DIELECTRIC AND TUNABLE BEHAVIOR OF LEAD STRONTIUM TITANATE CERAMICS AND COMPOSITES

A Thesis in
Materials
by
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Abstract

The needs of materials for microwave applications have been increasing due to the demands of mobile communication systems and it is preferable for most applications to be manufactured inexpensively using the least amount of space possible. One of the ideas presented to achieve this goal is to reduce the number of components. By changing certain properties under a specific electric and/or magnetic field condition, a component is able to have more than one function, which decreases the number of components necessary. Although microelectromechanical systems (MEMS), semiconductors, and ferrite based devices are available for tuning applications, ferroelectrics in the paraelectric regions and incipient ferroelectric materials are the most promising for low cost and miniaturized products over a wide frequency range of 1-10 GHz and higher frequencies.

Barium strontium titanate ((Ba, Sr)TiO₃ (BST)) is a considerably studied field dependent ferroelectric material. However, BST requires special techniques to prepare samples which show good reproducibility because the conventional mixed oxide method is not expected to offer high homogeneity due to low reactivity among the raw oxide chemicals of BST. On the contrary, lead strontium titanate ((Sr, Pb)TiO₃ (SPT)) permits much simpler processing due to the high reactivity of lead oxide, a raw oxide chemical, towards the other component oxides. Therefore, the SPT system has been selected as a potential candidate for the frequency agile ferroelectrics for electronics (FAME) applications.

Selected compositions, for example, Sr-Pb (0.7:0.3 by mole and 0.8:0.2 by mole) in the pure SPT system show the following properties: i) high relative permittivity, $\varepsilon_r$, ii) low tangent $\delta$ in the paraelectric states, iii) moderate DC bias dependence of $\varepsilon_r$ far above the transition temperatures, and iv) high DC bias dependence of $\varepsilon_r$ close to the transition temperatures. In addition, the SPT system does not show a significant composition dependence of the properties.

Because microwave applications need low capacitance materials in order to match the impedance for a device, the relative permittivity of the composition used should not be too high. Thus the $\varepsilon_r$ of the SPT system is tailored by the addition of non-ferroelectric low $\varepsilon_r$ and low tangent $\delta$ oxides such as magnesium oxide (MgO). In order to achieve low tangent $\delta$ in SPT based systems around room temperature, the composition, Sr-Pb (0.8:0.2 by mole), has been chosen as the SPT source of the composites.
The SPT-MgO composites show $\varepsilon_r \approx 100$, tangent $\delta$ less than 0.001 at room temperature and a frequency of 10 kHz using an LCR meter, and $Q \times$ frequency $\approx 700$ GHz in a microwave frequency range based on the Hakki-Coleman method at room temperature. The tunability is $\approx 0.02$ with a DC field of 20 kV/cm (the reference field to compare various materials) and $\approx 0.30$ with a DC field of 175 kV/cm at room temperature and at 10 kHz.

Mixing rules are analyzed for the best estimate relative permittivity of the composites. The $\varepsilon_r$ of the MgO based composites at room temperature and a frequency of 10 kHz show a reasonable agreement with the mixing model proposed by Wakino et al.

Besides the MgO based composites, other composite systems have been explored. Composites prepared from SPT and aluminum oxide (Al$_2$O$_3$) show unusually low temperature coefficients of dielectric permittivity and modest but relatively constant values of dielectric tunability over a wide temperature range. Composites prepared from SPT and zirconium oxide (ZrO$_2$) show the possibility to achieve higher $Q \times$ frequency values than most MgO based composites, but it would be difficult to achieve high density samples.

In the pure SPT system, detailed studies are focused upon a departure from the Curie-Weiss law above the Curie point, $T_c$. The studies reveal that the $T_c$ is unexpectedly below the Curie-Weiss temperature, $\theta$. In addition, unusually high values of weak AC field relative permittivity are observed at the transition temperatures. These behaviors have been traced to the inhomogeneity in the solid solutions, but further work is necessary to establish both the nano-scale and the amplitude of the composition fluctuations, which are enhancing the relative permittivity maximum at the $T_c$.

A more precise phase diagram has been established for the (Sr$_{1-x}$Pb$_x$)TiO$_3$ system in the important range of $x$ (0.05 - 0.30) for room temperature applications.
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4.2.5.9 Application of the mixing rules to the relative permittivity of SPT and composites prepared from SPT and MgO measured at 10 kHz and at 25 °C.

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(b) Dielectric properties; (3) Composite: SPT-MgO (0.95:0.05); (4) Composite: SPT-MgO (0.75:0.25 by weight) (5) Composite: SPT-MgO (0.60:0.40 by weight).

(c) Dielectric properties; (6) Composite: SPT-MgO (0.50:0.50); (7) Composite: SPT-MgO (0.40:0.60); (8) Composite: SPT-MgO (0.25:0.75 by weight).

(d) Dielectric properties; (9) Composite: SPT-MgO (0.05:0.95 by weight). …………………………………..

4.2.5.11 (a) Relative permittivity and Curie-Weiss behaviors of SPT and composites prepared from SPT and MgO at 10 kHz as a function of temperature. SPT:MgO by weight = 1 : 0 (0); 0.995 : 0.005 (1); 0.975 : 0.025 (2); 0.95 : 0.05 (3); 0.75 : 0.25 (4); 0.60 : 0.40 (5); 0.50 : 0.50 (6); 0.40 : 0.60 (7). ..………

(b) Relative permittivity and Curie-Weiss behaviors of SPT and composites with prepared from SPT and MgO at 10 kHz as a function of temperature. SPT:MgO by weight = 0.30 : 0.70 (8). ..………

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4.2.5.13 Curie-Weiss constants of SPT and composites prepared from SPT and MgO at 10 kHz. …………………….………………………

4.2.5.14 Reciprocal dielectric susceptibility of composites with parallel diphasic mixtures. …………………………….

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4.2.5.16 Q × frequency of (Sr0.8Pb0.2)TiO3 (SPT) ceramics and composites prepared from SPT and MgO measured using the parallel plate dielectric post resonator method. ……………………………

4.3.1 Room temperature Cu Kα X-ray diffraction patterns of (a) the mixture of calcined (Sr0.7Pb0.3)TiO3 (SPT) and Al2O3 and (b) sintered pellet prepared from SPT and Al2O3. …………………..……………

4.3.2 Comparison of room temperature Cu Kα X-ray diffraction patterns of (a) the sintered pellet prepared from SPT (x = 0.3) and Al2O3; (b) a number of SPT peaks refined by PRO-FIT, (c) SPT calculated based on the lattice parameter with CrRIne Crystallography 3.1, (d) selected peaks in the new phase refined by PRO-FIT, (e) SrAl12O19 (PDF#, 26-976), (f) SrAl12O19 (PDF#, 80-1195), (g) PbAl12O19 (PDF#, 20-558), (h) PbAl12O19 (PDF#, 80-1174), and (i) SrAl2O5 (PDF#, 2-964) ……..

4.3.3 Dielectric properties of composites prepared from SPT and Al2O3 as a function of temperature and freq.

4.3.4 Dielectric properties of composites prepared from SPT and Al2O3 as a function of temperature at 10 kHz in both cooling and heating cycles.

4.3.5 Dielectric properties of composites prepared from (Sr 1-xPbx)TiO3 (SPT) and aluminum oxide (Al2O3) as a function of temperature and applied DC bias field at 10kHz. ……………………..…….…………..

4.3.6 Dielectric tunability of composites prepared from SPT and Al2O3 as a function of temperature and applied DC bias field and temperature. (a) from 150 to 100 °C and (b) from ~90 to 40 °C. …………………

4.3.7 (a) Dielectric tunability and (b) relative permittivity and tangent δ of composites prepared from SPT and Al2O3 as a function of applied DC bias field and temperature. …………………

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(b) X-ray diffraction patterns of composites prepared from SPT and various oxides.

(i) Sintered composites from SPT and Al2O3. Sintered SPT, and Al2O3 chemicals. 
(ii) Sintered composites from SPT and MgAl2O4. Sintered SPT, and MgAl2O4 chemicals. 
(iii) Sintered composites from SPT and SnO2. Sintered SPT, and SnO2 chemicals. 
(iv) Sintered composites from SPT and ZrO2. Sintered SPT, and ZrO2 chemicals. ……..

(b) X-ray diffraction patterns of composites prepared from SPT and various oxides.

(i) Sintered composites from SPT, MgO, and ZrO2. (ii) Sintered pure SPT, (iii) MgO chemicals, and (iv) ZrO2 chemicals. ………………………………………………………………

4.4.2 Relative permittivity and tangent δ of composites fabricated from SPT and various oxides as a function of temperature and frequency. (a) Al2O3, (b) MgAl2O4, (c) SnO2, and (d) ZrO2 as the oxide which was added to SPT to make composites. ………………………………

4.4.3 Dielectric tunability of composites fabricated from SPT and (a) SnO2 and (b) ZrO2 as a function of temperature and DC bias field at 10 kHz upon cooling. …………………

6.1 Relative dielectric permittivity and reciprocal dielectric susceptibility of (Sr0.8Pb0.2)TiO3 (x = 0.2) ceramics as a function of temperature at 10 kHz upon cooling.
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1.1 Properties for conventional dielectric microwave applications

—Required properties and a figure of merit for conventional dielectric microwave applications—

1.1.1 Electromagnetic waves

Electromagnetic energy can propagate through free (empty) space as a wave motion in which transverse electric and magnetic fields are mutually orthogonal. In vacuum, the group velocity of the wave is the constant, \( c \), that is the ultimate velocity with which information may be transferred. As in all wave motion, the velocity, \( v \), is related to the frequency, \( f \), and the wavelength, \( \lambda \), of the wave by the relation

\[
v = f \lambda
\]

and the wave is described as a sin wave shown in Fig. 1.1.1 [1, 2]. The amplitude of the sin wave, \( E \), is derived from

\[
f(x) = E \sin(\theta) = E \sin(kx)
\]

\[
(\theta = \omega t = \frac{2\pi x}{\lambda} = \frac{2\pi f}{\lambda} x = k x)
\]

where \( x \) is the position of the wave or the distance the wave moves, \( \theta \) is an angle or phase, \( \omega \) is an angular velocity, \( T \) is a cycle, and \( k \) is a wave number. The unit of the amplitude is either voltage or current [1, 2].

1.1.2 Microwave (MW) frequency range and MW applications

The frequency, \( f \), and the corresponding wave length, \( \lambda \), cover a huge range and for convenience, this spectrum is divided into regions which are of interest for various types of applications. This division in terms of wavelength and frequency is given in Fig. 1.1.2 (a) [3] and (b) [2]. Additionally, this division defines the part of the spectrum which is generally characterized as microwave, and identifies some of the very widely used communication applications which fall inside this range. Frequently, an electrical engineer will wish to focus upon the frequencies in the microwave region (0.3-300 GHz, i.e., \( 1 \times 10^{-3} \) m [2, 4, 5]; 0.1-300 GHz defined by national telecommunications and information administration (NTIA) [3]) which are of most interest to his or her particular customer base. Therefore, the frequency space is
Figure 1.1.1 Sin wave.
(a) relationship between phase and angular velocity.
(b) relationship among velocity, wavelength, frequency, and amplitude.
After Suzuki [1], with permission from the Nikkan Kogyo Shimbun.
Ref.: Williams [2].
Figure 1.1.2 (a) US frequency allocation chart. (i) whole chart, (ii) from low to microwave frequency, and (iii) up to cosmic-ray frequency.

After NTIA [3].
Figure 1.1.2 (b) Electromagnetic spectrum.
Taken from Williams [2].
divided into a sequence of bands (ranges) which are given as simple letter designators listed in Table 1.1.1 (a) [6], (b) [7], and (c) [8, 7].

The reasons for this engineering focus become evident in Fig. 1.1.3, which lists some of the important applications that fall into these different bands within the microwave range. The largest markets of these applications are ovens, radar, and communications [2]. Among them, the need for wireless communication systems emphasizes an increase in attention on dielectric materials for these applications [9] because the dielectrics can provide miniaturized devices [4, 5, 9]. This will be explained in detail in the next section. Table 1.1.2 (a)-(c) [10], and (d) [11] show frequencies used for cellular, cordless phones, and satellite mobile communication systems.

1.1.3 Merits of dielectrics used for MW applications

−Miniaturization of devices based on reduced velocity in the devices−

For a low absorption and largely transparent material, the electromagnetic wave propagates with a lower velocity in the material, \( v \), than the velocity in free space, \( c \), and the ratio of velocities is termed the refractive index of the material

\[
\frac{c}{v} = n
\]  

(1.1.4)

where \( n \) is the index of refraction or refractive index.

A velocity, \( v \), in a medium at a frequency, \( f \), is also given by

\[
v = \frac{c}{\sqrt{\varepsilon \mu}} = \frac{1}{\sqrt{\varepsilon_0 \varepsilon_r \mu_0 \mu_r}} = \frac{c}{\sqrt{\varepsilon \mu}}
\]  

(1.1.5)

where \( \varepsilon \) is dielectric permittivity, \( \varepsilon_0 \) is vacuum dielectric permittivity, \( \varepsilon_r \) is relative dielectric permittivity, \( \mu \) is magnetic permeability, \( \mu_0 \) is vacuum magnetic permeability, and \( \mu_r \) is relative magnetic permeability at the frequency, \( f \). In a non-magnetic transparent material, for example, a dielectric, Eq. (1.1.5) reduces

\[
v = \frac{c}{\varepsilon_r}
\]  

(1.1.6)

From Eq. (1.1.1), Eq. (1.1.7) is derived for a wave in the free space of the frequency, \( f_v \)

\[
c = f_v \lambda_v
\]  

(1.1.7)

The wavelength will be \( \lambda_v \), but in the material of the index, \( n \), \( f \) will be the same as \( f_v \).

Accordingly, from Eqs. (1.1.1), (1.1.7), and (1.1.6), \( \lambda \) must change, namely

\[
\frac{\lambda}{\lambda_v} = \frac{v}{c} = \frac{1}{\sqrt{\varepsilon_r}}
\]  

(1.1.8)
Table 1.1.1 (a) ITU frequency band designations

ITU frequency bands, nine bands in radiospectrum

<table>
<thead>
<tr>
<th>Band Number*</th>
<th>Symbols</th>
<th>Nomenclature</th>
<th>Frequency range**</th>
<th>Corresponding metric designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>VLF</td>
<td>Very low frequency</td>
<td>3 kHz – 30 kHz</td>
<td>Myriametric waves</td>
</tr>
<tr>
<td>5</td>
<td>LF</td>
<td>Low frequency</td>
<td>30 kHz – 300 kHz</td>
<td>Kilometric waves</td>
</tr>
<tr>
<td>6</td>
<td>MF</td>
<td>Medium frequency</td>
<td>300 kHz – 3 MHz</td>
<td>Hectometric waves</td>
</tr>
<tr>
<td>7</td>
<td>HF</td>
<td>High frequency</td>
<td>3 MHz – 30 MHz</td>
<td>Decametric waves</td>
</tr>
<tr>
<td>8</td>
<td>VHF</td>
<td>Very high frequency</td>
<td>30 MHz – 300 MHz</td>
<td>Metric waves</td>
</tr>
<tr>
<td>9</td>
<td>UHF</td>
<td>Ultra high frequency</td>
<td>300 MHz – 3 GHz</td>
<td>Decimetric waves</td>
</tr>
<tr>
<td>10</td>
<td>SHF</td>
<td>Super high frequency</td>
<td>3 GHz – 30 GHz</td>
<td>Centimetric waves</td>
</tr>
<tr>
<td>11</td>
<td>EHF</td>
<td>Extremely high frequency</td>
<td>30 GHz – 300 GHz</td>
<td>Millimetric waves</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td>300 GHz – 3000 GHz</td>
<td>Decimillimetric waves</td>
</tr>
</tbody>
</table>

Note

ITU: International telecommunications union.

* : Band number, n, covers from $0.3 \times 10^n$ Hz (hertz) to $3 \times 10^n$ Hz.

** : Lower limit exclusive and upper limit inclusive.

Prefix: k = kilo ($10^3$); M = mega ($10^6$); G = giga ($10^9$).

Ref: Radio regulations [6].
<table>
<thead>
<tr>
<th>Symbols</th>
<th>Nomenclature</th>
<th>Frequency range</th>
<th>Wave length</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELF</td>
<td>Extremely low frequency</td>
<td>3 Hz – 30 Hz</td>
<td>100000 km – 10000 km</td>
</tr>
<tr>
<td>SLF</td>
<td>Super low frequency</td>
<td>30 Hz – 300 Hz</td>
<td>10000 km – 1000 km</td>
</tr>
<tr>
<td>ULF</td>
<td>Ultra low frequency</td>
<td>300 Hz – 3 kHz</td>
<td>1000 km – 100 km</td>
</tr>
<tr>
<td>VLF</td>
<td>Very low frequency</td>
<td>3 kHz – 30 kHz</td>
<td>100 km – 10 km</td>
</tr>
<tr>
<td>LF</td>
<td>Low frequency</td>
<td>30 kHz – 300 kHz</td>
<td>10 km – 1 km</td>
</tr>
<tr>
<td>MF</td>
<td>Medium frequency</td>
<td>300 kHz – 3 MHz</td>
<td>1 km – 100 m</td>
</tr>
<tr>
<td>HF</td>
<td>High frequency</td>
<td>3 MHz – 30 MHz</td>
<td>100 m – 10 m</td>
</tr>
<tr>
<td>VHF</td>
<td>Very high frequency</td>
<td>30 MHz – 300 MHz</td>
<td>10 m – 1 m</td>
</tr>
<tr>
<td>UHF</td>
<td>Ultra high frequency</td>
<td>300 MHz – 3 GHz</td>
<td>1 m – 10 cm</td>
</tr>
<tr>
<td>SHF</td>
<td>Super high frequency</td>
<td>3 GHz – 30 GHz</td>
<td>10 cm – 1 cm</td>
</tr>
<tr>
<td>EHF</td>
<td>Extremely high frequency</td>
<td>30 GHz – 300 GHz</td>
<td>1 cm – 1 mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300 GHz – 3 THz</td>
<td>1 mm – 0.1 mm</td>
</tr>
</tbody>
</table>

Ref: Sawicki [7], with permission from Mr. Sawicki.
Table 1.1.1 (c) IEEE Std. frequency band designations

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Nomenclature</th>
<th>Frequency range</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>High frequency</td>
<td>3 MHz – 30 MHz</td>
</tr>
<tr>
<td>VHF</td>
<td>Very high frequency</td>
<td>30 MHz – 300 MHz</td>
</tr>
<tr>
<td>UHF</td>
<td>Ultra high frequency</td>
<td>300 MHz – 1 GHz</td>
</tr>
<tr>
<td>L</td>
<td></td>
<td>1 GHz – 2 GHz</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>2 GHz – 4 GHz</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>4 GHz – 8 GHz</td>
</tr>
<tr>
<td>X</td>
<td></td>
<td>8 GHz – 12 GHz</td>
</tr>
<tr>
<td>Ku</td>
<td></td>
<td>12 GHz – 18 GHz</td>
</tr>
<tr>
<td>K</td>
<td></td>
<td>18 GHz – 27 GHz</td>
</tr>
<tr>
<td>Ka</td>
<td></td>
<td>27 GHz – 40 GHz</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>40 GHz – 75 GHz</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td>75 GHz – 110 GHz</td>
</tr>
<tr>
<td>mm</td>
<td>millimeter wavelength</td>
<td>110 GHz – 300 GHz</td>
</tr>
</tbody>
</table>

IEEE: Institute of electrical and electronics engineers.
Ref. : IEEE Std. 521™ [8].
Sawicki [7].
Figure 1.1.3 Microwave spectrum. 
Taken from Williams [2].
Table 1.1.2 (a) Parameters of some first-generation cellular standards

<table>
<thead>
<tr>
<th>Parameters</th>
<th>AMPS</th>
<th>C450</th>
<th>NMT 450</th>
<th>NTT</th>
<th>TACS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobile</td>
<td>824-849</td>
<td>450-455.784</td>
<td>453-457.5</td>
<td>925-940</td>
<td>890-915</td>
</tr>
<tr>
<td>Bass station</td>
<td>869-894</td>
<td>460-465.74</td>
<td>463-467.5</td>
<td>870-885</td>
<td>935-960</td>
</tr>
<tr>
<td>Channel bandwidth (kHz)</td>
<td>30</td>
<td>20</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Spacing between forward and reverse channels (MHz)</td>
<td>45</td>
<td>10</td>
<td>10</td>
<td>55</td>
<td>45</td>
</tr>
<tr>
<td>Speech signal</td>
<td>±12</td>
<td>±5</td>
<td>±5</td>
<td>±5</td>
<td>±9.5</td>
</tr>
<tr>
<td>FM deviation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control signal data rate (kbps)</td>
<td>10</td>
<td>5.28</td>
<td>1.2</td>
<td>0.3</td>
<td>8</td>
</tr>
<tr>
<td>Handoff decision is based on</td>
<td>Power received at base</td>
<td>Round-trip delay</td>
<td>Power received at base</td>
<td>Power received at base</td>
<td>Power received at base</td>
</tr>
</tbody>
</table>

AMPS, Advanced mobile phone service; TACS, Total access communication system; NMT, Nordic mobile telephone; NTT, Nippon telephone and telegraph.

Table 1.1.2 (b) Parameters of some second-generation cellular standards

<table>
<thead>
<tr>
<th>Parameters</th>
<th>IS-54</th>
<th>GSM</th>
<th>IS-95</th>
<th>PDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>TX frequencies (MHz)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mobile</td>
<td>824-849</td>
<td>890-915</td>
<td>824-849</td>
<td>940-956 and 1429-1453</td>
</tr>
<tr>
<td>Base station</td>
<td>869-894</td>
<td>935-960</td>
<td>869-894</td>
<td>810-826 and 1477-1501</td>
</tr>
<tr>
<td>Channel bandwidth (kHz)</td>
<td>30</td>
<td>200</td>
<td>1250</td>
<td>25</td>
</tr>
<tr>
<td>Spacing between forward and reverse channels (MHz)</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>30/48</td>
</tr>
<tr>
<td>Modulation</td>
<td>π/4</td>
<td>GMSK</td>
<td>BPSK/QPSK</td>
<td>π/4</td>
</tr>
<tr>
<td>Frame duration (ms)</td>
<td>40</td>
<td>4.615</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

IS-54, Interim standard-54 (United States digital cellular); PDC, Personal digital cellular (system in Japan); IS-95, United States digital cellular; GSM, Global system for mobile (communications systems in Europe); GMSK, Gaussian minimum-shift keying; BPSK, Binary phase-shift keying; QPSK, Quaternary phase-shift keying; DQPSK, Differential-quadrature phase-shift keying. (Definition based on Sclater and Markus [17]).

Table 1.1.2 (c) Digital cordless system parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CT2</th>
<th>DECT</th>
<th>PACS</th>
<th>PHS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency (MHz)</td>
<td>864-868</td>
<td>1880-1900</td>
<td>1850-1910 and 1930-1990</td>
<td>1895-1918</td>
</tr>
<tr>
<td>Channel spacing (kHz)</td>
<td>100</td>
<td>1728</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Duplexing</td>
<td>TDD</td>
<td>TDD</td>
<td>FDD</td>
<td>TDD</td>
</tr>
<tr>
<td>Channel rate (kbps)</td>
<td>72</td>
<td>1152</td>
<td>384</td>
<td>384</td>
</tr>
<tr>
<td>Transmitted power (mW)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>5</td>
<td>10</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>Peak</td>
<td>10</td>
<td>250</td>
<td>200</td>
<td>80</td>
</tr>
<tr>
<td>Frame duration (ms)</td>
<td>2</td>
<td>10</td>
<td>2.5</td>
<td>5</td>
</tr>
<tr>
<td>Channels per carrier</td>
<td>1</td>
<td>12</td>
<td>8</td>
<td>4</td>
</tr>
</tbody>
</table>

CT2, British standard; DECT, Digital European cordless telecommunication (standard); PHS, Personal handy phone system (in Japan); PACS, Personal access communication service (in the United States). TDD, Time-division duplexing; FDD, Frequency-division duplexing. Ref. for definition: Sclater and Markus [17].

After Godara [10], with permission from CRC press.
Table 1.1.2 (d) Frequency bands allocated to satellite transmission

<table>
<thead>
<tr>
<th>Frequency band</th>
<th>Frequency (Uplink / Downlink)</th>
<th>User</th>
<th>Service</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHF</td>
<td>400/225 MHz</td>
<td>Military</td>
<td>Mobile</td>
</tr>
<tr>
<td>L-band</td>
<td>1.6/1.5 GHz</td>
<td>Commercial</td>
<td>Mobile</td>
</tr>
<tr>
<td>S-band</td>
<td>3/2 GHz</td>
<td>Commercial</td>
<td>Satellite control</td>
</tr>
<tr>
<td>C-band</td>
<td>6/4 GHz</td>
<td>Commercial</td>
<td>Fixed</td>
</tr>
<tr>
<td>X-band</td>
<td>8/7 GHz</td>
<td>Military</td>
<td>Fixed/mobile</td>
</tr>
<tr>
<td>Ku-band</td>
<td>14/12 GHz</td>
<td>Commercial</td>
<td>Fixed</td>
</tr>
<tr>
<td>Ka-band</td>
<td>30/20 GHz</td>
<td>Commercial</td>
<td>Fixed</td>
</tr>
<tr>
<td>Ka-band</td>
<td>44/20 GHz</td>
<td>Military</td>
<td>Fixed/mobile</td>
</tr>
</tbody>
</table>

Taken from Ryan [11], with permission from CRC press.
Thus the wave length in the dielectric is proportional to $\frac{1}{\sqrt{\varepsilon_r}}$, so that to keep wave interaction devices small, increased values of $\varepsilon$ will be important. This argument, however, cannot be taken too far since electrical impedance, $Z$ (of the dielectric scales as $\frac{1}{\varepsilon}$ (or $\frac{1}{\text{capacitance}}$)) becomes too small for practical systems when $\varepsilon$ (capacitance) is too large.

### 1.1.4 Requirements for MW applications

The dielectrics for the microwave applications are required to have specific major properties: i) reasonable relative permittivity, $\varepsilon_r$ [12], ii) high Q factor (quality factor $= \frac{1}{\text{tangent } \delta}$) [4, 5, 9, 12-14] or high $Q \times$ frequency [15], and iii) low temperature coefficient of frequency [4, 5, 9, 12-14]. Additional goals to manufacture products would address cost-effectiveness, smaller size, reliability, and simpler processing for products [2].

Reasonable relative permittivity is necessary to obtain the impedance match of a dielectric for a device, and 50 $\Omega$ is the required impedance value because of the characteristic value of many microwave systems [2, 16]. In addition, relatively high dielectric constants are preferable since the miniaturization of the device would be possible. Preferable values are determined by the possible dimension of the device and frequencies or modes at which the device is operated [12]. Because the main polarization mechanism of ionic microwave dielectrics in the microwave frequency range is ionic polarization, relative permittivity is expected to be constant in this region [4]. This explanation will be described in more detail later in Sect. 1.1.7.

### 1.1.5 Several resonant modes in MW devices

Several resonant modes that are used in applications are a TE$_{01\delta}$ mode (only transverse electric (TE) waves exist: transverse electric field perpendicular to the propagation direction of an electromagnetic wave [17]), a TM$_{01\delta}$ mode (only transverse magnetic (TM) waves exist: transverse magnetic field perpendicular to the propagation direction of an electromagnetic wave [17]), and a TEM mode (transverse electromagnetic (TEM) wave: both the electric and magnetic waves exist: transverse electric and magnetic fields perpendicular to the propagation direction of an electromagnetic wave [17]) [18, 14, 5] (Fig. 1.1.4). Dielectric resonators have radiation losses because the resonators fabricated from the dielectrics cannot hold electromagnetic fields and should have metallic conductors on the outsides of the resonators [5]. The TE$_{01\delta}$ mode is used for
Figure 1.1.4 Major resonant modes.
D, the outside diameter or diameter of a conductor; d, the inside diameter or diameter of a dielectric for TE\textsubscript{01δ}; \ell, the height of the dielectric; L, the height of the conductor for TE\textsubscript{01δ}; \lambda, wave length.
After Wakino [18].
circular cylinder shaped dielectric resonators, the TEM mode is for circular cylinders with hole (coaxial) shaped dielectric resonators, and the TM\textsubscript{010} mode is for cylindrical dielectric resonators. Furthermore, the TEM mode is also used in stripline resonators [5].

### 1.1.6 Issues on Q factors

An unloaded Q factor, $Q_U$, for a dielectric in a resonator is described by Eq. (1.1.9) [19]

$$Q_U = \frac{2\pi f_o}{\frac{\text{Energy stored in a resonant circuit}}{\text{Energy lost in a resonant circuit}}}$$

(1.1.9)

where $f_o$ is the resonance frequency of the dielectric in the resonator. Thus a device with a high Q material shows a sharp attenuation constant [5]. In other words, tangent $\delta$ should be low due to the optimization of signal intensity and due to the number of possible channels within a specific frequency range [9].

The unloaded Q factor of a resonant circuit, $Q_U$, is also given by Eq. (1.1.10)

$$\frac{1}{Q_U} = \frac{1}{Q_d} + \frac{1}{Q_C} + \frac{1}{Q_R}$$

(1.1.10)

where $Q_d$ is a Q factor caused by a dielectric, $Q_C$ is a Q factor by a conductor, and $Q_R$ is a Q factor by radiation [12].

TE\textsubscript{018} mode resonators have dielectrics on low relative permittivity stands inside metal containers [4]. A demerit of these systems is that the size becomes large because of the necessity of the metallic outside containers, while a merit is that $Q_U$ factors become large due to the high $Q_C$ factors. Because the dielectrics do not need electrodes, the conduction is from the dielectrics which have low conductivity. The TE\textsubscript{018} mode resonators are used in devices required for high Q, for example, oscillators [5]. The dielectrics of TEM mode resonators need electrodes on them. Therefore, the $Q_U$ factors of the TEM mode resonators are low because the $Q_C$ factors become low. A disadvantage of the TEM mode resonators is that $Q_U$ factors become low because $Q_C$ and $Q_R$ factors are low. Meanwhile, an advantage of these resonators is to be able to fabricate smaller sizes of devices [5, 15] compared with the TE\textsubscript{018} and TM\textsubscript{018} mode resonators. The TEM resonators, thus, are used in mobile communication systems [5]. As described before, the TEM mode is also used in the stripline resonators. Characteristics of the TM\textsubscript{018} mode resonators are to have medium sizes of devices and medium $Q_U$ factors among the three types of resonators [5].
1.1.7 Real and imaginary parts of relative complex permittivity based on the lattice
dynamic theory

There are four major polarization mechanisms: space charge, dipolar polarization, ionic
polarization, and electronic polarization (Fig. 1.1.5) [20], but the main polarization mechanism
of the conventional microwave dielectrics in the microwave frequency band is ionic because the
electronic polarization is small compared with the ionic polarization. Dielectric properties at a
constant temperature may be calculated based on the lattice dynamics, for example, the rigid ion
model [4, 21, 22]. The rigid ion model assumes that ions are treated as point charges and that the
motion of positive and negative ions in opposite directions cause relative permittivity under an
alternating current (AC) field, E. In other words, no electronic polarizability exists. When all
positive ions whose charges are \( +Ze \) (Z: Valance and e: Electrical charge) are displaced by \( u_1 \)
and all the negative ions whose charges are \( -Ze \) are displaced by \( u_2 \), then the polarization is
given by Eq. (1.1.11) with a unit cell volume, \( v \).

\[
P = \frac{Ze(u_1 - u_2)}{v} \quad (1.1.11)
\]

The motion of the positive ions is expressed as Eq. (1.1.12) using the Lorentz field and \( \beta \)
which is a force constant to account for the restoring force, \( \beta u \)

\[
m_1 \frac{\partial^2 u_1}{\partial t^2} = Ze \left( E + \frac{P}{3\epsilon_o} \right) - \beta (u_1 - u_2) \quad (1.1.12)
\]

where \( m_1 \) is the mass of the positive ions.

For the negative ions,

\[
m_2 \frac{\partial^2 u_2}{\partial t^2} = -Ze \left( E + \frac{P}{3\epsilon_o} \right) - \beta (u_2 - u_1) \quad (1.1.13)
\]

where \( m_2 \) is the mass of the negative ions.

Using Eqs. (1.1.11), (1.1.12), and (1.1.13), Eq. (1.1.14) is obtained

\[
m \left( \frac{\partial^2 P}{\partial t^2} \right) = \frac{(Ze)^2}{v} \left( E + \frac{P}{3\epsilon_o} \right) - \beta P \quad (1.1.14)
\]

where \( m \) is the reduced mass, i.e., \( m = \frac{m_1 \cdot m_2}{m_1 + m_2} \).

When the damping factor, \( \gamma \), is added to Eq. (1.1.14), Eq. (1.1.15) is given by

\[
m \left( \frac{\partial^2 P}{\partial t^2} + \gamma \frac{\partial P}{\partial t} \right) = \frac{(Ze)^2}{v} \left( E + \frac{P}{3\epsilon_o} \right) - \beta P \quad (1.1.15)
\]
Figure 1.1.5 Contribution of polarization on real and imaginary parts of complex permittivity, $\varepsilon'$, and $\varepsilon''$, as a function of frequency. After Moulson and Herbert [20] p. 68.
When the electric field, $E$, is applied as $\exp(-i\omega t)$, the solution of Eq. (1.1.15) is

$$
\varepsilon^*(\omega) - 1 = \frac{(Z\varepsilon)^2}{\omega_T^2} = \frac{-\omega_T^2 (\varepsilon(0) - 1)}{\omega_T^2 - \omega^2 - i\gamma\omega}
$$

(1.1.16)

Eq. (1.1.16) is modified further, and complex relative permittivity, $\varepsilon^*(\omega)$, at the angular frequency, $\omega$, is obtained by the following equation.

$$
\varepsilon^*(\omega) - \varepsilon(\omega) = \frac{\omega^2 (\varepsilon(0) - \varepsilon(\omega))}{\omega_T^2 - \omega^2 - i\gamma\omega}
$$

(1.1.17)

$\varepsilon(0)$ is relative permittivity at a lower frequency than the microwave frequency. In other words, this frequency may be 0. $\varepsilon(\omega)$ is relative permittivity due to the electronic polarization and in this case, $\varepsilon(\omega)$ is 1. In addition, $\omega_T$ is longitudinal optical angular frequency. The real and imaginary parts of complex permittivity, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$, respectively, are obtained as shown in the equations below.

$$
\varepsilon'(\omega) = \varepsilon(\omega) + \omega_T^2 (\varepsilon(0) - \varepsilon(\omega)) \frac{\omega_T^2 - \omega^2}{(\omega_T^2 - \omega^2)^2 + (\gamma\omega)^2}
$$

(1.1.18)

$$
\varepsilon''(\omega) = \omega_T^2 (\varepsilon(0) - \varepsilon(\omega)) \frac{\gamma\omega}{(\omega_T^2 - \omega^2)^2 + (\gamma\omega)^2}
$$

(1.1.19)

Because the $\omega_T$ of most ionic crystals shows the range from $10^{12}$ to $10^{13}$ Hz, $\omega_T^2 \gg \omega^2$ when $\omega$ is in the microwave range, $10^9$ through $10^{10}$ Hz.

$$
\varepsilon'(\omega) = \varepsilon(0)
$$

(1.1.20)

$$
\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = \frac{\gamma}{\omega_T^2}
$$

(1.1.21)

$$
\frac{1}{\tan \delta} \frac{\omega}{2\pi} = Q \cdot f = \frac{1}{2\pi} \frac{\omega_T^2}{\gamma} = \text{constant}
$$

(1.1.22)

From Eqs. (1.1.20) and (1.1.22), relative permittivity and $Q \times$ frequency become constant in the microwave region. Because the microwave applications need high $Q$ values and $Q \times$ frequency is assumed to be constant in the microwave range, a figure of merit for the microwave dielectrics is $Q \times$ frequency.

In this section, constant relative permittivity and $Q \times$ frequency at a fixed temperature is explained based on the damped oscillator model. However, this model determines some of the loss behaviors because it has restrictions in use. Thus loss tangents on phonon transport theory...
covers a wider range of temperature as a function of frequency, temperature, and relative permittivity than those based on the damped oscillation model [23] (see Sect. 4.2.4).

### 1.1.8 Issues on temperature coefficients of relative permittivity and resonant frequency

It is possible to calculate relative permittivity, $\varepsilon_r$, of dielectric rods to use the resonant frequency of a TE$_{0ml}$ mode using the parallel plate dielectric post resonator method or post resonant method [24, 25 and references therein]

$$\varepsilon_r = \left( \frac{\lambda_o}{\pi D} \right)^2 \left( u^2 + v^2 \right) + 1$$

(1.1.23)

$$v^2 = \left( \frac{\pi D}{\lambda_o} \right)^2 \left[ \left( \frac{\lambda_o}{\lambda_g} \right)^2 - 1 \right]$$

(1.1.24)

$$\lambda_o = \frac{c}{f_o}, \lambda_g = \frac{2h}{\ell}, \ell = 1, 2, 3, \ldots$$

(1.1.25)

where $D =$ diameter, $h =$ height, $\lambda_o =$ the free space resonance wavelength, $c =$ the light velocity in vacuum, $\lambda_g =$ the guiding wavelength in the dielectric transmission line, $f_o =$ resonant frequency, and $u^2 =$ a value related to $v^2$.

A change in temperature, $\Delta T$, causes a change in relative permittivity, $\Delta \varepsilon_r$, a change in the diameter, $\Delta D$, a change in the length, $\Delta h$, and a change in $\Delta f_o$ for the TE$_{011}$ mode. The following equation is obtained for isotropic materials [24, 25]

$$\tau_e = -2 \left( 1 + \frac{W}{\varepsilon_r} \right) \left( \tau_f + \alpha_l \right)$$

(1.1.26)

where $\tau_e =$ temperature coefficient of relative permittivity, $\tau_f =$ temperature coefficient of resonant frequency, $\alpha_l =$ linear thermal expansion coefficient, and $W =$ the ratio of electric field energy stored outside to electric field energy stored inside a dielectric rod.

If $\varepsilon_r$ is large and $\frac{D}{h}$ is nearly two, the electric energy is stored inside the sample. Then Eq. (1.1.26) is reduced to Eq. (1.1.27) because $\frac{W}{\varepsilon_r}$ becomes small values like 0.01 [24, 25].

$$\tau_e = -2 \left( \tau_f + \alpha_l \right)$$

(1.1.27)
For example, assuming that \( \alpha_l \) is \( 1 \times 10^{-5} \, ^\circ\text{C}^{-1} \) as a value of conventional ceramics, then \( \tau_e \) would be \( -2 \times 10^{-5} \, ^\circ\text{C}^{-1} \) in order to achieve \( 0 \times 10^{-5} \, ^\circ\text{C}^{-1} \) for the value of \( \tau_f \), namely, zero as the temperature coefficient of the resonant frequency.

Moreover, paraelectric materials would show the relation, Eq. (1.1.28) according to Harrop’s observation based on samples with \( \alpha_l = 1 \times 10^{-5} \, ^\circ\text{C}^{-1} \) [26].

\[
\tau_e = -\alpha_l \cdot \epsilon_r
\]  
(1.1.28)

Eq. (1.1.29) is obtained from Eqs. (1.1.27) and (1.1.28).

\[
\tau_f = \alpha_l \left( \frac{\epsilon_r}{2} - 1 \right)
\]  
(1.1.29)

Fig. 1.1.6 shows the relationship between \( \tau_f \) and \( \epsilon_r \) [4]. Some materials such as TiO_2 showed close to the linear relationship between \( \tau_f \) and \( \epsilon_r \), but materials like SrTiO_3 and BaO-TiO_2-Nd_2O_3-PbO showed behaviors far from the linear relationship. If one assumes that the thermal expansion coefficients of a specimen are \( \sim 10^{-5} \, ^\circ\text{C}^{-1} \), one could estimate the temperature coefficients of resonant frequencies of the specimen by Eq. (1.1.29). However, this is not the general rule, and one needs to remember that Eq. (1.1.29) is obtained based on the assumptions. Thus temperature coefficients of some materials are beyond these estimates.

### 1.2 Various tunable applications

--- Needs for tunable devices and brief description of various tunable applications ---

Most microwave devices are required to be miniaturized and manufactured inexpensively. Tunable devices have the potential of miniaturization and cost reduction because they will be able to decrease the number of parts in the devices. For example, conventional filters have specific frequencies to cover. When these filters are required to transmit and receive signals which belong to different frequencies, at least two filters are necessary. However, if tunable filters cover the two frequencies to change their resonant frequencies under a specific condition, then these filters have the roles of both transmitting and receiving signals. Therefore, the number of the filters will be decreased.

Mechanical tuning systems and ferrite, ferroelectric, semiconductor, superconductor, acoustic, and microelectromechanical systems (MEMS) devices will be described briefly in this section. Additionally, significant properties for the tunable devices will be summarized concisely at the end of this section.
Figure 1.1.6 Temperature coefficient of resonant frequency, $\tau_f$, as a function of relative permittivity, $\varepsilon_r$.

Taken from Ohuchi [4].
A simple way to tune a property of a material is to do it mechanically if the material is supposed to change the property. Metallic tuning screws allow limited tuning ranges [27]. In order to achieve a wide tuning range and low insertion loss, the mechanical tuning by dielectrics [27, 28] or high temperature superconductors (HTSs) [27, 29] has been reported. There are disadvantages to the mechanical tuning systems and these include a slow tuning speed due to the slow movement of a mechanical part [30] and a difficulty in accurate positioning [30]. Meanwhile, one of the merits of these systems is a large power handling capability [31]. A relatively high frequency for the operation of mechanical tuning devices reported would be Ka-band (operating frequency: 26-38 GHz in the literature) as phase shifters [28].

Electrically tunable ferrite filters are used in scanning receivers, radar, and microwave test equipment. These devices have a wide electric tuning range compared with varactors, ferroelectrics, and MEMS [32]. Magnetically tuning ferrite filters are also available, and they offer a multi-octave tuning range, very high selectivity, spurious free resonance, and compact size [31]. Ferrimagnetic yttrium-iron-garnet (YIG) single crystal spheres are often used as major ferrite tunable materials under DC magnetic fields [32, 33]. A couple of drawbacks of the YIG filters are that the YIG often needs an external thermostat because YIG is not stable with temperature [33] and that the limitation of power starts at relatively low power levels [33]. In addition, the ferrite devices are costly compared with MEMS and ferroelectric devices [34]. The maximum frequency studied would be W band (75-110 GHz) with hexagonal ferrite filters [35].

Other potential magnetic devices using magnetic materials are based on a magnetostatic wave (MSW) which propagates in ferrimagnetic single crystal films such as liquid phase epitaxial (LPE) grown YIG films. The MSWs have three pure modes: magnetostatic surface waves (MSSW), magnetostatic forward volume waves (MSFW), and magnetostatic backward volume waves (MSBV). The frequency limits of these devices are dependent on internal magnetic fields and modes used, depending on the orientation of the bias magnetic field relative to the YIG films and the propagation direction [36, 31]. The MSW devices and subsystems offer instantaneous bandwidths of up to 1 GHz at the operating frequencies in the range between 0.5 and 26.5 GHz [36]. However, the MSW devices need further improvement to replace current surface acoustic wave (SAW) devices and the YIG spheres [32].

Direct current (DC) dependent ferroelectrics or incipient ferroelectrics are used in the tunable devices and the materials enable the devices to be simple, cost-effective, and to control a microwave resonant frequency [15]. Ferroelectric varactors show similar properties to semiconductor varactors between 10 and 20 GHz. Although the ferroelectric varactors keep
similar quality (Q) factor values over the above frequency range (10-20 GHz), the Q values of the semiconductor varactors drop in the same range (10-20 GHz) [37, 38]. Ferroelectric phase shifters have a high tuning speed, good tunability, high power handling capability, and lower power requirements than ferrite phase shifters [34]. Disadvantages of the ferroelectric systems are that the Q factors become low at frequencies of less than 10 GHz. Moreover, bulk systems are not suitable for integration with monolithic microwave integrated circuits (MMICs) compared with the semiconductor systems [37]. The ferroelectric devices are suitable for the operation at low frequencies up to 15 GHz, larger phase shift per dB loss, low losses, and large power handling capability [34]. Na$_{0.5}$K$_{0.5}$NbO$_3$ (NKN) has been studied up to 50 GHz as the tunable ferroelectric [37].

Regarding the comparison of three technologies for tunable applications: i) tunable ferroelectric thin films, ii) semiconductors, and iii) ferrites, the ferroelectric systems are superior to the other two methods since these two technologies do not satisfy the required properties such as high Q, low distortion, easy integration with microwave systems, and inexpensive manufacturing [16].

The semiconductor varactors show the high Q factors rather than the ferroelectric varactors at low frequencies, less than 10 GHz, and the semiconductors are suitable to integrate circuits. Nevertheless, the Q values decrease faster in the frequency range higher than 10 GHz [37]. There is the literature for the electrically tunable semiconductor devices [39-42].

The ceramic oxide family superconductors, HTSs, have critical temperatures above ~ 25 K [43]. HTS microwave filters have comparative properties such as sizes and Q factors with conventional waveguide and dielectric resonator filters [44]. In order to achieve the improvement of Q values further, HTS has been often used with dielectric substrates [44]. HTS and dielectric and/or ferroelectric tunable devices have been reported in the literature [45-47]. Yttrium barium copper oxide (YBa$_2$Cu$_3$O$_{7-\delta}$; YBCO) is a typical HTS material. The HTS devices have been studied to be operated up to 20 GHz [48].

Microwave acoustic devices have the potential to be miniaturized because the acoustic waves are slower than the electromagnetic waves and the devices are able to obtain a long delay on compact spaces [49, 50]. These devices are suitable for large quantity production due to a simple technology available for manufacturing such as lithography. Electrically tunable SAW filters with lithium niobate (LiNbO$_3$) [51] or hybrid GaAs (gallium arsenide)/LiNbO$_3$ [52] have been reported. Although the general SAW devices are operated at lower than 3 GHz, a frequency
multiplication enables these devices to operate at 5.84 GHz [53]. Non-tunable SAW devices have been operated at ~ 17 GHz [54].

The MEMS devices are attractive for switches in radar systems, filters, and communication systems because they are able to reduce weight, cost, size, and power dissipation [55]. Moreover, they are suitable for highly integrated multiband/multifrequency systems [56]. The MEMS applications are based on tunable MEMS devices like the varactors [57-60]. The frequencies of these devices are tuned by analog (continuous frequency) or digital (discrete center frequencies). The MEMS switches can be operated at high frequencies from 1 G to 60 GHz and have good isolation and little intermodulation distortion [38]. Moreover, the MEMS switches are operated under lower power consumption than the semiconductors because MEMS do not need a continuous DC current [38]. There are drawbacks to the MEMS devices and these include slower switching time and higher actuation voltages compared with the semiconductor switches [38]. Although series switches with metal-to-metal contacts have a problem with stiction, the usage of dielectric films extends the lifetime of the switches [38]. MEMS offers good qualities at higher frequencies, over 20 GHz, and a large phase shift per dB loss [38].

Besides the above methods, there are various tuning methods or materials such as acoustic (bulk acoustic wave) [61], piezoelectric [62], optical [48, 63-67], acousto-optic [68], electric and magnetic tuning [69: the use of electro/magnetorheological fluid; 70: ferroelectric/ferrimagnetic multilayer (BST/YIG), BST-barium strontium titanate], photonic crystals [71-73] or liquid crystals [74, 75] based on the Fréedericksz-effect which is related to dielectric anisotropy, that is, a change in dielectric constant or refraction index based on a specific orientation relative to excited radio frequency (RF)-field polarization at electro-static or magneto-static fields.

Required properties for tunable microwave devices are determined by applications, but the following paragraph will discuss several ideas related to these properties. One may classify the required properties according to two factors: i) devices’ properties and ii) aspects for (mass) production and/or products. Properties related to tuning are operating frequency, bandwidth, tuning range, tuning speed, selectivity, isolation, tuning linearity, sensitivity, hysteresis, reproducibility, aging effect, and/or stability at an operating temperature and atmosphere. Q factor or insertion loss is also an important factor. Power related performances are power handling capability, maximum field in which a material can withstand, power consumption, actuation voltage, and power dissipations. Modulation distortion is also a considerable factor.
Regarding the production and/or products, cost, integration with other devices, producibility, flexibility of design, size, weight, ruggedness, reproducibility and/or lifetime are significant.

To fabricate the tunable microwave devices for room temperature (RT), and 1-10 GHz and possibly higher frequency operation, and inexpensive manufacturing (and integration with other microwave devices), the ferroelectric based systems are the most promising among ferroelectrics, ferrites, HTSs, SAW devices, semiconductors, and MEMS devices. The HTS devices can be integrated with microwave devices such as ferroelectric based systems, but the HTS devices are not suitable for RT applications at present. Because the SAW devices are suitable for low frequency operation, for example, below 3 GHz, these devices cannot currently satisfy the requests for higher frequency applications. The ferrite systems are expensive and cumbersome. Although the semiconductors are suitable for applications at lower frequencies of less than 10 GHz and are also quite sensitive, these systems are costly. The MEMS devices are also expensive even though they are very sensitive. However, special applications which demand excellent qualities and which are not required to be manufactured inexpensively need the MEMS tunable devices.

1.3 Scope of tunable materials

Various materials have their own advantages and disadvantages, and these materials will be reviewed briefly. Ferroelectric based systems are the most promising for inexpensive room temperature and tunable microwave frequency applications at a frequency range of 1-10 GHz and at higher frequencies. Additionally, various ferroelectrics and related materials show non-linear behaviors, namely, the direct current (DC) dependence of relative permittivity. Thus the ferroelectric related materials will be summarized in the next section (Sect. 1.3.2).

1.3.1 Non-ferroelectric and non-incipient ferroelectric materials

1.3.1.1 Materials for mechanical tuning

Although metallic materials are available for mechanical tuning, metallic screws limit tuning ranges, and metallic disks decrease unloaded Q-factors of resonators even though the disks allow a wide tuning [27]. Therefore, dielectrics [27, 28] or high temperature superconductors (HTSs) [29] are candidate materials. There are disadvantages such as a slow tuning speed [30], while there are advantages such as a large power handling capability [31].
1.3.1.2 Magnetic materials (ferrites)

Magnetic metals are not suitable in the frequency range above 100 kHz because of a decrease in magnetic permeability and an increase in magnetic losses due to the skin effect, that is, current flowing on the surface of a conductive material instead of flowing through the conductor uniformly [1]. Therefore, ferromagnetic ceramics and films are used in frequencies above 1 GHz [76] based on the gyromagnetic effect [76, 77, 32]. Because of this effect, magnetization results from the rotation of electron charges such as spinning electrons moving within atoms [17]. There are important properties for the microwave ferrites such as saturation magnetization, ferromagnetic resonance linewidth, and spinwave resonance linewidth [77]. Required saturation magnetization depends on applications and necessary frequencies. The magnetic resonance property would be useful for the rough evaluation of the magnetic losses, and the spinwave resonance linewidth would demonstrate the ability to stand electric power [77]. Materials which have been studied as microwave devices are magnesium (Mg) ferrite, nickel (Ni) ferrite, lithium (Li) spinel ferrite, yttrium iron garnet (YIG), aluminium (Al) substituted YIG, gadolinium (Gd) substituted YIG, calcium (Ca) substituted YIG, hexaferrites such as barium (Ba) ferrite and strontium (Sr) ferrite [77, 32]. YIG is used as a typical tunable ferrite material [31, 32] and (LiFe)0.5Fe2O4 can also be used [31]. In addition, the hexaferrites have been studied because they would decrease electromagnetic heat and hysteresis, and they would improve tuning linearity [78, 79]. The hexagonal ferrites have been reported for applications at W band (up to 110 GHz) [35]. YIG films have been studied for MSW (magnetostatic wave) devices [36].

1.3.1.3 Semiconductors

The DC and radio frequency (RF) performances of solid-state devices depend on the properties of semiconductor materials, and the combination of the mechanical, thermal, and electrical properties of the fabricated semiconductor contributes to the DC and RF properties of the semiconductor device [80]. There are preferable properties such as a wide energy gap, low relative permittivity, high thermal conductivity, and a high electrical breakdown field [80]. Energy gap is related to the capability to support an internal electric field. Relative permittivity indicates that the capacitance loading of a device and the terminal impedance. Thermal conductivity demonstrates that the ability to remove heat from a device [80]. Silicon (Si), gallium arsenide (GaAs), indium phosphide (InP), silicon carbide (SiC), gallium nitride (GaN), diamond, and related compounds are used for conventional devices [80].
In the literature, there are applications for electrically tunable devices based on semiconductors such as Si varactors [38], GaAs varactors [38], GaAs MMIC (monolithic microwave integrated circuits) active inductors [41], GaAs laser [40], and InGaAsP-InP filters [81].

### 1.3.1.4 High temperature superconductors (HTSs)

HTSs show superconductivity at more than 25 K compared with metal superconductive materials [43]. A characteristic of HTSs is low surface resistance [44, 82]. This low resistance makes Q factors of HTSs high because HTSs take out conductive losses [82]. There are three major HTS microwave filters: i) HTS thin film planar filters, ii) hybrid dielectric/HTS filters, and iii) HTS thick film coated filters [44]. In addition, there are HTS materials such as yttrium-barium-copper-oxide compound (YBa$_2$Cu$_3$O$_{7-δ}$, YBaCuO) for electrically tunable devices [83, 47] and magnetically tunable devices [84], and thallium compound (Tl$_2$Ba$_2$CaCu$_2$O$_y$) for magnetically tunable devices [85].

### 1.3.1.5 Acoustic wave materials

The velocities of surface acoustic waves (SAWs) are some $10^5$ times smaller than the electromagnetic waves (in air), and this property makes it possible to miniaturize the SAW devices because the devices are able to obtain a long delay on compact spaces [50, 49, 86-88]. Devices such as SAW bandpass filters are small, light [50, 49, 86-88], reliable [87], and rugged [87, 88] (and can be designed to possess very sharp frequency selectivity and/or a linear phase response). These devices are suitable for mass production due to the use of a simple technology such as lithography [49]. The most common method to generate acoustic waves is to use piezoelectric materials [50]. The upper frequency limit is determined by the device wavelength which is related to the fundamental material parameters, photolithographic line resolution, and manufacturing tolerances [86]. The maximum usable frequency, $f_{\text{max}}$, is given by the following equations with the electromechanical coupling coefficient, $k^2$, and the acoustic time constant, $\tau$ [50]

$$f_{\text{max}} = \frac{2k^2}{\pi^3 \tau}$$  \hspace{1cm} (1.3.1)

$$\tau = \frac{1}{2\pi f Q}$$  \hspace{1cm} (1.3.2)
where \( f \) = a nominal operating frequency and \( Q \) = a quality factor measured at the frequency, \( f \). The major requirements for the acoustic piezoelectric materials for the SAW devices are high acoustic velocity, high piezocoupling coefficient, and/or temperature stability (low temperature coefficient of delay (TCD) or frequency (TCF)) [50, 86, 88].

Most common crystalline piezoelectric materials are quartz (\( \alpha \)-SiO\(_2\)) [50, 86], lithium niobate (LiNbO\(_3\)), or lithium tantalate (LiTaO\(_3\)) [50, 49, 86, 88]. Other available piezo-materials are lithium tetraborate (Li\(_2\)B\(_4\)O\(_7\); LBO), GaAs, SiC [50], silicon nitride (SiN) [86], zinc oxide (ZnO) [50, 49, 86], aluminium nitride (AlN) [50, 49, 86], potassium niobate (KNbO\(_3\)) [50, 49], lead zirconate titanate (PZT) solid solutions [50, 49], and poly(vinylidene fluoride) (PVDF) [50]. Although LBO has reasonable piezocoupling coefficient, wave velocity, and TCD [86], LBO can be dissolved in water and acid [88]. Beside these materials, langasite, ultrahard piezoelectrics, sapphire [50, 86], diamond [50, 49, 86], and piezomagnets are drawing attention [50]. The langasite (La\(_3\)Ga\(_5\)SiO\(_{14}\)) family which consists of langanite (La\(_3\)Ga\(_{11/2}\)Nb\(_{1/2}\)O\(_{14}\)) and langatate (La\(_3\)Ga\(_{11/2}\)Ta\(_{1/2}\)O\(_{14}\)), has disordered structures. Therefore, totally ordered (Ca, Sr)\(_3\)(Nb, Ta)Ga\(_5\)Si\(_5\)O\(_{14}\) crystals are expected to be stiffer, and to have lower dielectric permittivity and higher piezo-coupling [50]. Ultrahard binaries and diamond exhibit high acoustic-wave velocities [50]. Piezomagnetic acoustic materials are promising for future devices. Stable biasing magnets of neodymium-iron-boron (NdFeB) alloys and rare earth compounds such as samarium cobalt or samarium cobaltide (SmCo\(_5\)) have become available for the devices because biased magnetostriction is equivalent to piezomagnetism [50]. There are hybrid SAW devices such as poled piezoelectric material, Pb(Mn\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-Pb(Zr, Ti)O\(_3\) mounted on a LBO single crystal [89] or GaAs on LiNbO\(_3\) [52]. In order to improve withstanding power, electrodes have been investigated on the modification of aluminum (Al) with copper (Cu), nickel (Ni), magnesium (Mg), titanium (Ti), or tungsten (W), and on epitaxial Al [49]. SAW devices with a frequency multiplication have operated at \( \sim 6 \) GHz [53].

1.3.2 Ferroelectric and incipient ferroelectric materials

Some ferroelectric materials show the DC field dependence of relative permittivity, and ferroelectric tunable devices, in general, are based on this property. Requirements for these materials will be discussed later in detail (Sect. 1.4). Some materials of which the DC dependence of dielectric constant have been studied are summarized in Sect. 1.3.2.1. Thus all the materials described in the section below do not show high dielectric tunability. Sect. 1.3.2.2 will discuss major materials for microwave tunable applications.
1.3.2.1 Ferroelectrics and incipient ferroelectrics

Ferroelectrics and related materials studied for the DC field dependence of relative permittivity

Information on relative permittivity of various ferroelectrics and incipient ferroelectrics investigated at DC bias fields are compiled in the Landolt-Börnstein figures and tables [90, 91]. Oxide type materials studied are as follows: i) simple perovskite-type oxides such as potassium tantalate (KTaO$_3$) [92, 93], calcium titanate (CaTiO$_3$) [93], strontium titanate (SrTiO$_3$) [94, 95] (oxygen isotope exchanged SrTiO$_3$ [96]), barium titanate (BaTiO$_3$) [97, 98], cadmium titanate (CdTiO$_3$) [94], and lead zirconate (PbZrO$_3$) [99], ii) complex perovskite-type oxides like (Ln$_{1/2}$Na$_{1/2}$)TiO$_3$ (Ln = La and Nd) [93], lead scandium tantalate (Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ (PST)) [100, 101], lead indium niobate (Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$ (PIN)) [102], lead magnesium niobate oxide or lead magnesium niobate (Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN)) [103, 104], lead zinc niobate (Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ (PZN)) [105], and barium zirconium titanate (zirconium-modified barium titanate; Ba(Ti, Zr)O$_3$ (BTZ or BZT)) [106, 107], iii) solid solutions with perovskite-type oxides as end members, for example, barium strontium titanate ((Ba, Sr)TiO$_3$ (BST)) [97, 108-110], lead strontium titanate ((Pb, Sr)TiO$_3$) [111, 108], barium lead titanate ((Ba, Pb)TiO$_3$) [108], barium titanate stannate, barium titanium tin oxide, or barium titanostannate solid solutions of barium titanate and stannate (Ba(Sn, Ti)O$_3$) [106, 109], lead zirconate titanate or lead titanium zirconium oxide (Pb(Ti, Zr)O$_3$ (PZT)) [112, 109], barium lead zirconate ((Ba, Pb)ZrO$_3$) [113, 114], lead strontium zirconate ((Pb, Sr)ZrO$_3$) [114], potassium tantalate niobate ((KTa$_{1-x}$Nb$_x$)O$_3$ (KTN)) [115], silver tantalate niobate (Ag(Ta$_{1-x}$Nb$_x$)O$_3$ (ATN)) [116], (1-x)PMN-(x)PT (PT: lead titanate (PbTiO$_3$)) [109], and (1-x)PZN-(x)PT [117], iv) ternary or more than ternary solid solutions with perovskite-type oxides as constituents like (Pb, La)(Ti, Zr)O$_3$ (PLZT) [118, 109], (Ba, Ln)(Ti, M)O$_3$ (Ba$_{1-x}$Ln$_x$Ti$_{1-x}$M$_x$O$_3$; Ln = La, Sm, Gd, Dy; M = Al, Fe, Cr) [119], (Pb, La)(Ti, Zr, Sn)O$_3$ (PSnZT) [109], (Pb, La$_{0.5}$Li$_{0.5}$)(Ti, Zr)O$_3$ (PLLZT) [120], and Pb(Mg$_{1/3}$W$_{1/3}$)O$_3$-PbTiO$_3$-Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ (xPMW-0.35PT-(0.65-x)PNN) [121], v) tungsten bronze type oxides such as barium strontium niobate ((Ba, Sr)Nb$_2$O$_6$ (SBN)) [122], and vi) pyrochlore structure oxides such as cadmium pyroniobate (Cd$_2$Nb$_2$O$_7$) [123, 124].

Other than these oxide materials, inorganic substances, organic compounds, liquid crystals, and polymers have also been investigated. These are as follows: i) inorganic materials such as antimony sulfide iodide (SbSI) [125], sodium nitrite (NaNO$_2$) [126], rubidium nitrate (RbNO$_3$) [127], potassium di-hydrogen phosphate (KH$_2$PO$_4$ (KDP)) [128], ammonium sulfate ((NH$_4$)$_2$SO$_4$) [129], potassium iodate (KIO$_3$) [130] and related compounds [131], and alums such as (NH$_4$)Fe(SO$_4$)$_2$•2H$_2$O [132], ii) organic materials like dicalcium lead propionate
Various film samples have been prepared based on the above materials, especially oxides. In addition to these systems, niobium potassium sodium oxide (sodium potassium niobate; Na$_{0.5}$K$_{0.5}$NbO$_3$ (NKN)) [140], bismuth strontium tantalum oxide (strontium bismuth tantalate; SrBi$_2$Ta$_2$O$_9$ (SBT)) [141], bismuth zinc niobate (Bi$_2$O$_3$-ZnO-Nb$_2$O$_5$ (BZN)) pyrochlore [142, 143], and Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ (BMT) [144] films have been investigated.

We have selected (Pb, Sr)TiO$_3$ systems as a potential candidate among various materials. Sect. 1.4 will discuss the reasons for the selection.

1.3.2.2 **Typical ferroelectrics and incipient ferroelectrics for tunable microwave devices**

Typical tunable microwave incipient ferroelectrics and ferroelectrics are strontium titanate (SrTiO$_3$ (ST or STO)) [16, 36, 23], potassium tantalate (KTaO$_3$ (KT or KTO)) [16, 37, 23], and barium strontium titanate ((Ba$_{1-x}$Sr$_x$)TiO$_3$ (BST or BSTO)) compositions [16, 37, 23, 145, 146].

Besides these materials, materials which have been studied for microwave frequency properties are niobium potassium sodium oxide (Na$_{0.5}$K$_{0.5}$NbO$_3$ (NKN)) [147, 37, 140, 148], lead magnesium niobate (Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN)) [149], barium zirconium titanate (Ba(Ti, Zr)O$_3$ (BZT)) [150], bismuth strontium tantalum oxide (SrBi$_2$Ta$_2$O$_9$; SBT) [141], lead zirconate titanate (Pb(Zr, Ti)O$_3$ (PZT)) and donor doped PZT (e.g., La: (Pb, La)(Zr, Ti)O$_3$ (PLZT)) [149, 151], niobium silver tantalum oxide (Ag(Nb, Ta)O$_3$ (ATN)) [148], lead strontium titanate ((Pb, Sr)TiO$_3$ (PST or SPT)) [111], and Pb$_{0.99}$[Nb$_{0.02}$(Zr$_{1-x}$Sn$_x$)Ti$_{0.02}$]$_{0.98}$O$_3$ [149].

1.4 **Requirements for tunable ferroelectrics and possible applications**

- **Requirements and a figure of merit for tunable microwave ferroelectric applications and possible tunable microwave devices**

As described in Sect. 1.1, the major microwave applications are for ovens, radar, and communications. Applications for dielectrics to circuit elements are for dielectric resonators, dielectric substrates, dielectric guided wave lines, and capacitors [4]. Major required properties for conventional linear microwave dielectrics are as follows: i) reasonable relative permittivity, $\varepsilon_r$, ii) high Q factor (low tangent $\delta$) or high Q $\times$ frequency, and iii) low temperature coefficient of
frequency. A figure of merit for these systems is \( Q \times \) frequency. Some microwave dielectric ceramic applications are oscillators, filters, circuit substrates, wave-guided lines, dielectric antennas, and capacitors [4].

However, tunable microwave ferroelectrics need to have not only similar properties to the conventional microwave dielectrics but also some different properties. Several requirements for the ferroelectrics are i) reasonable \( \varepsilon_r \), ii) reasonable tunability, iii) high \( Q \) (or high \( Q \times \) frequency), iv) high \( K \)-factor (tunability \( \times \) \( Q \)), and v) high breakdown DC field. Additionally, vi) easy processing to prepare samples with specific transition temperatures, and vii) capability of thin film forms are required.

Each application needs a specific relative permittivity, especially to obtain the impedance match for other elements, and 50 \( \Omega \) is a typical impedance value. Unless materials show the DC field dependence of relative permittivity, the materials are not useful for the tunable devices. Required values of tunability are dependent on the applications. Dielectrics used for microwave applications are required to have high \( Q \). Similarly, microwave ferroelectrics should possess high \( Q \). As shown in Fig. 1.4.1, ferroelectrics show lower tangent \( \delta \) (high \( Q \)) in paraelectric regions at low frequencies (e.g., 10 kHz) before starting to increase tangent \( \delta \) far from the transition temperatures and close to the dielectric constant maxima at the phase transitions. Therefore, the materials should be used over the temperature range in which tangent \( \delta \) is low. Generally, \( Q \times \) frequency is to be considered constant at the microwave range unless a resonance does occur. Thus the value, \( Q \times \) frequency, is considered as a figure of merit for the microwave dielectrics. Regarding the tunable ferroelectrics, a figure of merit is \( K \)-factor, and high values are preferable for any kind of application. Because dielectric tunability becomes higher under higher DC fields, high breakdown DC field is desirable. In addition, higher tunability is observed closer to the phase transition, but tangent \( \delta \) also increases close to the phase transition temperature (Fig. 1.4.1). In order to obtain a reasonable \( K \)-factor, it is important to be able to control the phase transition temperature of a material. There are applications which need thin film forms. Therefore, it is advantageous to be able to fabricate thin films.

Various tunable applications have been reviewed in the literature [15, 16, 37, 23]. Filters [16, 37], phase shifters [16, 37, 23, 152-154], and varactors [37, 23] have been widely studied. Additionally, antennas [16, 155], amplifiers [15], capacitors [23], harmonic generators [15], limiters [16, 156], oscillator [16], phased arrays [37], phase modulator and mixer [15], resonators
Figure 1.4.1 Relative permittivity and tangent $\delta$ of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ ceramics as a function of temperature at 10 kHz upon cooling.
[157], substrates [23], switches [158], and wave detector [16] are considered as applications to need field dependent properties of ferroelectric or incipient ferroelectric materials.

In this section, changing resonant frequencies focuses on a change in relative permittivity (capacitance). However, other properties such as waveguide length, transmission line phase velocity, or refractive index are also available for these tunable devices. Fig. 1.4.2 shows tunable communication, sensor systems, and frequency agile properties for the tunable microwave application systems [159].

1.5 Merits of ferroelectric solid solution systems

− Necessity for tunable devices and DC field dependent ferroelectrics, and merits of solid solution systems over single phase systems −

In Sect. 1.3, various tunable materials are described. Among materials available for the creation of tunable devices, ferroelectrics are the most promising for inexpensive tunable microwave applications.

When non-tunable filters are used in a device, the number of necessary filters depend on the number of necessary frequencies. If a filter has various resonant frequencies, then the number of the filters will be reduced. Because there is a relationship between relative permittivity and resonant frequency in a setup (Fig. 1.5.1), a change in the relative permittivity means a change in the resonant frequency. DC field dependant ferroelectrics can change their relative permittivity with DC electric fields (Fig. 1.5.2). Thus these materials have the potential to reduce the number of parts in the devices.

An important requirement for these applications is a reasonable K-factor. Because dielectric tunability and tangent δ are increased as temperatures approach the dielectric constant maximum temperatures, the tangent δ values are reasonable in a specific temperature range above the transition temperatures. Thus it is required to control the transition temperature of the system to obtain reasonable K-factors, namely, reasonable tunability and tangent δ at an operating temperature. Solid solution systems which are able to modify the transition temperatures of these systems depending on their compositions are superior to the other ferroelectric single component systems.
MEMS, Microelectromechanical systems; FE, Ferroelectric; VCO, Voltage controlled oscillator.

$\Delta \varepsilon_{\text{r, eff}}$: Change in relative dielectric constant; $\Delta \lambda_g$: Change in waveguide length; $\Delta C$: Change in capacitance; $\Delta V_p$: Transmission line phase velocity; $\Delta n$: Change in refractive index; $\Delta f_0$: Change in resonant oscillating frequency; $\Delta \phi$: Change in insertion phase; $\Delta \tau$: Change in TTD (true time delay).

After Korn and Wu [159].
Figure 1.5.1 Relationship between relative permittivity and resonant frequency of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ ceramics using the parallel plate dielectric post resonator method at various temperatures.

Figure 1.5.2 Relative permittivity of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ ceramics as a function of DC bias field at 10 kHz.
1.6 Comparison of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) with the main tunable candidate (Ba$_{1-x}$Sr$_x$)TiO$_3$ (BST) – Main candidate BST, problems of BST, characteristics of SPT, and advantages of SPT over existing materials like BST –

Barium strontium titanate (BST) so far is the main candidate for tunable microwave ferroelectrics and has been widely studied (Sect. 1.3.2.2). The transition temperatures ($T_m$) of the BSTs vary from the $T_m$ of barium titanate (BT) ~ 130 °C [160] to lower temperatures (quantum paraelectric transition temperature ($T_{QPE}$) of strontium titanate ($T_{QPE}$: ~ 4K) [161] depending on samples) determined by the mole fraction of strontium [162-164]. Upon cooling, BT has three ferroelectric phase transitions from cubic to tetragonal, to orthorhombic, to rhombohedral [165], and strontium titanate does not show any ferroelectric phase transition [166]. Thus the phase transitions of BT reflect on the phase transitions of BST depending on the compositions [162-164]. A linear relationship between the mole fraction of strontium (or barium) and transition temperatures from the paraelectric to ferroelectric states based on dielectric constants was not observed clearly when BST contained less than 80 % strontium [162, 163]. Furthermore, inconsistency has been reported in the properties of typical tunable ferroelectric BST [34].

On the contrary, the (Sr, Pb)TiO$_3$ (SPT) system can change the transition temperatures from ~490 °C ($T_m$ of PbTiO$_3$ (PT)) [167] to lower temperatures [168, 169] when SPT is cooled. Dielectric constant vs. temperature plots show one maximum because PT has one phase transition from cubic to tetragonal upon cooling [170]. Dielectric constant maximum temperatures tended to be linearly proportional to the mole fraction of lead [168, 169] over wide composition ratios of samples.

Moreover, the SPT system has an advantage of easy processing. The highly possible raw chemicals for the preparation of BST are barium carbonate (BaCO$_3$) (or barium oxide (BaO)), strontium carbonate (SrCO$_3$), and titanium oxide (TiO$_2$), and those for SPT are lead oxide (PbO), SrCO$_3$, and TiO$_2$. The easy preparation of the SPT system would be expected due to the high reactivity of PbO compared with that of BaO resulted from the decomposition of BaCO$_3$. One of the indexes to evaluate the quality of ferroelectrics is relative permittivity, and we have prepared the SPT of which the relative permittivity was more than 20000 at the transition temperatures [171].

In addition, Sharpe and Brockus investigated the tunability and tangent $\delta$ of various materials, and the (Sr, Pb)TiO$_3$ system showed good properties [111]. Amoss et al. studied several ferroelectrics for the microwave switches and found that Sr$_{0.685}$Pb$_{0.315}$TiO$_3$ was the best in
performance among the materials they tested, for example, barium strontium titanate, lead calcium titanate, lead strontium nickel titanate, and lead strontium erbium titanate [158].

Table 1.6.1 summarizes comparisons between SPT and BST. Easy processing is a merit of the SPT system.

1.7 References

Table 1.6.1 Comparisons between SPT and the main tunable microwave ferroelectric, BST

<table>
<thead>
<tr>
<th></th>
<th>SPT</th>
<th>BST</th>
</tr>
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<tbody>
<tr>
<td>Reactivity among raw chemicals</td>
<td>high</td>
<td>not high</td>
</tr>
<tr>
<td>Chemistry (stoichiometry)</td>
<td>good</td>
<td>poor***</td>
</tr>
<tr>
<td></td>
<td>(present study)</td>
<td>(invariably difficult to achieve)</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>moderate</td>
<td>poor***</td>
</tr>
<tr>
<td></td>
<td>(present study; prepared under similar conditions)</td>
<td></td>
</tr>
<tr>
<td>Frequency dependence of</td>
<td>relatively low</td>
<td>moderate</td>
</tr>
<tr>
<td>relative permittivity</td>
<td>(present study)</td>
<td></td>
</tr>
<tr>
<td>Potential maximum temperature (°C)</td>
<td>~490 (Sr = 0 %)</td>
<td>~130 (Sr = 0 %)</td>
</tr>
<tr>
<td>Phase transition</td>
<td>1</td>
<td>3 (depending on composition)</td>
</tr>
<tr>
<td>Tangent δ (at low frequency and in paraelectric states)</td>
<td>relatively very low</td>
<td>moderate</td>
</tr>
<tr>
<td></td>
<td>(present study)</td>
<td></td>
</tr>
<tr>
<td>Relative permittivity</td>
<td>can be tailored</td>
<td>can be tailored</td>
</tr>
<tr>
<td>Tunability *</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>Composite properties**</td>
<td>relatively</td>
<td>not highly reproducible***</td>
</tr>
<tr>
<td>(e.g., relative permittivity)</td>
<td>reproducible</td>
<td>(special process needs)</td>
</tr>
<tr>
<td>Breakdown strength (Composites at RT)</td>
<td>high</td>
<td>moderate</td>
</tr>
<tr>
<td></td>
<td>(present study)</td>
<td></td>
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</tbody>
</table>

SPT, (Sr_{1-x}Pb_{x})TiO_{3}; BST, (Ba_{1-x}Sr_{x})TiO_{3}; Composite, i.e., ferroelectric and at least one additional phase, for example, in order to tailor the relative permittivity of the ferroelectric.

RT : room temperature.

*: depending on composition and measurement temperature.

**: SPT or BST and non ferroelectric and low relative permittivity oxide.

***: Special process allows the properties of BST to improve.


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Chapter 2
STATEMENT OF THE PROBLEM

2.1 Properties of SrTiO$_3$-PbTiO$_3$ solid solution system

Main requirements for frequency agile ferroelectric materials are as follows: to have i) direct current (DC) field dependence of relative permittivity, ii) low tangent $\delta$ (i.e., high Q), and iii) high reproducibility of properties. Strontium titanate and lead titanate (SrTiO$_3$-PbTiO$_3$) solid solution system has been selected as a potential candidate and studies on this system are the basis of this thesis work. Highest priorities of this study is to prepare samples which possess reproducible dielectric properties and low tangent $\delta$ and to carry out dielectric property measurements at low and high frequencies.

The SrTiO$_3$-PbTiO$_3$ solid solution system is prepared from moderate purity strontium carbonate (SrCO$_3$), lead oxide (PbO), and titanium oxide (TiO$_2$) using the conventional mixed oxide method. Because PbO tends to evaporate during heating, it is important to prepare high quality solid solutions.

Furthermore, it is important to be able to control the transition temperature of the solid solution system in order to achieve a high K-factor $Q = \frac{\text{tunability}}{\text{tangent } \delta}$ because dielectric tunability and tangent $\delta$ become higher as temperatures are closer to the transition temperature of the ferroelectric. Therefore, a solid solution system which shows a linear relationship between weak field dielectric constant maximum temperatures and compositions (i.e., the mole fraction of a component) is preferable. Moreover, it is desirable that the tunability and tangent $\delta$ in a specific temperature range above the transition temperature show a low composition dependence because the design of the system becomes simple if the properties do not show a composition dependence.

2.2 Composite systems

Because microwave application materials should take in consideration to the impedance match for devices, the reasonable range of relative permittivity exists. However, the relative permittivity of the SrTiO$_3$-PbTiO$_3$ solid solution system is higher than that of the desirable values. Therefore, the relative permittivity of the solid solutions should be tailored by the addition of materials. The materials used for tailoring the relative permittivity should be selected
from linear dielectric and non-ferroelectric oxides which have low reactivity with the solid solutions, especially PbO. Reasons are that linear dielectric and non-ferroelectric oxides would have relatively low dielectric constants and low tangent $\delta$ and that a complicated reaction between the oxides and PbO might ruin the tunability of the system and increase the tangent $\delta$ of the system. Additionally, a merit to use the non-ferroelectric oxides is that their properties such as relative permittivity and tangent $\delta$ would be independent of operating temperatures and frequencies. Magnesium oxide (MgO) is selected as a potential oxide. With caution, processing conditions have to be selected so that the effective tunability of the ferroelectric in the composite system would remain high and that the tangent $\delta$ of the composite system would become low.

The major research targets of the composite systems will address the characterization of tunability, tangent $\delta$, and microwave frequency properties, and maximum DC bias fields which the composites are able to withstand.

The properties of the composites could be dependent on non-ferroelectric oxides. If composites resulted from reactions between $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ (SPT) and an oxide (or oxides) show moderate tunability, low tangent $\delta$, and reasonable relative permittivity, one may select the oxide (or oxides) which have the possibility to react with SPT. Consequently, it is attractive to explore oxides, for example, aluminum oxide ($\text{Al}_2\text{O}_3$), magnesium aluminum oxide ($\text{MgAl}_2\text{O}_4$), tin oxide ($\text{SnO}_2$), and zirconium oxide ($\text{ZrO}_2$). These oxides are also worth studying in the composite form.

The relative permittivity of ferroelectrics, in general, show a temperature dependence. However, tunable materials with low temperature coefficients of relative permittivity are preferable. Therefore, it is also important to develop composites which have the low temperature coefficients of the relative permittivity and reasonable K-factors.

2.3 Outline of the thesis

This thesis will discuss the investigation of lead strontium titanate (SPT) into its preparation, relative permittivity, tangent $\delta$, and the DC bias dependence of dielectric properties, and the composition dependence of transition temperatures. In addition, the Curie-Weiss analysis is applied for the SPT system because these materials are used in paraelectric regions and the analysis is a method to characterize relative permittivity behaviors in the paraelectric states. Among the SPT system with various compositions, $(\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3$ is selected and studied in detail to understand the SPT solid solution system. A phase diagram based on relative permittivity is also completed with the SPT $(x = 0.05 - 0.30)$. 
In addition to the investigation of the SPT system, this thesis will discuss composite systems prepared from SrTiO$_3$-PbTiO$_3$ solid solutions and linear dielectric oxides. Research targets will include the preparation of the SPT-MgO composites, dielectric properties with or without DC field dependence, DC field strength, and microwave frequency dielectric properties. The effect of the composition of SPT and MgO has also been studied. Furthermore, composites are prepared from SPT and various oxides such as Al$_2$O$_3$, MgAl$_2$O$_4$, SnO$_2$, or ZrO$_2$ to develop tunable ferroelectric composites.
Chapter 3
MEASUREMENTS, RESULTS, AND DISCUSSION ON THE CHARACTERISTICS OF PURE (Sr$_{1-x}$Pb$_x$)TiO$_3$ SOLID SOLUTIONS

3.1 Sample preparation

- Processing of SrTiO$_3$-PbTiO$_3$ solid solution system -

Strontium lead titanate solid solution system was prepared by the conventional mixed oxide method. Suitable ratios of strontium carbonate (e.g., 99.9% purity SrCO$_3$, Aldrich), lead oxide (e.g., 99.9% purity PbO, Aldrich), and titanium oxide (e.g., 99.5% purity TiO$_2$, Alfa Aesar, 0.3 mol) were put in a plastic container (e.g., 500-mL propylene container) with yttrium-stabilized zirconia balls (e.g., 5-mm diameter, 200 g) and 2-propanol (e.g., A. C. S. spectrophotometric grade, ≥99.5% purity, Aldrich, 75 mL). 0.02 mol% extra PbO was added to the raw chemicals to compensate for weight loss during heating. The mixture was ball milled for 8 h and balls were removed from the mixture with a plastic sieve. Subsequently, the mixture was dried at room temperature and then in an oven at 80 °C for 3 h. The dried mixture was sieved with an 80-mesh plastic sieve (opening size: 180 µm), and the agglomerated powders were ground with an agate mortar and pestle. The sieved mixture was calcined in a platinum (Pt) dish covered by a Pt lid within an aluminum oxide (Al$_2$O$_3$) sagger at 1100 °C for 3 h. The heating rate was 5 °C per min and cooling rate was 2.5 °C per min. After the above procedure, the calcined powders were ball milled again for 20 h (e.g., 25 g calcined powders in a 60-mL plastic container with 100 g balls and 30 mL 2-propanol). Because the diameter of the 60-mL containers was shorter than the distance between two adjacent roles of a ball milling machine, the 60-mL container was placed in a special container of which the diameter was larger than the distance between the rolls. After ball milling, ball milled powders were dried and sieved in a way similar to that for the mixture of raw chemicals. The aggregated powders were ground in a yttrium-stabilized zirconia mortar with the same material pestle. The sieved reactants were pressed in a pellet form under low uniaxial pressures (e.g., 100 pounds for count 10, three times; 200 pounds for count 10, three times; 300 pounds for count 10, once; and 500 pounds for 30 seconds for 3/8-in (~0.95-cm) metal or plastic die) and then under an isostatic pressure, for example, 2500 kg/cm$^2$, at room temperature for 15 min. Pellets were sintered in the Pt dish in a sagger (e.g., Al$_2$O$_3$ or magnesium oxide (MgO)) at 1350 °C for 3 h to heat at a rate of 5 °C per min and to cool at a rate of 2.5 °C per min. To avoid weight loss during heating, the pellets were covered
with the sieved and calcined powders (e.g., sample-calcined powders (1:1 by weight) and the mixture of calcined lead zirconate (PZ) and zirconium oxide (Z) (e.g., PZ-Z (90:10 by weight); lead source was prepared from 99.999% purity PbO and 99.978% purity zirconium oxide (ZrO₂) and calcined in a tall flat-bottomed crucible (MgO) at 850 °C for 3 h; heating and cooling rates, 5 °C per min) was put on the outside of the Pt lid (the lead source weight was more than the sample weight: e.g., lead source-sample (2:1 by weight)). The lead source, the mixture of PZ and Z, was also pressed before using it.

The surfaces of the samples were polished with silicon carbide (SiC) grinding powders (e.g., #600: average grain size, 14 μm) as a final treatment. After polishing the pellets, the X-ray diffraction patterns of the samples were collected. Before dielectric property measurements were taken, the samples were coated with gold after the samples were annealed at 700 °C for 3 h on a Pt sheet on a ceramic plate (e.g., Al₂O₃). The heating rate was 10 °C per min and the cooling rate was 2.5 °C per min. Unnecessary gold was removed from the surfaces of the samples by sand paper (#600).

Silver wire was bonded on the surfaces of a sample with silver paste for cryogenic temperature dielectric property measurements. After the paste was dried, the samples were measured.

### 3.1.1 Reproducible data

Fig. 3.1.1.1 (a) and (b) show the dielectric properties of (Sr₁₋ₓPbₓ)TiO₃ (SPT) (x = 0.2) ceramic samples sintered in aluminum oxide (Al₂O₃) ceramic containers and a platinum (Pt) dish (in a sagger), respectively. The setups are shown in Fig. 3.1.1.2. Because samples sintered in the Pt dish possessed similar relative permittivity maxima as a function of temperature, the SPT ceramics should be sintered in the Pt dish. The high density Al₂O₃ ceramics might have low reactivity with lead oxide (PbO) but they might absorb the PbO during heating. Therefore, it could be difficult to achieve the similar atmosphere without heating the containers before using the containers which were used for heating materials with PbO.

Meanwhile, the Pt containers might be damaged by PbO at high temperatures such as sintering temperature, but the Pt containers are not expected to absorb the PbO. Additionally, at high temperatures, a Pt lid and Pt dish might make a closed system because of the deformation of the Pt due to the heat. Thus the Pt containers might offer a more similar atmosphere than the Al₂O₃ containers. These characteristics might be helpful to prepare samples which show similar dielectric constant maxima.
Figure 3.1.1 Relative permittivity and tangent δ of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.2$) ceramics sintered in different containers. (a) aluminum oxide containers and (b) platinum dish as a function of temperature at 10 kHz upon cooling. Sample 1 and Sample 2 were sintered in a similar setup; the setup is shown in Fig. 3.1.2 (a). Sample 3 and Sample 4 were sintered in a similar setup; the setup is shown in Fig. 3.1.2 (b).
Figure 3.1.2 Sintering setups for (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2) ceramics of which the results are shown in Fig. 3.1.1. (a) aluminum oxide containers and (b) platinum dish. Note: The outside of an aluminum oxide container, in a saggar, was sealed with a sealing compound shown in plot (a). Samples were covered with sieved and calcined powders.
Although ball milling conditions have not been optimized to prepare the samples, it is important to prepare similar powders before pressing. Average particle sizes, the size distribution, and the effect of stress gained during the ball milling should be considered. Moreover, the calcined powders before the ball milling might influence the condition of the powders afterward. Thus calcination conditions, for example, the packing of raw chemicals in a container, should be taken into consideration.
3.2 Characterization of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (\(x = 0.20, 0.25, \text{ and } 0.30\)) solid solutions

Pure \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (\(x = 0.20, 0.25, \text{ and } 0.30\)) ceramics are characterized to understand various physical and electrical properties desirable for tunable ferroelectrics. Sect. 3.2.1 will discuss the properties of materials used for low frequency dielectric property measurements and Sect 3.2.2 will describe samples used for high frequency dielectric property measurements.

3.2.1 Properties of materials used for low frequency dielectric property measurements

3.2.1.1 Sample preparation

As described in Sect. 3.1, \((\text{Sr}, \text{Pb})\text{TiO}_3\) compositions were prepared from strontium carbonate (99.9%+ purity \(\text{SrCO}_3\), Aldrich), lead oxide (99.9% purity \(\text{PbO}\), Aldrich), and titanium oxide (99.5% purity \(\text{TiO}_2\), Alfa Aesar) by mixing suitable ratios of \(\text{Sr}:\text{Pb}:\text{Ti}\). 0.02 mol % additional \(\text{PbO}\) was added to the raw chemicals to compensate for weight loss during heating. The raw chemicals were ball milled with 5-mm-yttrium-stabilized zirconia balls and 2-propanol for 8 h and then calcined in a platinum (Pt) dish (in a sagger) at 1100 °C for 3 h. The reactant powders were ball milled again, pressed in a pellet form using a cold isostatic pressure of 3000 kg/cm², and sintered in the Pt dish placed in a sagger at 1350 °C for 3 h with a lead source. Samples were cut for dielectric property measurements because a blocking circuit limited the maximum capacitance of the samples. The blocking circuit was necessary to use in order not to break an LCR meter during direct current (DC) bias measurements. Before the electrodes were coated on the samples, they were annealed at 700 °C for 3h.

3.2.1.2 X-ray diffraction pattern

Structural phases within the samples at room temperature were identified by their X-ray diffraction (XRD)-patterns using Cu Kα as an X-ray source (PDIV, SCINTAG, Inc.) The peak positions were determined in the range between 20 and 130 degrees two-theta by the program developed by Toraya, “PRO-FIT” [1]. The lattice parameters were obtained using the external reference, silicon powders and the program named “UNITCELL” [2].

The XRD patterns of calcined powders are shown in Fig. 3.2.1 (a) and the plot shows that raw chemicals were all reacted to form \((\text{Sr}, \text{Pb})\text{TiO}_3\). Fig. 3.2.1 (b) shows the typical XRD patterns of the sintered products and indicates a single phase formation in the sintered pellets. The crystal system of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) (\(x = 0.20, 0.25, \text{ and } 0.30\)) was a simple cubic at room temperature, and the lattice parameters of the compositions were 3.913, 3.915, and 3.917Å, respectively.
Figure 3.2.1 Room temperature Cu K_\alpha X-ray diffraction patterns of (a) as calcined powders and (b) sintered pellets. (i) and (iv) (Sr_{0.8}Pb_{0.2})TiO_3; (ii) and (v) (Sr_{0.75}Pb_{0.25})TiO_3; (iii) and (vi) (Sr_{0.7}Pb_{0.3})TiO_3.
3.2.1.3 Dielectric properties at low frequency

Dielectric properties were measured at a weak AC field of 1 V/cm on the gold electrode deposited samples using an LCR meter (4284A, Hewlett Packard) with or without a blocking circuit. A step mode was used in cooling cycles except for thermal hysteresis measurements. The LCR meter and oven were controlled by computer interfaces and other necessary components.

Fig. 3.2.2 shows the dielectric properties of SPT (x = 0.20, 0.25, and 0.30) ceramics in the temperature range from 190 to −180 °C and at frequencies of 1 k, 10 k, and 100 kHz. The transition temperatures (T_m) of the compositions, −59, −24, and 10 °C, relative permittivity, 1200, 2400, and 9100, and tangent δ values, < 0.0005, < 0.0005, and < 0.001 were measured at 25 °C and at 10 kHz, respectively. No relaxor-like behaviors were observed in these compositions.

Fig. 3.2.3 shows the dielectric properties of the SPT ceramics (x=0.20, 0.25, and 0.30) at 10 kHz in both cooling and heating cycles. Hysteresis was not observed at more than 10 °C above the transition temperatures, and the differences of transition temperatures between cooling and heating cycles were about 1 °C. As the content of strontium (Sr) went up in the samples, the relative permittivity at the transition temperature and the tangent δ maximum values increased.

Fig. 3.2.4 shows the Curie-Weiss behaviors of the SPT (x = 0.20, 0.25, and 0.30) ceramics at 10 kHz based on the cooling results. The Curie-Weiss constant, C, of the SPT (x = 0.20, T_m = −59 °C) was 9 × 10^4 °C in the temperature range from 130 to −45 °C and its Curie-Weiss temperature, θ, was −53 °C from the data. The C of the SPT (x = 0.25, T_m = −24 °C) was 1 × 10^5 °C in the temperature range from 150 to −10 °C, and its θ was calculated as −19 °C. The C of the SPT (x = 0.30, T_m = 10 °C) was 1 × 10^5 °C in the temperature range from 185 to 30 °C, and its θ was calculated as 16 °C. The compositions show similar Curie-Weiss constants in paraelectric states over wide temperature ranges of more than 100 °C.

Fig. 3.2.5 shows the effect of the mole fraction of lead (Pb), x in (Sr_{1-x}Pb_x)TiO_3, on the transition temperatures of the SPT based on the dielectric constant maxima at 10 kHz upon cooling. A linear relationship between the compositions and transition temperatures was observed. Sect. 3.5 will discuss a more precise phase diagram.

3.2.1.4 Thermal expansion properties

The thermal expansion coefficients of samples that were cut to a similar length of the reference, 6.54 mm fused silica, were measured using a dilatometer (Theta Industries, Inc.) at a rate of 2 °C per min upon cooling. Linear thermal expansion coefficients were calculated using
Figure 3.2.2 Dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics (x = 0.2, 0.25, and 0.3) as a function of temperature and frequency. (a) (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$, (b) (Sr$_{0.75}$Pb$_{0.25}$)TiO$_3$, and (c) (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$.

Temperature range, from 190 to –180 °C; Frequencies, at 1 k, 10 k, and 100 kHz.
Figure 3.2.3 Thermal hysteresis of dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics ($x = 0.2$, 0.25, and 0.3) as a function of temperature at 10 kHz. (a) (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$, (b) (Sr$_{0.75}$Pb$_{0.25}$)TiO$_3$, and (c) (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$. 

Figure 3.2.3 Thermal hysteresis of dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics ($x = 0.2$, 0.25, and 0.3) as a function of temperature at 10 kHz. (a) (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$, (b) (Sr$_{0.75}$Pb$_{0.25}$)TiO$_3$, and (c) (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$. 

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Figure 3.2.4 Curie-Weiss behaviors of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x=0.2$, 0.25, and 0.3) at 10 kHz in cooling cycles.

(a) (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ : $T_m= -59^\circ$C; $\theta= -53^\circ$C; $C=9 \times 10^4$ oC ($-45 < T < 130$).

(b) (Sr$_{0.75}$Pb$_{0.25}$)TiO$_3$: $T_m= -24^\circ$C; $\theta= -19^\circ$C; $C=1 \times 10^5$ oC ($-10 < T < 150$).

(c) (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$: $T_m= 10^\circ$C; $\theta= 16^\circ$C; $C=1 \times 10^5$ oC ($30 < T < 185$).

$T_m$, Transition temperature; $\theta$, Curie-Weiss temperature; $C$, Curie-Weiss constant; $T$, temperature.
Figure 3.2.5 Effect of $x$ in $(\text{Sr}_1-x\text{Pb}_x)\text{TiO}_3$ ceramics on their transition temperatures. $x = 0.2, 0.25, \text{ and } 0.3$. Transition temperatures were based on relative permittivity at 10kHz upon cooling.
the results of the thermal expansion on the samples of different compositions. The transition temperature based on the thermal expansion was the minimum point of a curve calculated by differentiating the results for nine-order polynomial fitting of the observed data at a specific temperature range, $T_m+10 - T_m-5$ (i.e., $-45 - -60$ °C for the SPT ($x = 0.2$); $-25 - -10$ °C for the SPT ($x = 0.25$); $20 - 5$ °C for the SPT ($x = 0.3$)).

Fig. 3.2.6 shows the typical thermal expansion and thermal expansion coefficients of the SPT ($x = 0.20$, 0.25, and 0.30) ceramies in cooling cycles. Assuming that a linear relationship between thermal expansion and temperature, thermal expansion coefficient $1 \times 10^{-5}$ °C$^{-1}$, was observed in the same temperature range used for calculating the Curie-Weiss constants of compositions on $x = 0.20$, 0.25, and 0.30, respectively.

Fig. 3.2.7 shows the typical thermal expansion and thermal expansion coefficients of the SPT ($x = 0.20$, 0.25, and 0.30) upon both cooling and heating. The transition temperature of the SPT ($x = 0.20$) on cooling was $-57 \pm 0.7$ °C at an average of three results and the transition temperature on heating was $-56 \pm 1$ °C. The transition temperatures of the SPT ($x = 0.25$) upon cooling and heating were $-24$ °C and $-22$ °C, respectively. The SPT ($x = 0.30$) showed $7$ °C as the transition temperature upon cooling and $6$ °C as that upon heating.

Both relative permittivity and thermal expansion as a function of temperature showed similar transition temperatures.

### 3.2.1.5 Dielectric tunability

Dielectric properties were also measured at various applied electric DC fields with a blocking circuit in order to investigate the dielectric tunability of the samples. Fig. 3.2.8 shows the temperature dependence of the dielectric constants with DC fields at 10 kHz. Fig. 3.2.9 shows the relative permittivity of the compositions (shown in Fig. 3.2.8) on the magnified scale. The relative permittivity was suppressed at DC bias fields, and tangent δ remained small or decreased to smaller values. The SPT ceramics with $x = 0.20$ and 0.25 showed two kinds of suppression in relative permittivity at high DC bias fields and in the ferroelectric states. This inhomogeneity could be related to the high relative permittivity and high tangent δ peak as a function of temperature.

From the above measurements and additional experiments at room temperature, the dielectric tunability of these materials was evaluated by using the relation given by Eq. (3.2.1), and the results of tunability are plotted in Fig. 3.2.10.
Figure 3.2.6 Thermal expansion and thermal expansion coefficients of $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ ($x = 0.2, 0.25, \text{and } 0.3$) in cooling cycles.
Figure 3.2.7 Thermal expansion and thermal expansion coefficients of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2, 0.25, and 0.3) upon both cooling and heating. (a) (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$, (b) (Sr$_{0.75}$Pb$_{0.25}$)TiO$_3$, and (c) (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$. 
Figure 3.2.8 Dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.2$, 0.25, and 0.3) ceramics as a function of temperature and applied electric DC bias field at 10kHz.

DC fields: –20, –15, –10, –5, and 0 kV/cm.

thicker lines: relative permittivity; thinner lines: dielectric loss tangent.

Figure 3.2.8 Dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.2$, 0.25, and 0.3) ceramics as a function of temperature and applied electric DC bias field at 10kHz.

DC fields: –20, –15, –10, –5, and 0 kV/cm.

thicker lines: relative permittivity; thinner lines: dielectric loss tangent.
Figure 3.2.9 Dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.2$, 0.25, and 0.3) ceramics as a function of temperature and applied electric DC bias field at 10 kHz. Relative permittivity at 0 kV/cm is beyond this scale.
Figure 3.2.10 Dielectric tunability of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2, 0.25, and 0.3) ceramics as a function of temperature and DC bias field at 10 kHz. (a) (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$, (b) (Sr$_{0.75}$Pb$_{0.25}$)TiO$_3$, and (c) (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$. Values at 25 °C were obtained as the results of different runs.
Dielectric tunability was given by the following equation

\[
\% \text{dielectric tunability} = \frac{\varepsilon(E_0) - \varepsilon(E)}{\varepsilon(E_0)} \times 100 \quad (E_0 = 0 \text{ kV/cm}) \quad (3.2.1)
\]

where \(\varepsilon(E)\) is relative dielectric permittivity at a DC field of \(E\).

As shown in Fig. 3.2.10, 25 °C dielectric tunability, 3, 15, and 70 %, with a DC bias field of 20 kV/cm at 10 kHz were measured on compositions with \(x = 0.20, 0.25,\) and 0.30, respectively.

Fig. 3.2.11 shows the dielectric responses of \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) ceramics before and after DC bias field measurements (the measurement temperature range was transition temperature ± 40 °C; DC bias fields were 0 ~ 20 ~ –20 ~ 0 kV/cm and the step field was 5 kV/cm; the sample was heated more than 100 °C above the transition temperature in order to remove the DC bias measurement influence). Although applied DC bias fields suppressed the relative permittivities of the SPT \((x=0.20, 0.25,\) and 0.30) ceramics, only a small reduction in relative permittivity and almost similar tangent \(\delta\) values were observed on the samples before and after the E-field measurements.

3.2.1.6 Microstructure studies

The microstructures of the SPT \((x = 0.20, 0.25,\) and 0.30) ceramics were studied using a scanning electron microscope (S-3500N, Hitachi) with fractured surfaces sputtered lightly by gold to detect secondary electrons. Fig. 3.2.12 shows the microstructures observed on the samples of various compositions. Two types of small size pores were observed. These pores could have two causes: i) the evaporation of volatile materials such as lead oxide and ii) the insufficient growth of grains. However, these pores do not greatly affect the dielectric and field tunable properties of the samples. Although the effect of the pores on breakdown field strength has not been investigated, these pores could not be greatly affected based on the field strength of the SPT \((x = 0.2)\)-magnesium oxide (MgO) composites in Sect. 4.2.3.

3.2.1.7 Summary

\((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) \((x = 0.20, 0.25,\) and 0.30) ceramics were prepared by the conventional mixed oxide method, and their dielectric properties, thermal expansion, and microstructure were measured as means to characterize the quality of the samples. The three compositions studied showed similar Curie-Weiss constant values \(1 \times 10^5 \text{ °C}\) and thermal expansion coefficients
Figure 3.2.11 Dielectric properties of (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics at 10 kHz upon cooling before and after DC bias field measurement. Solid lines, properties before measurement; Dotted lines, properties after measurement.

DC bias measurement conditions: temperature range was transition temperature ± 40 °C and the maximum DC bias field was 20kV/cm; the sample was heated to more than 100°C above its transition temperature (based on relative permittivity maximum) after DC bias measurement.
Figure 3.2.12 Scanning electron microscope (SEM) images of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x=0.2, 0.25, and 0.3) ceramic fractures obtained to detect secondary electrons. (a) x = 0.2, (b) x = 0.25, and (c) x = 0.3.
The transition temperatures of the compositions, –59, –24, and 10 °C, were measured on x = 0.20, 0.25, and 0.30, respectively, and the transition temperatures demonstrated a linear relationship with the composition, x, the mole fraction of Pb in lead strontium titanate. The dielectric tunability, 3, 15, and 70 %, were measured on samples with x = 0.20, 0.25, and 0.30 at 20 kV/cm and at 10 kHz, respectively. The tangent δ values, less than 0.001, were measured at 25 °C and at 10 kHz on all these samples. Furthermore, the \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (x = 0.20, 0.25, and 0.30) ceramics showed similar dielectric behaviors in the paraelectric states.

The study suggests the potentiality of the (Sr, Pb)TiO₃ system for the field tunable devices. It is noted that high quality (Sr, Pb)TiO₃ in bulk forms, which shows high dielectric constant maxima and low tangent δ in the paraelectric states, is easier to be prepared compared to (Ba, Sr)TiO₃.

### 3.2.2 Materials used for high frequency dielectric property measurements

The relative permittivity and tangent δ of pure \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) were characterized at the microwave frequency range, up to ~ 1 GHz using the parallel plate dielectric post resonator method or Hakki-Coleman method. Sect. 3.2.2.1 will discuss the temperature dependence of dielectric properties of SPT (x = 0.2 and 0.3) with additional low frequency data measured using an LCR meter. Sect. 3.2.2.2 will discuss the room temperature dielectric properties of SPT (x = 0.2) prepared under different conditions.

#### 3.2.2.1 Temperature dependence of SPT (x = 0.2 and 0.3) with additional data at low frequency

##### 3.2.2.1.1 Sample preparation and characterization

As described in Sect. 3.2.1, (Sr, Pb)TiO₃ compositions were prepared and dielectric properties of the samples were measured at low and high frequencies.

The low frequency dielectric properties were measured using an LCR meter (4284A, HP) which was controlled by computer, and the computer also controlled an oven for temperature dependent measurements. The samples were coated with gold after the samples were annealed. The low frequency measurements were carried out after the high frequency property characterization.

Dielectric properties at the high frequency were obtained using samples without electrodes based on the parallel plate dielectric post resonator method, the Hakki-Coleman
method [3-5] with a network analyzer (8510C, HP) and an S-parameter detector (8515A, HP). Dielectric constants were calculated using the values of resonant frequencies in the resonator (the position of the S$_{21}$ peak based on TE$_{011}$), and tangent δ (or Q = 1/tangent δ) was calculated by using the width of the S$_{21}$ peak at –3 dB with additional data such as insertion losses and the thickness and diameter of a sample. Equations to calculate dielectric constants and loss tangents were described in the literature [6].

3.2.2.1.2 Results and discussion

Fig. 3.2.13 shows the relative permittivity and tangent δ of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.2) at low and high frequencies. Fig. 3.2.14 shows the relative permittivity and tangent δ or resonant frequency of the SPT (x = 0.2) as a function of temperature. Fig. 3.2.15 shows the relative permittivity and tangent δ of SPT (x = 0.3). Table 3.2.1 (a) lists a description of the SPT (x = 0.2 and 0.3) ceramic samples and Table 3.2.1 (b) summarizes dielectric properties.

The high frequency measurements inside the oven showed different tangent δ values from those measured without using the oven. For example, the tangent δ of the SPT (x = 0.2) at 26 °C was 0.0011 measured without the oven, while that was 0.0016 and 0.0015 (run 1 and 2: two separate measurements) measured with the oven. The different tangent δ values observed in the setups with and without the oven could be due to the difference of surface resistance of different conducting plates which were used in the setups. In addition, tangent δ values were determined without subtracting the contribution of surface resistance values to the tangent δ values. However, a significant difference in relative permittivity at the high frequency was not observed in the setups with and without the oven. For example, relative permittivity of the SPT (x = 0.2) at 26 °C was 1170 measured without the oven and 1165 (run 1 and 2) measured with the oven. Relative permittivity and tangent δ showed similar and reproducible values as the result of two separate measurements (run 1 and 2) measured in the oven (Table 3.2.1 (b) and Fig. 3.2.13). Thus dielectric properties were measured as a function of temperature.

Relative permittivity at the high frequencies and the low frequency such as 10 kHz are similar, but tangent δ at the high frequencies and low frequencies showed differences. This discrepancy is not able to be explained clearly. The LCR meter measures capacitance and tangent δ based on the null-balance circuit. This method assumes that AC fields are uniformly applied through a sample, while the parallel plate dielectric post resonator method assumes that AC fields are distributed through a sample. The discrepancy could depend on these differences...
Figure 3.2.13 Relative permittivity, $\varepsilon_r$, and tangent $\delta$ of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.20$) ceramics as a function of temperature and frequency.

Note:  
w/o Oven: measurements at a constant temperature without using an oven. 
w Oven: temperature dependent measurements in the oven. 
HF: measurements based on the parallel plate dielectric post resonator method (i.e., Hakki-Coleman method) from $\sim$ 1.7 to 0.3 GHz. 
10 kHz and 100 kHz: measurements using an LCR meter (based on the null-balance circuit method). 
Run1 and 2: two separate runs.
Figure 3.2.14 (a) Relative permittivity, $\varepsilon_r$, and tangent $\delta$ and (b) $\varepsilon_r$ and resonant frequency in a setup with (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.20$) ceramics.

Note: The results of run 1 shown in Fig. 3.2.13.

HF: measurements based on the parallel plate dielectric post resonator method (i.e., Hakki-Coleman method).

10 kHz and 100 kHz: measurements using an LCR meter (based on the null-balance circuit method).
Figure 3.2.15 Relative permittivity, $\varepsilon_r$, and tangent $\delta$ of $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ ($x = 0.30$) ceramics. (a) magnified scale regarding tangent $\delta$ (0 - ca. 0.015) and (b) scale of tangent $\delta$ (0 - ca. 0.6).

Note: HF: measurement based on the parallel plate dielectric post resonator method (Hakki-Coleman method).

10 kHz and 100 kHz: measurements using an LCR meter (based on the null-balance circuit method).
Table 3.2.1 (a) Description of SPT ceramic samples

<table>
<thead>
<tr>
<th>Description</th>
<th>Composition (Sr_{1-x}Pb_x)TiO_3</th>
<th>Diameter (D) (cm)</th>
<th>Thickness (T) (cm)</th>
<th>D/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>x = 0.20</td>
<td>1.04</td>
<td>0.50</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>x = 0.30</td>
<td>1.06</td>
<td>0.49</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 3.2.1 (b) Dielectric properties of SPT ceramic samples

<table>
<thead>
<tr>
<th>Description</th>
<th>Composition</th>
<th>HF w/o Oven at 26 °C (run 1)</th>
<th>HF w Oven at 26 °C (run 2)</th>
<th>HF w Oven at 26 °C</th>
<th>10 kHz at 26 °C</th>
<th>100 kHz at 26 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(Sr_{0.8}Pb_{0.2})TiO_3</td>
<td>ε_r = 1170, tan δ = 0.0011</td>
<td>ε_r = 1165, tan δ = 0.0016</td>
<td>ε_r = 1165, tan δ = 0.0015</td>
<td>1160, tan δ = 0.0001</td>
<td>1160, tan δ = 0.0001</td>
</tr>
<tr>
<td>2</td>
<td>(Sr_{0.7}Pb_{0.3})TiO_3</td>
<td>ε_r = 8545, tan δ = 0.0086</td>
<td>ε_r = 8790, tan δ = 0.0090</td>
<td>ε_r = 8665, tan δ = 0.0005</td>
<td>8660, tan δ = 0.0006</td>
<td></td>
</tr>
</tbody>
</table>

Note:
HF: measurements based on the parallel plate dielectric post resonator method.
Sample 1 was measured at ~1.21 GHz; Sample 2 was measured at ~0.45 GHz.
Run 1 and 2: two separate runs.
10 kHz and 100 kHz: measurements using an LCR meter (based on the null-balance circuit method).
w/o Oven: measurements at a constant temperature without using an oven.
w Oven: temperature dependent measurements in the oven.
of the measurement assumptions. The parallel plate dielectric post resonator method has the capability to measure a broad range of dielectric constant samples (e.g., up to 900) experimentally [6] and, theoretically, it does not have a specific limitation [e.g., 4]. However, the necessary conditions of samples to measure tangent \( \delta \) are not clear. Further investigations are necessary to understand the accuracy of dielectric properties, especially tangent \( \delta \) by the resonant method.

3.2.2.2 High frequency and room temperature dielectric properties of SPT (\( x = 0.2 \))

3.2.2.2.1 Sample preparation and characterization

Four kinds of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) \((x = 0.2)\) samples were prepared. Samples #1, sample #2, and sample #3 (the number of samples: 2) were prepared from raw purity chemicals, strontium carbonate (99.9% + purity \( \text{SrCO}_3 \), Aldrich), lead oxide (99.9% purity \( \text{PbO} \), Aldrich), and titanium oxide (99.5% purity \( \text{TiO}_2 \), Alfa Aesar). Lots of chemicals used for sample #1 were different from those of sample #2 and sample #3. Sample #2 and sample #3 were ball milled under different conditions. After calcination, powders for sample #2 and sample #3 (and sample #1) were ball milled for 20 h. Then the powders were sieved to form products with specific sizes of powders. The powders for sample #3, however, were ball milled again for an additional 4 h after sieving. Sample #4 (the number of samples: 2) was prepared from high purity raw chemicals, \( \text{SrCO}_3 \) (99.995% purity, Aldrich), \( \text{PbO} \) (99.9995% purity, Alfa Aesar), and \( \text{TiO}_2 \) (99.999% purity, Aldrich). The powders for sample #4 were ball milled for only 20 h after calcination.

Dielectric properties at high frequencies were obtained by the parallel plate dielectric post resonator method [3-5] with a network analyzer (8510C, HP) and an S-parameter detector (8515A, HP). Equations to calculate dielectric constants and loss tangents were described in the publication [6].

3.2.2.2.2 Results

Table 3.2.2 shows the summary of dimensions and dielectric properties of the four kinds of samples. All the samples showed similar relative permittivity at room temperature and at ~ 1 GHz, but these samples showed different tangent \( \delta \) values. Further investigation is required to understand and improve tangent \( \delta \) of SPT samples in a microwave frequency range.
Table 3.2.2 Description and dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2) ceramics based on the parallel plate dielectric post resonator method

<table>
<thead>
<tr>
<th>Description</th>
<th>Diameter, D (cm)</th>
<th>Thickness, T (cm)</th>
<th>D/T</th>
<th>Density (g/cm$^3$)</th>
<th>RD (%)</th>
<th>$\varepsilon_r$</th>
<th>$\tan \delta$</th>
<th>Q</th>
<th>Resonance freq, f (GHz)</th>
<th>$Q \times f$ (GHz)</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>1.04</td>
<td>0.50</td>
<td>2.1</td>
<td>-----</td>
<td>---</td>
<td>1170</td>
<td>0.0011</td>
<td>910</td>
<td>1.21</td>
<td>1100</td>
<td>26</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1.03</td>
<td>0.54</td>
<td>1.9</td>
<td>5.66</td>
<td>98</td>
<td>1246</td>
<td>0.0012</td>
<td>827</td>
<td>1.12</td>
<td>926</td>
<td>25</td>
</tr>
<tr>
<td>Sample 3-1</td>
<td>1.04</td>
<td>0.52</td>
<td>2.0</td>
<td>5.53</td>
<td>96</td>
<td>1177</td>
<td>0.0032</td>
<td>307</td>
<td>1.17</td>
<td>359</td>
<td>25</td>
</tr>
<tr>
<td>-2</td>
<td>1.04</td>
<td>0.51</td>
<td>2.0</td>
<td>5.73</td>
<td>100</td>
<td>1212</td>
<td>0.0031</td>
<td>319</td>
<td>1.17</td>
<td>373</td>
<td>25</td>
</tr>
<tr>
<td>Sample 4-1</td>
<td>1.04</td>
<td>0.52</td>
<td>2.0</td>
<td>5.61</td>
<td>98</td>
<td>1243</td>
<td>0.0010</td>
<td>988</td>
<td>1.14</td>
<td>1126</td>
<td>24</td>
</tr>
<tr>
<td>-2</td>
<td>1.05</td>
<td>0.55</td>
<td>1.9</td>
<td>5.61</td>
<td>98</td>
<td>1245</td>
<td>0.0010</td>
<td>973</td>
<td>1.11</td>
<td>1080</td>
<td>24</td>
</tr>
</tbody>
</table>

RD: Relative density (= density/theoretical density (5.75 g/cm$^3$)).
Q: $1/\tan \delta$.

Note: Sample 1, 2, 3 : prepared from low purity raw chemicals, SrCO$_3$ (99.9% +), PbO (99.9%), and TiO$_2$ (99.5%).
lots of sample 1 were different from those of sample 2 and sample 3.
Sample 4 : prepared from high purity raw chemicals, SrCO$_3$ (99.995%), PbO (99.9995%), and TiO$_2$ (99.999%).
Sample 1, 2, 4 : ball milled for 20 h after calcination.
Sample 3 : after 20 h ball milling and sieving, ball milled for an additional 4 h.
Sample 1 : the results of 1 datum.
Sample 2, 3, 4 : the results of 3 data.
3.3 Characteristics and behaviors of phase transition in x = 0.3 composition of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT)

3.3.1 Deviation from the Curie-Weiss law and phase transition behaviors

3.3.1.1 Introduction

The literature on lead strontium titanate, (Pb, Sr)TiO$_3$, started to appear at the end of the 1940s [7-9] and, since then, dielectric properties of (Pb, Sr)TiO$_3$ ceramics [10-21], single crystals [22, 23], and thin films [21, 24-27] have been investigated.

In order to comprehend paraelectric state behaviors of ferroelectric materials, the Curie-Weiss analysis (Eq. 3.3.1.1) [28, 29] is often used, and temperature ranges in which the Curie-Weiss behaviors are observed, the Curie-Weiss constants, and the Curie-Weiss temperatures are important factors for understanding the materials

$$\frac{1}{\varepsilon_r - 1} = \frac{T - \theta}{C}$$

where $\varepsilon_r = \text{relative permittivity}$, $C = \text{the Curie-Weiss constant}$, $T = \text{Temperature}$, and $\theta = \text{the Curie-Weiss temperature}$. Regarding the 1st-order transition, $\theta$, is below its transition temperature based on relative permittivity, $T_c$ (ideal or theoretical transition temperature which does not show a frequency dependence) or $T_m$ (transition temperature at which a sample shows the maximum dielectric constant at a weak alternating current (AC) field and at a specific frequency), while the 2nd-order transitions are supposed to show that $\theta$ equals $T_c$ [30].

Nomura and Sawada [11] and Boganov and Khomutetskaia [12] showed a relatively well fitted Curie-Weiss behavior of (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics (by the interpretation of their data), but a previous report [20] and Sect. 3.2 showed a deviation from the Curie-Weiss law close to the phase transitions as the result of the reciprocal of dielectric constant of the (Sr, Pb)TiO$_3$ solid solution system as a function of temperature.

The Curie-Weiss behaviors of the materials have been studied from various viewpoints such as porosity [31], inhomogeneity [32-34], defect [35, 36], structural disorder [33], stress [37-39], grain size [40, 41], grain boundary layer [42], and the clamping effect on bulk samples over measurements [43]. Barium titanate (BaTiO$_3$ (BT)) with varied theoretical densities ranging between 83 and 99% (average grain sizes from 0.8 to 1.2 µm) showed the Curie-Weiss constants between $1.1 \times 10^5$ and $1.5 \times 10^5$ K [31]. The impurity which covered grains (and which was modeled as a serial diphase, in other words, part of the brick wall model) did not change the Curie Weiss constant, but more impurity lowered the Curie-Weiss temperature, $\theta$ [32]. The films
under tensile stress invariably showed lower $\theta$ than tensile free crystals, and the Curie-Weiss constants of the films in the tensile states were larger than those of the tensile free crystals [37-39]. However, the Curie-Weiss constant of the clamped KH$_2$PO$_4$ sample was similar to that of the KH$_2$PO$_4$ sample without clamping [43]. More than 98% theoretical density BT of which the grain sizes were between 0.07 and 1.7 $\mu$m showed similar Curie-Weiss constants, but the BT shifted the Curie-Weiss temperatures from low to high temperatures as the grain sizes of the samples increased [40]. This observation was explained based on the serial diphase model (see Sect. 4.2.5.4). Similarly, the BT with various grain sizes showed similar Curie-Weiss constants [31].

The deviation from the Curie-Weiss law has been often observed in relaxor materials such as Pb(Mg$_{1/3}$Nb$_{1/3}$)O$_3$ (PMN) [44], (Pb, La)(Ti, Zr)O$_3$ (PLZT) (P-L-Z (x:30:70)) (x = 5-20) [45], Ba(Ti, Zr)O$_3$ (Ti-Zr (70:30)) [46], and [Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$]$_{0.905}$[PbTiO$_3$]$_{0.095}$ [47; the effect of pressure on the deviation was in the literature]. In addition, KTa$_{1-x}$Nb$_x$O$_3$ (x = 15.7 %) crystals also showed such a deviation [48]. However, some relaxor SBN crystals did not show a deviation from the Curie-Weiss behavior due to the lack of stable polar nanodomains above the phase transition. They also observed the loss of non-linearity for the hysteresis measurements above the transition temperatures [49].

The appearance of micro-polar regions in the paraelectric state could cause such deviations. A source for the microscopic polarization is defects and, theoretically, samples with specific defects have been demonstrated to show the deviation of this nature [35]. In addition, the local microscopic inhomogeneity caused the finite polarization above the transition temperature due to the structural disorder [33].

The idea of the soft mode theory started to appear at the end of the 1940s as publications (Fröhlich [50]; some references in the literature [51]; and P. W. Anderson [52]), and Cochran developed the soft mode theory [53]. Ferroelectricity is caused by the softening of specific components or the lattice modes of vibration. Therefore, the deviation from the Curie-Weiss law for the displacive ferroelectrics may be discussed on the soft mode frequency observation. Rytz et al. showed that the deviation behavior of KTa$_{1-x}$Nb$_x$O$_3$ (x = 0.018) was related to the temperature dependence of the soft mode frequency [54]. Tokunaga [55, 56] theoretically demonstrated that the Curie-Weiss behavior had a relation to the soft mode behavior, namely, the displacive behavior, and the order-disorder behavior (caused by dipole-dipole interactions).

This section will discuss that the deviation from Curie-Weiss behavior for the SPT, its dielectric properties, and physical properties such as thermal expansion and lattice parameters.
3.3.1.2 Experimental procedure

The processing of (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics and the preparation of the samples for dielectric property measurements are described in Sect. 3.2 and the publication [20].

Dielectric properties were measured using LCR meters (4284A, HP). The higher temperature measurements up to ~190 °C were carried out in an ambient atmospheric condition using an oven of which the temperature was controlled by computer, and liquid nitrogen was used as the cooling medium. The lower temperature properties down to ~ −260 °C were measured using a cryogenic system in vacuum, and the temperature of the setup was controlled by computer. For cryogenic temperature measurements, the samples were (partially) covered with grease. In both cases, step modes in cooling cycles were used to carry out the measurements in order to achieve enough thermal stabilization. An AC field of 1 V/cm was used, and the data were collected at an average of four datum values. Higher and lower temperature data were connected at −15 °C, that is, 25 °C below the transition temperature of the (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ (~10 °C), a temperature at which an X-ray diffraction pattern analysis revealed a clear tetragonal phase.

The thermal expansion of the (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics was measured in cooling cycles using a dilatometer (Theta Industries, Inc) at a rate of 2 °C per min.

X-ray diffraction patterns were collected based on a θ-θ scan by a X-ray diffractometer (X2, Scintag, Inc.) in vacuum using a Cu K$_\alpha$ X-ray source. Tungsten powders (10-μm size, 99.99+% purity, Aldrich) were placed on a small area of the surface of a sample to coat it as a reference. The lattice parameters of the tungsten powders were determined with NIST standard silicon powders (SRM 640 c). Peak positions were obtained using PRO-FIT, the program developed by Toraya [1] and the lattice parameters were determined by Toraya’s program, UNITCELL [2].

Electric polarization was measured using a triangle wave at 1 Hz with a system based on a modified Sawyer-Tower circuit controlled by computer and the samples were immersed in fluid (Galden HT-200, CF$_3$-[(O-CF-CF$_3$-CF$_2$)$_n$-(O-CF$_2$)$_m$]-O-CF$_3$, temperature range: ~185~ −85 °C).
3.3.1.3 Results and discussion

Table 3.3.1.1 shows a summary of the measurements and description of the samples used for the studies. Sample 1 (1P: Polished sample 1), 2, and 3 were sintered at the same time, and they showed a similar dielectric behavior.

3.3.1.3.1 Dielectric properties

Fig. 3.3.1.1 shows the temperature dependence of relative permittivity and tangent $\delta$ of the (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.3) ceramics (sample 1P) at 1, 10, and 100 kHz from 190 to –260 °C. The relative permittivity vs. temperature plot showed one maximum at $T_m$ ~ 10 °C and at 10 kHz when the sample was cooled. The magnitude of the dielectric constant peaks strongly depended on the samples measured. The phase transition temperatures depend on the mole fraction of lead (or strontium) (and lead deficiency in the sample) [e.g., 11, 12] and grain sizes as shown in the Raman spectroscopy data [57].

Nomura and Sawada reported the maximum relative permittivity of the SPT (x = 0.3), ~4100 at –10 °C and at 1.034 MHz in vacuum [11], Boganov and Khomutetskaia showed ~21000 at ~5 °C and at 5 kHz in vacuum [12], Lavedan and Donaldson observed 3 °C (at 1 kHz) as the transition temperature [58], Griffiths showed 3550 at 14 °C and at 1 MHz [14], Falter observed ~16000 at ~10 °C and at 1 kHz [17], and Dibenedetto and Cronan obtained ~16000 at ~ –20 °C and at 1 kHz for their single crystals [23]. Lemanov et al. presented the equation to estimate the transition temperature of the (Sr$_{1-x}$Pb$_x$)TiO$_3$ to be –2 °C when x was 0.3 [18]. Relatively high and so far the largest value of the dielectric constant, nearly 30000, which could demonstrate the quality of the (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics, was also reported in the previous paper [20] and Sect. 3.2.

Fig. 3.3.1.2 shows the Curie-Weiss analysis results of the (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramic at 10 kHz (sample 1P) and calculated in the temperature range from 190 to 30 °C. The Curie-Weiss temperature of the sample, $\theta$, was above the transition temperature, $T_m$, and the deviation initiated from ~20 °C above the $T_m$. The Curie-Weiss constant calculated to be $1 \times 10^5$ °C and was similar to the value reported in the earlier publication [20] and Sect. 3.2. However, these values differ from the value, $5 \times 10^4$ °C, reported by Nomura and Sawada [11] mainly due to the different relative permittivity vs. temperature behavior in the samples.

In Fig. 3.3.1.1, there are three anomalies in the tangent $\delta$ vs. temperature plots (labeled as peak1, 2, and 3 from high to low temperature). A shoulder or weak peak at ~8 °C (peak 1) corresponded to the main dielectric constant maxima. Two additional strong tangent $\delta$ peaks at ~
Table 3.3.1.1 Summary of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramic samples

<table>
<thead>
<tr>
<th>Description</th>
<th>Shape</th>
<th>T (10$^{-3}$m)</th>
<th>Area (10$^{-6}$m$^2$)</th>
<th>Measurements</th>
<th>$\varepsilon_r$ max at 10 kHz</th>
<th>$\tan \delta$ max at 10 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Cylinder</td>
<td>4.9</td>
<td>48</td>
<td>TE</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Sample 1P</td>
<td>Cylinder</td>
<td>4.7</td>
<td>47</td>
<td>XRD, $\varepsilon_r$, $\tan \delta$</td>
<td>33000(10°C) 0.012(-95°C) 0.015(-210°C)</td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>Plate</td>
<td>1.1</td>
<td>4</td>
<td>$\varepsilon_r$, $\tan \delta$</td>
<td>35500(10°C) 0.012(-100°C) 0.015(-215°C)</td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td>Plate</td>
<td>1.1</td>
<td>4.3</td>
<td>$\varepsilon_r$, $\tan \delta$, P</td>
<td>33500(10°C) ------- -------</td>
<td></td>
</tr>
</tbody>
</table>

T: Thickness.
Sample 1P: Polished sample 1.
( ): the peak maximum temperature; the approximate temperatures for tangent $\delta$.
Peak 2 was closer to the relative permittivity peak.
Peak 3 was at the lowest temperature.
Measurements: methods used for the characterization of samples.
TE, Thermal expansion measurement; XRD, X-ray diffraction pattern measurement; P, Polarization vs. AC field (hysteresis loop) measurement.
Figure 3.3.1.1 Relative permittivity and tangent $\delta$ of (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics as a function of temperature at 10 kHz upon cooling (three tangent $\delta$ peaks are labeled as peak 1, 2, and 3 from high to low temperature).

Figure 3.3.1.2 Relative permittivity, $\varepsilon_r$, and reciprocal susceptibility of (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics as a function of temperature at 10 kHz upon cooling. $T_m = 10.4 \, ^\circ C; \theta = 17.3 \, ^\circ C; C = 1 \times 10^5 \, ^\circ C^{-1}$ ($190 > T > 30 \, ^\circ C$). 
Fit, Curie-Weiss behavior calculated in the temperature range from 190 to 30 $^\circ C$. $T_m$, transition temperature; $\theta$, Curie-Weiss temperature; $C$, Curie-Weiss Constant.
−95 °C (peak 2) and at ~ −210 °C (peak 3) were observed at 10 kHz, but they did not correspond to any relative permittivity anomalies. The magnitude and position of the peaks depended on the preparation, namely, the conditions of ferroelectric SPT in the samples. Also, the measurement frequency influenced the magnitude and position of the peaks. The peaks at lower frequency showed lower values of tangent δ maxima (peak 2 and 3) and moved the peaks (especially peak 2) to lower temperatures.

Fig. 3.3.1.3 shows the effect of measurement rates on tangent δ at 10 kHz using the cryogenic system only (sample 1P). When the rate became faster, the position of peak 2 became higher. In other words, when a step time per 0.5 °C changed from 6 min to 3 min to 1.2 min, then the maximum positions of tangent δ moved from −95 through −90 and −80 °C, respectively. However, the maximum position of the peak 3 did not show a clear cooling or heating rate dependence on the position of the tangent δ maximum.

From X-ray diffraction pattern studies, no structural changes closer to the occurrence of the dielectric loss anomaly (peak 2) were found (Sect. 3.3.2). It is quite possible that these features could be related to the physical motion or disturbances in the crystals.

It might be difficult to consider that each component of a well prepared solid solution contributes to the dielectric properties of the solution system. However, it is important to check each property to understand the solid solutions and/or to eliminate unnecessary options. A couple of components of SPT would be strontium titanate (SrTiO₃) and lead titanate (PbTiO₃). SrTiO₃ has the antiferrodistortive transition at ~ −168 °C (105 K), which is the closest transition temperature to ~ −100 °C [59-61], and PbTiO₃ would have a controversial transition from tetragonal to orthorhombic transition approximately −100 °C upon cooling because a number of researchers did not observe this transition [62]. By the addition of magnesium oxide (MgO), SPT (x = 0.3)-MgO (50:50 by weight) composites sintered at 1350 °C (Fig. 3.3.1.4) showed only one clear anomaly in tangent δ, namely, peak 3 at ~ −190 °C and an unclear feature of peak 2. As the ratio of Sr to Pb increased in the SPT samples, the transition temperatures, Tₘ, of relative permittivity shifted to lower temperatures and the positions of peak 2 (tangent δ) also moved to lower temperatures (Fig. 3.3.1.5). These observations suggest that peak 2 did not come from each component, but from the materials themselves. Peak 2 would be caused by the motion of domain walls. The formation of domains could be dependent on the samples, and similarly, peak 2 did not show a consistency among the samples.
Figure 3.3.1.3 Relative permittivity and tangent $\delta$ (peak 1, 2, and 3) of (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics as a function of temperature at 10 kHz upon cooling using the cryogenic system.

S6: step time, 6 min per 0.5 °C; S3: step time, 3 min per 0.5 °C; S1.2, step time, 1.2 min per 0.5 °C.
Figure 3.3.1.4 Relative permittivity, $\varepsilon_r$, and tangent $\delta$ of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.3)-MgO composite (50:50 by weight) as a function of temperature at 10 kHz upon cooling.

Figure 3.3.1.5 Relative permittivity and tangent $\delta$ of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics (x = 0.10 and 0.15) at 10 kHz as a function of temperature. Bolder curves, relative permittivity; Thinner curves, tangent $\delta$. 
There could be several possible reasons for the occurrence of the peak 3: i) a complex stress behavior such as different domain wall motion from the peak 2 tangent $\delta$, ii) a ferroic transformation similar to that observed in SrTiO$_3$ [59-61], and iii) behaviors related to polar and/or dipolar defects [63]. Aleksandrov et al. [64] and Hegenbarth et al. [65] studied the phase transition behaviors of the (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x \leq 0.15$) using the ultrasonic method. Hegenbarth et al. observed the clear phase transitions of which the origin was related to SrTiO$_3$ in the Sr rich compositions of the SPT ($x=0.02$ and 0.03). From Figs. 3.3.1.1 and 3.3.1.5, the SPT ($x=0.30$, 0.15, and 0.10) showed tangent $\delta$ (peak 3) around similar temperatures, ~ –210, –200, and –200 °C, respectively. Furthermore, the plots of reciprocal dielectric susceptibility vs. temperature (Fig. 3.3.1.2) show the change in a slope in the vicinity of peak 3, ~ –190 °C. Thus peak 3 could be related to the ferroelastic phase transition similar to that observed in SrTiO$_3$. The temperature dependence of electron diffraction using transmission electron microscope (TEM) might reveal the origin of peak 3.

3.3.1.3.2 Thermal expansion

Fig. 3.3.1.6 shows the thermal expansion and thermal expansion coefficients of the (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics (sample 1). A fitted curve was obtained based on superimposing the nine-order polynomial fitting of the experimental results in the specific temperature ranges, 550 to 15, 20 to 4, and 10 to –100 °C, and the plots were combined at 19 and 5 °C. From the fitted curve, thermal expansion coefficients were calculated. The transition temperature of the SPT ($x = 0.3$) ceramics using the minimum in the fitted thermal expansion coefficient vs. temperature plots was determined to be 8 ± 1 °C at an average of seven values. The thermal expansion coefficients of the (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics was $1 \times 10^{-5}$ °C$^{-1}$ from 190 to 30 °C in the temperature range in which the Curie-Weiss law was applied.

The value of the thermal expansion coefficient was similar to the value of the reciprocal of the Curie-Weiss constant over the same temperature range. Roberts [66] assumed that the Clausis-Mossotti equation and the Lorentz local field were applicable for the systems, namely, isotropic in nature, and the author obtained the relationship between the Curie-Weiss constant, $C$, and linear thermal expansion coefficient, $\alpha_l$

$$\frac{1}{C} = \alpha_l - \frac{1}{3\alpha} \frac{\partial \alpha}{\partial T} \quad (3.3.1.2)$$

where $\alpha$ is polarizability.
Figure 3.3.1.6 Thermal expansion and thermal expansion coefficients of (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics upon cooling.

TE, thermal expansion; TEC, thermal expansion coefficient;
TE, Fit, fitted curve (temperature range: 550 ~ 15 °C; 20 ~ 4 °C;
10 ~ –100 °C; overlapping temperature, 19 and 5 °C);
TEC, Fit, differentiation of TE, Fit (Fitting condition is the same as TE, Fit).
Harrop [67] also derived the relationship for the intrinsic temperature coefficient of capacitance or relative permittivity of a solid (with the Lorentz approximation and the application of the Clausius-Mosotti equation) and the thermal expansion of a ferroelectric material (Eq. 3.3.1.3). In addition, the materials were assumed to have low tangent $\delta (< 0.001)$ for the simple relationship; otherwise, additional terms for the extrinsic loss contribution were necessary in Eq. 3.3.1.3

$$\frac{1}{\varepsilon_r} \left( \frac{\partial \varepsilon_r}{\partial T} \right)_p = \frac{1}{\varepsilon_r} \left( \varepsilon_r - 1 \right) \left( \varepsilon_r + 2 \right) \left( \frac{1}{3 \alpha_m} \left( \frac{\partial \alpha_m}{\partial T} \right) - \alpha_l \right) + \alpha_l$$  (3.3.1.3)

where $\varepsilon_r$ is the relative permittivity of a material, $\alpha_m$ is the polarizability of a macroscopic volume, $V$, and $\alpha_l$ is the linear thermal expansion coefficient of the material. In terms of the capacitance, the equation for high dielectric constant materials ($\varepsilon_r \gg 1$) reduces to

$$\frac{1}{C} = \frac{\partial \left( \frac{1}{\varepsilon_r} \right)}{\partial T} = - \frac{1}{\varepsilon_r^2} \left( \frac{\partial \varepsilon_r}{\partial T} \right)_p = - \frac{1}{\varepsilon_r^2} \left( \varepsilon_r - 1 \right) \left( \varepsilon_r + 2 \right) \left( \frac{1}{3 \alpha_m} \left( \frac{\partial \alpha_m}{\partial T} \right) - \alpha_l \right) - \frac{\alpha_l}{\varepsilon_r}$$  (3.3.1.4)

Since $\varepsilon_r$ is larger than 1, Eq. 3.3.1.4 reduces to

$$\frac{1}{C} = \alpha_l - \frac{1}{3 \alpha_m} \left( \frac{\partial \alpha_m}{\partial T} \right)$$  (3.3.1.5)

Thus Eq. 3.3.1.5 is the same as Eq. 3.3.1.2.

Harrop assumed $\frac{1}{3 \alpha_m} \left( \frac{\partial \alpha_m}{\partial T} \right)$ as a negligible term and $\varepsilon_r$ was high. Consequently, Eq. 3.3.1.5 reduces to equations

$$- \frac{1}{\varepsilon_r^2} \left( \frac{\partial \varepsilon_r}{\partial T} \right)_p = \frac{1}{C} = \alpha_l$$  (3.3.1.6)

or

$$\frac{1}{\varepsilon_r} \left( \frac{\partial \varepsilon_r}{\partial T} \right)_p = - \varepsilon_r \alpha_l$$  (3.3.1.7)

He demonstrated that a linear relationship between $\varepsilon_r$ and $\frac{1}{\varepsilon_r} \left( \frac{\partial \varepsilon_r}{\partial T} \right)_p$ using materials of which the $\alpha_l$ was approximately $1 \times 10^{-5} \degree C^{-1}$. Therefore, the reciprocal of the Curie-Weiss constant would be empirically close to the value of linear thermal expansion, assuming the isotropic systems with comparatively very small polarizability contributions (and this is represented by very low tangent $\delta$ values).
When a material changes, for example, thermally and/or elastically, the atoms in the material vibrate. Atoms which are chained one-dimensionally vibrate either longitudinally (along the chain) or transversely (normal to the chain). Fig. 3.3.1. (a) and (b) describe two kinds of displacements based on the movement of an atom which occupies a unit cell: i) parallel to the direction of the wave propagation (longitudinal wave) and ii) perpendicular to the direction (transverse wave). Assuming that each atom is influenced by the nearest neighbor atoms, the system reduces to the one-dimensional model shown in Fig 3.3.1 (c).

Fig. 3.3.1.8 (a) shows one-dimensionally and alternatively arranged particles with two different masses, and the model leads to two vibrational modes, optical modes in which two kinds of particles vibrate in opposite signs and acoustic modes in which all the particles vibrate in the same sign (Fig. 3.3.1.8 (b) and (c)). Fig. 3.3.1.8 (d) describes optical and acoustic branches of the dispersion curves for the one-dimensional lattice which has the same spacing between two kinds of particles (with two masses) arranged alternatively [68-70].

The ferroelectricity occurs due to the softening of the specific optic modes and dielectric constant or the Curie-Weiss constant is related to the soft optic modes (transverse mode). However, thermal expansion/thermal expansion coefficient or strain is related to the acoustic modes [68]; linear thermal expansion is described as a longitudinal mode. It is thus difficult to establish the relationship between the Curie-Weiss constant and thermal expansion coefficient theoretically. There are, however, materials which do show the relationship with assumptions.

3.3.1.3.3 X-ray diffraction pattern

Fig. 3.3.1.9 shows the splitting of X-ray diffraction (XRD) peaks of the SPT (x = 0.3) ceramic (sample 1P) from 20 to −15 °C into two components assuming that the two components with $K_{\alpha1}$ and $K_{\alpha2}$ peaks were in the observed peaks at each temperature. If a tetragonal system was assumed, then component 1 (C1) became 224 peak, and component 2 (C2) was 422 peak. The calculated peak maximum of C1 and C2 from “PRO-FIT” [1] and the relative intensities of C1 and C2 are shown in Fig. 3.3.1.10. Although the transition temperature, $T_m$, of the $(\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3$ ceramics based on relative permittivity as a function of temperature at 10 kHz upon cooling was 10 °C, the XRD peaks could be possible to be decomposed into two components over a wide temperature range above the $T_m$. It was also possible to split the XRD peaks into the peaks of $K_{\alpha1}$ and $K_{\alpha2}$ at lower temperatures than the $T_m$ assuming the presence of one component (i.e., the system was cubic). Above 10 °C, the relative intensity of the weaker component, C1, was less than 10 %, and its peak maximum was the shoulder of the main peak.
Figure 3.3.1.7 (a) Longitudinal and (b) transverse waves of identical atoms, and (c) simple chain model for identical atoms.

$k$, wave vector; $a$, spacing between two adjacent atoms.

After Sakudo [70] p.19, with permission from Shokabo.

Figure 3.3.1.8 (a) Chain of alternatively arranged particles of masses, M and m (M > m), at a uniform spacing, a, and single force constant, $\beta$, (b) transverse optic branch, (c) transverse acoustic branch, and (d) dispersion curves for simple diatomic chain shown in (a). k, wave vector or wave number; M or m, atomic mass (M > m); $\beta$, force constant; a, atomic spacing; $\omega$, angular frequency.

Ref.: 1) Sakudo [70] pp. 23 and 25, 2) Musgrave [68] p.64, and 3) Ghatak [69]. (a)–(c) After ref. 1, with permission from Shokabo and (d) taken from ref. 2, with permission from Acoustical Society of America.

2) Reprinted from Musgrave, Crystal acoustics, the Acoustical Society of America USA, 2003; The previous edition was published by Holden-Day, Inc.
Figure 3.3.1.9 Splitting of X-ray diffraction pattern (XRD) peaks of (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics into two components.
If a cubic system is assumed, then two peaks indicate Cu K$_{α1}$ and Cu K$_{α2}$ peaks; If a tetragonal system is assumed, then two peaks indicate Cu K$_{α1}$ and Cu K$_{α2}$ of 224 and 422 peaks.
Figure 3.3.1.10 Observed $T_{\text{max}}$ (peak maximum temperature) and the relative intensity of component 1 (C1) and 2 (C2) of $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ ($x = 0.3$) ceramics. Tetragonal phase is assumed to decompose observed X-ray diffraction peaks. C1, 224 peak; C2, 422 peak.
Therefore, the separation into two peaks was not very accurate. Upon cooling, a component for the \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) system, \(\text{PbTiO}_3\), changes from a cubic to a tetragonal at the phase transition [71] similar to the well studied isomorphic \(\text{BaTiO}_3\) [72]. The SPT system should also be treated in the same way as well studied systems.

In order to determine the temperature dependence of lattice parameters of the SPT \((x = 0.3)\), tungsten \((\text{W})\) powders were used as a reference because the diffraction peaks of the \(\text{W}\) did not overlap the SPT peaks and did not affect the positions of the SPT peaks. Since the thermal expansion of silicon \((\text{Si})\) has been studied more compared with the \(\text{W}\) from room temperature to liquid nitrogen temperature [73] and the lattice parameter of NIST silicon powders \((\text{SRM 640 c})\) is precisely known at room temperature [74], the silicon powders were used to refine the lattice parameters of the tungsten powders. The temperature dependence of thermal expansion of the \(\text{Si}\) was obtained by the data of Lyon et al. [75]. To obtain the values related to the \(\text{Si}\) thermal expansion at a specific temperature, a nine-order polynomial fitting was applied to refine the data. Fig. 3.3.1.11 shows the lattice parameters of the \(\text{Si}\) and those of the \(\text{W}\) using the \(\text{Si}\) as a reference. After the refined lattice parameters of the \(\text{W}\) was obtained, a linear relationship between observed values and temperature was assumed, and the lattice parameters of the \(\text{W}\) were finally determined. Observed and calculated lattice parameters of the tungsten are shown in Fig. 3.3.1.11. Fig. 3.3.1.12 shows the temperature dependence of the lattice parameters of the \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) ceramics. In order to calculate the lattice parameters of the ceramics at various temperatures, three \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) peaks, 301, 400, and 422, and two tungsten peaks, 310 and 321, were used in the cubic states and five diffraction peaks, 103, 004, 400, 224, and 422, and the two tungsten peaks were used in the tetragonal states. Because the 004 peak was in the shoulder of the main 400 peak at 10 °C, the 004 peak was not used to calculate the lattice parameter of the SPT at 10 °C.

The XRD peaks in the tetragonal state were obvious at –15 °C, a temperature which was 25 °C below the \(T_m\) (based on dielectric constant data). From 10 to 0 °C, the lattice parameter, \(c\), showed higher values compared to the value at –5 °C. It could be due to two reasons: i) the incorrect assumption that the system had a single tetragonal phase at each temperature instead of assuming a mixture of cubic and tetragonal phases and ii) the low resolution of the X-ray diffraction pattern data.

A number of authors have reported the X-ray diffraction results of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) solid solution system [11, 76-79, 19, 80-83]. For the composition \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) \((x = 0.4)\), relative permittivity as a function of temperature was measured, and conflicted values of the transition
Figure 3.3.1.11 Lattice parameters of tungsten (W) powders normalized with silicon (Si) powders. Si powders: NIST 640C [74], a, 5.4311946 Å at 22.5 °C, thermal expansion coefficient (TEC), $2.581 \times 10^{-6}$ °C$^{-1}$. The TEC was used to calculate the lattice parameter of Si at 25 °C. TEC at other temperatures was based on Lyon et al. [75]. The lattice parameters of W were calculated based on the linear relationship between observed values and temperature.

Figure 3.3.1.12 Lattice parameters of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.3) ceramics as a function of temperature. Tetragonal system was assumed to occur at 10 °C; Fitting for cubic system was carried out using the data above 10 °C; Fitting for tetragonal phase was carried out using the data below 0 °C.
temperatures, ~65 °C [11, 12, 18], ~75 °C [79] and below room temperature, 16 °C [19], have
been reported. Calos et al. and Kuo et al. concluded (Sr0.5Pb0.5)TiO3 as cubic and Wang et al.
described (Sr1-xPbx)TiO3 (0 < x ≤ 0.3) as the tetragonal system at room temperature. It is, in
general, more difficult to assign the accurate crystal phase of (Sr1-xPbx)TiO3 compositions with
transition temperatures closer to room temperature because it is difficult to obtain the high
resolution X-ray diffraction data, especially at low angles. The present study on the
(Sr0.7Pb0.3)TiO3, which showed the sharp dielectric constant anomalies in relative permittivity vs.
temperature behaviors, demonstrated that the tetragonal phase based on the XRD analysis was
clearly detected at 25 °C below the Tm based on the dielectric constant vs. temperature plots. It
was also possible to split the observed peaks into Kα1 peak and Kα2 peak assuming the cubic
phase (by the curve fitting) in the apparent tetragonal state around 20 °C below the Tm.

3.3.1.3.4 Polarization

Fig. 3.3.1.13 shows the temperature dependence of hysteresis loop curves of the
(Sr0.7Pb0.3)TiO3 ceramics (sample 3), and Fig. 3.3.1.14 shows the plots of remnant polarization
and squared remnant polarization as a function of temperature. At 60 (Tm+50) °C (Tm: 10 °C, the
phase transition temperature based on dielectric constant as a function of temperature at 10 kHz
upon cooling), a linear relationship between the polarization and the AC field was observed (Fig.
3.3.1.13). Non-linear behavior was clearly noted at 40 °C (Tm+30), and the remnant polarization
was detectable at 25 °C (Tm+15).

The phase transition would be of second-order for three reasons: i) clear hysteresis was not
observed at the Tm, ii) squared remnant polarization, $P_r^2$ vs. temperature showed the liner
relationship between ~5 and ~25 °C, and iii) the temperature at which $P_r^2$ was zero (~ 7.5 °C) was
not above the θ ~ 14 °C.

Polarization, P, and AC field, E, bear the following relationship, with vacuum
permittivity, $\varepsilon_o$, and relative permittivity, $\varepsilon_r$.

$$\frac{\partial P}{\partial E} = \varepsilon_o (\varepsilon_r - 1)$$  \hspace{1cm} (3.3.1.8)

In Fig. 3.3.1.15, the measured 10 kHz relative permittivity of the same sample used for
the hysteresis measurements and calculated relative permittivity using the polarization data at 1
Hz are plotted. Because the (Sr0.7Pb0.3)TiO3 ceramics did not show an appreciable frequency
dependence of relative permittivity (Fig. 3.3.1.1), the calculated values were similar to those
measured at 10 kHz.
Figure 3.3.1.13 (a) Hysteresis loops of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.3$) ceramics at 1 Hz above the transition temperature (10°C). The transition temperature was based on relative permittivity maximum at 10 kHz upon cooling. (value conducted from the relative permittivity vs. temperature measurements).
Figure 3.3.1.13 (b) Hysteresis loops of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.3) ceramics at 1 Hz at the transition temperature and below the transition temperature. Transition temperature, 10 °C, measured from the dielectric constant vs. temperature plot at 10 kHz upon cooling.
Figure 3.3.1.14 Remnant polarization, \( P_r \), and \( P_r^2 \) of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3 \) (\( x = 0.3 \)) ceramics at 1 Hz as a function of temperature.

The temperature range for linear fitting based on \( P_r^2 \) was between 5 and \(-25 \, ^\circ \text{C}\). \( P_r^2 \) was 0 at 7.4 \, ^\circ \text{C}.

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<th>( P_r^2 ) (µC²/cm⁴)</th>
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Figure 3.3.1.15 Relative dielectric permittivity and reciprocal relative dielectric susceptibility of (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics as a function of temperature.
i) Values based on capacitance measured at 10 kHz and ii) values calculated from the polarization data at 1 Hz.
$T_m = 9.5\, ^\circ\text{C}$; $\theta = 13.8\, ^\circ\text{C}$; $C = 1 \times 10^5\, ^\circ\text{C}^{-1}$ ($60 \equiv T \equiv 30\, ^\circ\text{C}$) for 10 kHz data;
$\theta = 13.9\, ^\circ\text{C}$, $C = 9 \times 10^4\, ^\circ\text{C}^{-1}$ ($60 \equiv T \equiv 30\, ^\circ\text{C}$) for polarization data.
$T_m$, relative permittivity maximum; $\theta$, Curie-Weiss temperature; $C$, Curie-Weiss constant; $T$, temperature.
3.3.1.3.5 Deviation from the Curie-Weiss law

Upon cooling, the SPT \((x = 0.3)\) ceramics showed the deviation from the Curie-Weiss behavior about 20 °C above the phase transition, \(T_m\), obtained from the dielectric constant vs. temperature plot at 10 kHz. In cooling cycles, thermal expansion coefficients started to deviate at around 90 °C above the \(T_m\) and showed a distinct change at 5 °C above the \(T_m\).

The microscopic polarization in micro-polar regions above \(T_m\) could contribute to the deviation from the theoretical Curie-Weiss behavior. In other words, this local polarization could reduce the slope of reciprocal of the relative dielectric susceptibility as a function of temperature. The micro-polar regions could delay the onset of ferroelectricity, (i.e., domain polarization or macroscopic polarization) which could start to decrease the relative permittivity rapidly. Consequently, the \(T_m\) of SPT could become below \(\theta\).

The displacement of atoms from their average lattice positions was observed in the literature [84, 85]. Therefore, it is suggested that local lead ion displacements may tend to break up the coherence of the ferroelectric soft mode leading to the development of local micro-polar regions at temperatures above \(T_m\) (the weak field dielectric maximum). An evidence of the reduced coherence would be the observation of the thermal expansion which showed the deviation from the linear relationship with temperature, which was observed far above \(T_m\), because the thermal expansion reflects the behavior of \(\sqrt{p^2} \ (p: \text{root mean square (rms) polarization})\). In addition, a second consequence of the reduced coherence would be a reduction in the rate of decrease of dielectric stiffness \((1/\varepsilon_w)\) with temperature vs. the rate observed in the perfect lattice. These local micro-polar regions could contribute to a delay to lower the temperature for the formation of macro-polar domains, which would be the primary cause of the catastrophic decrease of weak field polarizability. This loss causes an increase in dielectric stiffness (decrease in relative permittivity) evidenced in the dielectric constant behaviors of normal ferroelectrics below \(T_c\). It appears probable that this delay contributes to lower \(T_m\) permitting a continuing increase of \(\varepsilon_w\).

In introduction section, various sources are described for the deviation of the Curie-Weiss law; for example, porosity, chemical inhomogeneity, chemical defects, and mechanical stress. Among them, changes in physical properties, for example, thermal expansion coefficients, could cause stress and, hence, be a source for the detectable polarization in the paraelectric region. In addition, the change in crystal symmetry and/or the formation of local ferroelectric domains near the phase transition could contribute to the stress. Porosity, chemical inhomogeneity, and chemical defects could have less possibilities because sample 1 showed 99 % theoretical density...
measured by the Archimedes method, the \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) ceramics showed a sharp relative permittivity as a function of temperature at the phase transition, and the tangent \(\delta\) values of the SPT \((x = 0.3)\) ceramics in the paraelectric regions between \(\sim 10^\circ\text{C}\) above the \(T_m\) and a temperature far from the \(T_m\), at which obvious conductivity started, were less than 0.0005 at 10 kHz.

Furthermore, it is important to investigate these deviation behaviors from a viewpoint of the soft mode frequency. Additional contributions to the deviation could be as follows: i) the order-disorder behavior which \(\text{PbTiO}_3\) shows near the displacive phase transition [3.3.1-80] and ii) the small nanopolar \(\text{PbTiO}_3\) clusters, if presented in the SPT.

### 3.3.1.4 Summary

SPT \((x = 0.3)\) ceramics showed one maximum at \(\sim 10^\circ\text{C}\) in the relative permittivity vs. temperature behavior at 10 kHz upon cooling in the temperature range from 190 to \(-260^\circ\text{C}\). Thermal expansion coefficients upon cooling showed the transition temperature of the \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) ceramics at \(\sim 10^\circ\text{C}\). The analysis of X-ray diffraction data extracted at various temperatures also suggested the phase transformation of the SPT \((x = 0.3)\) approximately \(10^\circ\text{C}\).

Upon cooling, the deviation from the Curie-Weiss law was observed almost up to \(20^\circ\text{C}\) above the dielectric maximum, \(T_m\), of \(10^\circ\text{C}\). The thermal expansion coefficient started showing the deviation nature from \(90^\circ\text{C}\) above the \(T_m\) and the main anomaly at \(\sim 5^\circ\text{C}\) above the \(T_m\). The lattice parameters measured in the cubic region (from \(T_m + 50^\circ\text{C}\)) did not show a strong deviation with temperature and experimentally followed the temperature dependence upon cooling. Hysteresis loop plots showed an s-type shape (non-linearity) at \(30^\circ\text{C}\) above the \(T_m\), and remnant polarization was clearly detectable at \(15^\circ\text{C}\) above the \(T_m\). The deviation from the Curie-Weiss behavior could be caused by some of the several regions associated with the physical state of the material and/or atoms and hence by the micro polarization.

The tangent \(\delta\) of the \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) ceramics as a function of temperature showed two distinct anomalies. The peak at \(\sim -95^\circ\text{C}\) (peak 2) was supposed to be associated with the domain wall motion because the dielectric constant and thermal expansion behavior did not show a corresponding anomaly in this temperature range and the X-ray diffraction pattern did not indicate any structural change. Therefore, the obvious reason left was due to be domain wall related behavior. Furthermore, neither the SPT \((x = 0.3)\)-magnesium oxide (MgO) composites nor the SPT of \(x=0.15\) and 0.10 showed the anomaly in the relative permittivity vs. temperature.
measurements. These observations also suggested that the anomaly of tangent $\delta$ (peak 2) was strongly due to the domain wall motion.

The anomaly observed in the tangent $\delta$ of the ($\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3$ at the temperature, $\sim – 210 ^\circ \text{C}$ (peak 3), which was observed in most SPT samples, could be due to the following reasons: i) different types of domain wall motions from those observed in peak 2 tangent $\delta$, ii) an antiferrodistortive phase transition similar to that observed in SrTiO$_3$, and/or iii) behaviors due to the presence of polar and/or dipolar defects. Even though a clear dielectric constant anomaly was not apparent in that temperature range, the reciprocal dielectric susceptibility vs. temperature showed a change in slope at $\sim –190 ^\circ \text{C}$. The anomaly of tangent $\delta$ was also presented in the SPT ($x = 0.15$ and 0.10) and SPT ($x = 0.3$)-MgO composites at $\sim –200$, $\sim –200 ^\circ \text{C}$, and $\sim –190 ^\circ \text{C}$, respectively. The anomaly, thus, could be more closely associated with the ferroelastic phase transition of SrTiO$_3$ rather than the domain wall motion or defects of the SPT.

Sect. 3.4 will describe the effect of sintering conditions on dielectric properties of SPT ($x = 0.2$). It will add additional information to estimate the source of peak 3 as the ferrodistortive phase transition similar to that observed in SrTiO$_3$. 

3.3.2 X-ray diffraction peak analysis on phase transition and line broadening

3.3.2.1 Introduction

(Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ (SPT) showed the dielectric constant maximum as a function of temperature around 10 $^\circ$C relatively independent of frequency. Moreover, the SPT showed low dissipation factors in the paraelectric state but with the maximum in tangent $\delta$ from approximately –50 to –100 $^\circ$C in the ferroelectric state depending on measurement frequencies from 1 k to 100 kHz (Sect. 3.2). Lewis [87] suggested that an increase in loss tangents in the ferroelectric states was caused mainly by domain wall motion. Postnikov et al. [88] reported the interaction between 90$^\circ$ domain walls and point defects made loss tangents high. Härdtl [89] modeled the damping of 90$^\circ$ domain walls by point defects such as oxygen vacancies and demonstrated this behavior could also increase loss tangents. Guo et al. [90] explained dielectric losses due to a polarization fluctuation mechanism in the lead barium niobate system, but this system had strong relaxor ferroelectric characters.

If dielectric behaviors such as dielectric constant maxima are related to the phase transition of a crystal system, we are able to observe changes in X-ray diffraction patterns. In case the dielectric behaviors such as tangent $\delta$ are related to the ferroelectric domain wall motion, changes in line broadening of X-ray peaks could be observed. The line broadening is caused by both an instrument and a specimen. Reasons for the line broadening by the specimen are small crystallites (crystallite domains, i.e., units with the same d-spacing and orientation), the effects of stacking and twin faults and subgrain structures (e.g., small-angle boundaries), overlapping of more than one diffraction line, heterogeneous strain, structural disorder, dislocation, point defects, inhomogeneous chemistry [91-95]. However, they may be classified as two factors: i) the size (coherent length) effect perpendicular to the direction of the incident X-rays and ii) the inhomogeneity effect parallel to the direction of the incident X-rays due to various d-spacings.

Therefore, the X-ray diffraction line broadening or sharpening denotes to estimate the changes in crystallite domains. The concept of these domains is different from that of ferroelectric domains observed in a ferroelectric material in the ferroelectric state at alternating current (AC) fields. In both cases, one expects the dynamic motion related to crystals and/or ferroelectrics when the sample is cooled or heated.

Several equations have been proposed to estimate sizes and/or strain (for homogenous materials such as metals) in materials based on the line widths of the X-ray diffraction peaks [96,
Williamson and Hall examined size and strain effects on the line broadening and obtained Eq. (3.2.2.1) [98]

$$\beta = \beta_{\text{size}} + \beta_{\text{strain}} = \frac{\lambda}{t \cos \theta} + 2 \eta \tan \theta$$  \hspace{1cm} (3.3.2.1)

where $\beta =$ total integral width, $\beta_{\text{size}} =$ integral width due to size, $\beta_{\text{strain}} =$ integral width due to strain, $\lambda =$ X-ray wavelength, $\theta =$ diffraction angle, $t =$ crystallite domain size, and $\eta =$ strain. Eq. (3.3.2.1) is modified by multiplying $\frac{\cos \theta}{\lambda}$.

$$\beta \frac{\cos \theta}{\lambda} = 2 \eta \frac{\sin \theta}{\lambda} + \frac{1}{t}$$  \hspace{1cm} (3.3.2.2)

Using the above relation between $\beta \frac{\cos \theta}{\lambda}$ and $\frac{\sin \theta}{\lambda}$, the size is obtained by the reciprocal of the y intersect, and the strain is calculated by the half of the slope. At least two peaks with different Bragg reflection indices, $m_h m_k m_l$ and $n_h n_k n_l$ ($m \neq n$; $m = 1, 2, 3, \ldots$; $n = 1, 2, 3, \ldots$), are necessary for the calculation. Instead of considering the strain effects observed in the homogeneous specimen, the inhomogeneous effect such as various d-spacings due to the chemical inhomogeneity (and strain in the ferroelectric state) is suitable to explain the line broadening of the inhomogeneous specimen such as ferroelectric solid solution systems like SPT.

X-ray diffraction analysis is used to explore structural consequences of the ferroelectric phase transition, the temperature dependence of line broadening, and the effect of size and inhomogeneity especially in the ferroelectric state. This section will discuss the effect of the crystal system change on dielectric constants and the effect of widths on loss tangents based on the preliminary results.

### 3.3.2.2. Experimental

#### 3.3.2.2.1 Material

$(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ (SPT) ($x = 0.3$) ceramics was prepared with high purity raw chemicals (99.995% purity SrCO$_3$; 99.9995% purity PbO; and 99.999% purity TiO$_2$). X-ray diffraction analysis was carried out on the surface of the sample.
3.3.2.2 Measurements

3.3.2.2.1 Dielectric properties

The dielectric properties of a gold-coated sample were measured with an LCR meter (4284A, HP) at a constant rate.

3.3.2.2.2 X-ray diffraction pattern analysis

A surface of the bulk sample was polished, and a small amount of tungsten (W) powders (10-µm size, 99.99+% purity, Aldrich) were placed on it as a reference. The X-ray diffraction patterns of the sample were collected by an X-ray diffractometer (X2, Scintag, Inc.) with a Cu Kα X-ray source by the θ-θ scanning method using a cold stage for temperature dependent measurements. The values of Kα1 peaks were determined using the computer program, “PRO-FIT” [1] and peak positions were corrected with the tungsten powders by the difference between the observed and calculated W peak positions. The lattice parameters of the W powders were refined with silicon (Si) powders (SRM 640c, NIST) and the computer program, “UNITCELL” [2], using a mixture of the tungsten and silicon powders. The lattice parameter of the Si powders at 22.5 °C was specified in the NIST certificate [74], and the lattice parameter at 25 °C was obtained by the thermal expansion coefficient value described in the NIST certificate. Thermal expansion values at different temperatures were based on Lyon et al. [75] and Roberts [99].

Fig. 3.3.2.1 shows the calculated lattice parameter of the Si powders, and Fig. 3.3.2.2 shows observed and calculated lattice parameters of the W powders. Fig. 3.3.2.3 shows the comparison of the lattice parameter of the calculated W powders with the values based on the literature [100] (25 °C value referred to the calculated value at 25 °C shown in Fig. 3.3.2.2), and the difference between the calculated and reference values was less than 0.02 %.

X-ray diffraction patterns at 25, 0, −25, and −195 °C were collected between 20 and ~160 degrees two-theta to check the crystal system of the SPT. In order to investigate the temperature dependence of the line broadening and the size and inhomogeneity effects, 1 1 1 and 2 2 2 peaks were selected. Because the crystal system of the SPT changes from cubic to tetragonal upon cooling, other peaks such as 2 0 0 and 4 0 0 peaks could be preferable to estimate the motion of the crystallite domains. However, the 1 1 1 and 2 2 2 peaks were selected because they did not split into two components in the tetragonal system and permitted easy stripping Kα2 from the mixture of Kα1 and Kα2 peaks.

Before the X-ray diffraction peaks were analyzed in detail, the integral widths were obtained assuming pseudo-Voigt function for the peak fitting with “PRO-FIT” [1],
Figure 3.3.2.1 Temperature dependence of silicon lattice parameters.
Silicon used: NIST SRM 640 C.
The value in the NIST certificate was used as 22.5 °C value. 25 °C value was obtained from the 22.5 °C value and thermal expansion coefficient in the NIST certificate.
25 - 20 °C values were based on the NIST certificate (SRM 640 C) [74];
50 - 150 °C values were based on the literature by Lyon et al. [75];
100 - 50 °C values were based on the literature by Roberts [99].
Figure 3.3.2.2 Lattice parameters of tungsten (W) powders.
Si (silicon), Calculated: temperature dependence of Si lattice parameter shown in Fig 3.3.2.1;
W, Observed: observed values of W in a mixture of W and Si powders;
W, Calculated: calculated values of W based on a linear fitting between observed values and temperature.

Figure 3.3.2.3 Comparison of calculated tungsten (W) values with reference W values based on the literature. (W value at 25 °C in this experiment was used to calculate reference values).
33, 34, 34+Cal, and 36 in Touloukian et al. [100];
34+Cal: Calculated values with data for 34.
\[ \beta = 1/ \left( \frac{1}{\eta_l} + \frac{1}{\eta_h} \right) \left( \frac{1+A}{\sqrt{\pi \ln 2}} \right) + \frac{A}{\eta_l + (1-\eta_h)\sqrt{\pi \ln 2}} \times \frac{2}{\pi H} \]  

(3.3.2.3)

where \( A \) = peak asymmetry, \( H \) = full width at half maximum (FWHM), \( \eta_l \) = decay rate on the low angle side, \( \eta_h \) = decay rate on the high angle side [101]. The Bragg angles of the samples were corrected by the tungsten powders. An instrumental background was estimated by the Si powders. Although the NIST silicon powders had strain in them, annealed samples were not used. The position of the Si was interpolated using two peaks, and widths were also interpolated at the same position as the SPT was observed.

3.3.2.3 Results and discussion

3.3.2.3.1 Dielectric properties

Fig. 3.3.2.4 shows the dielectric responses of the \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) as a function of temperature and frequency. The transition temperature, \( T_m \), of the sample based on relative permittivity was \( \sim 15^\circ C \), and the loss tangent maxima were observed at \(-50^\circ C \) (1 kHz) and \(-40^\circ C \) (10 kHz), respectively. The SPT prepared from low purity raw chemicals (3N) showed the transition temperature \( \sim 10^\circ C \) (Sect. 3.2). The high purity (4 - 5N) SPT sample showed higher transition temperature, and this difference could be due to impurities in the lower quality oxides lowering \( T_m \) and/or a slight difference of the mixing ratio between lead and strontium.

3.3.2.3.2 X-ray diffraction pattern

3.3.2.3.2.1 Change in crystal system

The \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) (SPT) system showed a cubic system at 25 \( ^\circ C \), and the lattice constant was 3.917\AA, which was the same value observed for the lower purity SPT at room temperature in Sect 3.2 and the earlier publication [20].

Fig. 3.3.2.5 (plot (a) and (b)) shows selected X-ray diffraction peaks at 25, 0, \(-25\), and \(-195^\circ C \). X-ray diffraction peaks started to change at 0 \( ^\circ C \) upon cooling. Plot (a) shows 4 0 0 as \( h \) \( k \) \( l \), and plot (b) is for 4 2 0. Regarding 4 0 0 peaks, two peaks, \( K_{o1} \) and \( K_{o2} \) were observed at 25 \( ^\circ C \). Three peaks, namely, a mixture of 0 0 4 \( K_{o1} \), 0 0 4 \( K_{o2} \), 4 0 0 \( K_{o1} \), and 4 0 0 \( K_{o2} \) were observed at 0 and \(-25^\circ C \). Four peaks, namely, 0 0 4 \( K_{o1} \), 0 0 4 \( K_{o2} \), 4 0 0 \( K_{o1} \), and 4 0 0 \( K_{o2} \) were clearly observed at \(-195^\circ C \). 0 0 4 peaks were due to the formation of the tetragonal system. In
Figure 3.3.2.4 Dielectric responses of (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics as a function of temperature and frequency.
Figure 3.3.2.5 X-ray diffraction patterns of (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ ceramics at various temperatures. (a) 4 0 0 and (b) 4 2 0 as h k l (the Bragg reflection indices: primary reflection from the set of planes (h k l)).
plot (b), the change in X-ray diffraction peaks was also observed at 0 °C when the sample was cooled.

One of the components which could be in the SPT, lead titanate, shows the tetragonal system in the ferroelectric region [71]. Strontium titanate which could be in the SPT also shows a phase change from cubic to tetragonal upon cooling [102]. The SPT at liquid nitrogen temperature showed a tetragonal system, and an obvious change in the crystal system was not observed from 0 °C to the liquid nitrogen temperature. Therefore, the SPT system did not have additional phase transitions from the transition temperature to –195 °C.

### 3.3.2.3.2.2 Temperature dependence of line broadening

Fig. 3.3.2.6 shows the temperature dependence of integral widths of (a) (Sr0.7Pb0.3)TiO3 sample without subtracting the instrumental contributions, (b) silicon powders (SRM 640 C), that is, the background due to the instrument, and (c) (Sr0.7Pb0.3)TiO3 sample after subtracting the background. The silicon powders (plot (b)) did not show an obvious temperature dependence of the line broadening. However, the (Sr0.7Pb0.3)TiO3 sample showed a temperature dependence (plot (a)). Consequently, plot (c) also showed a temperature dependence. This would be due to dynamic changes in crystallite domains.

Therefore, the further analysis to separate two factors, size and inhomogeneity effects was proceeded using the Williamson-Hall equation (Eq. 3.3.2.2) (Fig. 3.3.2.7). However, it is difficult to obtain any conclusive summary. Reasons might be explained as follows: i) the selection of the peaks was not sufficient to link the line broadening and the behavior of tangent δ and ii) enough intensity might not be obtained for a detailed analysis because the area of the sample was small and the instrument was used for a limited time.

To use annealed silicon powders (e.g., to seal Si powders in a quartz tube under an argon (Ar) atmosphere (~ 0.2 × 10^5 Pa; 99.99% purity) and heat at 1000 °C [103]) would be better for a further precise analysis. In addition, the width of the sample was determined by subtracting the width of the instrument from the observed width. However, it would require that the width by sample itself be determined [e.g., 93, 94].
Figure 3.3.2.6 Integral widths as a function of temperature. (a) \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) and instrumental contributions, (b) instrumental contribution obtained using silicon powders (SRM 640 C), and (c) \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) contribution after the instrumental contribution was subtracted.
Figure 3.3.2.7 Analysis of line broadening of $(\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3$ ceramics based on size and inhomogeneity effects.
3.3.3 The effect of dopants on dielectric properties – Analysis of relaxation behavior and structure

3.3.3.1 Introduction

There are various methods to influence tangent $\delta$ of a system at a specific temperature and frequency. One of the ideas presented to prepare samples with low tangent $\delta$ is to dope an element in the system. Although a uniform doping is possible to use a solution with a dopant, there might be the difficulty of removing an anion specie after doping. Therefore, the doping sources were selected among oxides and carbonates.

Fig. 3.3.3.1 shows the crystal structure of $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ (SPT) $(x = 0.3)$ which is the perovskite. Strontium (Sr) and lead (Pb) occupy the A-site of the perovskite, and titanium (Ti) occupies the B-site of the perovskite. Table 3.3.3.1 (a) lists possible candidates for A-site doping, and Table 3.3.3.1 (b) lists possible candidates for B-site doping [104-107]. Cerium oxide (CeO$_2$) and samarium oxide (Sm$_2$O$_3$) were selected among the various oxides and carbonates. The reasons are as follows: (i) the A-site doping could be expected to be easier than the B-site doping, (ii) cerium (Ce) and samarium (Sm) have 12 as a coordination number, which is same as the coordination number of Sr and Pb, (iii) Ce and Sm have multi-oxidation states (Ce: III and IV (maximum coordination number: 12); Sm: II and III (maximum coordination number, 8 for Sm$^{2+}$; 12 for Sm$^{3+}$) [104], and (iv) the handling of CeO$_2$ and Sm$_2$O$_3$ powders is easy. For example, barium (Ba), calcium (Ca), lanthanum (La), Ce, or Sm shows 12 as the coordination number. If vacancies and/or defects introduced by the preparation of the samples mainly contributes to the tangent $\delta$ of the samples, elements which have multi oxidation states might be desirable since these elements might compensate for charges occurred by the defects and/or vacancies. Chemicals with La element might have a problem with handling because lanthanum oxide (La$_2$O$_3$) has the possibility to absorb water and lanthanum carbonate is generally available as hydrated chemicals such as La$_2$(CO$_3$)$_3$·8H$_2$O [107].

Fig. 3.3.3.2 shows dielectric properties of 0.5 wt% CeO$_2$ doped SPT (Ce-SPT (0.000637:1 by mole) (plot (a)) and 0.5 wt% Sm$_2$O$_3$ doped SPT (Sm-SPT (0.000630:1 by mole)) (plot b). Because the tangent $\delta$ of both samples increased after doping, further investigation will be required to reduce the tangent $\delta$ of the SPT system. The CeO$_2$ doped sample showed similar relative permittivity maxima at various frequencies, while the Sm$_2$O$_3$ doped sample showed an unusual relaxation behavior.
Figure 3.3.3.1 Crystal structure of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.3).
(a) Side view.
(b) Top view.
(c) Top view after removing the top oxygen.
Table 3.3.3.1 (a) Possible ion of A-site doping for \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Oxid. state</th>
<th>Coordination Number (CN)</th>
<th>Radius (Å)</th>
<th>Source</th>
<th>Substance name</th>
<th>MW (g/mol)</th>
<th>m.p. (°C)</th>
<th>Density (g/cm³)</th>
<th>(\text{MTiO}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>2</td>
<td>12</td>
<td>1.44</td>
<td>SrCO₃</td>
<td>Strontium carbonate</td>
<td>147.63</td>
<td>1494</td>
<td>3.5</td>
<td>(\text{SrTiO}_3)</td>
</tr>
<tr>
<td>Pb</td>
<td>2</td>
<td>12</td>
<td>1.49</td>
<td>PbO</td>
<td>Lead oxide</td>
<td>223.2</td>
<td>886*</td>
<td>9.53*</td>
<td>(\text{PbTiO}_3)</td>
</tr>
<tr>
<td>Mg</td>
<td>2</td>
<td>8</td>
<td>0.89</td>
<td>MgO</td>
<td>Magnesium oxide</td>
<td>40.304</td>
<td>2825</td>
<td>3.6</td>
<td>(\text{MgTiO}_3)</td>
</tr>
<tr>
<td>Ca</td>
<td>2</td>
<td>12</td>
<td>1.34</td>
<td>CaCO₃</td>
<td>Calcium carbonate</td>
<td>100.087</td>
<td>825(d.)</td>
<td>2.83</td>
<td>(\text{CaTiO}_3)</td>
</tr>
<tr>
<td>Ba</td>
<td>2</td>
<td>12</td>
<td>1.61</td>
<td>BaCO₃</td>
<td>Barium carbonate</td>
<td>197.336</td>
<td>1555</td>
<td>4.2865</td>
<td>(\text{BaTiO}_3)</td>
</tr>
<tr>
<td>Mn</td>
<td>2</td>
<td>8</td>
<td>0.96</td>
<td>MnO</td>
<td>Manganese (II) oxide</td>
<td>70.937</td>
<td>1839</td>
<td>5.37</td>
<td>(\text{MnTiO}_3)</td>
</tr>
<tr>
<td>Co</td>
<td>2</td>
<td>8</td>
<td>0.90</td>
<td>CoO</td>
<td>Cobalt (II) oxide</td>
<td>74.932</td>
<td>1830</td>
<td>6.44</td>
<td>(\text{CoTiO}_3)</td>
</tr>
<tr>
<td>Ni</td>
<td>2</td>
<td>6</td>
<td>0.69</td>
<td>NiO</td>
<td>Nickel (II) oxide</td>
<td>74.692</td>
<td>1955</td>
<td>6.72</td>
<td>(\text{NiTiO}_3)</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>6</td>
<td>0.73</td>
<td>CuO</td>
<td>Copper (II) oxide</td>
<td>79.545</td>
<td>1446</td>
<td>6.31</td>
<td>(\text{CuTiO}_3)</td>
</tr>
<tr>
<td>Zn</td>
<td>2</td>
<td>8</td>
<td>0.90</td>
<td>ZnO</td>
<td>Zinc oxide</td>
<td>81.39</td>
<td>1974</td>
<td>5.6</td>
<td>(\text{ZnTiO}_3)</td>
</tr>
<tr>
<td>Nb</td>
<td>2</td>
<td>-</td>
<td>-----</td>
<td>NbO</td>
<td>Niobium (II) oxide</td>
<td>108.905</td>
<td>1936</td>
<td>7.30</td>
<td>(\beta)</td>
</tr>
<tr>
<td>La</td>
<td>3</td>
<td>12</td>
<td>1.36</td>
<td>La₂O₃</td>
<td>Lanthanum oxide</td>
<td>325.809</td>
<td>2305</td>
<td>6.51</td>
<td>(\text{LaTiO}_3)</td>
</tr>
<tr>
<td>Ce</td>
<td>4</td>
<td>12</td>
<td>1.14</td>
<td>Ce₂O₃</td>
<td>Cerium (IV) oxide</td>
<td>172.114</td>
<td>2400</td>
<td>7.65</td>
<td>(\text{CeTiO}_3)</td>
</tr>
<tr>
<td>Sm</td>
<td>3</td>
<td>12</td>
<td>1.24</td>
<td>Sm₂O₃</td>
<td>Samarium (III) oxide</td>
<td>348.72</td>
<td>2335</td>
<td>7.6</td>
<td>(\text{SmTiO}_3)</td>
</tr>
<tr>
<td>Si</td>
<td>2</td>
<td>-</td>
<td>-----</td>
<td>SiO</td>
<td>Silicon (II) oxide</td>
<td>44.085</td>
<td>&gt;1702*</td>
<td>2.18</td>
<td>(\beta)</td>
</tr>
</tbody>
</table>

Ref.: D. R. Lide ed., Handbook of chemistry and physics on CD-ROM [104].

Oxid. state: oxidation state; CN: coordination number;
Source: source of an element to a system, but coordination number is not necessary to be the same as description on the left side; MW: molecular weight;
m. p.: melting point; d.: decomposes.
\(\text{MTiO}_3\): observed in references; Crystal structures do not mean perovskites.

Ref.: PDF files, Sets 1-53, ICDD, PA, USA except marked as (α) and (β);
(α) : Found in the database, SciFinder Scholar , American Chemical Society;
(β) : Found neither in the PDF files nor in the SciFinder Scholar.
*
Research chemicals, metals and materials, Alfa Aesar, 1999-2000: Alfa Aesar catalog
**
Not listed in the catalog of Alfa Aesar.

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116
Table 3.3.3.1 (b) Possible ion of B-site doping for (Sr$_{1-x}$Pb$_x$)TiO$_3$

<table>
<thead>
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<th>Atom</th>
<th>Oxid. state</th>
<th>CN (max)</th>
<th>Radius (Å)</th>
<th>Source Substance name</th>
<th>MW</th>
<th>m.p. (°C)</th>
<th>density (g/cm$^3$)</th>
<th>PbMO$_3$/SrMO$_3$</th>
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<tbody>
<tr>
<td>Ti</td>
<td>4</td>
<td>6</td>
<td>0.61</td>
<td>TiO$_2$ Titanium (IV) oxide</td>
<td>79.866</td>
<td>1843</td>
<td>4.23</td>
<td>PbTiO$_3$, SrTiO$_3$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8</td>
<td>0.74</td>
<td>TiO$_2$ Titanium (IV) oxide</td>
<td>79.866</td>
<td>1843</td>
<td>4.23</td>
<td>PbTiO$_3$, SrTiO$_3$</td>
</tr>
<tr>
<td>V</td>
<td>4</td>
<td>6</td>
<td>0.58</td>
<td>VO$_2$ Vanadium (IV) oxide</td>
<td>82.941</td>
<td>1967</td>
<td>4.339</td>
<td>SrVO$_3$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8</td>
<td>0.72</td>
<td>VO$_2$ Vanadium (IV) oxide</td>
<td>82.941</td>
<td>1967</td>
<td>4.339</td>
<td>SrVO$_3$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6</td>
<td>0.79</td>
<td>VO Vanadium (II) oxide</td>
<td>66.941</td>
<td>1789</td>
<td>5.758</td>
<td>SrVO$_3$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6</td>
<td>0.64</td>
<td>V$_2$O$_3$ Vanadium (III) oxide</td>
<td>149.881</td>
<td>2067</td>
<td>4.87</td>
<td>SrVO$_3$</td>
</tr>
<tr>
<td></td>
<td>4 and 5</td>
<td>-</td>
<td>-----</td>
<td>V$<em>6$O$</em>{13}$* Vanadium (IV, V) oxide</td>
<td>513.64</td>
<td>-</td>
<td>-</td>
<td>SrVO$_3$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6</td>
<td>0.54</td>
<td>V$_2$O$_5$ Vanadium (V) oxide</td>
<td>181.880</td>
<td>670</td>
<td>3.35</td>
<td>SrVO$_3$</td>
</tr>
<tr>
<td>Cr</td>
<td>4</td>
<td>6</td>
<td>0.55</td>
<td>CrO$_2$ Chromium (IV) oxide</td>
<td>83.995</td>
<td>≈400(d.)</td>
<td>4.89</td>
<td>PbCrO$_3$(α),SrCrO$_3$</td>
</tr>
<tr>
<td>Cr</td>
<td>3</td>
<td>6</td>
<td>0.62</td>
<td>Cr$_2$O$_3$ Chromium (III) oxide</td>
<td>151.990</td>
<td>2329</td>
<td>5.22</td>
<td>PbCrO$_3$(α),SrCrO$_3$</td>
</tr>
<tr>
<td>Y</td>
<td>3</td>
<td>6</td>
<td>0.90</td>
<td>Y$_2$O$_3$ Yttrium oxide</td>
<td>225.810</td>
<td>2438</td>
<td>5.03 (β)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9</td>
<td>1.08</td>
<td>Y$_2$O$_3$ Yttrium oxide</td>
<td>225.810</td>
<td>2438</td>
<td>5.03 (β)</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>4</td>
<td>6</td>
<td>0.72</td>
<td>ZrO$_2$ Zirconium (IV) oxide</td>
<td>123.223</td>
<td>2709</td>
<td>5.68</td>
<td>PbZrO$_3$, SrZrO$_3$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>9</td>
<td>0.89</td>
<td>ZrO$_2$ Zirconium (IV) oxide</td>
<td>123.223</td>
<td>2709</td>
<td>5.68</td>
<td>PbZrO$_3$, SrZrO$_3$</td>
</tr>
<tr>
<td>Nb</td>
<td>4</td>
<td>6</td>
<td>0.68</td>
<td>NbO$_2$ Niobium (IV) oxide</td>
<td>124.905</td>
<td>1901</td>
<td>5.9</td>
<td>SrNbO$_3$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6</td>
<td>0.64</td>
<td>Nb$_2$O$_5$ Niobium (V) oxide</td>
<td>265.810</td>
<td>1512</td>
<td>4.6</td>
<td>SrNbO$_3$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>8</td>
<td>0.74</td>
<td>Nb$_2$O$_5$ Niobium (V) oxide</td>
<td>265.810</td>
<td>1512</td>
<td>4.6</td>
<td>SrNbO$_3$</td>
</tr>
<tr>
<td>Hf</td>
<td>4</td>
<td>6</td>
<td>0.71</td>
<td>HfO$_2$ Hafnium (IV) oxide</td>
<td>210.49</td>
<td>2774</td>
<td>9.68</td>
<td>PbHfO$_3$, SrHfO$_3$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8</td>
<td>0.83</td>
<td>HfO$_2$ Hafnium (IV) oxide</td>
<td>210.49</td>
<td>2774</td>
<td>9.68</td>
<td>PbHfO$_3$, SrHfO$_3$</td>
</tr>
<tr>
<td>Ta</td>
<td>4</td>
<td>6</td>
<td>0.68</td>
<td>Ta$_2$O$_5$** Tantalum (IV) oxide</td>
<td>212.947</td>
<td>-</td>
<td>10.0</td>
<td>SrTaO$_3$(α)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6</td>
<td>0.64</td>
<td>Ta$_2$O$_5$ Tantalum (V) oxide</td>
<td>441.893</td>
<td>1784</td>
<td>8.2</td>
<td>SrTaO$_3$(β)</td>
</tr>
<tr>
<td>W</td>
<td>4</td>
<td>6</td>
<td>0.66</td>
<td>WO$_2$ Tungsten (IV) oxide</td>
<td>218.54</td>
<td>1500-1700(d.)</td>
<td>10.8</td>
<td>SrWO$_3$(c)</td>
</tr>
</tbody>
</table>

Ref : D. R. Lide ed., Handbook of chemistry and physics on CD-ROM [104].

Oxid. state, oxidation state; CN, coordination number;
Source, source of an element to a system, but coordination number is not necessary to be the same as description on the left side; MW, molecular weight;
m. p., melting point; d., decomposes; t1, transition to β-quartz; t2, transition to tridymite; t3, transition to cristobalite.
PbMO$_3$/SrMO$_3$ : Observed in references. Crystal structures do not mean to be perovskites.

Ref : PDF files, Sets 1-53, ICDD, PA, USA. except marked as (α) and (β);
(α) : Found in the database, SciFinder Scholar, American Chemical Society;
(β) : Found neither in the PDF files nor in the SciFinder Scholar;
* : Research chemicals, metals and materials, Alfa Aesar, 1999-2000 (Alfa Aesar catalog);
** : Not listed as powder chemicals in the catalog of Alfa Aesar.
Figure 3.3.3.2 Dielectric properties of (a) CeO$_2$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) and (b) Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$ as a function of temperature and frequency upon cooling. The ratio of raw chemicals for SPT: Sr-Pb-Ti (0.7:0.3:1 by mole). The ratio of raw chemicals for CeO$_2$ and Sm$_2$O$_3$ doping: CeO$_2$-SPT (0.005:1 by weight) and Sm$_2$O$_3$-SPT (0.005:1 by weight).
In this section, the properties of the Sm$_2$O$_3$ doped ceramics will be discussed in order to understand the unusual enhancement of relative permittivity of the SPT system.

3.3.3.2 Experimental

The dopant, Sm$_2$O$_3$, was added to the raw chemicals, strontium carbonate (SrCO$_3$), lead oxide (PbO), and titanium oxide (TiO$_2$) (Sr-Pb-Ti (0.7:0.3:1)). The content of the dopant was adjusted to be 0.5 wt% to SPT. The mixture of the raw chemicals were calcined, and then pressed pellets were sintered at 1350 °C for 3 h; doped samples were prepared in a way similar to that used for pure SPT samples described in Sect. 3.2.1.

3.3.3.3 Results and discussion

3.3.3.3.1 X-ray diffraction pattern

Fig. 3.3.3.3 shows the X-ray diffraction patterns of (a) the mixture of PbO, SrCO$_3$, TiO$_2$ and Sm$_2$O$_3$, (b) the mixture of PbO, SrCO$_3$, and TiO$_2$, (c) calcined Sm$_2$O$_3$ doped SPT, (d) calcined SPT, (e) sintered Sm$_2$O$_3$ doped SPT, and (f) sintered SPT. Both the mixtures (a) and (b) did not show an obvious difference, but calcined powders showed a difference in X-ray diffraction patterns of the reacted powders. Doped samples showed shoulder peaks along with the main peaks, and they could be caused by the slower calcining process due to the existence of Sm$_2$O$_3$. Fig. 3.3.3.4 shows the effect of calcination temperature on X-ray diffraction patterns of the calcined SPT powders, and the powders processed at lower temperatures showed similar shoulder peaks. However, sintered products with or without the dopant did not show any noticeable differences on a macroscopic level except for the colors of the samples. The pure SPT samples prepared under conditions similar to those used for the doped samples showed dark brown, but the Sm$_2$O$_3$ doped samples showed dark red.

3.3.3.3.2 Thermal expansion

Fig. 3.3.3.5 shows the thermal expansion and thermal expansion coefficients of the Sm$_2$O$_3$ doped SPT in a cooling cycle. The sample was cut to a length similar to that of a fused silica reference, 6.54 mm, and the measurement rate was 2 °C per min. The transition temperature based on the thermal expansion was – 2 °C, which was obtained from differentiating a fitted curve between 10 and – 5 °C by a nine-order polynomial fitting.
Figure 3.3.3.3 X-ray diffraction patterns of (a) the mixture of PbO, SrCO₃, TiO₂, and Sm₂O₃, (b) the mixture of PbO, SrCO₃, and TiO₂, (c) calcined Sm₂O₃ doped SPT, (d) calcined SPT, (e) sintered Sm₂O₃ doped SPT, and (f) sintered SPT.

SPT : (Sr₁₋ₓPbx)TiO₃.
The ratio of raw chemicals:
  Pb:Sr:Ti = 0.3:0.7:1 by mole for Sm₂O₃ doped samples.
  Sm₂O₃:SPT = 0.005:1 by weight for Sm₂O₃ doped samples.
  Pb:Sr:Ti =0.3:0.7:1 by mole for SPT samples.
Figure 3.3.3.4 The effect of calcination temperature on X-ray diffraction patterns of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) \((x = 0.3)\) ceramics. The samples were calcined in a aluminum oxide crucible (without being placed in a sagger). (a) at 1100 °C, (b) at 1000 °C, and (c) at 900 °C for 3h.
Figure 3.3.3.5 Thermal expansion and thermal expansion coefficients of Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$ upon cooling.

The ratio of raw chemicals:

Sr:Pb:Ti = 0.7:0.3:1 by mole and Sm$_2$O$_3$:(Sr$_{1-x}$Pb$_x$)TiO$_3$ = 0.005:1 by weight.

TE, Thermal expansion; TEC, Thermal expansion coefficient.
3.3.3.3 Dielectric properties

Fig. 3.3.3.6 shows the relative permittivity, $\varepsilon_r$, (the real part of relative complex permittivity, $\varepsilon_r'$) and tangent $\delta$ or the imaginary part of relative complex permittivity, $\varepsilon_r''$, of the Sm$_2$O$_3$ doped SPT ($\varepsilon_r$ and tangent $\delta$ in plot (a); $\varepsilon_r$ and $\varepsilon_r''$ in plot (c)) and the pure SPT ($\varepsilon_r$ and tangent $\delta$ in plot (b); $\varepsilon_r$ and $\varepsilon_r''$ in plot (d)). The SPT did not show the frequency dependence of dielectric properties except in the ferroelectric region, but the Sm$_2$O$_3$ doped SPT ceramics showed frequency dependent behaviors.

Fig. 3.3.3.7 shows the thermal hysteresis of dielectric behavior measured from 100 Hz through 1 MHz. Fig. 3.3.3.8 shows dielectric properties as a function of temperature at 10 kHz upon both cooling and heating. In the paraelectric and ferroelectric state far from the transition temperature, no hysteresis was observed at a frequency of 10 kHz.

Fig. 3.3.3.9 shows the dielectric constant and reciprocal dielectric susceptibility of the Sm$_2$O$_3$ doped SPT as a function of temperature at 10 kHz. Fig. 3.3.3.10 shows the Curie-Weiss analysis of relative permittivity upon cooling at 10 kHz. Plot (a) superimposes dielectric constant vs. temperature upon cooling and heating and plot (b) superimposes tangent $\delta$ vs. temperature in cooling and heating cycles. Table 3.3.3.2 summarizes dielectric constant, tangent $\delta$, the imaginary part of relative complex permittivity at a peak maximum, and the results of the Curie-Weiss analysis.

It is surprising that the data taken at 10 kHz follows the Curie-Weiss law rather precisely right to the dielectric maximum, that is, the departure observed in the pure SPT solid solutions near $T_m$ associated with the micro-polar mechanism was not evident. However, the value of the Curie-Weiss constant, $C$, was changed from $C \sim 1 \times 10^5 \, ^\circ\text{C}$ in the undoped SPT ceramics to $C \sim 4 \times 10^5 \, ^\circ\text{C}$. It is possible that the local field associated with the trivalent ions could pin the breathing modes of the micro-polar regions (i.e., expanding and shrinking the regions) which would eliminate the departure near $T_m$. More work would be needed to validate this hypothesis and explain the change of the Curie-Weiss constant.

3.3.3.4 Imaginary part of complex permittivity, $\varepsilon_r''$, vs. real part of complex permittivity, $\varepsilon_r'$

An alternating current (AC) through a media is given by the following equations [108-109]
Figure 3.3.3.6 Dielectric properties as a function of temperature and frequency.
(a) Sm₂O₃ doped (Sr₁₋ₓPbx)TiO₃ ceramics (Sr-Pb-Ti for raw chemicals (0.7:0.3:1 by mole) and Sm₂O₃-(Sr₁₋ₓPbx)TiO₃ for raw chemicals (0.005:1 by weight)) and (b) (Sr₁₋ₓPbx)TiO₃ (x = 0.3) ceramics.
Figure 3.3.3.6 Dielectric properties of (c) Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics (the ratio of raw chemicals: Sr:Pb:Ti = 0.7:0.3:1 by mole and Sm$_2$O$_3$:(Sr$_{1-x}$Pb$_x$)TiO$_3$ = 0.005:1 by weight), and (d) (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.3) as a function of temperature and frequency.

\( \varepsilon' \), real part of complex permittivity (thinner curves).

\( \varepsilon'' \), imaginary part of complex permittivity (bolder curves).
Figure 3.3.3.7 Temperature dependence of dielectric properties of Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics at 100, 1 k, 10 k, 100 k, and 1 MHz frequencies upon cooling and heating. (the ratio of raw chemicals: Sr:Pb:Ti = 0.7:0.3:1 by mole and Sm$_2$O$_3$:(Sr$_{1-x}$Pb$_x$)TiO$_3$ = 0.005:1 by weight).

Figure 3.3.3.8 Temperature dependence of dielectric properties of Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics at 10 kHz upon both cooling and heating. (the ratio of raw chemicals: Sr:Pb:Ti = 0.7:0.3:1 by mole and Sm$_2$O$_3$:(Sr$_{1-x}$Pb$_x$)TiO$_3$ = 0.005:1 by weight).
Figure 3.3.3.9 Relative permittivity, $\varepsilon_r$, and reciprocal susceptibility, $1/(\varepsilon_r - 1)$, of Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics as a function of temperature and frequency (100, 1 k, 10 k, 100 k, and 1 MHz) in a cooling cycle.

The ratio of raw chemicals:

$\text{Sr:Pb:Ti} = 0.7:0.3:1$ by mole and $\text{Sm}_2\text{O}_3:(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3 = 0.005:1$ by weight.
Figure 3.3.3.10 Curie-Weiss behavior of Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics at 10 kHz upon cooling and (a) relative permittivity upon both cooling and heating and (b) tangent $\delta$ upon both cooling and heating.

Curie-Weiss analysis temperature range, $52.5 > T > -2 \, ^\circ C$; Curie-Weiss constant, $C$, $3.5 \times 10^5 \, ^\circ C$; Curie-Weiss temperature, $\theta$, $-14.4 \, ^\circ C$; Transition temperature, $T_m$, $-2.7 \, ^\circ C$. 
Table 3.3.3.2 Dielectric properties and the results of the Curie-Weiss analysis

<table>
<thead>
<tr>
<th>Frequency</th>
<th>ε', Real part (maximum)</th>
<th>ε', Imaginary part (peak maximum)</th>
<th>Real part, the real part of complex permittivity;</th>
<th>Imaginary part, the imaginary part of complex permittivity;</th>
<th>– 3 °C: Tm, transition temperature based on maximum of dielectric constant;</th>
<th>θ, Curie-Weiss temperature;</th>
<th>C, Curie-Weiss constant;</th>
<th>Range, temperature range in which Curie-Weiss analysis was applied.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Hz</td>
<td>5800(141 °C)</td>
<td>44200(-3 °C)</td>
<td>0.50(103 °C)</td>
<td>0.53( 8 °C)</td>
<td>1.04(-22 °C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1kHz</td>
<td>400(181 °C)</td>
<td>32200(-3 °C)</td>
<td>0.33(144 °C)</td>
<td>0.21( 8 °C)</td>
<td>0.44(-18 °C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10kHz</td>
<td>26800(-3 °C)</td>
<td>0.26(192 °C)</td>
<td>0.17(14 °C)</td>
<td>0.18(-18 °C)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>100kHz</td>
<td>24400(-3 °C)</td>
<td>0.18(37 °C)</td>
<td>0.08(-19 °C)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1MHz</td>
<td>23100(-3 °C)</td>
<td>0.24(85 °C)</td>
<td>0.05(-13 °C)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frequency</td>
<td>ε, Real part (maximum)</td>
<td>ε′, Imaginary part (peak maximum)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100Hz</td>
<td>5800(141 °C)</td>
<td>44200(-3 °C)</td>
<td>2800(114 °C)</td>
<td>27000(-5 °C)</td>
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<tr>
<td>1kHz</td>
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<td>32200(-3 °C)</td>
<td>12200(150 °C)</td>
<td>7400(-5 °C)</td>
<td></td>
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</tr>
<tr>
<td>10kHz</td>
<td>26800(-3 °C)</td>
<td>2800(-4 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100kHz</td>
<td>24400(-3 °C)</td>
<td>1400( 6 °C)</td>
<td>1300(-3 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1MHz</td>
<td>23100(-3 °C)</td>
<td>800(-5 °C)</td>
<td>800(-5 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Curie-Weiss behavior</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Frequency</td>
<td>Tm (°C)</td>
<td>θ (°C)</td>
<td>C (°C)</td>
<td>Range (°C)</td>
<td>Correlation Factor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>--------</td>
<td>--------</td>
<td>------------</td>
<td>---------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100Hz</td>
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<td>-6.4</td>
<td>4.6 x 10^5</td>
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<td>0.99991</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1kHz</td>
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<td>-11.3</td>
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<td>92.5&gt;T&gt; 5</td>
<td>0.99990</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10kHz</td>
<td>-2.7</td>
<td>-14.4</td>
<td>3.5 x 10^5</td>
<td>52.5&gt;T&gt;-2</td>
<td>0.99990</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100kHz</td>
<td>-2.7</td>
<td>-10.9</td>
<td>2.5 x 10^5</td>
<td>25 &gt;T&gt; 2.5</td>
<td>0.99992</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1MHz</td>
<td>-2.8</td>
<td>-7.9</td>
<td>1.9 x 10^5</td>
<td>40 &gt;T&gt; 5</td>
<td>0.99992</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ I_o = i\omega C_o V \]  
\[ I = i\omega C V \]  
(3.3.3.1)

(3.3.3.2)

where \( I \) is current, \( \dot{I} \) is current 90° in advance of \( I \), \( i (=\sqrt{-1}) \) is imaginary part, \( \omega \) is angular frequency, \( C \) is capacitance, \( \dot{C} \) is capacitance 90° in advance of \( C \), \( V \) is voltage, \( \dot{V} \) is voltage 90° in advance of \( V \), and the subscript o means values in vacuum. Complex relative permittivity, \( \varepsilon_r^* \), is given by

\[ \varepsilon_r^* = \frac{\dot{I}}{I_o} = \frac{\dot{C}}{C_o} = \varepsilon_r' - i\varepsilon_r'' \]  
(3.3.3.3)

where \( \varepsilon_r' \) is the real part of relative complex permittivity, and \( \varepsilon_r'' \) is the imaginary part of relative complex permittivity. \( \varepsilon_r \) is same as relative permittivity or dielectric constant. Tangent \( \delta \) is given by

\[ \text{tangent} \ \delta = \frac{\varepsilon_r''}{\varepsilon_r'} \]  
(3.3.3.4)

Fig. 3.3.3.11 shows \( \varepsilon_r'' \) as a function of \( \varepsilon_r' \), the Cole-Cole plot in the frequency range from 100 Hz to 1 MHz, but conventional closed circles were not observed. Three kinds of relaxation mechanisms were observed at 190 and 150 °C in plot (a) of Fig. 3.3.3.11, plot (b) and (c) show two types of relaxation at 100, 50, and 25 °C. Plot (d) - (f) show one type of relaxation at 0, −2.7 (transition temperature at 10 kHz on cooling), −25, −50, and −100 °C.

3.3.3.5 Discussion on the electrical property observation

Table 3.3.3.3 lists the dielectric behaviors of various kinds of ferroelectric materials [110-118]. Relative permittivity of the Sm$_2$O$_3$ doped SPT as a function of temperature near the phase transition increased as the measurement frequencies decreased, but the transition temperature did not show much frequency dependence as shown in Fig 3.3.3.6. Thus these behaviors are different from the relaxors.

Fig. 3.3.3.12 shows the real and imaginary parts of relative complex permittivity as a function of frequency from 100 Hz through 1 MHz at certain temperatures. Two kinds of effects are considered for understanding dielectric behaviors as a function of frequency: i) resonance and ii) relaxation (Fig. 3.3.3.13) [119]. The resonance is caused by materials themselves independent of the shapes of samples or by a measurement setup depending on the dimensions of
Figure 3.3.3.11 Imaginary part, $\varepsilon''$, vs. real part, $\varepsilon'$, of complex permittivity of Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics between 100 Hz and 1 MHz (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1, 2, 3, 4, 5, 6, 8, 10, 20, 30, 40, 50, 60, 80, 100, 200, 300, 400, 500, 600, 800, and 1000 kHz).

(a) 190 and 150, (b) 100 and 50, (c) 25, (d) 25, 0, and $-2.7$, (e) $-25$, $-50$, and $-100$ and (f) $-100$ °C.

Transition temperature based on relative permittivity at 10 kHz upon cooling.
## Table 3.3.3.3 (a) Frequency dependent dielectric behaviors of several ferroelectrics

<table>
<thead>
<tr>
<th>Description</th>
<th>Relative permittivity</th>
<th>Tangent $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Magnitude at $T_m$</td>
<td>Transition temp, $T_m$</td>
</tr>
<tr>
<td>Observed</td>
<td>Larger at lower freq.</td>
<td>Constant or higher at higher freq.</td>
</tr>
<tr>
<td>Normal Ferroelectrics</td>
<td>Constant or larger at low freq.</td>
<td>Constant</td>
</tr>
<tr>
<td>Pinched Ferroelectrics</td>
<td>Constant or larger at lower freq.</td>
<td>Higher at higher freq.</td>
</tr>
<tr>
<td>Relaxors</td>
<td>Larger at lower freq.</td>
<td>Higher at higher freq.</td>
</tr>
<tr>
<td>Order-Disorder Ferroelectrics</td>
<td>Larger at lower freq.</td>
<td>Higher at higher freq.</td>
</tr>
<tr>
<td>Antiferroelectrics</td>
<td>Constant</td>
<td>Higher at higher freq.</td>
</tr>
<tr>
<td>Debye type</td>
<td>Larger at lower freq.</td>
<td>Constant or higher at higher freq.</td>
</tr>
<tr>
<td>Maxwell-Wagner-Sillars type</td>
<td>Larger at lower freq.</td>
<td>Constant or higher at higher freq.</td>
</tr>
</tbody>
</table>

A summary is based on examples from the literature.

**Observed**: observed in $Sm_2O_3$ doped $(Sr_1-xPbx)TiO_3$.

* This behavior would not be related to relative permittivity, but be due to domain wall motion.

** Tangent $\delta$ might start to increase at lower freq. upon heating and the order of tangent $\delta$ magnitude might depend on the temperature.

1. e.g., $(Sr_1-xPbx)TiO_3$ ($x = 0.3$) (present study) and $(Ba_{1-x}Sr_x)TiO_3$ in Fielding [110].
2. e.g., $Ba(Sn_{1-x}Ti_x)O_3$ in Fielding [110].
3. e.g., $(Pb, La)(Zr, Ti)O_3$ (PLZT) ($x/65/35$) in Fielding [110].
4. e.g., $NaNO_2$ in Hatta [111].
5. e.g., $(Pb, La)((Zr, Ti), Sn))O_3$ (Pb/La/Zr/Ti/Sn 97/2/53/12/35) in Fielding [110].
6. e.g., Plots theoretically derived from the Debye model in Oka [112].
7. e.g., $BaFe_{1/2}Nb_{1/2}O_3$ in Raevski et al. [113].
8. e.g., Superlattice layers of $(Ba_{1-x}Sr_x)TiO_3$ (BST) ($x = 0.2$) and BST ($x = 0.8$) in O’Neill et al. [114].
9. e.g., glass beaded polystyrene composites in Perrier and Bergeret [115].
10. e.g., ceramic composite: ferrite, $(Ni_{0.5}Zn_{0.5})Fe_{2+1}O_4$ and ferroelectric, $BaTiO_3$ in Zhi and Chen [116].
Table 3.3.3 (b) Frequency dependent dielectric behaviors of several ferroelectrics

<table>
<thead>
<tr>
<th>Description</th>
<th>Real part of complex permittivity</th>
<th>Imaginary part of complex permittivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Magnitude at $T_m$</td>
<td>Transition temp, $T_m$</td>
</tr>
<tr>
<td>Observed</td>
<td>Larger at lower freq.</td>
<td>Constant or higher at higher freq.</td>
</tr>
<tr>
<td>Normal Ferroelectrics(^1)</td>
<td>Constant or larger at lower freq.</td>
<td>Constant</td>
</tr>
<tr>
<td>Pinched Ferroelectrics(^2)</td>
<td>Constant or larger at lower freq.</td>
<td>Constant</td>
</tr>
<tr>
<td>Relaxors(^3)</td>
<td>Larger at lower freq.</td>
<td>Higher at higher freq.</td>
</tr>
<tr>
<td>Order-Disorder Ferroelectric(^4)</td>
<td>Larger at lower freq.</td>
<td>Higher at higher freq.</td>
</tr>
<tr>
<td>Antiferroelectrics(^5)</td>
<td>Constant</td>
<td>Constant</td>
</tr>
<tr>
<td>Debye type Ferroelectrics(^6)</td>
<td>Larger at lower freq.</td>
<td>Higher at higher freq.</td>
</tr>
<tr>
<td>Maxwell- Wagner-Sillars type Ferroelectrics(^7)</td>
<td>Larger at lower freq.</td>
<td>Higher at higher freq.</td>
</tr>
</tbody>
</table>

A summary is based on examples from the literature.

**Observed**: observed in Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$.

* This behavior would not be related to relative permittivity, but be due to domain wall motion.

1 e.g., (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x=0.3) (present study)
2 e.g., Ba(Ti$_{1-y}$Ce$_y$)O$_3$ (y = 0.06) in Chen et al. [117].
3 e.g., 0.95 PMN-0.05 PZT in Gridnev [118].
4 e.g., NaNO$_3$ in Hatta [111].
5 e.g., (Pb, La)((Zr, Ti), Sn)O$_3$ (Pb/La/Zr/Ti/Sn 97/2/53/12/35) in Fielding [110].
6 e.g., Plots theoretically derived from the Debye model in Oka [112].
7 e.g., BaFe$_{12}$Nb$_{12}$O$_{33}$ in Raevski et al. [113].
Figure 3.3.12 Real part, $\varepsilon'$, and imaginary part, $\varepsilon''$, of complex permittivity of Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics as a function of frequency between 100 ($10^2$ Hz) and 1 MHz ($10^6$ Hz).

(a) 190 and 150, (b) 100 and 50, (c) 25, (d) 25, 0, and $-2.7$, (e) $-25$, $-50$, and $-100$, and (f) $-100$ °C.

$-2.7$ °C, transition temperature based on relative permittivity at 10 kHz upon cooling.
Figure 3.3.3.13 Real and imaginary parts of complex permittivity, $\varepsilon'$, and $\varepsilon''$, as a function of frequency, $f$. (a) resonance type and (b) relaxation type. After Geyer [119].
the samples. In addition, the resonance is observed in the real and imaginary parts of complex permittivity. In this case, both real and imaginary parts did not show a resonance. Therefore, the relaxation was obviously observed in the Sm₂O₃ doped SPT samples.

There are classifications of Cole-Cole plots ($\varepsilon_r$ vs. $\varepsilon_i$), for example, the Debye (D), Cole-Cole (CC), Davidson-Cole (DC), Havriliak-Negami (HN), Kohlrausch-Williams-Watts (KWW), Grant, and Maxwell-Wagner-Sillars (MWS) types [120-137]. A summary is listed in Table 3.3.3.4.

A simple relaxation type is the Debye type, which shows a semicircle. The Debye type, which has a single relaxation time, is shown in Fig. 3.3.3.14 [123], and permittivity is described in the following equations. The Debye model is often observed for polar gases and dilute solutions of polar liquids [124]

$$
\varepsilon_r^* (\omega) = \varepsilon_r (\infty) + \frac{\varepsilon_r (0) - \varepsilon_r (\infty)}{1 + i\omega\tau} 
$$

(3.3.3.5)

$$
\varepsilon_r' (\omega) = \varepsilon_r (\infty) + \frac{\varepsilon_r (0) - \varepsilon_r (\infty)}{1 + (\omega\tau)^2} 
$$

(3.3.3.6)

$$
\varepsilon_r'' (\omega) = \frac{(\varepsilon_r (0) - \varepsilon_r (\infty))\omega\tau}{1 + (\omega\tau)^2} 
$$

(3.3.3.7)

$$
tangent \delta = \frac{\varepsilon_r''}{\varepsilon_r'} = \frac{(\varepsilon_r (0) - \varepsilon_r (\infty))\omega\tau}{\varepsilon_r (0) + \varepsilon_r (\infty)(\omega\tau)^2} 
$$

(3.3.3.8)

where $\omega$ is an angular frequency, $\varepsilon_r^*$ is relative complex permittivity, $\varepsilon_r(\infty)$ is relative permittivity at a high frequency (e.g., $\omega = \infty$; there are materials which show constant relative permittivity at a frequency below an optical frequency ($\omega = \infty$)), $\varepsilon_r(0)$ is relative permittivity at a low frequency (e.g., $\omega = 0$; there are materials which show static (constant) relative permittivity at a frequency above the frequency ($\omega = 0$)), $i = \sqrt{-1}$ is the imaginary part, and $\tau$ is relaxation time [138, 124, 120].

A common mechanism to enhance dielectric constants is the MWS type (or Maxwell-Wagner type, and this also shows a similar type to the Debye type [139, 124]. The MWS type will be explained in the following text.

The surface charges, $\sigma$, at the interface of two species (dielectrics), 1 and 2, is given by

$$
\sigma = \varepsilon_o \left( \varepsilon_{r1} E_1 - \varepsilon_{r2} E_2 \right) 
$$

(3.3.3.9)
Table 3.3.3.4 Behaviors of Cole-Cole plots based on examples

<table>
<thead>
<tr>
<th>Type</th>
<th>$\varepsilon''$ vs. $\varepsilon'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed</td>
<td>Arc and non-closed arc, e.g., curved line</td>
</tr>
<tr>
<td>Debye$^{1-4}$</td>
<td>Semicircle</td>
</tr>
<tr>
<td>Cole-Cole$^{5, 2-4}$</td>
<td>Arc</td>
</tr>
<tr>
<td>Davidson-Cole$^{6, 2-4}$</td>
<td>Distorted arc</td>
</tr>
<tr>
<td>Havriliak-Negami$^{7, 8, 3, 4}$</td>
<td>Distorted arc</td>
</tr>
<tr>
<td>Kohlrausch-Williams-Watts (KWW)$^{9-13, 3, 4}$</td>
<td>Distorted arc</td>
</tr>
<tr>
<td>Grant diagrams$^{14, 2}$</td>
<td>Closed arc and non-closed arc</td>
</tr>
<tr>
<td>Maxwell-Wagner-Sillars$^{15-18}$</td>
<td>Nearly Debye type</td>
</tr>
<tr>
<td>Relaxors$^{19}$</td>
<td>Cole-Cole type</td>
</tr>
<tr>
<td>Order-Disorder$^{20}$</td>
<td>Cole-Cole type (or near Debye type)</td>
</tr>
<tr>
<td>Normal ferroelectrics$^{21}$</td>
<td>No obvious relaxation (resonance)</td>
</tr>
</tbody>
</table>

$\varepsilon'$, the real part of complex permittivity;
$\varepsilon''$, the imaginary part of complex permittivity.

Observed: Observed in Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$.

Note: behaviors are based on examples from the literature.

1: Debye [120];
2: Bunget and Popescu [121].
3: Böttcher, and Bordewijk [122].
4: Amo [123].
5: Cole and Cole [124].
6: Davidson and Cole [125].
7: Havriliak and Negami [126].
8: Havriliak and Havriliak [127].
9: Kohlrausch [128].
10: Kohlrausch [129].
11: Williams and Watts [130].
12: Williams and Watts [131].
13: Williams [132].
14: Grant [133].
15: Maxwell [134].
16: Wagner [135].
17: Sillars [136].
18: Daly et al. [137].
19: Gridnev [118].
20: Hatta [111].
21: Present study, (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.3).
Figure 3.3.3.14 Real and imaginary parts of complex permittivity as a function of frequency and some specific parameters depending on a relaxation model (plot a, c, e, g, and k) and Cole–Cole plots (plot b, d, f, h, and l). a, b: Debye; c, d: Cole-Cole; e, f: Davidson-Cole; g, h: Harviliak-Negami; k, l: KWW. After Amo [123].
where \( \varepsilon_0 \) is vacuum relative permittivity, \( \varepsilon_m \) is the relative permittivity of species (dielectric) \( n \) (\( n=1 \) or 2), and \( E_n \) is the normal component of the field in the interface. The alternating fields of the complex notation are given by

\[
E_1^*(t) = x^* e^{i\omega t} \quad E_2^*(t) = y^* e^{i\omega t}
\]  

(3.3.10)

The surface charge carried by the conduction of two dielectrics of which the conductivity are \( \gamma_1 \) and \( \gamma_2 \) is given by

\[
\sigma^*(t) = \int \left[ (\gamma_1 E_1^* - \gamma_2 E_2^*) dt = (\gamma_1 x^* - \gamma_2 y^*) \right] i\omega dt = \frac{1}{i\omega} (\gamma_1 E_1^* - \gamma_2 E_2^*) + \text{const.}
\]  

(3.3.11)

where const. may be neglected if the field is switched on for a long time.

Complex charge is also given by the following equation based on charge density.

\[
\sigma^*(t) = \varepsilon_o \left[ \varepsilon_{r1} E_1^*(t) - \varepsilon_{r2} E_2^*(t) \right]
\]  

(3.3.12)

From Eqs. (3.3.11 and 3.3.12), the generalization of Eq. (3.3.9) under dynamic conditions is obtained.

\[
\left( \varepsilon_o \varepsilon_{r1} - \frac{\gamma_1}{i\omega} \right) E_1^* = \left( \varepsilon_o \varepsilon_{r2} - \frac{\gamma_2}{i\omega} \right) E_2^*
\]  

(3.3.13)

In case \( \gamma_1 = 0 \) (i.e., only component 2 is a conductor), all the power dissipation occurs in the inclusions. Consequently, Sillars derived the power loss with the Ohm’s law

\[
W = \frac{1}{2} \gamma_2 |E_2^*|^2
\]  

(3.3.14)

where \( W \) is the power loss per unit volume of the inclusion, and \( E_2^* \) is the field within the inclusion (sample 2). For heterogenous dielectrics containing the volume fraction, \( q \), of spheroids of the given axial ratio (\( \lambda = a/b \)), the real and imaginary parts of relative complex permittivity are given by

\[
\varepsilon_r'(\omega) = \varepsilon_r(\infty) + \frac{\varepsilon_{rl}N}{1 + (\omega\tau)^2}
\]  

(3.3.15)

\[
\varepsilon_r''(\omega) = \frac{\varepsilon_{rl}N\omega\tau}{1 + (\omega\tau)^2}
\]  

(3.3.16)

Spheroids are assumed to be ellipsoids with the axis \( a \) in the field direction and the equal axis \( b = c \) perpendicular to the field. \( \tau \), \( N \), and \( \varepsilon_r(\infty) \) are given by the following equations.

\[
\tau = \frac{\varepsilon_o \left( \varepsilon_{rl}'(\lambda - 1) + \varepsilon_{r2}' \right)}{\gamma_2}
\]  

(3.3.17)
\[ N = q \frac{\lambda^2 \varepsilon_{r1}}{\varepsilon_{r1} \left( \lambda - 1 \right) + \varepsilon_{r2}} \]  
(3.3.3.18)

\[ \varepsilon_r(\infty) = \varepsilon_{r1} \left[ 1 + q \frac{\lambda \left( \varepsilon_{r2} - \varepsilon_{r1} \right)}{\varepsilon_{r1} \left( \lambda - 1 \right) + \varepsilon_{r2}} \right] \]  
(3.3.3.19)

Eqs. (3.3.3.15 and 3.3.3.16) is similar to the Debye type Eqs. (3.3.3.6 and 3.3.3.7). Sillars assumed that the conductivity of dielectric 1 was null \((\gamma_1 = 0)\) and electrostatic interaction was negligible because two adjacent spheroids (sample 2) were far from each other. Therefore, the increase in volume fraction of species 2 (conductor) caused a deviation from the Debye model [115].

The validity of the MWS model for a system would be determined by checking out the constancy of \(\frac{\varepsilon_r(\omega_1) - \varepsilon_r(\omega_2)}{\varepsilon_r(\omega_1)}\) \((\varepsilon_r(\omega_n)\text{ is relative permittivity at a specific frequency, }\omega_n;\text{ n is 1 or 2)}\) as a function of temperature (Fig. 3.3.3.15). Fig. 3.3.3.16 shows the typical Cole-Cole plot observed in the MWS type sample [137].

Other widely known equations than the Debye type are the CC type (Eq. 3.3.3.20), the DC type (Eq. 3.3.3.21), and the HN type (Eq. 3.3.3.22). The CC type is suitable for many polar materials [127], the DC type is for a different kind of polar liquids from the CC type materials, for example, propylene glycol [127], and the HN type was found in polymers such as polycarbonate [127].

The CC type which shows a semicircle is an empirical equation [124] (Fig. 3.3.3.14 [123]). In case \(\beta\) is 1, then the CC type becomes the D type.

\[ \varepsilon_r^*(\omega) = \varepsilon_r(\infty) + \frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{1 + (i\omega\tau)^\beta} \]  
(3.3.3.20)

The DC type is also an empirical equation [125] (Fig. 3.3.3.14 [123]).

\[ \varepsilon_r^*(\omega) = \varepsilon_r(\infty) + \frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{1 + i\omega\tau} \]  
(3.3.3.21)

If \(\alpha\) is 1, then the equation expresses the D type.

The HN type is also based on experimental results [126, 127] (Fig. 3.3.3.14).

\[ \varepsilon_r^*(\omega) = \varepsilon_r(\infty) + \frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{1 + (i\omega\tau)^\beta} \]  
(3.3.3.22)
Figure 3.3.3.15 Dielectric properties of Sm$_2$O$_3$ doped (Sr$_{1-x}$Pb$_x$)TiO$_3$ ceramics (the ratio of raw chemicals: Sr:Pb:Ti = 0.7:0.3:1 by mole and Sm$_2$O$_3$:(Sr$_{1-x}$Pb$_x$)TiO$_3$ = 0.005:1 by weight) as a function of temperature at 10 kHz upon cooling.

Left scale: relative permittivity, Right scale: $\frac{\varepsilon_r(n \ Hz) - \varepsilon_r(1 \ MHz)}{\varepsilon_r(1 \ MHz)}$ where n is 100, 1 k, 10 k or 100 k.

Figure 3.3.3.16 Cole-Cole plot of multi-polymer layer sample for the MWS behavior.

Taken from Daly et al. [137].

MWS (Maxwell-Wagner-Sillars).
When both $\alpha$ and $\beta$ are 1, the above equation presents the D type. In case $\alpha$ is 1, the HN type is the same as the CC type. If $\beta$ is 1, then the HN type is the same as the DC type.

A general formula for the complex dielectric permittivity may be expressed as

$$\varepsilon_i^*(\omega) = \varepsilon_r(\infty) + \left(\varepsilon_r(0) - \varepsilon_r(\infty)\right) \int_0^\infty \left[-\frac{d \phi(t)}{dt}\right] \exp(-i\omega t) \, dt$$  \hspace{1cm} (3.3.3.23)

where $\phi(t)$ is dielectric decay or relaxation function [130, 121, 132]. If $\phi_D(t) = \exp\left(-\frac{t}{\tau}\right)$, the above equation leads to the Debye type, Eq.(3.3.3.5) [130-132]. $\phi_{HN}(t) = \frac{1}{\left(1+i\omega\tau\right)^\alpha}$ is used to describe the HN type [121]. Williams et al. proposed an empirical decay or relaxation function, Eq.(3.3.3.24) [130-132].

$$\phi_{KWW}(t) = \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^\beta\right] \hspace{1cm} (0<\beta\leq 1)$$  \hspace{1cm} (3.3.3.24)

This type is called Kohlrausch-Williams-Watts, KWW type [132] (Fig. 3.3.3-14).

Another method to describe the relaxation is based on stochastic approaches, and models such as the HN and KWW types have been demonstrated to be included in the proposed equations [140, 141].

Grant demonstrated that direct current (DC) conductive species showed a deviation from the ideal Debye type behavior at low frequency regions [133] (Fig. 3.3.3.17). Fig. 3.3.3.18 shows the Cole-Cole plots of Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ as an example [142]. In the equivalent circuit of plot (c) in Fig.3.3.3.17, the real and imaginary parts of complex permittivity are given by [133]

$$\varepsilon_i^*(\omega) = \varepsilon_r(\infty) + \frac{\varepsilon_{r1}(\omega)}{1 + \left(\omega \tau_1\right)^2}$$  \hspace{1cm} (3.3.3-25)

$$\varepsilon_i^\prime\prime(\omega) = \frac{\varepsilon_{r1}\omega \tau_1}{1 + \left(\omega \tau_1\right)^2} + \frac{\sigma(0)}{\varepsilon_\infty \omega}$$  \hspace{1cm} (3.3.3-26)

$$\text{tangent } \delta = \frac{\varepsilon_i^\prime\prime(\omega)}{\varepsilon_i^\prime(\omega)} = \frac{\sigma'(\omega)}{\sigma'(\omega)}$$  \hspace{1cm} (3.3.3-27)

$$\tau_1 = \frac{\varepsilon_\infty \varepsilon_i^\prime(\omega)}{\sigma_1(\omega)}$$  \hspace{1cm} (3.3.3-28)

where $\omega$ is an angular frequency, $\varepsilon_{r1}(\omega)$ is the relative permittivity of capacitor 1, $\varepsilon_r(\infty)$ is relative permittivity at a high frequency (e.g., $\omega = \infty$), $\sigma_1(\omega)$ is DC conductivity of conductor 1, $\sigma(0)$ is
Figure 3.3.3.17 Diagrams of complex conductivity (plot e, f, g, and h) and complex permittivity (plot i, j, k, and l) corresponding to four equivalent circuits (plot a, b, c, and d).

\( \omega \) = angular frequency. Taken from Grant [133].

\( \varepsilon_n \) = permittivity of species n (1 for species 1; 2 for species 2); \( \varepsilon_\infty \) for permittivity at high frequency (= \( \infty \)); \( \sigma_n \) = DC conductivity of species n; \( \sigma_\infty \) for conductivity at low frequency (= 0).

Figure 3.3.3.18 The Cole-Cole plots of Ni\(_{0.8}\)Zn\(_{0.2}\)Fe\(_2\)O\(_4\).

\( \epsilon' \), real part of complex permittivity; \( \epsilon'' \), imaginary part of complex permittivity; \( \nu \), frequency.

Taken from Bunget and Popescu [142] p. 292.

DC conductivity at a low frequency (e.g., $\omega = 0$), $\varepsilon_o$ is vacuum permittivity, and $\tau_1$ is the relaxation time of the capacitor 1. The admittance, $Y$, of a unit cube (with parallel plane electrodes) may be expressed

$$Y = i\omega \varepsilon_o \varepsilon_r^* = i\omega \varepsilon_o \left(\varepsilon'_r - i\varepsilon''_r\right)$$  \hspace{1cm} (3.3.3.29)

$$Y = \sigma^* = \sigma' + i\sigma''$$  \hspace{1cm} (3.3.3.30)

From Eqs. (3.3.3.29 and 3.3.3.30), the following equations are obtained.

$$\sigma' = \omega \varepsilon_o \varepsilon''_r$$  \hspace{1cm} (3.3.3.31)

$$\sigma'' = \omega \varepsilon_o \varepsilon'_r$$  \hspace{1cm} (3.3.3.32)

If the circuit satisfies Eqs. (3.3.3.31 and 3.3.3.32), then the Cole-Cole plot of conductivity becomes semicircular. Therefore, the correction of DC conductivity and the usage of modified values makes the Cole-Cole plots semicircular.

$$\sigma'' = \omega \left(\varepsilon' - \varepsilon_\infty\right)$$  \hspace{1cm} (3.3.3.33)

From plot (a) of Fig. 3.3.3.11, three kinds of relaxation mechanisms were observed at 190 and 150 °C. Plot (b) and (c) of Fig. 3.3.3.11 show two types of relaxation at 100, 50, and 25 °C. Plot (d) ~ (f) in Fig. 3.3.3.11 present one type of relaxation at 0, −2.7 (10 kHz weak field dielectric maximum temperature), −25, −50, and −100 °C. Low frequency behaviors at high temperature such as 190 and 150 °C could be due to conductivity which is often observed at higher temperatures than the transition temperatures. However, the lower frequency behaviors at lower temperatures such as 25 °C or behaviors at much lower temperatures, for example, the transition temperature could be due to conductive species which were connected to the mobile matrix. In other words, there could be the contribution of ferroelectric domain motion which became active at a temperature near the phase transition upon cooling.

### 3.3.3.6 SEM

The fractured surfaces of Sm$_2$O$_3$ doped SPT which were sputtered by gold were observed using a scanning microscope (S-3500N, Hitachi) to detect secondary ions (Fig. 3.3.3.19). The structure was similar to that observed in pure SPT (Sr-Pb (0.7:0.3 and 0.75:0.25 by mole)) samples (see Fig 3.2.12) on a macroscopic scale.
Figure 3.3.3.19 Microstructure of Sm$_2$O$_3$ doped SPT observed using scanning electron microscope (SEM) to detect secondary electrons. (a) $\times$ 1000 and (b) $\times$ 5000.
3.3.3.7 TEM

Fig. 3.3.3.20 shows the electron diffractions using a transmission electron microscope (TEM) (philips 420). TEM samples were prepared by the conventional sample process. The pellets were cut and polished to the thickness of 10~30 micrometers and finally a sample that was on a copper grid, was ionmilled. The final conditions of ionmill to prepare samples for TEM measurements were as follows: voltage, 5 kV; current, 8 mA; angle, 12 degrees. Diffraction patterns were obtained using selected area diffraction using 120 kV as an accelerating voltage. Two adjunct spots were observed in the doped Sm$_2$O$_3$ sample. This observation could be due to the twin boundary, low angle boundary, or weak ordering effects.

More detailed studies will be required to explore the origin of the such diffraction spots.

3.3.3.8 Comments

Sm$_2$O$_3$ doped SPT ceramics showed unusual relaxation behaviors. Because the doped SPT ceramics showed high tangent $\delta$ over a wide temperature range, the conductive species would contribute to the observed relaxation behaviors. Further studies of TEM will reveal how Sm$_2$O$_3$ was incorporated in the SPT matrix and it will be helpful to understand the mechanism of the unusual enhancement of relative permittivity at lower frequencies.

It is tempting to think of the doped SPT samples as two-phase structures with different conductivities. Subsequently, the effective geometry could be changing as a function of frequency. Because of the conductivity, it is not possible to close the $\varepsilon_r(0)$ vs. $\varepsilon_r(\infty)$ arcs. The validity of the MWS model would be determined by checking out the constancy of $\frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{\varepsilon_r(0)}$. Since there is no obvious new structure in $\Delta\varepsilon$ vs. T, it appears that the MWS model could be the most likely major contributor to the observed behaviors. Additional electrical property characterization will be necessary to explain the relaxation behaviors observed in the Sm$_2$O$_3$ doped sample.
Figure 3.3.3.20 Electron diffractions of (a) pure SPT, (b) Sm$_2$O$_3$ doped SPT, and (c) magnified image of (b).
3.4 Factors influencing weak field relative dielectric permittivity (maximum) of (Sr\(_{1-x}\)Pb\(_x\))TiO\(_3\) (SPT) (x = 0.2) solid solution system and the effect of full width at half maximum (FWHM) of X-ray diffraction peaks on the relative permittivity maximum

3.4.1 Introduction

In well behaved ferroelectric solid solutions such as (Ba\(_x\)Sr\(_{1-x}\))TiO\(_3\) and (Sr\(_{1-x}\)Pb\(_x\))TiO\(_3\), we have come to regard that the temperature dependence of the weak field dielectric permittivity, \(\varepsilon_{rw}\), measured at the radio frequencies (e.g., the range between 1 kHz and 1 MHz) as a simple indication of solid solution quality and homogeneity. With a Curie-Weiss constant, \(C_\varepsilon \sim 10^5\) which is expected in the paraelectric phase of a ferroelectric perovskite, at 2 °C away from the thermodynamic instability at the Curie point, \(T_c\), one may expect \(\varepsilon_{rw} \sim 50000\) in a near perfect homogeneous composition.

Until the need for the pyroelectric imaging community because of the necessary element for the application, a rounded \(\varepsilon_{rw}\) peak near room temperature in (Ba\(_{0.7}\)Sr\(_{0.3}\))TiO\(_3\) composition with \(\varepsilon_{rw-max} \sim 15000\) was considered very good (\(\varepsilon_{rw-max}\): weak field dielectric permittivity maximum). Functionally, the need in the pyroelectric images for a very sharp dielectric constant peak as a function of temperature, which would be prevented under weak direct current (DC) bias fields, leads to the application of much more sophisticated wet chemical processing because this processing proceeds in (Ba\(_{0.7}\)Sr\(_{0.3}\))TiO\(_3\) composition with \(\varepsilon_{rw-max} > 30000\) and with a weak field under character for the phase change at the \(T_c\).

For (Sr\(_{0.8}\)Pb\(_{0.2}\))TiO\(_3\), because of the much more aggressive reaction character of lead (Pb) cations, we expected that the homogenization of the solid solution would be much easier and hence were delighted to find that even in early processing a sharp dispersion free dielectric maximum with \(\varepsilon_{rw-max} \sim 35000\) was quite readily achieved under careful processing.

More detailed analysis of the dielectric data has, however, revealed several unusual features of the behaviors which are targets to this section and begin to call into question the naive assumption that the highest permittivity at the weak field dielectric maximum temperature is necessary with the most perfect homogeneous solid solution.

3.4.2 Experimental

Strontium lead titanate solid solutions were prepared using the conventional mixed oxide method. Suitable ratios of strontium carbonate (SrCO\(_3\)), lead oxide (PbO), and titanium oxide (TiO\(_2\)), namely, Sr-Pb-Ti (0.8:0.2:1) were ball milled and calcined at 1100 °C for 3 h.
calcined powders were ball milled again, and most samples were sintered at 1350 °C for 3 h after cold isostatic pressing. The pressed samples were covered with the calcined and sieved SPT powders, and the pressed mixture of lead zirconate and zirconia were also used as a lead source when most samples were sintered. The surfaces of samples were polished with silicon carbide (SiC) grinding powders (#600; average grain sizes, 14 µm).

Room temperature powder X-ray diffraction patterns were collected using an X-ray diffractometer with a Cu Kα X-ray source (PDIV, Scintag, Inc). Dielectric properties were measured using LCR meters (4284A, HP). Higher temperature properties up to ~ 190 °C were measured in an ambient atmospheric condition using an oven which was controlled by computer, and liquid nitrogen was used as a cooling medium. Lower (cryogenic) temperature properties down to ~ −260 °C were measured using a cryogenic system in vacuum, and temperature was controlled by computer. In both cases, step modes were used to carry out the measurements. In case of high temperature measurements, the step time was 0.25 sec at a temperature interval of 0.5 °C depending on the slope of capacitance vs. temperature plots because a steeper slope made the interval narrower. For the cryogenic temperature measurements, a step time was 1 min at a constant temperature interval of 0.5 °C. The data were collected at an alternating current (AC) of 1 V/cm and at an average of four datum values. Higher and lower temperature data were connected at −5 °C. There were measurements which were carried out beyond the above conditions.

### 3.4.3 Results and discussion

#### 3.4.3.1 Effect of containers and ovens for sintering on the dielectric properties of SPT (x=0.2)

Around the same time, the samples were prepared by using the relatively low purity chemicals, (SrCO₃ (99.9%+, Aldrich), PbO (99.9%, Aldrich), and TiO₂ (99.5%, Alfa Aesar)), different containers (ceramics or platinum), and different heating conditions (box ovens; constant heating up to the sintering temperature or rapid heating up to 700 °C and then constant heating up to the sintering temperature). Table 3.4.1 (a) summarizes a description of six samples, and Table 3.4.1 (b) lists the dielectric properties and the Curie-Weiss analysis at 10 kHz. Fig. 3.4.1 shows the dielectric properties of the six samples at 10 kHz as a function of temperature upon cooling. Figs. 3.4.2 and 3.4.3 show the dielectric properties as a function of temperature and frequency upon cooling and the thermal hysteresis of dielectric properties at 10 kHz. Fig 3.4.4 shows the results of the Curie-Weiss analysis. Each sample showed a similar dielectric constant
Table 3.4.1 (a) Description of samples sintered under various conditions

<table>
<thead>
<tr>
<th>Description</th>
<th>Oven</th>
<th>Heating rate</th>
<th>Container material</th>
<th>Shape</th>
<th>Thickness (mm)</th>
<th>Area (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Conventional box type oven</td>
<td>5 °C/min</td>
<td>Ceramics (1)</td>
<td>Disk</td>
<td>1.06</td>
<td>49.6</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Conventional box type oven</td>
<td>5 °C/min</td>
<td>Platinum (2)</td>
<td>Disk</td>
<td>1.20</td>
<td>49.0</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Conventional box type oven</td>
<td>5 °C/min</td>
<td>Platinum (2)</td>
<td>Disk</td>
<td>1.18</td>
<td>49.4</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Box type oven</td>
<td>Rapid up to 700 °C</td>
<td>Ceramics (3)</td>
<td>Disk</td>
<td>1.15</td>
<td>49.0</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Conventional box type oven</td>
<td>5 °C/min</td>
<td>Ceramics (1)</td>
<td>Disk</td>
<td>1.19</td>
<td>49.4</td>
</tr>
<tr>
<td>Sample 6</td>
<td>Conventional box type oven</td>
<td>5 °C/min</td>
<td>Ceramics (1)</td>
<td>Disk</td>
<td>1.19</td>
<td>48.0</td>
</tr>
</tbody>
</table>

Note: Ceramics (1): A sample was on a platinum sheet in double ceramic containers in a ceramic sagger (Fig.3.1.2 (a)).
Platinum (2): A sample was in a platinum dish in a ceramic sagger (Fig.3.1.2 (b)).
Ceramics (3): A sample was on a platinum sheet in double ceramic containers.

Table 3.4.1 (b) 10 kHz dielectric properties of samples sintered under various conditions

<table>
<thead>
<tr>
<th>Description</th>
<th>(\varepsilon_r) at (T_m)</th>
<th>(T_m) (°C)</th>
<th>(C) (°C)</th>
<th>(\theta) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>48000</td>
<td>-61</td>
<td>8.8 \times 10^4</td>
<td>-53</td>
</tr>
<tr>
<td>Sample 2</td>
<td>42000</td>
<td>-60</td>
<td>9.0 \times 10^4</td>
<td>-54</td>
</tr>
<tr>
<td>Sample 3</td>
<td>41000</td>
<td>-60</td>
<td>9.1 \times 10^4</td>
<td>-53</td>
</tr>
<tr>
<td>Sample 4</td>
<td>31000</td>
<td>-60</td>
<td>9.0 \times 10^4</td>
<td>-54</td>
</tr>
<tr>
<td>Sample 5</td>
<td>27000</td>
<td>-60</td>
<td>8.9 \times 10^4</td>
<td>-54</td>
</tr>
<tr>
<td>Sample 6</td>
<td>27000</td>
<td>-60</td>
<td>9.1 \times 10^4</td>
<td>-54</td>
</tr>
</tbody>
</table>

\(\varepsilon_r\): relative permittivity; \(T_m\): transition temperature at 10 kHz upon cooling,
\(C\): Curie-Weiss constant; \(\theta\): Curie-Weiss temperature.
Figure 3.4.1 (a) Effect of containers and box-type oven for sintering on dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.2) prepared from low purity raw chemicals:
Dielectric properties as a function of temperature at 10 kHz upon cooling in vacuum.
Sample 1, 5, and 6 were sintered in ceramic containers (in a sagger) at a constant heating rate (see setup in Fig 3.1.2 (a)); sample 1 and 6 were sintered in the same setting; sample 5 was sintered without sealing compounds between a ceramic lid and container;
Sample 2 and 3 were sintered in a platinum dish (in a sagger) at the constant heating rate (see setup in Fig. 3.1.2 (b)).
Sample 4 were sintered in ceramic containers at a rapid rate up to 700 °C and then at the constant rate.
Constant heating rate : 5 °C/min.
Rapid rate for sample 4 : about 10 min to be 700 °C from room temperature.

Note : Because samples sintered in only ceramic containers showed extremely various relative permittivity maximum peaks, SPT samples were prepared using the platinum dish.
Figure 3.4.1 (b) Effect of containers and box-type oven for sintering on dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.2): Dielectric properties as a function of temperature at 10 kHz upon cooling.

Measurement conditions: AC field, 1 V/cm; Averaging number, 4.

Temperature $> -5^\circ$C:
- Atmospheric condition; step time, 0.25 sec; step interval, $\leq 0.5^\circ$C
- (step interval depending on increase or decrease in rate of capacitance or relative permittivity as a function of temperature).

Temperature $< -5^\circ$C:
- Vacuum condition; step time, 1 min; step interval, 0.5 $^\circ$C.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Relative permittivity</th>
<th>Tangent δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>-250</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-200</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-150</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-50</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.00</td>
<td>1kHz</td>
<td>0.01</td>
</tr>
<tr>
<td>0.01</td>
<td>1kHz</td>
<td>0.01</td>
</tr>
<tr>
<td>0.02</td>
<td>1kHz</td>
<td>0.01</td>
</tr>
<tr>
<td>0.03</td>
<td>1kHz</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Figure 3.4.2** Effect of containers and box-type oven for sintering on dielectric properties of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) \((x = 0.2)\): Dielectric properties as a function of temperature and frequency upon cooling.

(i) Sample 1, (ii) Sample 2, (iii) Sample 3, (iv) Sample 4, (v) Sample 5, and (vi) Sample 6.

Sample 1, 5, and 6 were sintered in ceramic containers (in a sagger) at a constant heating rate.
Sample 2 and 3 were sintered in a platinum dish (in a sagger) at the constant heating rate.
Sample 4 were sintered in ceramic containers at a rapid rate up to 700 °C and then at the constant rate.

Measurement conditions: AC field, 1 V/cm; averaging number, 4.

Temperature > − 5 °C:
Atmospheric condition; step time, 0.25 sec; step interval : ≤ 0.5 °C
(depending on increase or decrease in rate of capacitance or relative permittivity as a function of temperature).

Temperature < − 5 °C:
Vacuum condition; step time, 1 min; step interval, 0.5 °C.
Figure 3.4.3 Effect of containers and box-type oven for sintering on dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) ($x = 0.2$): Dielectric properties at 10 kHz in cooling and heating cycles. 
(i) Sample 1, (ii) Sample 2, (iii) Sample 3, (iv) Sample 4, (v) Sample 5, and (vi) Sample 6. Sample 1, 5, and 6 were sintered in ceramic containers (in a sagger) at a constant heating rate. Sample 2 and 3 were sintered in a platinum dish (in a sagger) at the constant heating rate. Sample 4 were sintered in ceramic containers at a rapid rate up to 700 °C and then at the constant rate.
Measurement conditions: AC field, 1 V/cm; averaging number, 4.
Temperature < – 5 °C:
Vacuum condition; step time, 1 min; step interval, 0.5 °C.
Figure 3.4.4 Effect of containers and box-type oven for sintering on Curie-Weiss behaviors of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.2): Dielectric properties at 10 kHz in cooling cycles as a function of temperature as the results of two measurements combined at −5 °C.

(i) Sample 1, (ii) Sample 2, (iii) Sample 3, (iv) Sample 4, (v) Sample 5, and (vi) Sample 6.

Sample 1, 5 and 6 were sintered in ceramic containers (in a sagger) at a constant heating rate; Sample 2 and 3 were sintered in a platinum dish (in a sagger) at the constant heating rate; Sample 4 were sintered in ceramic containers at a rapid rate up to 700 °C and then at the constant rate.

$\varepsilon_r$, relative permittivity; Range, temperature range in which Curie-Weiss analysis was applied; Fit, fitted curve.

(i) $C=9 \times 10^4$ °C, $\theta=-53$ °C, $T_m=-61$ °C, 150.0 > $T$ > −42.5 °C, r=0.99990.

(ii) $C=9 \times 10^4$ °C, $\theta=-54$ °C, $T_m=-60$ °C, 160.0 > $T$ > −47.5 °C, r=0.99990.

(iii) $C=9 \times 10^4$ °C, $\theta=-53$ °C, $T_m=-60$ °C, 160.0 > $T$ > −45.0 °C, r=0.99990.

(iv) $C=9 \times 10^4$ °C, $\theta=-54$ °C, $T_m=-60$ °C, 170.0 > $T$ > −45.0 °C, r=0.99990.

(v) $C=9 \times 10^4$ °C, $\theta=-54$ °C, $T_m=-60$ °C, 172.5 > $T$ > −45.0 °C, r=0.99990.

(vi) $C=9 \times 10^4$ °C, $\theta=-54$ °C, $T_m=-60$ °C, 152.5 > $T$ > −42.5 °C, r=0.99990.

C, Curie-Weiss constant; $\theta$, Curie-Weiss temperature; $T_m$, transition temperature at 10 kHz; T, temperature; r, correlation factor.
behavior except the value around the transition temperature. In paraelectric regions, the six samples showed low tangent $\delta$, but the behaviors of tangent $\delta$ peaks around relative permittivity maximum peaks were different. In addition, the differences of the tangent $\delta$ values were observed near the relative permittivity peaks in both cooling and heating cycles. Tangent $\delta$ peak values around $-200$ °C were similar among the samples.

3.4.3.2 Effect of sintering temperature on the dielectric properties of SPT (x = 0.2)

The ceramic samples were prepared from high purity raw chemicals, SrCO$_3$ (99.995%, Aldrich), PbO (99.9995%, Alfa Aesar), and TiO$_2$ (99.999%, Aldrich), and pressed pellets were sintered around the same time using a platinum dish (inside a sagger) in a conventional box oven at a heating rate of 5 °C/min but at various temperatures (1375, 1350, 1300, and 1250 °C). Table 3.4.2 lists a description of the samples and the dielectric properties. Fig. 3.4.5 shows the 10 kHz dielectric properties of the samples sintered at various temperatures, and Figs. 3.4.6 and 3.4.7 show the frequency dependence, thermal hysteresis, AC field, and measurement rate dependence of dielectric properties as a function of temperature. The samples sintered at 1300 and 1250 °C showed lower density and relatively lower relative permittivity compared with those sintered at 1350 and 1375 °C. Tangent $\delta$ vs. temperature plots showed two kinds of peaks. The tangent $\delta$ peaks close to the main relative permittivity peaks showed the thermal hysteresis, AC field and measurement rate dependence, while the other tangent $\delta$ peaks did not show an obvious dependence of measurement conditions at the certain frequency, 10 kHz. Fig. 3.4.8 shows the Curie-Weiss behaviors of the samples. The samples which were sintered at lower temperatures showed lower Curie-Weiss constants.

3.4.3.3 Effect of sintering atmosphere on the dielectric properties of SPT (x = 0.2)

SPT ceramics were prepared from high purity SrCO$_3$ (99.995%, Aldrich), PbO (99.9995%, Alfa Aesar), and TiO$_2$ (99.999%, Aldrich). The samples were sintered under different sintering conditions: i) sintered in a platinum dish (inside a sagger) in a conventional box type oven, namely in air, at 1350 °C and ii) sintered on a platinum sheet in a tube flowing oxygen (O$_2$) gas around 1350 °C. The formed samples were covered with the calcined and sieved SPT powders. An additional lead source (calcined lead zirconate and zirconium oxide (PZ-Z)) was used for the sintering of the sample in a box type oven (this sample is labeled as Air sample). Meanwhile, the lead source (PZ-Z) was not used for the sample sintered flowing O$_2$ (this sample
Table 3.4.2 Description of samples sintered at various temperatures and dielectric properties at 10 kHz

<table>
<thead>
<tr>
<th>Description (Sintering temp (°C))</th>
<th>Shape</th>
<th>Thickness (mm)</th>
<th>Area (mm²)</th>
<th>Density (g/cm³)</th>
<th>ε&lt;sub&gt;r&lt;/sub&gt; at T&lt;sub&gt;m&lt;/sub&gt;</th>
<th>T&lt;sub&gt;m&lt;/sub&gt; (°C)</th>
<th>C (°C)</th>
<th>θ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1375</td>
<td>Part of a disk</td>
<td>1.15</td>
<td>43.2</td>
<td>5.67</td>
<td>41000</td>
<td>-58</td>
<td>9.1 × 10⁴</td>
<td>-51</td>
</tr>
<tr>
<td>1350</td>
<td>Part of a disk</td>
<td>1.30</td>
<td>20.0</td>
<td>5.62</td>
<td>36000</td>
<td>-58</td>
<td>9.0 × 10⁴</td>
<td>-50</td>
</tr>
<tr>
<td>1300</td>
<td>Disk</td>
<td>1.11</td>
<td>50.2</td>
<td>5.39</td>
<td>21000</td>
<td>-58</td>
<td>8.0 × 10⁴</td>
<td>-50</td>
</tr>
<tr>
<td>1250</td>
<td>Part of a disk</td>
<td>0.96</td>
<td>28.2</td>
<td>5.43</td>
<td>9000</td>
<td>-48</td>
<td>7.4 × 10⁴</td>
<td>-48</td>
</tr>
</tbody>
</table>

The area of a sample was calculated from the diameters of the sample measured by a scaler or obtained using a computer program after taking the picture of the sample on a scaled graph.

The density of a sample was measured by the Archimedes method at an average of three results.

ε<sub>r</sub>, relative permittivity; T<sub>m</sub>, transition temperature at 10 kHz upon cooling; C, Curie-Weiss constant; θ, Curie-Weiss temperature.
Figure 3.4.5 Effect of sintering temperature on dielectric properties of \((\text{Sr}_{1-x}\text{Pb}_{x})\text{TiO}_3\) \((x = 0.2)\). Samples were sintered at 1375, 1350, 1300, and 1250 °C and prepared from high purity raw chemicals.

Measurement conditions: Average of 4 data at 10 kHz (measured at 100, 1 k, 10 k, 100 k, and 1 MHz) as a function of temperature upon cooling.

Temperature > – 5 °C: Atmospheric condition; step time, 0.25 sec; step interval, ≤ 0.5 °C (depending on increase or decrease in rate of capacitance or relative permittivity as a function of temperature).

Temperature < – 5 °C: Vacuum condition; step time, 1 min; step interval, 0.5 °C.
Figure 3.4.6 Effect of sintering temperature on dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2). (a) 1375 and (b) 1350 °C. (i) Frequency dependence (100, 1k, 10k, and 100kHz), (ii) Thermal hysteresis, (iii) AC field dependence (1, 5, and 10 V/cm), (iv) Measurement rate dependence (S1, 1 min as a step time; S2, 2 min as a step time). Measurement conditions: Average of 4 data in vacuum less than –5 °C upon cooling at a step interval of 0.5 °C and at a rate of 1 min as a step time except S2 results.
Figure 3.4.7 Effect of sintering temperature on dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2). (a) 1300 and (b) 1250 °C. (i) Frequency dependence (100, 1k, 10k, and 100kHz), (ii) Thermal hysteresis, (iii) AC field dependence (1, 5, and 10 V/cm) (iv) Measurement rate dependence (S1, 1 min as a step time; S2, 2 min as a step time). Measurement conditions: Average of 4 data in vacuum less than −5 °C upon cooling at a step interval of 0.5 °C and at a rate of 1 min as a step time except S2 results.
Figure 3.4.8 Effect of sintering temperature on Curie-Weiss behaviors of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2) at 10 kHz in cooling cycles at (i) 1375, (ii) 1350, (iii) 1300, and (iv) 1250 °C. 

$\varepsilon_r$, relative permittivity; Range, temperature range in which Curie-Weiss analysis was applied; Fit, fitted curve: Curie-Weiss plots based on the application of the data in the temperature ranges. 

Measurement conditions: Average of 4 data at 10 kHz upon cooling. 

Temperature $> -5 \, ^\circ$C: Atmospheric condition; step time, 0.25 sec; step interval, $\leq 0.5 \, ^\circ$C (depending on increase or decrease in rate of capacitance or relative permittivity as a function of temperature). 

Temperature $< -5 \, ^\circ$C: Vacuum condition; step time, 1 min; step interval, 0.5 °C. 

(i) C=9×10$^4$ °C , $\theta$=−51 °C , $T_m$=−58 °C , 152.5>T>−40.0 °C, r=0.99990. 
(ii) C=8×10$^4$ °C , $\theta$=−50 °C , $T_m$=−58 °C , 150.0>T>−37.5 °C, r=0.99990. 
(iii) C=8×10$^4$ °C , $\theta$=−50 °C , $T_m$=−58 °C , 160.0>T>−35.0 °C, r=0.99990. 
(iv) C=7×10$^4$ °C , $\theta$=−48 °C , $T_m$=−55 °C , 167.5>T>−30.0 °C, r=0.99990. 

C, Curie-Weiss constant; $\theta$, Curie-Weiss temperature; $T_m$, Transition temperature at 10 kHz. 
T: Temperature, r: Correlation factor.
is labeled as O2 sample). The color of the sample sintered with flowing O2 showed white, which remained similar to the color of pressed samples before sintering. However, the sample sintered in the box type oven with the supply of lead oxide by the lead source turned dark. The supply of lead oxide by the lead source (PZ-Z) to the samples would affect the color of the samples. When calcined powders covered the samples (and it might prevent the lead oxide from supplying the samples), the color of the samples remained similar to that before sintering without turning dark.

Table 3.4.3 lists a description of the samples. Fig. 3.4.9 shows the effect of the atmosphere, in air (using the conventional box oven) or in an O2 atmosphere, on dielectric properties as a function of temperature at 10 kHz upon cooling. Fig. 3.4.10 shows the frequency dependence, thermal hysteresis, AC field, and measurement rate dependence of dielectric properties as a function of temperature. Furthermore, Fig. 3.4.11 shows the Curie-Weiss behavior of the samples.

“Air sample” showed higher dielectric constant at the transition temperature (~35000 at −58 °C) than “O2 sample” did (~20000 at −59 °C). Both samples showed similar Curie-Weiss constant, 9 × 10^4 °C, but “O2 sample” showed slightly higher Curie-Weiss constant. The sample sintered at 1300 °C showed similar relative permittivity (~20000 at −58 °C) to “O2 sample,” but the Curie-Weiss constant of the sample sintered at 1300 °C (8 × 10^4 °C) was lower than that of the “O2 sample.” Additionally, “O2 sample” showed higher tangent δ maximum at low temperature, 0.019 at −200 °C. Meanwhile, “Air sample” showed 0.014 at −200 °C, and the 1300 °C sample did not show an obvious peak maximum but a shoulder 0.017 at −200 °C.

### 3.4.3.4 Effect of additional ball milling for calcined powders on the dielectric properties of SPT (x = 0.2)

The samples were prepared from the relatively low purity chemicals (SrCO3 (99.9%+, Aldrich), PbO (99.9%, Aldrich), and TiO2 (99.5%, Alfa Aesar)). Calcined powders were ball milled using yttrium-stabilized zirconia balls (5 mm in diameter) for 20 h, and pressed samples were sintered in a platinum dish (inside a sagger) in a conventional box oven (the sample may be called as the sample without the extra ball milling). After 20 h ball milling and sieving, the sieved powders were ball milled again with yttrium-stabilized zirconia cylinders (3/8-in diameter) for 4 h. After pressing, the samples were sintered in the same way as the sample without extra ball milling (the sample may be called as the sample with the extra ball milling).
Table 3.4.3 Description of samples sintered in air and flowing oxygen and dielectric properties at 10 kHz

<table>
<thead>
<tr>
<th>Description (Sintering condition)</th>
<th>Shape</th>
<th>Thickness (mm)</th>
<th>Area (mm²)</th>
<th>Density (g/cm³)</th>
<th>$\varepsilon_r$ at $T_m$</th>
<th>$T_m$ (°C)</th>
<th>C (°C)</th>
<th>$\theta$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>Part of a disk</td>
<td>1.21</td>
<td>28.6</td>
<td>5.50</td>
<td>37000</td>
<td>−58</td>
<td>8.8 × 10^4</td>
<td>−50</td>
</tr>
<tr>
<td>flowing O₂</td>
<td>Disk</td>
<td>1.20</td>
<td>47.5</td>
<td>5.60</td>
<td>20000</td>
<td>−59</td>
<td>9.4 × 10^4</td>
<td>−53</td>
</tr>
<tr>
<td>1350 (air)</td>
<td>Part of a disk</td>
<td>1.30</td>
<td>20.0</td>
<td>5.62</td>
<td>36000</td>
<td>−58</td>
<td>9.0 × 10^4</td>
<td>−50</td>
</tr>
</tbody>
</table>

1350 (air) is the same sample (1350) described in Table 3.4.2.

The area of a sample was calculated from the diameters of the sample measured by a scaler or obtained using a computer program after taking the picture of the sample on a scaled graph.

The density of a sample was measured by the Archimedes method at an average of three results.

$\varepsilon_r$, Relative permittivity; $T_m$, Transition temperature at 10 kHz on cooling; C, Curie-Weiss constant; $\theta$, Curie-Weiss temperature.
Figure 3.4.9 Effect of atmosphere (air or oxygen (O$_2$)) on temperature dependence of dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.2$) prepared from high purity raw chemicals.

In air, sintered in a conventional box oven.

In flowing O$_2$, sintered in a tube furnace in which O$_2$ flowed.

Measurement conditions: Average of 4 data at 10 kHz upon cooling.

Temperature $> -5^\circ$C: Atmospheric condition; step time, 0.25 sec; step interval, $\leq 0.5^\circ$C (depending on increase or decrease in rate of capacitance or relative permittivity as a function of temperature).

Temperature $< -5^\circ$C: Vacuum condition; step time, 1 min; step interval, 0.5 $^\circ$C.
Figure 3.4.10 Effect of sintering atmosphere (air or O₂) on dielectric properties of (Sr₁₋ₓPbx)TiO₃ (x = 0.2). (a) In air: sintered in a conventional box oven, and (b) flowing O₂: sintered in a tube furnace in which O₂ flowed. (i) Frequency dependence (1kHz, 10kHz, and 100kHz), (ii) Thermal hysteresis, (iii) AC field dependence (1, 5, and 10 V/cm) (iv) Measurement rate dependence (S1, 1 min as a step time; S2, 2 min as a step time). Measurement conditions: Average of four data in vacuum less than −5 °C on cooling at a step interval of 0.5 °C and at a rate of 1 min as a step time except S2 results.
Figure 3.4.11 Effect of sintering atmosphere (air or O₂) on Curie-Weiss behavior of (Sr₁₋ₓPbx)TiO₃ (x = 0.2).

(i) Sintered in a conventional oven and in the air (ii) Sintered in a tube furnace flowing O₂
 εᵣ, relative permittivity; Range, temperature range in which Curie-Weiss analysis was applied; Fit, Fitted curve.

Measurement conditions: Average of 4 data at 10 kHz upon cooling.

Temperature > − 5 °C: Atmospheric conditions; step time, 0.25 sec; step interval, ≤ 0.5 °C
(depending on increase or decrease in rate of capacitance or relative permittivity as a function of temperature).

Temperature < − 5 °C: Vacuum conditions; step time, 1 min; step interval, 0.5 °C.

(i) C=9×10⁴ °C , θ=−50 °C , Tₘ=−58 °C, 165.0>T>−42.5 °C, r=0.99990.
(ii) C=9×10⁴ °C , θ=−53 °C , Tₘ=−59 °C, 177.5>T>−37.5 °C, r=0.99990.

C, Curie-Weiss constant; θ, Curie-Weiss temperature; Tₘ, Transition temperature at 10 kHz; T, temperature; r, correlation factor.
Table 3.4.4 lists a description of the samples. Fig 3.4.12 shows the relative permittivity and tangent δ of the samples as a function of temperature in cooling cycles at 10 kHz. Fig. 3.4.13 shows the measurement condition dependence of dielectric properties: frequency (1, 10, and 100 kHz), thermal hysteresis, AC field (1, 5, and 10 V/cm), and rate (1 and 2 min as a step time at a step temperature interval of 0.5 °C). Fig. 3.4.14 shows the results of the Curie-Weiss analysis of the samples. The dielectric constant at the transition temperature was ~45000 at −58 °C for the sample with the extra ball milling and ~25000 at −57 °C for the sample without the extra ball milling. The dielectric constant of the sample without the additional ball milling was expected to be similar to the values of the samples in Table 3.4.1, ~40000 at −60 °C, but the samples showed a difference. Therefore, the ball milling conditions and/or conditions to prepare similar calcined powders before pressing are also important factors to obtain samples which have reproducible dielectric properties. Thus the specification of the conditions will be necessary. The additional ball milling influenced the dielectric constant around the transition temperatures and tangent δ behaviors. Both samples showed similar tangent δ values at low temperature, 0.015 around −205 °C, as the maximum for the sample with the extra ball milling and 0.015 at −205 °C as a shoulder for the sample without the extra ball milling. However, the rest of tangent δ values, especially in the ferroelectric states, were different.

3.4.3.5 Summary of dielectric properties of (Sr₁₋ₓPbₓ)TiO₃ (x = 0.2)

Sintering conditions such as sintering temperature, atmosphere, and containers affected relative permittivity values at transition temperatures. Additionally, powders before pressing, for example, the effects of ball milling and purity of raw chemicals, influenced relative permittivity at the transition temperatures. A sufficient sintering temperature range existed and lower sintering temperatures such as 1300 and 1250 °C lowered relative permittivity at the transition temperatures and the Curie-Weiss constants. The sample sintered in flowing oxygen gas showed lower relative permittivity than did the one sintered in a conventional box oven (for the present study), but it showed a similar Curie-Weiss constant. The samples showed one peak in relative permittivity vs. temperature plots, but they showed two obvious tangent δ peaks in tangent δ vs. temperature plots, peaks near the transition temperature based on relative permittivity ~−60 °C and peaks at lower temperature ~−200 °C. However, some samples showed one maximum at ~−60 °C and a shoulder at ~−200 °C in tangent δ vs. temperature plots. The tangent δ peaks around −60 °C showed a difference depending on the samples. In addition, these peaks depended
Table 3.4.4 Description of samples with and without additional ball milling before the samples were pressed

<table>
<thead>
<tr>
<th>Description</th>
<th>Shape</th>
<th>Thickness (mm)</th>
<th>Area (mm²)</th>
<th>Density (g/cm³)</th>
<th>εᵣ at Tₘ</th>
<th>Tₘ (°C)</th>
<th>C (°C)</th>
<th>θ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>with additional ball milling</td>
<td>Disk</td>
<td>1.87</td>
<td>47.9</td>
<td>5.63</td>
<td>46000</td>
<td>−58</td>
<td>9.0 × 10⁴</td>
<td>−50</td>
</tr>
<tr>
<td>without additional ball milling</td>
<td>Disk</td>
<td>1.81</td>
<td>47.2</td>
<td>5.66</td>
<td>24000</td>
<td>−57</td>
<td>9.1 × 10⁴</td>
<td>−51</td>
</tr>
</tbody>
</table>

The area of a sample was calculated from the diameters of the sample measured by a scaler or obtained using a computer program after taking the picture of the sample on a scaled graph. The density of a sample was measured by the Archimedes method at an average of three results.

εᵣ, Relative permittivity; Tₘ, Transition temperature at 10 kHz upon cooling; C, Curie-Weiss constant; θ, Curie-Weiss temperature.
Figure 3.4.12 Effect of additional ball milling on dielectric properties of $(Sr_{1-x}Pb_x)TiO_3$ $(x = 0.2)$ ceramic.
Sample 1: Additionally ball milled with cylinder media for 4 h after 20 h ball milling of calcined powders and sieving.
Sample 2: No additional ball milling after 20 h ball milling of calcined powders and sieving.
Measurement conditions: Average of 4 data at 10 kHz upon cooling.
a) Temperature $> -5$ °C: Atmospheric condition; step time, 0.25 sec; step interval, $\leq 0.5$ °C (depending on increase or decrease in rate of capacitance or relative permittivity as a function of temperature).
b) Temperature $< -5$ °C: Vacuum condition; step time, 1 min; step interval, 0.5 °C.
Figure 3.4.13 Effect of additional ball milling on dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2) ceramic.

Samples with (a) additional ball milling and (b) no additional ball milling. (i) Frequency dependence (1k, 10k, and 100kHz), (ii) Thermal hysteresis, (iii) AC field dependence (1, 5, and 10 V/cm) (iv) Measuring rate dependence (S1, 1 min as step time; S2, 2 min as step time). Measurement conditions: Average of 4 data in vacuum in the range of less than –5 °C upon cooling at a step interval of 0.5 °C.
Figure 3.4.14 Effect of additional ball milling on Curie-Weiss behavior of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2) ceramics.

(i) Sample 1: Ball milled with cylinder media for 4 h after 20 h ball milling of calcined powders and sieving.
(ii) Sample 2: No additional ball milling after 20 h ball milling of calcined powders and sieving.

$\varepsilon_r$, relative permittivity; Range, temperature range in which Curie-Weiss analysis was applied; Fit, curve obtained by fitting in the temperature range.

Measurement conditions: Average of 4 data at 10 kHz on cooling.

Temperature $\geq -5$ °C: Atmospheric condition; step time, 0.25 sec; step interval, $\leq 0.5$ °C

Temperature $\leq -5$ °C: Vacuum condition; step time, 1 min; step interval, 0.5 °C.

(i) $C=9 \times 10^4$ °C, $\theta=-50$ °C, $T_m=-58$ °C, 152.5$T>-42.5$ °C, $r=0.99990$.
(ii) $C=9 \times 10^4$ °C, $\theta=-51$ °C, $T_m=-57$ °C, 152.5$T>-42.5$ °C, $r=0.99990$.

$C$, Curie-Weiss constant; $\theta$, Curie-Weiss temperature; $T_m$, transition temperature at 10 kHz upon cooling; $T$, temperature; $r$, correlation factor.
on measurement conditions like thermal hysteresis, AC field, and measurement rate. Therefore, the tangent δ peaks close to the relative permittivity maxima could be due to the motion of domains. On the contrary, the tangent δ peaks around −200 °C did not show a measurement condition dependence such as thermal hysteresis, AC field, and measurement rate. In addition, the samples sintered in an oxygen atmosphere showed higher tangent δ values than the samples sintered in air, or in a box oven, at a similar temperature, 1350 °C. The samples sintered in the box oven at lower temperatures such as 1300 and 1250 °C showed higher values than the samples sintered at higher temperatures, for example, 1375 and 1350 °C. There are possibilities for the tangent δ peaks: i) a different type of domain wall motion from that observed in tangent δ peaks around −60 °C, ii) an antiferrodistortive phase transition similar to that observed in strontium titanate [102], and iii) behaviors due to polar and/or dipolar defects [63, 143]. Among them, ii) the ferroic transformation might have a higher possibility because these peaks demonstrated that a lower dependence of measurement conditions. Moreover, the samples showed similar values around −200 °C.

3.4.3.6 Room temperature X-ray diffraction peak analysis (preliminary results)

The powder X-ray diffraction patterns of some samples were collected at room temperature using an X-ray source of Cu Kα, and they were analyzed by the program, PRO-FIT, developed by Toraya [1].

Fig. 3.4.15 (a) shows the relative permittivity of samples which were sintered under the same condition as an experimental setup, but which showed different relative permittivity at the transition temperatures. These were the results of sample 1 and sample 6 listed in Table 3.4.1. Fig. 3.4.15 (b) shows the full width at half maximum (FWHM) and the relative intensity of the samples. The high and low relative permittivity samples did not show a specific orientation because they showed similar relative intensity behaviors. But the high relative permittivity sample showed wider FWHM than did the low relative permittivity sample. The samples sintered at various temperatures showed a similar tendency: higher dielectric constant samples showed wider FWHM. The samples with and without the additional ball milling showed a similar tendency: higher relative permittivity samples showed wider FWHM.

The broader FWHM is caused by the instrument and samples. There are many reasons related to materials, mainly, the size effects and lattice imperfection effects. The size effects include small crystallites and the lattice imperfection effects include heterogeneous strain,
Figure 3.4.15 Preliminary room temperature X-ray diffraction peak analysis of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) ($x = 0.2$) ceramics with different relative permittivity maximum. Two samples were sintered under similar conditions, e.g., in ceramic containers. High permittivity sample (Sample 1 in Fig.3.4.1). Low permittivity sample (Sample 6 in Fig.3.4.1).

(a) Dielectric properties of SPT at 10 kHz upon cooling.
(b) Preliminary FWHM and relative intensity results of the high and low relative permittivity maximum samples (shown in plot (a)).

$\varepsilon_r$, relative permittivity; FWHM, full width at half maximum.

Fig. 3.4.16 (a) shows the effect of strain on the peak profiles, that is, the effect of d-spacings parallel to (along) the direction of an incident X-rays [144]. Tensile and uniform strain, namely, enlarged d-spacing, moves the position of the peak to a lower angle without changing the shape of the peak profile. Meanwhile, compressed and uniform strain, namely, shortened d-spacing, shifts the position to a higher angle. However, heterogeneous strain changes a peak profile and makes it broader. The position of the peak depends on the average of d-spacings. If the average value of d-spacings is larger (like the tensile condition) than the original d-spacing, then the position becomes lower. When the average value of d-spacings is smaller than the original value without deforming, like the compressed condition, the position becomes higher. If a d-spacing of each crystallite shows a different value influenced by the chemistry or mechanical conditions, then a peak would be broadened.

Fig. 3.4.16 (b) shows the size effect on the broadening of peak profiles, that is, the effect of size perpendicular to incident X-rays [145]. If the X-ray diffracts at an only Bragg angle ideally, then a peak profile becomes sharp and hence the profile is a line without a width. However, generally, the X-ray diffracts at a range containing the Bragg angle, and hence the peak profile becomes wider. In other words, the peak has a specific width. This width depends on the coherent length of crystallites perpendicular to the incident X-rays, and small size crystallites make the profile broader.

Therefore, more heterogeneity (various d-spacings) along the direction of the incident X-ray and smaller size coherent X-ray areas perpendicular to the incident X-ray cause broader FWHM. Because the room temperature is far above the transition temperatures of these samples (about −60 °C), the strain hardly contributed to the various d-spacings. The solid solution system has the possibility to have chemical inhomogeneity, and it could thus cause different d-spacings. Therefore, it would be reasonable to think of the micro chemical inhomogeneity as a major contributor to the peak widths instead of the strain. In addition, the contribution from the small crystallites cannot be ignored. However, the samples sintered at higher temperatures also showed wider FWHM than the samples sintered at low temperatures. Because the samples sintered at higher temperatures were expected to have larger grains, the major reason of wide FWHM would be due to the lattice imperfection.

Further study will be necessary to pin down the precise origin of such behaviors. The contribution of each component will reveal the mechanism of relative permittivity.
Figure 3.4.16 (a) Effect of lattice strain on X-ray diffraction peak profile and position assuming samples of which the sizes perpendicular to incident X-rays are the same (not shown in the plots).

- \(d_o\), spacing of a sample without strain.
- \(d_T\), spacing of a sample with tensile strain.
- \(d_C\), spacing of a sample with compressed strain.
- \(d_{Hi}\), spacing of a sample with heterogeneous strain.

Assuming Average of \(\sum d_{Hi} = d_o\)

After Cullity [93] p.287, with permission from Mrs. Cullity.
Figure 3.4.16 (b) Effect of size on (i) X-ray diffraction, and (ii) and (iii) schematic X-ray diffraction peaks for a sample which has m layers with a spacing, d, and thickness, t (= m·d).

In plot (ii), samples diffract around a Bragg angle, namely, from lower limit to upper limit (i.e., sketch for small crystallite samples).

In plot (iii), samples diffract at a Bragg angle only under ideal conditions.

Xmn, X-ray which inclicts on layer m from 0 (surface) to m (bottom); n is B, θ₁, or θ₂; B satisfies the Bragg diffraction; θ₁ determines upper limit of a diffraction angle and θ₂ determines lower limit of a diffraction angle.

Xmn', X-ray which is diffracted by layer m.

I, Intensity; β, FWHM (full width at half maximum).

2θ₁ – 2θ₂ depends on a number of m and increases as the value of m decreases.

After Cullity et al. [144]. pp. 168 and 169, with permission from Prentice Hall.
3.4.4 Comparison of the observation with previous studies

There are various factors which influence relative permittivity, and many results on huge relative permittivity samples have been reported. A number of factors which influence relative permittivity are categorized as follows: i) measurement conditions, ii) materials, iii) processing, and iv) additional components such as dopants. This section will review the literature on materials with huge relative permittivity and on factors which influence the relative permittivity of materials in order to compare our observations with the previous investigation.

Relative permittivity is calculated from the capacitance and dimensions of a sample. Therefore, there are factors related to measurement conditions which influence relative permittivity values: for example, measurement conditions of capacitance (the selection of an instrument, calibration method, temperature, frequency, measurement rate, the direction of the measurement such as cooling or heating, measurement atmosphere, AC field, DC field, pressure (stressed), strain, and energy irradiation), the accuracy of the dimensions of a sample and the condition of electrodes (uniformity, thickness, contact between electrodes and the sample, and contact between the electrodes and, for example, the pins of a fixture for measurements). When the thickness of an matrix which contains an insulting substance (e.g., dielectric) is used to calculate the dielectric constant of the insulator and the thickness of the insulator is different from that of the matrix, then the effective relative permittivity of the insulator is obtained [146]. Stress free KH2PO4 (KDP) and rochelle salt showed higher relative permittivity than the strain free samples [146]. SrTiO3 thin films showed the effect of stress on relative permittivity than the strain free samples [146]. SrTiO3 thin films showed the effect of stress on relative permittivity [147] and the relative permittivity of compressive strain samples was higher than those of tensile strain samples [148]. 0.9 % Nb (niobium) doped KTaO3 (KTa1-xNbxO3) decreased relative permittivity under higher pressure/DC field conditions [149]. Ultraviolet (UV) irradiation enhanced the relative permittivity of SrTiO3 [150] and KTaO3 [151]. The authors proposed two models to explain the UV enhancement behaviors: i) polar cluster model and ii) Maxwell-Wagner or Maxwell-Wagner-Sillars model (see the end of this section), namely, metallic cluster model. NaNO2 single crystals, which showed order-disorder transitions, demonstrated higher relative permittivity at lower frequencies [111]. KDP showed the measurement direction dependence of relative permittivity based on the crystal axis [152].

Although CaCu3Ti4O12 [153] and Cu2Ta4O12 [154] showed high relative permittivity, it could be due to an external mechanism [154]. Some bulk compositions or solid solution systems showed the (intrinsic) enhancement of the dielectric constant. The specific composition of solid
solution systems such as the tungsten bronze crystal $K_2O$-$SrO$-$Nb_2O_5$ system ($K_2O$-$SrO$-$Nb_2O_5$ (11.88:40.10:48.02)) [155] or $K Ta_{0.9} Nb_{0.1} O_3$ [156] showed high relative permittivity. There were solid solutions such as PZT ($PbTiO_3$-$P bZrO_3$) [157] in which high dielectric constants were observed near and/or at the morphotropic phase boundaries [157-159]. $^{18}O$ substituted $SrTi^{16}O_3$ or $SrTi(16O_{1-x}^{18}O_x)_3$ showed high relative permittivity [160-162] when $x = 0.37$ [160] or $x = 0.38$ [161], while $SrTi^{16}O_3$ showed lower values at similar temperatures without showing any peak maximum [161]. Relaxors showed high dispersive relative permittivity [163], and lower frequency dielectric constant maxima were higher than values at higher frequencies [163, 164, 146, 149].

$(Pb_{1-x}Ca_x)BO_3$ (B: various B-site ions with different radius) ($x = 0.50$ or 0.75) shows relative permittivity, $\varepsilon_r$, $\sim$59 when the radius of the B-site ion, $r_B$, is 0.059 nm and $x$ is 0.75, while it shows $\varepsilon_r$, $\sim$26 when $r_B$ is 0.072 nm and $x$ is 0.75. The authors explained that the mobility of the B-site ion in the octahedron of the perovskites enhanced the relative permittivity of the system [165]. The same authors observed that $AZrO_3$ or $A(Mg_{1/3}Nb_{2/3})O_3$ (A: various A-site ions with various polarizability, e.g., Pb, Ba, Sr, and Ca) showed higher relative permittivity when A-site ions show higher average electric polarizability [165, 166].

Superlattices observed on some thin films showed the enhancement of relative permittivity. However, the reason of the enhancement in some (similar) systems was not revealed clearly [167, 168]. There were authors who explained the enhancement by the model based on the rigid body motion of a domain wall lattice, the motion of a single particle type in a sinusoidal washboard potential [168].

Pure homogeneous (organic or inorganic) polymers such as polyacene quinone radical (PAQR) polymers showed high dielectric constants due to nomadic polarization [169]. The nomadic polarization is due to the drift of either free protons or electronic carriers along the long domains. In addition, the polarization shows large electronic polarization of which the response is reversible, and is usually hysteresis free which is different from the piezoelectric and ferroelectric types [170, 171, 169].

The effects of processing such as an oxygen (O$_2$) annealing [172] on the enhancement of relative permittivity was observed. According to the authors, this enhancement may be due to the effects of the improvement in grain sizes and crystallinity [172]. The effect of sizes and crystallinity of (Ba, Sr)TiO$_3$ films on relative permittivity were observed [173]. The grain size effects were observed in (Ba$_{0.65}$Sr$_{0.35}$)TiO$_3$ thin films [174] and bulk BaTiO$_3$ (BT) ceramics [40]. The relative permittivity of LiNbO$_3$ single crystals with various concentrations of defects was
calculated with assumptions, and the higher concentrations of the Li site vacancies lowered the relative permittivity of the system [175]. Amorphous LiNbO₃ thin films with defects and micronetworks similar to the crystalline LiNbO₃ thin films showed high relative permittivity due to the Li ion transfer to (the vacancy of) the adjacent O-octahedron unit. Meanwhile, the crystal LiNbO₃ did not show high relative permittivity because Li ions in crystal LiNbO₃ were not able to move to the vacancy of the adjacent O-octahedrons. The authors demonstrated that this anomaly was not caused by the interfacial effect between the electrodes and film [176].

The composite, NaNO₂ in synthetic opals, which consisted of closely packed silica spheres, showed a relatively higher dielectric constant than the dielectric constant of the opals or NaNO₂ single crystals along the b-axis. The enhancement was explained by the interaction of liquid NaNO₂ with the NaNO₂ itself and with the silica spheres of the opal [177].

Percolation conductivity was used to explain the behavior of the metal-insulator composite, Ag particles dispersed in the KCl matrix. As the volume fraction of the metal increased, the relative permittivity of the system rose drastically after the percolation threshold [178]. The large dielectric constant of CH(IrCl₆)y (e.g., y = 0.010) compared with CH(I)y (e.g., y = 0.0207) was explained by percolation dielectric conductivity [179].

Doping is a method to enhance the relative permittivity of a system. Lanthanum (Ln) doping PZT, PLₙZT(4/30/70) films showed a different dielectric constant and tangent δ. Ln, the elements of lanthanide series of which the sizes were larger or equal to that of Gd, stayed mainly on the A-sites. La, Ce, Pr, and Nd on the A-site showed an obvious increase in dielectric constant. Th, Dy, Y, and Ho (amphoteric), Gd on the A-sites and Er on the B-sites did not show an obvious increase in dielectric constant. Tm, Yb, and Lu in the B-sites showed a slight increase in dielectric constant [180]. La doped PbTiO₃ had the possibility to have A-site and/or B-site vacancies, (Pb₁₋ₓ/Lax)TiO₃ (PLT-A) and/or (Pb₁₋ₓ/Lax)Ti₁₋ₓ/4O₃ (PLT-B). 15 % La-modified PbTiO₃ with the A-site vacancies showed high relative permittivity at the transition temperature [181], but the results were doubtful [182]. Ca doped SrTiO₃, Sr₁₋ₓCaₓTiO₃ (x=0.0107) crystal showed high permittivity at its peak maximum [183].

A well-known external mechanism which enhances dielectric constant is the Maxwell-Wagner-Sillars (MWS) or Maxwell-Wagner (MW) effect. This effect is generally associated with the inhomogeneous conductor or semiconductor nature of the samples [116, 184-189, 113, 114] such as BaTiO₃ with ferrite (Ni₀.₅Zn₀.₇)Fe₂.₁O₄ (NZFO) [116], CuO doped (Ba₀.₈Sr₀.₂)(Ti₀.₉Zr₀.₁)O₃ (BSTZ) and associated with surface barrier layer capacitors (BLCs) or reduction-reoxidation layers which showed high effective dielectric constant [187]. The
enhancement of relative permittivity by polycrystalline semiconductors were explained by the Maxwell-Wagner layer model assuming that grain boundary layers were highly resistive. Therefore, if high resistivity layers were formed on grains of a substance, for example, n-type oxide materials, then the substance might show the enhancement of dielectric constant [184]. There are various methods to create the n-type oxides: i) to sinter a ferrite under reducing conditions and then cool it under too high oxygen pressure [184] or ii) to introduce a small amount (≪ 1%) of trivalent ions such as Gd$^{3+}$, La$^{3+}$, Sb$^{3+}$, Y$^{3+}$, and rare earth ions in the Ba (Ba$^{2+}$) sites of BaTiO$_3$ (i.e., the A-site of the perovskite) and/or pentavalent ions such as Nb$^{5+}$, Ta$^{5+}$ in the Ti (Ti$^{4+}$) sites of BaTiO$_3$ (i.e., the B-site of the perovskite) [185]. There were a number of systems which showed the MWS behavior: semiconductors [184] such as La$_{0.9}$Sr$_{0.1}$MnO$_3$ [184], Nb doped BaTiO$_3$ [188], and Li and Ti doped NiO [189], systems like BaFe$_{1/2}$Nb$_{1/2}$O$_3$ (BFN) [113], and superlattice films with (Ba$_{1-x}$Sr$_x$)TiO$_3$ (BST) (x = 0.2) and BST (x = 0.8) [114]. La$_{0.9}$Sr$_{0.1}$MnO$_3$ would be described as (La$^{3+}$$_{0.9}$Sr$^{2+}$$_{0.1}$)(Mn$^{3+}$_{1-δ}Mn$^{4+}$$_{δ}$)O$_{2-δ}$ (δ ≈ 0.1) and a rod sample showed high relative permittivity [186].

Therefore, the observation that the inhomogeneity of the system enhanced relative permittivity is extremely new, and further studies will be necessary to understand the mechanisms of relative permittivity in detail.
3.5 Phase diagram

Studies on additional \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) compositions with \(x = 0.05, 0.10, \text{and} 0.15\)

3.5.1 Introduction

The phase transitions of strontium titanate and lead titanate \((\text{SrTiO}_3\text{-PbTiO}_3)\) solid solution system based on the relative permittivity measurements have been studied over the entire composition range \([11, 12, 190, 19, 21]\) including the compositions rich in \(\text{SrTiO}_3\) \([15, 18, 191, 65]\). The \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) system \((0.1 \leq x \leq 0.9)\) showed a linear relationship between transition temperatures and the mole fraction of lead \((\text{Pb})\), \(x\). However, SPT \((x \leq 0.1)\) has been reported to have complex dielectric behaviors. Boganov and Khomutetskaia measured the dielectric constant of SPT \((x = 0.1)\) down to \(-200^\circ\text{C}\) as a function of temperature at 5 kHz in vacuum, and they observed one maximum \([12]\). Martin et al. observed two maxima in dielectric constant vs. temperature plots of the SPT \((x = 0.04, 0.05, 0.06, 0.08, \text{and} 0.10)\) at 800 Hz in an oil, that is, they showed an additional second anomaly presented at a lower temperature beside the main peaks \([15]\). The main peak was pressure sensitive, and its position moved to the lower temperature when measured under higher pressures. Moreover, the magnitude of the peak reduced with the pressures. On the contrary, the second peak (the anomaly at the lower temperature) was relatively independent of the pressure. Under higher pressures, both the peaks merged into one, and the merged peak still showed the pressure dependence.

Besides the observation of the two peaks by Martin et al., Lemanov et al. showed the presence of a shoulder on the dielectric constant peak in SPT but only for the \(x = 0.06\) composition among the samples \((x=0.002, 0.005, 0.01, 0.02, 0.06, (0.08 \text{ and} 0.2))\) they studied \([18]\). Obviously, there is a need for better understanding of this behavior in the higher end of \(\text{Pb}\) rich compositions in the SPT system.

This section will discuss the relative permittivity and tangent \(\delta\) of SPT \((x=0.05, 0.10, \text{and} 0.15)\) as a function of temperature and their phase transition behaviors as a function of composition to support and extend further the results of the previous section (Sect. 3.2) \([20]\).

3.5.2 Processing of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\)

Strontium lead titanate solid solutions were prepared using the conventional mixed oxide method. Suitable ratios of strontium carbonate \((99.9\%+ \text{purity SrCO}_3, \text{Aldrich})\), lead oxide \((99.9\% \text{ purity PbO, Aldrich})\), and titanium oxide \((99.5\% \text{ purity TiO}_2, \text{Alfa Aesar})\) were placed in a plastic container with yttrium-stabilized zirconia balls \((5\text{-mm diameter})\) and 2-propanol (A. C. 181
S. spectrophotometric grade, ≥99.5% purity, Aldrich). Extra 0.02 mole% lead oxide was added to compensate for weight loss during heating. The mixture was ball milled for 8 h, and balls were removed from the mixture. The mixture was dried at room temperature and then in an oven at 80 °C for 3 h. The dried mixture was sieved with an 80-mesh plastic sieve, and the agglomerated powders were ground with an agate mortar and pestle. The sieved mixture was calcined in a platinum dish within an aluminum oxide sagger at 1100 °C for 3 h. The heating and cooling rates were 5 °C and 2.5 °C per min, respectively. After the above procedure, the calcined powders, which were crushed roughly using a yttrium-stabilized zirconia mortar with the same material pestle, were ball milled again for 20 h, dried, and sieved in a way similar to that used for the mixture of raw chemicals. The agglomerated powders were ground in the yttrium-stabilized zirconium oxide mortar with the same material pestle. The sieved reactants were pressed in a pellet form under low uniaxial pressures and then under an isostatic pressure of 2500 kg/cm² at room temperature. Pellets were sintered in the platinum dish in an aluminum oxide sagger at 1350 °C for 3 h, while heating at a rate of 5 °C per min and cooling at a rate of 2.5 °C per min. To avoid the weight loss during heating, the pellets were covered with the sieved and calcined powders (e. g., sample-calcined powders (approximately 1:1 by weight) and a lead source, the mixture of calcined lead zirconate and zirconium oxide, was also used. The lead source, which was also pressed in a pellet form, was placed on the outside of the platinum dish, and the weight of the lead source was more than that of the sample.

X-ray diffraction patterns were collected using an X-ray diffractometer (PDIV, Scintag, Inc.) with Cu Kα as an X-ray source on the surfaces of the polished and sintered samples. Dielectric property measurements were carried out with samples which were coated with gold after they were annealed at 700 °C for 3 h. The typical heating and cooling rates were 10 °C and 2.5 °C per min, respectively, for the annealing process. Silver wires were attached to the surfaces of the sample with silver paste for the cryogenic temperature measurements. After drying the paste, the dielectric properties on the samples were measured.

3.5.3 Results and discussion on X-ray diffraction analysis

An X-ray diffractometer was used to characterize the samples at room temperature. Peak positions were determined by the program, “PRO-FIT” [1], and lattice parameters were calculated and refined by the program, “UNITCELL” [2], using an external reference, silicon powders.
Fig. 3.5.1 shows the X-ray diffraction patterns of the surfaces of typical sintered ceramic pellets, \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) \((x = 0.05, 0.10, \text{and } 0.15)\). When SPT \((x = 0.05)\) pellets were sintered under a condition in which the ratio of a lead source weight to a sample weight was approximately 2:1, an unidentified peak (X-ray source, Cu K\(\alpha\)) was observed around 20.3 degrees two-theta. To obtain single phase samples, the ratio of a lead source weight to a sample was increased to 4.

The lattice parameters, a, of the SPT compositions \((x = 0.05, 0.10, \text{and } 0.15)\) at room temperature were 3.907, 3.909, and 3.911 Å, respectively using the data measured between 20 and approximately 130 degrees two-theta. These were the additional values included with the previous data [20] (Sect. 3.2) and plotted on the graph along with one of the reference values of strontium titanate (ST) [192] (Fig. 3.5.2). A linear relationship was observed over a wide composition range. The value, \(\frac{d a}{dx}\), was 0.04 Å, which is close to the value, \(3.7 \times 10^{-2}\) Å, reported by Lemanov et al. [18].

**3.5.4 Results and discussion on dielectric properties**

Dielectric properties were measured using an LCR meter (4284A, HP) at an alternating current (AC) field of 1 V/cm. Higher temperature properties (from 190 °C) were measured in air and nitrogen gas atmosphere, and cryogenic (lower) temperature properties (from room temperature through –260 °C) were measured under vacuum. Data obtained using the two systems were combined at –5 °C.

Fig. 3.5.3 shows the plots of relative permittivity and tangent \(\delta\) of the \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) \((x = 0.05)\) ceramics as a function of temperature from –50 °C to –260 °C and frequency at 1 k, 10 k, and 100 kHz. Although the relative permittivity vs. temperature plots showed a frequency dependence (the values at the lower frequencies were higher), the transition temperatures at 1 k, 10 k, and 100 kHz were ~ –190 °C and did not show much difference. The second peak at ~240 °C observed by Martin et al. [15] was not detected in our measurements down to –260 °C. Tangent \(\delta\) vs. temperature plots showed one maximum and some fluctuations at lower temperatures than the temperature at which the maximum peak was observed. The higher frequency tangent \(\delta\) maximum was smaller in magnitude compared to the lower frequency maximum, and the values in the temperature range at which the fluctuations were observed were almost independent of frequencies at 1 k, 10 k, and 100 kHz even though the behaviors were dependent on the frequencies.
Figure 3.5.1 Room temperature Cu Kα X-ray diffraction patterns of the surfaces of sintered (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.05, 0.10, and 0.15) ceramic pellets.
Figure 3.5.2 Lattice parameters of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) ceramics at room temperature as a function of x in (Sr$_{1-x}$Pb$_x$)TiO$_3$. ST, SrTiO$_3$. A reference value was taken from Swanson et al. [192].

Figure 3.5.3 Relative permittivity and tangent $\delta$ of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.05) ceramics upon cooling as a function of temperature and frequency.
Fig. 3.5.4 shows the relative permittivity and tangent $\delta$ of the SPT ($x = 0.10$) ceramics as a function of temperature from $–50 \, ^\circ C$ to $–260 \, ^\circ C$ and of frequency at 1 k, 10 k, and 100 kHz. Relative permittivity vs. temperature showed the frequency dependence in the ferroelectric phase with two maxima: the main peak at around $–145 \, ^\circ C$ and the second peak at $–190 \, ^\circ C$. These anomalies are in good agreement with the results of Martin et al. [15]. The position of the main peak was different from that of the peak observed by Martin et al., but the second peak showed in the vicinity of the temperature at which Martin et al. observed the second peak. Tangent $\delta$ vs. temperature plots showed an abrupt increase around the transition temperature of the main dielectric constant peak and also the second maximum in the temperature range from $–200$ to $–230 \, ^\circ C$ depending on the measurement frequencies. Tangent $\delta$ also showed a frequency dependence, and the higher frequency tangent $\delta$ maximum was smaller in magnitude compared to the low frequency maximum around the same temperature $–210 \, ^\circ C$. However, the frequency dependence of tangent $\delta$ in the temperature range close to the dielectric constant maximum was of the opposite trend, and the higher frequency tangent $\delta$ maximum was higher in magnitude.

Fig. 3.5.5 shows the relative permittivity and tangent $\delta$ of the SPT ($x = 0.15$) ceramics as a function of temperature from $–50 \, ^\circ C$ through $–260 \, ^\circ C$ and of frequency at 1 k, 10 k, and 100 kHz. The dielectric constant vs. temperature also showed two maxima: the main peak at about $–100 \, ^\circ C$ and the second small peak at around $–230 \, ^\circ C$. Tangent $\delta$ vs. temperature plots showed two maxima: the first peak close to the main dielectric peak and the second peak around $–200 \, ^\circ C$. The frequency dependence of tangent $\delta$ of the SPT ($x = 0.15$) was similar to that of the SPT ($x = 0.10$).

Fig. 3.5.6 shows the temperature dependence of the dielectric constant and tangent $\delta$ of the SPT ($x = 0.05, 0.10,$ and $0.15$) ceramics at 10 kHz. The relative permittivity peak of the SPT ($x = 0.05$) and the second peak of the SPT ($x = 0.10$) showed the maximum around the same temperature, $–190 \, ^\circ C$. Because of the lack of structural information, the reason why the two peaks showed the maximum at a similar temperature is not clear. In addition, the origin of the second peak in the SPT ($x = 0.15$) at $–230 \, ^\circ C$ was not explicit, either. Since the normal changes in relative permittivity vs. temperature behaviors are due to the phase transitions, there is the possibility of a subtle or weak phase transformation. In addition, the presence of defect dipoles could be responsible for the occurrence of this secondary peak.

The first tangent $\delta$ peak of the SPT ($x = 0.10$ and $0.15$) could be due to the motion of domain walls as we have concluded in the case of the SPT ($x = 0.30$) (Sect. 3.3.2).
Figure 3.5.4 Relative permittivity and tangent δ of (Sr\textsubscript{1-x}Pb\textsubscript{x})TiO\textsubscript{3} (x = 0.10) ceramics upon cooling as a function of temperature and frequency.

Figure 3.5.5 Relative permittivity and tangent δ of (Sr\textsubscript{1-x}Pb\textsubscript{x})TiO\textsubscript{3} (x = 0.15) ceramics upon cooling as a function of temperature and frequency. The inset shows the dielectric properties on expanded temperature (from $-175$ to $-250$ °C) and relative permittivity scales.
Figure 3.5.6 Temperature dependence of relative permittivity and tangent $\delta$ of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.05, 0.10, \text{ and } 0.15$) ceramics at 10 kHz upon cooling.

Figure 3.5.7 Phase transition temperatures, $T_m$, of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.05, 0.10, 0.15, 0.20, 0.25, \text{ and } 0.30$) ceramics based on relative permittivity, $\varepsilon_r$, at 10 kHz upon cooling as a function of $x$ in (Sr$_{1-x}$Pb$_x$)TiO$_3$. $T_{m2}$, temperature at which relative permittivity as a function of temperature showed a weak peak at 10 kHz. Correlation factor of linear fitting, 0.996. Correlation factor of quadratic fitting, 0.9996.
secondary peaks in the SPT, for \( x = 0.10 \) and 0.15, could possibly be related to the ferrodistortive transformation of strontium titanate (ST) rich lattice regions. The temperatures of the maximum tangent \( \delta \) vs. temperature plots at 10 kHz upon cooling, −195, −200, and −200 °C along with the mole fraction of Pb, \( x = 0.05, 0.10, \) and 0.15, respectively are also closer to the temperature of the ferroelastic phase change from a cubic to a tetragonal suggested in strontium titanate upon cooling (e.g., −168 °C (105 K) [102], −163 °C [193, 194], or −173 °C [195]). It is important to describe that tangent \( \delta \) is generally more sensitive to the small structural changes in the materials. However, the SPT (\( x=0.05 \)) showed only one tangent \( \delta \) peak, and it could be due to the combination effects of the domain wall motion and the phase transition similar to that observed in ST because the position was very close to the suggested the transition temperature of ST, around −168 °C. The second peak could be also explained based on the defect dipoles in the SPT composition.

Fig. 3.5.7 shows the transition temperatures of the \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (\(x = 0.05, 0.10, 0.15, 0.20, 0.25, \) and 0.30) based on the dielectric constant maxima at 10 kHz upon cooling as a function of \( x \) in the \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\). A good linear relationship was observed for compositions from \( x = 0.15 \) to 0.30 and above that range, the correlation factor was more than 0.999. From 0.05 to 0.30, the correlation factor by a linear fitting was 0.996. The second-polynomial curve fitting showed a better correlation factor of 0.9996.

Fig. 3.5.8 shows the Curie-Weiss behavior of the SPT (\( x=0.05, 0.10, \) and 0.15) at 10 kHz, and there are gaps in the plots because the two datum segments measured with two different systems were combined at −5 °C and plotted. The SPT (\( x = 0.05 \)), showed the Curie-Weiss temperature, \( \theta \), 6 °C above its transition temperature for the data analyzed in the temperature range from 40 to −175 °C and the Curie-Weiss constant for this composition was \( 7 \times 10^4 \) °C. The SPT (\( x = 0.10 \)) demonstrated \( \theta \), 8 °C above its transition temperature as derived from the dielectric data taken in the temperature range from 60 to −130 °C. The Curie-Weiss constant was \( 8 \times 10^4 \) °C. The SPT (\( x = 0.15 \)) showed \( \theta \) of 8 °C above the transition temperature from 100 to −80 °C temperature range and the Curie-Weiss constant calculated was \( 8 \times 10^4 \) °C. The unusual deviation from the Curie-Weiss behavior was thus observed from the dielectric constant data taken on the SPT samples we investigated.

Fig. 3.5.9 shows the composition dependence of the Curie-Weiss constant. The SPT with \( x = 0.05, 0.10, 0.15, \) and 0.20 showed an increase in the Curie-Weiss constant along with the composition and the SPT with \( x = 0.25 \) and 0.30 showed a constant value of \( C \approx 1 \times 10^5 \) °C.
Figure 3.5.8 Curie-Weiss behaviors of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) ($x = 0.05$, 0.10, and 0.15) at 10 kHz upon cooling. SPT ($x = 0.05$), $T_m = -189 \, ^\circ C$, $\theta = -183 \, ^\circ C$, $C = 7 \times 10^4 \, ^\circ C$ ($40 > T > -175 \, ^\circ C$); SPT ($x = 0.10$), $T_m = -145 \, ^\circ C$, $\theta = -137 \, ^\circ C$, $C = 8 \times 10^4 \, ^\circ C$ ($60 > T > -130 \, ^\circ C$); SPT ($x = 0.15$), $T_m = -99 \, ^\circ C$, $\theta = -92 \, ^\circ C$, $C = 8 \times 10^4 \, ^\circ C$ ($100 > T > -80 \, ^\circ C$). $T_m$, transition temperature; $\theta$, Curie-Weiss temperature; $C$, Curie-Weiss constant; $T$, temperature.

Figure 3.5.9 Curie-Weiss constants of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.05$, 0.10, 0.15, 0.20, 0.25, and 0.30) ceramics as a function of $x$ in (Sr$_{1-x}$Pb$_x$)TiO$_3$. 
3.5.5 Summary

The SPT (x=0.05, 0.10, and 0.15) ceramics were prepared using the mixed oxide method, and their dielectric properties and phase transition were studied at 10 kHz in cooling cycles. The SPT with x = 0.05 showed one maximum in the relative permittivity vs. temperature plots at –190 °C and one major peak in tangent δ vs. temperature plots at –195 °C. The SPT with x = 0.10 showed the main relative permittivity peak at –145 °C and the second peak at –190 °C. In addition, The SPT (x = 0.10) showed the first tangent δ peak at –150 °C and the major second peak at –200 °C with a shoulder around –230 °C. The major dielectric constant peak in the SPT with x = 0.15 occurred at –100 °C, and the second peak was observed at –230 °C. The SPT with x = 0.15 also showed the two tangent δ peaks at –110 °C and at –200 °C.

The first and major dielectric constant peak in all the cases could be associated with the phase transitions from paraelectric to ferroelectric phases, and reasons for the occurrence of the secondary peaks were not fully understood due to the lack of sufficient data.

The SPT (x = 0.10 and 0.15) showed two tangent δ peaks. The peaks which were closer to the major relative permittivity peaks could be due to the domain wall motion, and the second ones could be related to the phase transition of the rich secondary ferroic strontium titanate regions or clusters. The main tangent δ peak in the SPT with x = 0.05 might have been the combined effects of the domain wall motion and the ferrodistortive phase transition similar to that observed in strontium titanate.

The plot of the lattice parameter vs. the mole fraction of Pb in the (Sr_{1-x}Pb_x)TiO_3, x (= 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30) showed a linear relationship. The phase transition based on the relative permittivity measurements at 10 kHz upon cooling showed a linear relationship with the composition.

The SPT with x=0.05, 0.10, and 0.15 showed the deviation from the ideal Curie-Weiss behavior, and the Curie-Weiss constant increased as the lead content in the composition increased, but the values were constant in the case of the SPT x = 0.25 and 0.30.
3.6 References


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4.1 Composite synthesis (tailoring dielectric properties of (Sr, Pb)TiO$_3$)

The processing of calcined (Sr, Pb)TiO$_3$ composition powders are described in Sect. 3.1. The calcined powders were ball milled for 20 h, and magnesium oxide (e.g., 99.998% purity MgO, Alfa Aesar, 10 g) was added to the reactant powders (e.g., 10 g) in a plastic container (e.g., a 30-mL polypropylene container) with yttrium-stabilized zirconia cylinders (e.g., 3/8-in (~ 0.95-cm) diameter, 100g) and 2-propanol (e.g., A. C. S. spectrophotometric grade, ≥99.5% purity, 30 mL). Because the diameter of the 30-mL containers was shorter than the distance between two adjacent roles of a ball milling machine, the 30-mL container was placed in a special container of which the diameter was larger than the distance between the rolls. The powders were mixed for 4 h, and the cylinders were separated from the mixed powders and 2-propanol using a plastic sieve. The powders were dried in a hood to remove the organic solvent, held at 80 °C for 3 h, and sieved with an 80-mesh plastic sieve (opening size: 180 µm). When the powders were larger than the opening size of the sieve, they were ground with an agate mortar and pestle. Pellets were formed from the mixed powders with uniaxial and cold isostatic pressing (CIP) (e.g., under a pressure of 3000 kg/cm$^2$). When required shapes are neither cylinders nor disks, then it is better to make larger cylinders or disks than required sizes and to cut the demanded shape of a sample after sintering. In case the removal of water was necessary, the samples were heated to 300 °C on a platinum (Pt) sheet on a ceramic plate. An example process was as follows: the formed samples were heated up to 110 °C at a rate of 0.1 °C per min and held for 12 h, heated to 300 °C at the same rate again and held at 300 °C for 6 h, and cooled to room temperature at a rate of 2.5 °C per min. Unpressed powders covered the formed disks and a pressed lead source (the mixture of calcined lead zirconate and zirconium oxide powders) were placed on the outside of a Pt lid. Then, the disks were sintered in the Pt dish placed in a sagger at 1350 °C for 3 h. The heating and cooling rates were 5 °C and 2.5 °C per min, respectively. The surfaces of the samples were polished and the samples were annealed at 700 °C for 3 h. In case electrodes were necessary for the electrical measurements, the surfaces of samples were coated with gold.

In order to form a suitable shape, a binder (e.g., polyacryl resin or polyvinyl alcohol (PVA)) is sometimes necessary. The following text will describe the preparation process of
samples with the binder. Firstly, the binder was placed in a glass beaker, and a solvent such as acetone was pored to make a solution. Secondly, the solution was added to the calcined and sieved powders to make the content of the binder ~ 3 wt% per the calcined powders. While the solvent evaporated, the mixture was stirred. Thirdly, the dried mixture was sieved with the 80-mesh plastic sieve. If the agglomerates were larger than the opening size of the sieve, they were ground with the agate mortar and pestle in a way similar to that used for the powders without the binders. The sieved powders were pressed in required forms. The formed samples were burned out on a Pt sheet on a ceramic plate. An example profile was as follows: heated at a rate of 0.25 °C per min; held at 110 °C for 1 h, at 300 °C for 2 h, and at 550 °C for 3 h; cooled at a rate of 2.5 °C per min.
4.2 (Sr\textsubscript{1-x}Pb\textsubscript{x})TiO\textsubscript{3}-MgO composites

4.2.1 The effect of preparation routes on dielectric properties

It is noted that the preparation routes of samples have outstanding effects on the properties of final products. Containers used for calcination may affect the quality for the properties of calcined powders and sintered products. This section will discuss the effects of a platinum container used for the calcination of powders and sintering for the pellets of composites, (Sr\textsubscript{1-x}Pb\textsubscript{x})TiO\textsubscript{3} (SPT) and magnesium oxide (MgO). The influence of containers on the quality of the products will be discussed based on the results of composite dielectric properties.

4.2.1.1 Composites sintered at 1350 °C

MgO was added to calcined SPT powders, and then the mixture of SPT and MgO were sintered. The composite pellets were polished, cut if necessary for measurements, and coated with gold electrodes for dielectric property measurements.

Fig. 4.2.1.1 shows the dielectric behaviors of composite (\(\alpha\)), SPT (\(x = 0.3\))-MgO (50:50 by weight). The source SPT powders for the composites were calcined in an aluminum oxide (Al\textsubscript{2}O\textsubscript{3}) crucible and composite (\(\alpha\)) were sintered in an Al\textsubscript{2}O\textsubscript{3} dish (which was in a ceramic sagger). Although the pure SPT (\(x = 0.3\)) showed the transition temperature (T\textsubscript{m}) of relative permittivity \(\sim 10 \, ^\circ\text{C}\) at 10 kHz upon cooling, composite (\(\alpha\)) showed the higher T\textsubscript{m} \(\sim 40 \, ^\circ\text{C}\) at 10 kHz upon cooling.

Fig. 4.2.1.2 shows the comparison of the dielectric properties of composite (\(\alpha\)) and composite (\(\beta\)) of the same composition (SPT (\(x = 0.3\))-MgO (50:50 by weight)). Composite (\(\beta\)) was sintered in a platinum (Pt) dish and prepared from SPT powders calcined in the Pt dish. The purities of raw chemicals used were somewhat different in both cases: composite (\(\alpha\)): PbO (99.9995% purity, Alfa Aesar), SrCO\textsubscript{3} (99.995% purity, Aldrich), and TiO\textsubscript{2} (99.999% purity, Aldrich); composite (\(\beta\)): PbO (99.9% purity, Aldrich), SrCO\textsubscript{3} (99.9% purity, Aldrich), and TiO\textsubscript{2} (99.5% purity, Alfa Aesar)). However, both composites were prepared with the same purity MgO (99.998% purity, Alfa Aesar). The SPT (\(x = 0.3\)) used as the source for composite (\(\alpha\)) and composite (\(\beta\)) showed T\textsubscript{m} as sintered products, approximately 10 °C at 10 kHz (the precise T\textsubscript{m} of the sintered SPT prepared from calcined powders which were also used in composite (\(\alpha\)) and composite (\(\beta\)) were 12 °C and 10 °C, respectively). The SPT source of composite (\(\alpha\)) was prepared from the high purity chemicals. However, the effect of the raw chemical purities on the
Figure 4.2.1.1 Dielectric properties of ceramic composite \((\alpha)\) as a function of temperature and frequency upon cooling. Composite \((\alpha)\): \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) \((x = 0.3)\)-magnesium oxide (MgO) \((50:50 \text{ by weight})\). The composites were sintered in an aluminum oxide \((\text{Al}_2\text{O}_3)\) dish with SPT powders calcined in an \(\text{Al}_2\text{O}_3\) crucible.

Figure 4.2.1.2 Dielectric properties of composite \((\alpha)\) and composite \((\beta)\) at 10 kHz upon cooling as a function of temperature. Composites: \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) \((x=0.3)\)-magnesium oxide (MgO) \((50:50 \text{ by weight})\). Composite \((\alpha)\) were sintered in an alumina \((\text{Al}_2\text{O}_3)\) dish and SPT source composition was calcined in an \(\text{Al}_2\text{O}_3\) crucible. SPT was prepared from high purity raw chemicals. Composite \((\beta)\) were sintered in a platinum (Pt) dish and SPT source was calcined in the Pt dish. SPT was prepared from low purity chemicals.
transition temperatures of the SPT (x = 0.2)-MgO composites (the raw chemicals for the SPT was calcined in the Pt dish and the composites and pure SPT were sintered in the Pt dish) was not obviously observed. For example, the $T_m$ of the high purity SPT and that of the composites of which source was the high purity SPT were $-55$ and $-65$ °C, respectively. This difference was small compared to the difference observed between composite ($\alpha$) ($T_m$: $\sim 40$ °C) and composite ($\beta$) ($T_m$: $\sim 5$ °C).

Fig. 4.2.1.3 (a) shows the full width at half maximum (FWHM) of the SPT in the pure SPT system (of which the source was similar to the source of composite ($\alpha$)), composite ($\alpha$), and composite ($\beta$). Fig. 4.2.1.3 (b) shows the FWHM of the MgO component in composite ($\alpha$) and composite ($\beta$). X-ray diffraction patterns were collected at room temperature using an X-ray diffractometer with Cu K$_{\alpha}$ as an X-ray source (PDIV, SCINTAG, Inc.) and the patterns were analyzed by the program, “PRO-FIT” [1].

As a result, i) the SPT calcined in an Al$_2$O$_3$ crucible and ii) the SPT in the mixture of MgO and SPT which was calcined in the Al$_2$O$_3$ crucible showed similar values of FWHM. The mixing of the MgO to the SPT did not show much effect on the FWHM of the SPT component. After sintering, the SPT components in the composites did not show a significant difference in FWHM, but the pure SPT showed a decrease in the FWHM. On the contrary, the FWHM of the SPT calcined in the Pt dish showed lower than that of the SPT calcined in the Al$_2$O$_3$ crucible. Plot (b) shows changes in the FWHM of the MgO component in the mixture of the SPT and MgO before and after sintering. The FWHM of the MgO component in the composites sintered in both containers (Al$_2$O$_3$ and Pt containers) reduced compared to the values before sintering. The transition temperatures of the composites would thus be influenced depending on the chemical and/or mechanical boundary conditions and physical states of the SPT in the composites. The increase in the transition temperature of the composites ($\alpha$) would be due to the calcined SPT powders (and chemistry or physical conditions of the SPT) prepared by the Al$_2$O$_3$ container under the following conditions: Calcination: heating rate, 5 °C per min; soak condition, 1100 °C for 3 h; cooling rate, 2.5 °C per min; Sintering: heating rate, 5 °C per min; soak condition, 1350 °C for 3 h; cooling rate, 2.5 °C per min. Consequently, it was attempted to reduce the FWHM of the SPT to calcine raw chemicals in a Pt container and hence to make the transition temperature of the composites similar to that of the pure SPT.

The values of the FWHM caused by specimens were related to crystallite sizes and/or crystal imperfection (e.g., strain) [2-4]. Thus the materials calcined in the Pt container were
Figure 4.2.1.3 Full width at half maximum (FWHM) of (a) (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) and (b) magnesium oxide (MgO).

- **SPT(i)**: SPT calcined in an aluminum oxide ($Al_2O_3$) container.
- **SPT(1)**: Mixture of MgO and calcined SPT in $Al_2O_3$.
- **SPT(ii)**: Sintered in an $Al_2O_3$ container using calcined SPT in an $Al_2O_3$ container.
- **SPT(2)**: Composite ($\alpha$), sintered in $Al_2O_3$.
- **SPT(3)**: Mixture of MgO and calcined SPT in a platinum (Pt) container.
- **SPT(4)**: Composite ($\beta$), sintered in Pt.
- **MgO(1)**: Mixture of MgO and calcined SPT in $Al_2O_3$.
- **MgO(2)**: Composite ($\alpha$), sintered in $Al_2O_3$.
- **MgO(3)**: Mixture of MgO and calcined SPT in Pt.
- **MgO(4)**: Composite ($\beta$), sintered in Pt.

SPT of samples (i), (ii), (1), and (2) were prepared from high purity raw chemicals. SPT of sample (3) and (4) were prepared from low purity raw chemicals.

Initial ratio for SPT, Sr:Pb:Ti = 0.7:0.3:1.
suggested to have larger size crystallites and/or lower crystallite imperfection of SPT because the narrower FWHM were observed.

As shown in Fig. 4.2.1.2, the relative permittivity maximum of composite (α) as a function of temperature is lower than that of composite (β). The processing of SPT and the purity of chemicals also affect the maximum intensity of relative permittivity of the pure SPT (see Sect. 3.4). In addition, the composites prepared from high purity SPT (x = 0.2) sources showed lower relative permittivity maxima of the composites compared with those of the composites prepared from the low purity SPT (x = 0.2) sources (not shown in this dissertation). Therefore, the lower relative permittivity of the composites prepared from the high purity SPT source could be due to the processing of the composites and the purity of the source chemicals for the SPT.

Fig. 4.2.1.4 shows scanning electron microscope (SEM) (S-3500N, Hitachi) images of the fractures of pressed powders and fractured surfaces of the ceramic samples obtained to detect secondary electrons. Image (a) shows the mixture of the calcined SPT powders and MgO, the approximate particle sizes in both materials are approximately 1 µm. Image (b) shows the composites (α) sintered in the Al₂O₃ container (T_m ~ 40 °C) and image (c) shows the composites (β) sintered in the Pt container (T_m ~ 10 °C). The micrographs of both the composites show bright parts which mostly consist of small particles ~ 1 µm and the agglomeration of particles and the darker parts which represent a matrix and have the particle agglomerates of several µm in size.

Assuming that the bright particles indicate the MgO, some MgO particles remained similar sizes, and some became bigger after sintering. The decrease in the FWHM of the MgO was observed after sintering. This decrease could be due to the grain growth and subsequently the reduction in strain (crystal imperfection). The FWHM of the SPT did not change before and after sintering, but the sizes of dark particles became larger after sintering. Thus the crystallite imperfection of the SPT must compensate for the effect of the SPT crystallites. In other words, to show similar FWHM of the SPT, the crystallite imperfection also would increase. If the crystallites (which were assumed not to be detected by SEM) did not change in size, then the crystallite imperfection would not be changed.

On the contrary, if the dark particles indicate the MgO, then the MgO grew at least a few-µm size particles. The major reason of the reduction in the FWHM of the MgO could be due to the growth of grains. Meanwhile, the SPT did not show the grain growth and remained similar.
Figure 4.2.1.4 Scanning electron microscope (SEM) micrographs of various samples obtained to detect secondary electrons (SE).
(a) Mixture of MgO and SPT (x = 0.3) calcined in an Al₂O₃ container.
(b) Composite (α) sintered in an Al₂O₃ container.
(c) Composite (β) sintered in a Pt container.
(d) SPT sintered in an Al₂O₃ container at 1350 °C.
(e) MgO sintered at 1350 °C.
SPT prepared from high purity raw chemicals: (a), (b), and (d).
SPT prepared from low purity raw chemicals: (c).
MgO: Magnesium oxide.
SPT: (Sr₁₋ₓPbx)TiO₃ (x = 0.3).
Al₂O₃: Aluminum oxide.
Pt: Platinum.
condition possessed in the calcined SPT. Additionally, the FWHM of the SPT remained similar values (see the end of this section to obtain further information).

Image (d) is the micrograph of the pure SPT ($x = 0.3$) ceramics prepared with the high purity chemicals using the Al$_2$O$_3$ containers. Although grains had some pores, but they were in good contacts each other. Thus these contacts resulted in relatively dense samples. Furthermore, grain sizes were between a few tens µm and 10 µm. This suggests that the good grain growth in the samples which eventually would reflect in the reduction of the FWHM of the SPT.

Image (e) shows the pure MgO ceramics which were sintered at 1350 °C for 3 h under conditions similar to those used for sintering the composites and pure SPT. There were particles which were approximately 1 µm and the agglomeration of particles which were about a few µms. Cavities or pores which were observed in the pure SPT system and the SPT based composites were not noted.

Fig. 4.2.1.5 shows 10 kHz dielectric properties of composite ($\alpha$), SPT ($x = 0.3$)-MgO (SPT: prepared from the high purity raw chemicals and calcined in the Al$_2$O$_3$ containers) as a function of temperature and DC field. Plot (a) shows higher suppression of dielectric constant at higher DC fields and plot (b) indicates from 5 to 10 % tunability at 20 kV/cm near the $T_m$ ($= \sim$40 °C) in the temperature range from $T_m + 40$ to $T_m - 20$ °C. Plot (c) shows the K-factor less than 100 at 20 kV/cm.

The data for tunability and K-factor were the results at 10 kHz in a cooling cycle. Dielectric tunability and K-factor are calculated by the following equation.

$$\%\text{dielectric tunability}=\frac{\varepsilon(E_o)-\varepsilon(E)}{\varepsilon(E_o)}\times100\quad(E_o=0\text{ kV/cm})\quad(4.2.1.1)$$

$$\text{K-factor}=\frac{\%\text{ tunability}\times100}{\text{tunability}}\quad(4.2.1.2)$$

The K-factor in the plot was calculated from tangent $\delta$ measured without applying DC bias fields, that is, without using a blocking circuit.

Fig. 4.2.1.6 shows the temperature dependence of the relative permittivity and tangent $\delta$ of composite ($\beta$), SPT ($x = 0.3$)-MgO (SPT: prepared from the low purity chemicals and in the Pt container). The transition temperature of the composites $\sim$4 °C at 10 kHz was close to that of the pure SPT samples $\sim$10 °C. Tangent $\delta$ increased around 50 °C, but it remained less than 0.005
Figure 4.2.1.5 (a) Relative permittivity, (b) dielectric tunability, and (c) K-factor of composite ($\alpha$) at 10 kHz as a function of DC bias field and temperature.

Composite ($\alpha$): (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) ($x = 0.3$)-magnesium oxide (MgO) (50:50 by weight). SPT powders were calcined and composites were sintered in Al$_2$O$_3$ containers.

The sample was measured at 10 kHz with DC fields, up to 20 kV/cm, upon cooling.

K-factor was calculated from tangent $\delta$ measured without a blocking circuit, i.e., without applying DC bias fields.
Figure 4.2.1.6 Dielectric properties of ceramic composite (β) as a function of temperature and frequency upon cooling. Composite (β): (Sr_{1-x}Pb_{x})TiO_{3} (SPT) (x = 0.3)-magnesium oxide (MgO) (50:50 by weight). Composites were sintered in a platinum (Pt) dish using calcined SPT powders in the Pt dish.
around room temperature. Relative permittivity slightly far above the transition temperature did not show a frequency dependence.

Fig. 4.2.1.7 shows the temperature dependence of dielectric properties of composite (β) at 10 kHz under DC bias. Plot (a) shows the suppression of relative permittivity at higher DC fields and relatively very small change in tangent δ. Small steps in tangent δ were due to the use of the blocking circuit and an LCR meter (4284A, HP) while the LCR meter needed to vary measurement conditions for a continuous measurement to achieve the optimization of the system. When the LCR meter was used and the command “auto” was selected as “range” to optimize a measurement impedance range automatically, the meter showed a step at a specific spot such as 170 pF or 550 pF because the measurement conditions were changed at the specific capacitance for the optimization. Although the capacitance of the samples were of the order of tens pF, the blocking circuit multiplied the capacitance 10 times higher and measuring capacitance became in the range which the meter tried to optimize. Therefore, the use of two devices caused the artificial steps in the tangent δ vs. temperature plots. The dielectric tunability of composite (β) at 20 kV/cm and in the temperature range from $T_m+40$ to $T_m+15$ °C ($T_m \sim 5$ °C) is from 10 to 20 % as shown in plot (b). The dielectric tunability and K-factor of composite (β) up to 40 kV/cm are shown in Fig. 4.2.1.8. Composite (β) showed dielectric tunability approximately 35 % (plot (a)) and K-factor values ~ 200 (plot (b)) at 10 kHz and at 25 °C.

The studies suggest that it is important to prepare a composite with a transition temperature similar to the transition temperature of pure SPT. The use of the Pt container for the calcination of the SPT powders definitely helped to synthesize the high quality composites with the transition temperature similar to that of pure SPT. Such composites showed good dielectric tunability, K-factor, and overall dielectric properties at room temperature compared to the samples prepared using the Al₂O₃ containers.

**4.2.1.2 Composites sintered at higher temperature, 1500 °C**

An objective for this study is to develop tunable materials for room temperature applications and the materials should have low tangent δ in that temperature range. The transition temperature of composite (β) was ~ 4 °C at 10 kHz. Although the transition temperature was below room temperature, the tangent δ was still higher at room temperature and till ~ 50 °C compared to values in typical paraelectric states where these values were constant or stabilized. Therefore, its advisable to bring the transition temperature ~ 4 °C further down, so
Figure 4.2.1.7 (a) Relative permittivity and tangent \( \delta \), (b) dielectric tunability of composite (\( \beta \)) as a function of DC bias field and temperature.

Composite (\( \beta \)): \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) \((x = 0.3)\)-magnesium oxide (MgO) 

(50:50 by weight); SPT powders were calcined and ceramics were prepared in a platinum (Pt) container.

Measurements were carried out at 10 kHz with DC fields up to 20 kV/cm bias upon cooling.

K-factor was calculated using tangent \( \delta \) measured without DC bias, i.e., without a blocking circuit.

Steps in tangent \( \delta \) were due to the use of the blocking circuit, which multiplied capacitance 10 times higher than the real values, and the use of an LCR meter (4284A, HP), which automatically optimized a measurement range when “auto” was selected as “range.”

When the measurement range was changed, the steps were observed.
Figure 4.2.1.8 Temperature dependence of (a) dielectric tunability and (b) K-factor of composite (\( \beta \)).

Composite (\( \beta \)) (\( \text{Sr}_{1-x}\text{Pb}_x\text{TiO}_3 \) (SPT) \( x = 0.3 \)-magnesium oxide (MgO) (50:50 by weight).

SPT powders and ceramics were prepared in a platinum (Pt) container. Measurements were carried out at 10 kHz with DC bias fields up to 40 kV/cm upon cooling.

K-factor was calculated with tangent \( \delta \) measured without applying DC bias, i.e., without a blocking circuit.
that improved tangent $\delta$ can be achieved at room temperature. Transition temperatures in the SPT system can be adjusted by modifying the ratio of lead (Pb) to strontium (Sr) in the SPT samples. The decrease in a Pb/Sr ratio decreases the transition temperature of the composite. Alternatively the ratio of Pb to Sr can be also changed by heating at a temperature at which lead oxide volatilizes. The selection of the suitable heating temperature and length will make the transition temperature of the samples to be far below room temperature. Composite ($\gamma$) were sintered at 1500 °C for 3 h. The source materials used for composite ($\gamma$) were the same as those used for composite ($\beta$).

Fig. 4.2.1.9 shows the dielectric properties of composite ($\gamma$) as a function of frequency, tangent $\delta$ values decreased substantially at room temperature compared to composite ($\beta$) sintered at 1350 °C. Furthermore, composite ($\gamma$) showed smaller frequency dependence of relative permittivity and tangent $\delta$ around room temperature.

Fig. 4.2.1.10 shows the temperature dependence of dielectric tunability and K-factor at 10 kHz with a DC field, up to 40 kV/cm. Dielectric tunability and K-factor were calculated from Eqs. (4.2.1.1 and 4.2.1.2). K-factor was calculated from tangent $\delta$ values measured with DC bias field, that is, without using the blocking circuit. The dielectric tunability of the sample turned higher at measurement temperatures closer to the transition temperatures of the samples. Composite ($\gamma$) showed low room temperature tunability ~20 % at 40 kV/cm compared with the value of composite ($\beta$) (of which the tunability was more than 30 % at room temperature). Reasons are that measurement temperatures were far above the transition temperature of composite ($\gamma$) compared to composite ($\beta$) and that tunability becomes lower as a measurement temperature becomes further above the transition temperature. However, composite ($\gamma$) showed higher K-factor ~400 at room temperature compared to the value ~ 175 obtained on composite ($\beta$). This observation is mainly due to the substantial decrease in tangent $\delta$ at room temperature.

Fig. 4.2.1.11 shows the SEM micrographs of the lightly gold sputtered fracture samples using composite ($\gamma$) and composite ($\beta$). Large cavities in composite ($\gamma$) are observed in dark particles which were similar to those observed in the pure SPT images (Fig. 4.2.1.4 (d)). The darker contrast particles might indicate the SPT. This assumption suggested that composite ($\gamma$) had larger SPT particles, which were quite reasonable to conclude from the high temperature sintering and subsequent grain growth behavior in these materials.
Figure 4.2.1.9 Dielectric properties of ceramic composite ($\gamma$) as a function of temperature and frequency upon cooling. Composite ($\gamma$): (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT)-magnesium oxide (MgO) (50:50 by weight); composite ($\gamma$) were prepared from the SPT ($x = 0.3$) source which was calcined in a platinum (Pt) container and composite ($\gamma$) were sintered in a ceramic container at 1500 °C.
Figure 4.2.1.10 Temperature dependence of (a) dielectric tunability and (b) K-factor of composite ($\gamma$).

Composite ($\gamma$) were prepared with calcined ($\text{Sr}_{1-x}\text{Pb}_x\text{TiO}_3$) (SPT) ($x = 0.3$) in a platinum (Pt) and sintered at 1500 °C in a ceramic container. Measurements were carried at 10 kHz up to 40 kV/cm upon cooling. K-factor was calculated with tangent $\delta$ measured without a blocking circuit, i.e., without applying DC bias fields.
Figure 4.2.1.11 Scanning electron microscope (SEM) micrographs of composites prepared from \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) \((x = 0.3)\) and magnesium oxide (MgO). Secondary electron (SE) images of 
(a) Composite (β) sintered at 1350 °C
(b) Composite (γ) sintered at 1500 °C.
In Fig. 4.2.1.4, two cases were discussed for the observation of the SEM images: if the MgO indicated the brighter or darker parts of the image. It would be reasonable to conclude that the MgO indicated the brighter parts and that the SPT indicated the darker parts.
4.2.2 Properties of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) \((x = 0.20, 0.25, \text{ and } 0.30)\)-MgO composites

This section will discuss the effects of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) sources on the preparation of SPT-magnesium oxide (MgO) composites and the dielectric properties of the composites.

4.2.2.1 Introduction

Microwave devices are attractive due to the widespread use of wireless communication systems. For example, there is a need to decrease the number of parts in cellular phones to create filters which have the roles of both transmitting and receiving electromagnetic waves. If ferroelectrics change their relative permittivity at applied direct current (DC) fields, then ferroelectric filters have various resonant frequencies. In other words, these filters would have both transmitter and receiver sections. There are microwave tunable applications such as filters [5], antennas [6, 7], capacitors [8, 9], phase shifters [6, 8], and resonators [10, 11].

These materials are required to have the following properties: i) low tangent \(\delta\) (high \(Q\) values, \(Q = 1/\text{tangent } \delta\)) in operating frequency and temperature ranges, ii) reasonable relative permittivity, iii) reasonable DC field dependence of dielectric constant, namely, reasonable tunability, and iv) easy processing of samples.

Solid solutions between lead titanate and strontium titanate, \((\text{Sr}_{1- x}\text{Pb}_x)\text{TiO}_3\) (SPT), are selected as a potential material because this SPT system \((x=0.20, 0.25, \text{ and } 0.30)\) showed room temperature tangent \(\delta\) values of less than 0.001 at 10 kHz. Dielectric tunabilities of 3, 15, and 70 \% were measured on the SPT ceramics with \(x = 0.20, 0.25, \text{ and } 0.30\) with a 20 kV/cm bias field at a frequency of 10 kHz and at 25 °C. However, the relative permittivity of the samples was more than 500 at room temperature (Sect. 3.2). Therefore, appropriate ratios of non-ferroelectric low relative permittivity low tangent \(\delta\) oxides, for example, MgO, were added to the SPT system to tailor relative permittivity of the SPT component. A reason is that it is necessary to make the capacitance of the materials suitable for the microwave applications in order to achieve the impedance matching.

4.2.2.2 Experimental

\((\text{Sr, Pb})\text{TiO}_3\) compositions were prepared from strontium carbonate (99.9\%+ \(\text{SrCO}_3\) purity, Aldrich), lead oxide (99.9\% \(\text{PbO}\), Aldrich), and titanium oxide (99.5\% \(\text{TiO}_2\), Alfa Aeser) by mixing suitable ratios of \(\text{Sr:Pb:Ti}\). Extra 0.02 mol\% \(\text{PbO}\) was also added to the mixture of raw chemicals to compensate for weight loss during heating. The raw materials were ball milled in 2-propanol using 5-mm-\(\phi\) yttrium-stabilized zirconia balls for 8 h and then calcined in a platinum
(Pt) dish in a sagger at 1100 °C for 3 h. The reactant powders were ball milled and magnesium oxide (99.998% purity MgO, Alfa Aesar) was added to the powders. They were mixed by ball milling with 2-propanol using 3/8-in yttrium-stabilized zirconia cylinders for 4 h. Pellets were formed from the mixed powders with uniaxial press and cold isostatic pressing under a cold isostatic pressure of 3000 kg/cm². Formed disks were sintered in the Pt dish placed in a sagger at 1350 °C for 3 h with a lead source. The samples were cut for the dielectric property measurements if necessary. Before electrodes were coated on the samples, the surfaces of the samples were polished and the samples were annealed at 700 °C for 3 h.

Dielectric properties were measured in an oven using an LCR meter (4284A, Hewlett Packard), and the oven and LCR meter were controlled by computer. Dielectric properties were measured in cooling cycles using a step mode. Thermal hysteresis was obtained using measurements upon both cooling and heating.

Dielectric tunability was calculated from the following equation

$$\% \text{dielectric tunability} = \frac{\varepsilon(E_o) - \varepsilon(E)}{\varepsilon(E_o)} \times 100 \quad (E_o \approx 0 \text{ kV/cm}) \quad (4.2.2.1)$$

where $\varepsilon(E)$ is relative permittivity at a DC field of $E$.

### 4.2.2.3 Results and discussion

The phase identification of composite samples was carried out using their X-ray diffraction (XRD) patterns (X-ray source, Cu K$_\alpha$) (PDIV, SCINTAG, Inc) at room temperature. The XRD patterns of the mixtures of calcined (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) ($x=0.20$, $0.25$, and $0.30$) powders and MgO are shown in Fig. 4.2.2.1 (a). Fig. 4.2.2.1 (b) shows the typical XRD patterns of the surfaces of the sintered composites. Only SPT and MgO phases were observed.

The microstructure of the samples were studied using the scanning electron microscope, (SEM) (S-3500N, Hitachi). SEM samples were prepared by coating gold on the surfaces of samples: i) fractures of uniaxially pressed mixtures of the calcined SPT and MgO powders and ii) the sintered composites. Fig. 4.2.2.2 (a) (images obtained to detect back scattered electrons) shows the typical microstructure of the pressed mixtures with the SPT and MgO before sintering, and Fig. 4.2.2.2 (b) (images obtained to detect secondary electrons) shows the typical microstructure of the sintered composites. In Fig. 4.2.2.2 (a), the materials show different contrasts. Brighter parts of which the shapes were mostly cubes, could indicate the MgO and dark parts could show the SPT. The particle sizes of the MgO were close to or less than a few µm. However, the particle sizes of the SPT were not clear. The observed sizes were less than 1
Figure 4.2.2.1 Typical room temperature Cu Kα X-ray diffraction patterns of (a) the mixture of calcined (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) and magnesium oxide (M) and (b) the sintered products. i: x = 0.20, ii: x = 0.25, and iii: x = 0.30.
Figure 4.2.2.2 Typical scanning electron microscope (SEM) microstructure of
(a) the mixtures of calcined (Sr$_{1-x}$Pb$_x$)TiO$_3$ and magnesium oxide (MgO)
(back scattered electrons were detected).
i: $x=0.2$, ii: $x=0.25$, and iii: $x=0.3$ (the fractures of pressed samples).
(b) sintered composites made from (Sr$_{1-x}$Pb$_x$)TiO$_3$ and MgO
(secondary electrons were detected).
i: $x=0.20$, ii: $x=0.25$ and iii: $x=0.30$ (the fractures of sintered products).
µm, namely, a few tenths µm. The sintered composites showed small particles (approximately 1 µm), continuous phases with cavities which could indicate the SPT, and unidentified phases. Small cavities ~ 1 µm could be caused by the evaporation of volatile materials.

Fig. 4.2.2.3 shows the dielectric properties of the composites prepared from the SPT (x = 0.20, 0.25, and 0.30) and MgO in the temperature range from 190 to –180 °C and at 10 k, 100 k, and 1 MHz frequencies. Fig. 4.2.2.4 shows the dielectric responses of the composites in both cooling and heating cycles at 10 kHz. The transition temperatures, T_m, of the compositions (x = 0.20, 0.25, and 0.30), –61, –27, and 7 °C, relative permittivity, 110, 160, and 250, and tangent δ values, around 0.0005, 0.001, and 0.002, were observed at 25 °C and at 10 kHz, respectively. The previously prepared composites with the SPT (x = 0.3) and MgO showed T_m ~ 4 °C (in Sect. 4.2.1). The processing of the composites could influence the properties such as transition temperatures. Thus the composites should be prepared under specific conditions to control the quality of products, for example, the length and rate of a rotation for ball milling to mix SPT powders and MgO.

The tangent δ values of the composites were less than 0.001 at 10 kHz in the paraelectric state, more than 100 °C above the transition temperatures. The transition temperatures of SPT (x = 0.20, 0.25, and 0.30) were –59, –24, and 10 °C at 10 kHz, respectively. The respective composites also showed similar transition temperature shown in Fig. 4.2.2.5. The small differences in transition temperatures could be caused by the reaction between SPT and MgO, the evaporation of PbO from the SPT, and/or the physical state of the SPT component in the composites. The XRD patterns did not show phases resulted from the reaction of SPT and MgO. However, the microstructure observed by the SEM and dielectric behaviors, especially in the ferroelectric regions, could demonstrate that the SPT components in the composites were different from that in the pure SPT solid solutions. Far above the transition temperature such as 100 °C above the transition temperature, the dissipation factors were around 0.0005 at 10 kHz. These values were close to the values of the pure SPT at the same frequency.

The relative permittivity of (Sr_{1-x}Pb_x)TiO_3 (x = 0.20, 0.25, and 0.30)-MgO composites as a function of temperature upon both cooling and heating showed a small thermal hysteresis up to ~ 30 °C above their transition temperatures, but there were not significant differences in dissipation factors. The differences in the transition temperatures between cooling and heating cycles were approximately 1 °C, and the reduction in relative permittivity was within 2 % under the present measurement conditions (rate, ~ 1.5 °C per min).
Figure 4.2.2.3 Dielectric properties of (Sr_{1-x}Pb_x)TiO_3-MgO composites as a function of temperature and frequency.
i: x = 0.20, b: ii = 0.25, and iii: x = 0.30.
Figure 4.2.2.4 Dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$-MgO composites as a function of temperature at 10 kHz in both cooling and heating cycles. i: $x = 0.20$, ii: $x = 0.25$, and iii: $x = 0.30$. 
Figure 4.2.2.5 Transition temperatures, $T_m$, of $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ (SPT)-MgO composites as a function of $x$ in $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$. $T_m$ was based on relative permittivity maximum temperature at 10 kHz upon cooling.

Figure 4.2.2.6 Thermal expansion and thermal expansion coefficients of $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ (SPT)-MgO composites upon cooling.
The thermal expansion of the samples were measured using a dilatometer (Theta Industries, Inc.) at a rate of 2 °C per min. The samples were cut to a similar length of the reference, 6.54 mm fused silica. Fig. 4.2.2.6 shows the thermal expansion and thermal expansion coefficients of the composites. Although the pure SPT system showed the obvious transition temperatures, the composites did not clearly show transition temperatures. The peaks of the composites in relative permittivity vs. temperature plots were broad (Fig. 4.2.2.3 and 4.2.2.4), and the grains of the composites were not connected well (Fig. 4.2.2.2), while the pure SPT showed sharp dielectric constant peaks and well connected grains (Sect. 3.2). These differences could cause different observations on the thermal expansion behaviors. The thermal expansion coefficients of the composites were calculated, assuming a linear relationship between thermal expansion and temperature in the temperature range from 500 °C to transition temperature. The composites showed similar thermal expansion coefficients $1.2 \times 10^{-5} \, ^\circ\text{C}^{-1}$.

Because the relative permittivities of the composites were tailored to around 300 at transition temperatures, the DC field dependence of dielectric properties were measured. Fig. 4.2.2.7 shows the dielectric properties as a function of temperature and DC bias field. The steps of tangent $\delta$ were observed due to the use of the LCR meter and the blocking circuit, which was necessary not to break the LCR meter during applied DC bias measurements (see Sect. 4.2.3). Increases in loss tangent values were not observed apparently. As the applied DC bias field increased, the relative permittivity was suppressed.

Fig. 4.2.2.8 shows the dielectric tunability of the composites with the SPT ($x = 0.2, 0.25,$ and $0.3$) at 10 kHz using Eq. (4.2.2.1). Dielectric tunability at 25 °C with compositions on 0.2, 0.25, and 0.3 was 3, 7, and 18% at 20 kV/cm, respectively, and tunability at 50 °C above the transition temperature was 8.5, 8, and 7%, respectively, with a DC field of 20 kV/cm at 10 kHz with less than 0.001 tangent $\delta$. Additionally, the composites showed 2-3% dielectric tunability at 90 °C above their transition temperatures. Hysteresis was observed near and far above the transition temperature. However, the composites prepared from the SPT ($x = 0.20$) and MgO did not show hysteresis far from the transition temperature. The composites showed relatively flat relative permittivity in the ferroelectric region, and this behavior was not observed among the pure SPT. It could be due to reasonable connectivity between SPT and MgO and/or the interaction between SPT and MgO. The reasonable connectivity and/or interphase materials resulted from the reaction between SPT and MgO could be helpful to avoid the hysteresis of dielectric constants at DC bias fields.
Figure 4.2.2.7 Dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$-MgO composites as a function of temperature and DC bias field at 10 kHz. i: $x=0.2$, ii: $x=0.25$ and iii: $x=0.3$. Data at fields: −20, −15, −10, −5, and 0 kV/cm; all applied fields: 0 − 20 − 20 − 0 kV/cm (5 kV/cm as a step field). Transition temperature of composites: −61 °C ($x=0.2$), −27 °C ($x=0.25$), and 7 °C ($x=0.3$). Steps of loss tangents occurred due to the use of a blocking circuit and an LCR meter.
Figure 4.2.2.8 Dielectric tunability of (Sr$_{1-x}$Pb$_x$)TiO$_3$-MgO composites as a function of temperature and DC bias field at 10 kHz. i: $x = 0.2$, ii: $x = 0.25$ and iii: $x = 0.3$. Applied DC fields: 0, 5, 10, 15, 20, 15, 10, 5, 0, -5, -10, -15, -20, -15, -10, and 0 kV/cm. Transition temperatures ($T_m$) of composites without DC bias: $-61 \, ^\circ C$ ($x = 0.2$), $-27 \, ^\circ C$ ($x = 0.25$), and $7 \, ^\circ C$ ($x = 0.3$).
4.2.2.4 Summary

(Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.20, 0.25, and 0.30)-MgO ceramic composites were fabricated, and their dielectric properties, thermal expansion behaviors, and microstructure were studied.

The composites with SPT (x = 0.20, 0.25, and 0.30) showed their transition temperatures –61, –27, and 7 °C, respectively. These transition temperatures were linearly proportional to x in (Sr$_{1-x}$Pb$_x$)TiO$_3$. The SPT (x=0.20, 0.25, and 0.30)-MgO composites showed dielectric tunability, 3, 7, and 18%, respectively, with a DC field of 20 kV/cm bias field at 10 kHz and loss tangent values, less than 0.002 were measured at 25 °C and at a frequency of 10 kHz.
4.2.3 Dielectric properties of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2)-MgO composites under direct current (DC) bias field and after DC bias field measurements

4.2.3.1 Introduction [e.g., 12-14]

A phenomenon, ferroelectricity occurring in a displacive ferroelectric from a paraelectric to ferroelectric state upon cooling is considered to be caused by the softening of specific components or the lattice modes of vibration at the phase transition. In addition, the relative permittivity of the ferroelectric as a function of temperature often shows the maximum at the phase transition temperature.

In order to explain the magnitude of relative permittivity, polarizability, that is, the degree of relative movement of the charges (e.g., ions for a specific ferroelectric) is necessary. Two kinds of sources are possible to produce the polarizability: i) an external applied field which makes the electrical polarizability of a ferroelectric (broadly speaking, dielectric) and ii) a local field which is not necessary to be the same as the external applied field and which causes the electric polarizability of an entity within the ferroelectric (the dielectric). The magnitude of relative permittivity of the ferroelectric is related to the polarizability caused by the external applied field and the relationship between relative permittivity and polarization (net charges with a certain direction; in a sense, the magnitude of polarizability) is given by Eq. (4.2.3.1). The relationship among dielectric displacement, field, and permittivity or polarization is given by Eq. (4.2.3.2) and polarization caused by the dielectric phenomenon of a species (e.g., a non-linear dielectric) is given by Eq. (4.2.3.3)

\[
\varepsilon_r = 1 + \eta = 1 + \chi^{-1} = 1 + \frac{P}{\varepsilon_o E} \quad \text{(4.2.3.1)}
\]

\[
D = \varepsilon E = \varepsilon_r \varepsilon_o E = \varepsilon_o E + P \quad \text{(4.2.3.2)}
\]

\[
P = \varepsilon_o \eta E = \varepsilon_o \chi^{-1} E \quad \text{(4.2.3.3)}
\]

\[
D = \varepsilon E = \varepsilon_r \varepsilon_o E = \varepsilon_o E + \varepsilon_o \eta E = \varepsilon_o E + \varepsilon_o \chi^{-1} E = \varepsilon_o \left(1 + \chi^{-1}\right) E \quad \text{(4.2.3.4)}
\]

where $D$ is a dielectric displacement, $E$ is an electric field, $\varepsilon$ is dielectric permittivity, $\varepsilon_o$ is dielectric permittivity in vacuum, $\varepsilon_r$ is relative dielectric permittivity, $P$ is dielectric polarization, $\eta$ is dielectric susceptibility, and $\chi$ is dielectric stiffness (i.e., the reciprocal of the dielectric susceptibility). $\chi$ is often referred to as dielectric susceptibility and $\chi^{-1}$ is often used to describe the reciprocal of dielectric susceptibility, namely, dielectric stiffness in the literature. However,
in this text, $\chi$ is used as the reciprocal of dielectric susceptibility. Eq. (4.2.3.4) gives how to obtain the relation described in Eq. (4.2.3.1).

Free energy, electric field, and dielectric stiffness may be described as a function of polarization described in Eqs. (4.2.3.5-7) for the ferroelectric which shows a non-linear behavior

$$G = \frac{1}{2} \alpha P^2 + \frac{1}{4} \beta P^4 + \frac{1}{6} \gamma P^6$$  \hspace{1cm} (4.2.3.5)

$$\frac{\partial G}{\partial P} = E = \alpha P + \beta P^3 + \gamma P^5$$  \hspace{1cm} (4.2.3.6)

$$\frac{\partial^2 G}{\partial P^2} = \frac{\partial E}{\partial P} = \chi = \alpha + 3\beta P^2 + 5\gamma P^4$$  \hspace{1cm} (4.2.3.7)

where $G$ is free energy, and $\alpha$, $\beta$, and $\gamma$ are constants.

Because $P$ is small or null in the paraelectric state, Eq. (4.2.3.7) leads to

$$\chi = \alpha$$  \hspace{1cm} (4.2.3.8)

and, moreover, the constant $\alpha$ may be proportional to temperature based on experimental observations

$$\chi = \chi_0 (T - \theta) = \frac{T - \theta}{C}$$  \hspace{1cm} (4.2.3.9)

where $T$ is temperature, $\chi_0$ is dielectric stiffness which is proportional to $T$, $\theta$ is the Curie-Weiss temperature, and $C$ is the Curie-Weiss constant.

The ferroelectric shows a non-linear behavior, for example, the direct current (DC) dependence of relative permittivity. Assuming that the first and second terms of the right side of Eq. (4.2.3.7) contribute only to the dielectric stiffness because of small $P$ values, the dielectric stiffness for the non-linear ferroelectric, $\chi_{nl}$, may be given by the following equation with the relation in Eq. (4.2.3.9)

$$\chi_{nl} = \frac{(T - \theta)}{C} + 3\beta P_{ind}^2$$  \hspace{1cm} (4.2.3.10)

where $P_{ind}$ is polarization induced at a DC field. Polarization becomes higher at a higher DC field shown in Eq. (4.2.3.3), and higher induced polarization also makes higher dielectric stiffness in Eq. (4.2.3.10). On the contrary, relative permittivity becomes lower because the reciprocal of relative dielectric stiffness is relative dielectric permittivity. Thus we expect higher tunability (i.e., a change in relative permittivity at a DC bias field) at higher DC bias fields. When a measurement temperature is closer to the transition temperature (precisely speaking, the Curie-
Weiss temperature), the contribution of the first term of Eq. (4.2.3.10), \( \frac{(T - \theta)}{C} \), to the dielectric stiffness, \( \chi_{nl} \), becomes lower and, furthermore, induced polarization is easily increased by a lower DC field due to the softening of the system for the displacive ferroelectric. Thus higher tunability is expected as the measurement temperatures are approaching the phase transition temperatures. In order to exhibit the change of relative permittivity under DC bias, the ferroelectric does not need to be in the ferroelectric state nor to have spontaneous polarization.

Dielectric tunability is defined as the degree of DC field dependence of the capacitance or relative permittivity, and the tunability increases at higher DC fields and near the phase transition as described previously. Because polarizability, that is, the relative movement of species which have charges (in this case, ions are major species) is suppressed more under higher DC fields, lower relative permittivity is expected under the same condition. Thus higher tunability will be observed at higher DC bias fields. Higher tunability is expected near the phase transition because higher relative permittivity near the phase transition is suppressed at DC fields to a level similar to the values at temperatures not close to that of the phase transition. Generally, materials which show higher relative permittivity without DC bias fields are preferable in order to achieve higher tunability. This is true for temperature dependant tunability measurements. However, if the system is changed, higher relative permittivity materials are not necessary to refer to higher tunable materials. For example, there are ferroelectrics which do not show a strong DC bias dependence of relative permittivity even though their relative permittivity is high. In addition, a diphase composite with a ferroelectric and non-ferroelectric (e.g., composite with relatively low dielectric constant compared with the pure ferroelectric) has the possibility to show similar tunability the pure ferroelectric possesses, depending on the selection of components and on the structure of the components.

K-factor is defined by tunability over tangent \( \delta \), and high K-factor is preferable for all kinds of applications. To achieve a higher K-factor, higher tunability and/or lower tangent \( \delta \) is required. Higher tunability is obtained at higher DC fields until the tunability reaches its saturation range or the sample is broken. However, low tangent \( \delta \) values are achieved at a specific temperature range and at a fixed frequency such as 10 kHz. The range is in the paraelectric state which is not close to the phase transition and which is not far above the phase transition. The reasons are that tangent \( \delta \) becomes higher close to the phase transition and in the ferroelectric state due to the motion of domains and micro-polar regions in the paraelectric state.
and that of domain walls in the ferroelectric state. Furthermore, tangent $\delta$ in the paraelectric region and far above the phase transition increases due to the movement of conductive species.

Sect. 4.2.2. describes that $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ (SPT) $(x = 0.2)$-magnesium oxide (MgO) composites showed the lowest tangent $\delta$ at room temperature and at a frequency of 10 kHz among the composites studied. In addition, the composites showed tunability at room temperature and at 10 kHz. Tunable microwave ferroelectrics are required to have a higher K-factor, namely, higher tunability and lower tangent $\delta$. Tunability would be increased at higher DC bias fields. Thus the SPT $(x = 0.2)$-MgO was selected and prepared again to study their characteristics, the effect of density on tunability, and properties at cryogenic temperatures and at high DC bias fields. Additionally, several dielectric property data before and after DC bias measurements will be described in this section.

4.2.3.2 Experimental

The suitable ratio of strontium carbonate (SrCO$_3$), lead oxide (PbO), and titanium oxide (TiO$_2$) (Sr-Pb-Ti (0.8:0.2:1)) were mixed and calcined. Low dielectric constant oxide, MgO, was added to the SPT compositions in a ratio of 50:50 by weight. Pressed pellets were sintered at 1350 °C. The densities of the composites were calculated based on the dimensions and weights of the composites.

The dielectric properties of the composite samples at low frequencies (e.g., 10 kHz) were measured using LCR meters (4284A, HP). Thinner samples were measured in silicon oil or silicon rubber under an ambient atmosphere. Cryogenic temperature measurements were carried out in vacuum. Two kinds of blocking circuits (BCs; 2kV (volts) maximum BC, 2kV BC and 4kV maximum BC, 4kV BC) were used to protect the LCR meters during DC bias measurements.

The tunability and K-factor of the composites at various DC fields were calculated using the following equations

$$\text{tunability} = \frac{\varepsilon_r(E_o) - \varepsilon_r(E)}{\varepsilon_r(E_o)} \quad (4.2.3.11)$$

$$K - \text{factor} = \frac{\varepsilon_r(E_o) - \varepsilon_r(E)}{\varepsilon_r(E_o)} \times \frac{1}{\tan \delta} \quad (4.2.3.12)$$

where $\varepsilon_r(E)$ is relative permittivity at E kV/cm and $E_o$ is 0 kV/cm.
4.2.3.3 Results

4.2.3.3.1 Reproducibility of 10 kHz dielectric tunability at room temperature

In Sect. 4.2.2, the SPT (x = 0.2)-MgO composites showed the transition temperature $-61^\circ$C, relative permittivity $\sim 110$, and tangent $\delta$ less than 0.0005 without applying DC bias at 10 kHz and at 25 $^\circ$C. 25 $^\circ$C dielectric tunability was 0.02 with a DC field of 20 kV/cm at a frequency of 10 kHz. Freshly prepared SPT (x = 0.2)-MgO composites showed the transition temperature $-63^\circ$C, relative permittivity $\sim 130$, and tangent $\delta$ less than 0.0005 without applying DC bias at 10 kHz and at 25 $^\circ$C. Dielectric tunability was 0.02 with a DC field of 20 kV/cm at 10 kHz and at 25 $^\circ$C. The two composites showed different relative permittivity at room temperature and the difference was nearly 10 %. However, they showed similar dielectric tunability and low tangent $\delta$. A careful processing for mass production will reduce a difference in dielectric constant values. The fixture used for the characterization is shown in Fig. 4.2.3.1.

4.2.3.3.2 Effect of composite density on dielectric tunability

A freshly prepared sample was cut from a disk of which the density was 4.3 g/cm$^3$. Low density sample was cut from a plate of which the density was 3.8 g/cm$^3$. The plate was sintered after forming by uniaxial pressing only (without cold isostatic pressing). The high and low density composites were measured in silicon oil and showed the transition temperatures, $-63$ and $-56$ $^\circ$C at 10 kHz upon cooling, respectively. Fig. 4.2.3.2 shows the DC bias dependence of relative permittivity and tangent $\delta$ of the two composites. Artificial steps of tangent $\delta$ vs. temperature plots during the DC bias measurements were observed, and they were the artifacts of the setup. This will be explained in detail based on the measurement results in Sect. 4.2.3.3.4.

Fig. 4.2.3.3 shows dielectric tunability as a function of DC field and temperature at 10 kHz. The high density samples showed hysteresis near the transition temperature, but the low density samples showed a relatively low hysteresis around the transition temperature. At room temperature, both the composites showed a similar tunability 0.02, but they showed a different hysteresis behavior. The high density samples did not show a significant hysteresis around room temperature, but the low density showed hysteresis. Fig. 4.2.3.4 shows the DC bias dependence of tunability at $T_m + 80$ $^\circ$C ($T_m$: weak field dielectric maximum temperature). Although the low density samples showed the hysteresis over the DC bias fields, the high density samples showed the hysteresis at less than 10 kV/cm.
Figure 4.2.3.1 Fixture used for dielectric property measurements.
Figure 4.2.3.2 10 kHz relative permittivity and tangent $\delta$ of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) ($x = 0.2$)-MgO (50:50 by weight) composites as a function of temperature and DC field. Last five runs at $-20$, $-15$, $-10$, $-5$, and $0$ kV/cm of all applied fields ($0$, $5$, $10$, $15$, $20$, $15$, $10$, $5$, $0$, $-5$, $-10$, $-15$, $-20$, $-15$, $-10$, $-5$, and $0$ kV/cm).
(a) Sample 1 (0.45 mm in thickness): High density sample was cut from 4.3 g/cm$^3$ composites and measured in silicon oil ($T_m$, $-63$ °C).
(b) Sample 2 (0.32 mm in thickness): Low density sample was cut from 3.8 g/cm$^3$ composites and measured in silicon oil ($T_m$, $-56$ °C).
$T_m$: Dielectric constant peak maximum temperature at 10 kHz upon cooling.
Figure 4.2.3.3 10 kHz dielectric tunability of (Sr$_{1-x}$Pb$_x$)$_2$TiO$_3$ (SPT) ($x = 0.2$)-MgO (50:50 by weight) composites as a function of temperature and DC bias. Last five runs at $-20$, $-15$, $-10$, $-5$, and $0$ kV/cm of all applied DC fields ($0$, $5$, $10$, $15$, $20$, $15$, $10$, $5$, $0$, $-5$, $-10$, $-15$, $-20$, $-15$, $-10$, $-5$, and $0$ kV/cm).

(a) Sample 1 (0.45 mm in thickness): High density sample was cut from 4.3 g/cm$^3$ composites and measured in silicon oil ($T_m -63$ °C).
(b) Sample 2 (0.32 mm in thickness): Low density sample was cut from 3.8 g/cm$^3$ composites and measured in silicon oil ($T_m -56$ °C).

$T_m$: Dielectric constant peak maximum temperature at 10 kHz upon cooling.
Figure 4.2.3.4 Dielectric tunability of high and low density (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) 
(x = 0.2)-MgO (50:50 by weight) composites as a function of DC bias fields at 10 kHz and 
at T$_m$ + 80 °C.

Applied fields: 0, 5, 10, 15, 20, 15, 10, 5, 0, −5, −10, −15, −20, −15, −10, −5, and 0 kV/cm.

(a) Sample 1 (0.45 mm in thickness): High density sample was cut from 4.3 g/cm$^3$ 
composites and measured in silicon oil at 17 °C (T$_m$ = −63 °C).

(b) Sample 2 (0.32 mm in thickness): Low density sample cut from 3.8 g/cm$^3$ composites 
and measured in silicon oil and at 24 °C (T$_m$ = −56 °C).
Fig. 4.2.3.5 shows the effect of composite density on dielectric properties under the DC bias fields at 10 kHz and at 25 °C. The high density sample was prepared to thin and polish the sample shown in Fig. 4.2.3.4 (current sample, 0.23 mm in thickness; previous sample, 0.45 mm in thickness). Both high and low density samples were measured in silicon rubber. The high density samples did not show a significant hysteresis, but the low density samples showed a notable hysteresis. Furthermore, it is noted that the high density composite covered with silicon rubber or in the setup (see Fig. 4.2.3.12) did not show an obvious hysteresis at lower DC bias fields even though the thicker sample showed the hysteresis when it was measured in silicon oil (Fig. 4.2.3.4.1). The conditions of a sample are important to avoid hysteresis while applying DC bias. Because these composites are not planned to be used near the phase transition in order to achieve low tangent δ, high density samples are preferable for tunable ferroelectric devices.

### 4.2.3.3.3 Dielectric properties at cryogenic temperature

Fig. 4.2.3.6 shows the thermal hysteresis of dielectric properties of the composites, and the small hysteresis was observed near the phase transition and in the ferroelectric state. Fig. 4.2.3.7 shows the effect of the blocking circuit (2kV BC) on dielectric properties measured using the cryogenic system. Tangent δ values with or without the 2kV BC were significantly different. A reason is that the cryogenic system was not calibrated using a calibration with standard air capacitors (1 p, 10 p, 100 p, and 1 nF) (note: an open calibration to compensate for the open circuit of the setup was carried out) when the 2 kV BC was used. When the setup with the 2 kV BC was compensated for the open circuit and calibrated using standard capacitors, tangent δ did not show an obvious difference between the setups with and without using the 2 kV BC (Fig. 4.2.3.8). The difference of dielectric constant between the measurements with and without the BC was low, approximately 1 %.

Fig. 4.2.3.9 shows the DC bias dependence of dielectric properties at DC bias fields up to 40 kV/cm. Fig. 4.2.3.10 shows the dielectric tunability of the composites, and Fig. 4.2.3.11 shows the K-factor of the composites calculated from tangent δ values measured without applying DC bias, that is, without the BC. The relative permittivity and tangent δ were suppressed at higher DC fields over a wide temperature range.

### 4.2.3.3.4 Tunability at high DC fields

To achieve higher tunability, it is necessary to apply higher DC fields to the composites. The fixture shown in Fig.4.2.3.1 did not permit stable and noise free measurement data of the
Figure 4.2.3.5 Relative permittivity and tangent δ of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2)-MgO (50:50 by weight) composites as a function of DC bias field at 10 kHz and at 25 °C. Applied fields: 0, 5, 10, 15, 20, 30, 40, 50, 60, 50, 40, 30, 20, 15, 10, 5, and 0 kV/cm and similar sequence of negative fields.

(a) Sample 3 (0.23 mm in thickness) : High density sample was cut from 4.3 g/cm$^3$ composites and polished sample 1 (sample 1: 0.45 mm in thickness). Sample 3 was measured in silicon rubber.

(b) Sample 2 (0.32 mm in thickness): Low density sample was cut from 3.8 g/cm$^3$ composites and measured in silicon rubber.

$T_m$: Dielectric constant peak maximum temperature at 10 kHz upon cooling.
Figure 4.2.3.6 Dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites in vacuum at 10 kHz as a function of temperature upon both cooling and heating. Sample 3 (thickness: 0.23 mm) was measured.

Figure 4.2.3.7 Dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites in vacuum as a function of temperature at 10 kHz upon cooling with and without 2-kilo-volts maximum blocking circuit (2kV BC). Sample 3 (thickness: 0.23 mm) was measured without standard capacitor calibration. w/o, without; w, with.
Figure 4.2.3.8 Dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites in vacuum as a function of temperature at 10 kHz upon cooling with and without 2-kilo-volts maximum blocking circuit (2kV BC). Sample 3 (thickness: 0.23 mm) was measured in silicon rubber after standard capacitor calibration.

Figure 4.2.3.9 Dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites in vacuum as a function of temperature and DC bias field at 10 kHz using 2kV BC. Increasing DC bias: Black curves; Returning DC bias: Gray curves. Applied fields: 0, 2.5, 5, 7.5, 10, 15, 20, 25, 30, 35, 40, 35, 30, 25, 20, 15, 10, 7.5, 5, 2.5, 0 kV/cm. Sample 3 (0.23 mm in thickness) used: High density sample cut from 4.3 g/cm$^3$ composites. $T_m$: Dielectric constant peak maximum temperature at 10 kHz upon cooling, −63 °C. 2kV BC: 2-kilo-volts maximum blocking circuit.
Figure 4.2.3.10 Dielectric tunability of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites in vacuum as a function of temperature and DC bias field at 10 kHz with 2kV BC. (a) $T_m$ through $T_m + 90^\circ C$ and (b) 25 $^\circ C$ and $T_m$ through $T_m - 190^\circ C$.

Applied fields: 0, 2.5, 5, 7.5, 10, 15, 20, 25, 30, 35, 40, 35, 30, 25, 20, 15, 10, 7.5, 5, 2.5, 0 kV/cm.

Sample 3 (0.23 mm in thickness) used: High density sample was cut from 4.3 g/cm$^3$ composites. $T_m$: Transition temperature at 10 kHz upon cooling without applying DC bias, $-63^\circ C$.

2kV BC: 2-kilo-volts maximum blocking circuit.
Figure 4.2.3.11 K-factor of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites in vacuum as a function of temperature and DC bias field at 10 kHz with 2kV BC. (a) $T_m$+90 °C through $T_m$+30 °C and (b) $T_m$+20 °C through $T_m$−190 °C.

Applied fields: 0, 2.5, 5, 7.5, 10, 15, 20, 25, 30, 35, 40, 35, 30, 25, 20, 15, 10, 7.5, 5, 2.5, 0 kV/cm.

Sample 3 (0.23 mm in thickness) used: High density sample was cut from 4.3 g/cm$^3$ composites.

$T_m$: Transition temperature at 10 kHz on cooling without applying DC bias, −63 °C.

2kV BC: 2-kilo-volts maximum blocking circuit.

Figure 4.2.3.12 Special fixture used for dielectric property measurements.
thin sample which had 0.23 mm in thickness. Therefore, the sample was measured in a different setup (Fig. 4.2.3.12). In addition, the new setup might enable the sample to be measured at higher DC fields. The breakdown fields of air (relative permittivity, \( \varepsilon_r \), 1.00), silicon oil (\( \varepsilon_r \) 2.8), and polymers such as polystyrene (\( \varepsilon_r \) 2.5), polyethylene (\( \varepsilon_r \) 2.2), polysulfone (\( \varepsilon_r \) 3.1), and polypropylene (\( \varepsilon_r \) 2.5) are 30, 140, 200, 1800, 3200, and 3840 kV/cm, respectively [15]. Thus the sample in silicon rubber would increase breakdown fields than that in air or silicon oil if the sample has a higher breakdown field than air or silicon oil. Fig. 4.2.3.13 shows the temperature dependence of relative permittivity and tangent \( \delta \) of the SPT (x = 0.2)-MgO composites in the DC field range between 0 and 90 kV/cm over the temperature range from 35 to –100 °C at 10 kHz with the two kilovolts maximum blocking circuit (2kV BC) at the specific measurement AC field, 4 V/cm. The transition temperature of the sample without applying the DC bias fields (\( T_m \)) was about –64 °C. As described before, the steps of tangent \( \delta \) were noted in tangent \( \delta \) vs. temperature plots during the DC bias field measurements.

Fig. 4.2.3.14 shows the observed capacitance values of the composite using the LCR meter and the 2kV BC, but relative permittivity was not calculated (calculated dielectric constant values were shown in Fig. 4.2.3.13). The tangent \( \delta \) showed the steps at the specific capacitance, ~550 pF. Fig. 4.2.3.15 shows the observation of steps by an air capacitor of which the capacitance was changed manually, and the figure also demonstrates that the steps occurred at the specific capacitance value. The artificial steps of tangent \( \delta \) vs. temperature plots during the DC bias measurements were the artifacts of the setup. These behaviors were due to the optimization of measurement conditions of the LCR meter (4284A, HP) under the measurement conditions and the BC which multiplies the capacitance 10 times higher than real capacitance values. These tangent \( \delta \) steps were also noted at ~170 pF as an observed capacitance.

Fig. 4.2.3.16 (a) and (b) show the tangent \( \delta \) and tunability of the SPT (x = 0.2)-MgO composites at 10 kHz as a function of temperature and DC field.

Dielectric constant and tangent \( \delta \) were suppressed at DC bias fields, and the discontinuity of tangent \( \delta \) was caused by the use of the blocking circuit and the LCR meter as explained earlier. Higher tunability was observed at higher fields. At 25 °C, the relative permittivity was ~ 120, tangent \( \delta \) was less than 0.0005 without DC fields, and tunability was 0.19 with a 90 kV/cm field and at a 10 kHz frequency.

Fig. 4.2.3.16 (c) and (d) show K-factors which were calculated using two types of tangent \( \delta \) values: (i) tangent \( \delta \) at 10 kHz measured at a different time from that of the DC bias
Figure 4.2.3.13 Dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites at 10 kHz as a function of temperature and DC bias field with 2kV BC. Returning DC bias: 90, 80, 70, 60, 50, 40, 30, 25, 20, 15, 10, 7.5, 5, 2.5, and 0 kV/cm (0 ~ 90 ~0 kV/cm). Sample 3 (0.23 mm in thickness) used: High density sample was cut from 4.3 g/cm$^3$ composites and measured in silicon rubber. $T_m$: Dielectric constant peak maximum temperature at 10 kHz upon cooling, $-64 \, ^\circ$C.

Figure 4.2.3.14 Artificial tangent $\delta$ values of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO composites with DC bias fields at a capacitance of around and more than 550 pF due to the use of 2k-volts maximum blocking circuit and LCR meter (4284A, HP). Applied DC fields: $-15, -10, -7.5, -5, -2.5$, and 0 kV/cm. Blocking circuit shows 10 times higher capacitance. Calculated relative permittivity is shown in Fig. 4.2.3.13.
Figure 4.2.3.15 Changes in tangent $\delta$ values at a capacitance of ca. 550 pF caused by manually changed capacitance using an air capacitor, 2k-volts maximum blocking circuit, and LCR meter (4284A, HP).
Figure 4.2.3.16 (a) Tangent $\delta$ of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites at 10 kHz as a function of temperature and DC bias field with 2kV BC. Returning DC bias: 90, 80, 70, 60, 50, 40, 30, 25, 20, 15, 10, 7.5, 5, 2.5, 0 kV/cm (0 - 90 - 0 kV/cm). Sample 3 (0.23 mm in thickness) used: high density sample was cut from 4.3 g/cm$^3$ and composites were measured in silicon rubber. $T_m$: Dielectric constant peak maximum temperature at 10 kHz upon cooling, $-64$ °C.

Figure 4.2.3.16 (b) Dielectric tunability of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites at 10 kHz as a function of temperature and DC bias field with 2kV BC. Returning DC bias: 90, 80, 70, 60, 50, 40, 30, 25, 20, 15, 10, 7.5, 5, 2.5, 0 kV/cm (0 - 90 - 0 kV/cm). Sample 3 (0.23 mm in thickness) used: High density sample was cut from 4.3 g/cm$^3$ composites and measured in silicon rubber. $T_m$: Dielectric constant peak maximum temperature at 10 kHz upon cooling, $-64$ °C.
Figure 4.2.3.16 K-factor of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50) composites at 10 kHz as a function of temperature and DC bias field with 2kV BC.

(c) K-factor calculated based on tangent $\delta$ measured without 2kV BC and without applying DC bias.

(d) K-factor calculated based on tangent $\delta$ measured at DC bias fields.

Returning DC bias: 90, 80, 70, 60, 50, 40, 30, 25, 20, 15, 10, 7.5, 5, 2.5, 0 kV/cm (0 - 90 - 0 kV/cm).

Sample 3 (0.23 mm in thickness) used: High density sample was cut from 4.3 g/cm$^3$ composites and measured in silicon rubber.

$T_m$: Dielectric constant peak maximum temperature at 10 kHz upon cooling, $-64$ °C.
measurements, that is, tangent $\delta$ measured without the blocking circuit and without applying DC bias fields (plot (c)) and (ii) tangent $\delta$ values measured during DC bias measurements, that is, tangent $\delta$ measured with DC bias fields (plot (d)). K-factor calculated from tangent $\delta$ measured without DC fields was $\sim$ 400 at 10 kHz and at 25 °C and K-factor calculated from tangent $\delta$ values measured with DC bias fields was $\sim$ 700 under the same conditions. Because the samples showed the suppression of loss tangents at DC bias fields, K-factors tended to be higher when calculated using tangent $\delta$ values measured at the DC bias fields. Fig. 4.2.3.17 shows the reproducibility of relative permittivity and tunability of the composites at 90 kV/cm as the maximum DC field and small differences were noted.

Fig. 4.2.3.18 (a) shows the relative permittivity and tangent $\delta$ of the composites before DC bias measurements at 175 kV/cm as the maximum DC field. Fig. 4.2.3.18 (b) shows the 10 kHz tunability at specific temperatures. The tunability was obtained with decreasing fields from a DC field of 175 kV/cm as the highest DC field using the 4 kV maximum BC (4kV BC). However, the 4 kV BC did not permit accurate measurements of tangent $\delta$. Additionally, it caused the hysteresis of relative permittivity at lower DC bias fields with measuring AC fields of 12 - 14 V/cm. The 10 kHz tunability was 0.30 at 25 °C with a DC field of 175 kV/cm (Fig. 4.2.3.18 (b)). Calculated K-factors using tangent $\delta$ measured without the 4kV BC are shown in Fig. 4.2.3.18 (c). 10 kHz K-factor value was $\sim$ 800 at 25 °C with a field of 175 kV/cm. The composites were able to withstand the high DC field, 175 kV/cm. The breakdown field of ceramics ($\varepsilon_r$, 5.5~7.5) and that of high voltage ceramic-barium titanate composite and filler ($\varepsilon_r$, 500~6000) is 80~140 kV/cm and 20 kV/cm, respectively [15]. The value, 175 kV/cm, is not a breakdown field and is not obtained by a standard test. However, it could be due to the fact that the thin sample had a good composition quality. Table 4.2.3.1 summarizes the results of these composites.

4.2.3.3.5 Effect of storage conditions on dielectric tunability

Fig. 4.2.3.19 shows the relative permittivity and tangent $\delta$ of the (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO composite sample at room temperature and at 10 kHz. The sample was placed at room temperature under a conventional atmosphere and then stored in a desiccator for about 4 months. The sample showed similar relative permittivity and tangent $\delta$ at 10 kHz independent of storing conditions when DC bias fields were not applied to the sample. However, the sample placed in air showed the asymmetrical behavior of relative permittivity at DC bias fields even though the
Figure 4.2.3.17 Reproducibility of (Sr0.8Pb0.2)TiO3-MgO (50:50 by weight) composite dielectric properties at 10 kHz and at 25 °C with DC bias fields (0 - 90 - 0 kV/cm) using 2kV BC. Sample 3 (0.23 mm in thickness) used: High density sample was cut from 4.3 g/cm³ composites and measured in silicon rubber.

Tm: Dielectric constant peak maximum temperature at 10 kHz upon cooling, −64 °C.

2kV BC: 2-kilo-volts maximum blocking circuit.

Figure 4.2.3.18(a) Relative permittivity and tangent δ of (Sr0.8Pb0.2)TiO3-MgO (50:50 by weight) composites at 10 kHz without 2kV BC.

Sample 3 (0.23 mm in thickness) used: High density sample was cut from 4.3 g/cm³ composites and measured in silicon rubber.

Tm: Dielectric constant peak maximum temperature at 10 kHz upon cooling, −64 °C.

2kV BC: 2-kilo-volts maximum blocking circuit.
Figure 4.2.3.18 (b) Dielectric tunability and (c) K-factor of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites at 10 kHz as a function of temperature and DC bias field. K-factor was calculated using tangent δ values presented in plot (a).

Sample 3 (0.23 mm in thickness) used: High density sample was cut from 4.3 g/cm$^3$ composites and measured in silicon rubber.

T$_m$: Dielectric constant peak maximum temperature at 10 kHz upon cooling, $\sim$64 °C.

2kV BC: 2-kilo-volts maximum blocking circuit.
Table 4.2.3.1 Summary of tunability and K-factor of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.2)-MgO (50:50 by weight) composites at 10 kHz and at 25 ℃

<table>
<thead>
<tr>
<th>Description</th>
<th>Thickness (mm)</th>
<th>Condition</th>
<th>BC</th>
<th>Field (kV/cm)</th>
<th>Tunability</th>
<th>K-factor*** (tan δ w/o DC fields)</th>
<th>K-factor**** (tan δ at DC fields)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample 1</td>
<td>0.45</td>
<td>in Si oil</td>
<td>2kV</td>
<td>20</td>
<td>0.02*</td>
<td>60</td>
<td>--</td>
</tr>
<tr>
<td>sample 2</td>
<td>0.23</td>
<td>in Si rubber (1)</td>
<td>2kV</td>
<td>20</td>
<td>0.02*</td>
<td>20</td>
<td>--</td>
</tr>
<tr>
<td>sample 3</td>
<td>0.23</td>
<td>in Vacuum</td>
<td>2kV</td>
<td>20</td>
<td>0.02*</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>sample 4</td>
<td>0.23</td>
<td>in Si rubber (2)</td>
<td>2kV</td>
<td>20</td>
<td>0.02*</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>90</td>
<td>0.19**</td>
<td>370</td>
<td>690</td>
</tr>
<tr>
<td>sample 5</td>
<td>0.23</td>
<td>in Si rubber (2)</td>
<td>4kV</td>
<td>20</td>
<td>0.03**</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>90</td>
<td>0.18**</td>
<td>520</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>175</td>
<td>0.30**</td>
<td>840</td>
<td></td>
</tr>
</tbody>
</table>

Sample 1 was cut from a disk of which the density was 4.3 g/cm$^3$ and measured in silicon oil.
Sample 2 - 5 were thinned and polished using sample 1.
Si: Silicon; two kinds of silicon rubber were used in the experiments.
BC: Blocking circuit; two kinds of BCs were used in the experiments. 2kV: 2-kilo-volts as the maximum voltage. 4kV: 4-kilo-volts as the maximum voltage. 4kV BC did not permit accurate measurements of tangent δ values.
* : An average of two results.
** : One measurement result.
*** : K-factor was calculated from tangent δ measured at a different time from that of DC bias measurement, i.e., without applying DC fields and without using the BCs.
****: K-factor was calculated from tangent δ measured on the same time at which capacitance was measured.
Figure 4.2.3.19 Effect of storage conditions on DC bias field dependence of relative permittivity and tangent δ of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites at 10 kHz and at 25 °C with 2kV BC.

Sample (i) : Kept at room temperature and under atmosphere.
Sample (ii) : Sample (i) stored in a desiccator for ~ 4 months.

Sample 3 (0.23 mm in thickness) used: High density sample was cut from 4.3 g/cm$^3$ composites and measured in silicon rubber.
sample did not show a clear hysteresis during bias measurements. The sample stored in the desiccator did not show an asymmetrical behavior. Water or a substance stored in the measuring system would cause this behavior. It would be important to consider how to store the composites. Because the composite was in silicon rubber, the water or substance was not expected to influence the dielectric constant measurements. A couple of solutions to avoid this unusual behavior are as follows: i) to store composites under a special condition, for example, in a dessicator, or ii) to store composites in vacuum, for example, to make a device with a composite in vacuum or to seal a composite in glass under vacuum.

4.2.3.3.6 Degradation due to DC bias: Dielectric properties after DC bias measurements

Fig. 4.2.3.20 (a) and (b) show two examples to demonstrate the degradation of the (Sr0.8Pb0.2)TiO3-MgO composite due to the application of DC fields. Plot (a) shows a reduction in dielectric constant and an increase in tangent δ after applying DC bias fields up to 175 kV/cm. An electric DC field of 175 kV/cm was not applied to the sample before the measurement. On the contrary, plot (b) does not show an obvious difference of dielectric properties before and after applying DC bias fields, up to 90 kV/cm, but the composite had already been subjected to 175 kV/cm, which was more than the 90 kV/cm now applied.

The history of application of DC fields appeared to influence dielectric properties, and further investigation is necessary to understand the degradation mechanism.

4.2.3.3.7 Effect of DC bias on the relative permittivity maxima of composites

Fig. 4.2.3.21 shows the effect of DC bias fields on the relative permittivity maxima of the (Sr0.8Pb0.2)TiO3-MgO composite samples as a function of temperature. Under DC bias, the dielectric constant peak maximum temperature is expected to increase. Fig 4.2.3.22 shows the results of pure (Sr1-xPbx)TiO3 (SPT) (x = 0.2) as an example. The decrease in the maximum temperature of the composites could be due to the effect of stress of the SPT component in the composite matrix or the artificial effect of the SPT component in the composites. This tendency was also observed in the SPT (x = 0.25 and 0.3)-MgO composites (not shown in this dissertation).

Further studies will be necessary to understand the behavior.
Figure 4.2.3.20 Change in dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO composites (50:50 by weight) due to the application of DC bias fields: dielectric properties before and after DC bias measurements.  
(a) Before and after DC bias measurement up to 175 kV/cm as the maximum field and at several temperatures in the temperature range from room temp to −20 °C. 
(b) Before and after DC bias measurements up to 90 kV/cm as the maximum field and in the temperature range from 35 to −115 °C; Sample was subjected to 175 kV/cm as the maximum field before 90 kV/cm measurements. 
Sample 3 (0.23 mm in thickness) used: High density sample was cut from 4.3 g/cm$^3$ composites and measured in silicon rubber.
Figure 4.2.3.21 Transition temperatures of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50) composites as a function of DC bias fields.
Transition temperatures ($T_m$) were based on dielectric constant maximum at 10 kHz with DC bias fields.
(i) Sample in silicon rubber was measured up to 90 kV/cm.
(ii) Sample was measured up to 40 kV/cm in vacuum.
Sample 3 (0.23 mm in thickness) used: High density sample was cut from 4.3 g/cm$^3$ composites and measured in silicon rubber.

Figure 4.2.3.22 Transition temperatures of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ ceramics as a function of DC bias fields.
Transition temperatures ($T_m$) were based on dielectric constant maximum at 10 kHz with DC fields.
4.2.3.4 Summary

The results suggested the highest electric field tolerance, 175 kV/cm, of the samples. The fact that the samples were able to take high fields at room temperature and the K-factor values ~ 800 made these composites the most suitable tunable microwave ferroelectrics reported so far. Further measurements will establish their usefulness for microwave ferroelectric devices such as tunable filters.
4.2.4 Dielectric properties over a wide frequency range between low and microwave frequencies

4.2.4.1 Introduction

Frequency agile ferroelectrics have been widely studied for various applications [16-20]. Some tunable materials based on the frequency agile ferroelectrics have been prepared by the addition and/or doping of low permittivity low tangent δ oxides to paraelectric–ferroelectric perovskites to achieve lower tangent δ and/or to dilute the relative permittivity of the pure substances of which the relative permittivity shows a direct current (DC) bias field dependence [21-24].

Subsequently, frequency agile microwave ferroelectrics were prepared from (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.20, 0.25, and 0.30) and magnesium oxide (MgO). The composites with SPT (x = 0.20, 0.25, and 0.30) showed reasonable dielectric tunability, 0.03, 0.07, and 0.18, respectively, with a 20 kV/cm bias field at 10 kHz and at room temperature. The SPT (x = 0.20, 0.25, and 0.30)-MgO composites showed low tangent δ values, 0.0005, 0.001, and 0.002, respectively, under the same conditions described in the above (Sect. 4.2.2) [24]. Additionally, the composites will show higher tunability at higher DC fields because the SPT (x = 0.20)-MgO composites showed tunability 0.30 with a DC field of 175 kV/cm at room temperature (Sect. 4.2.3).

Because the SPT (x = 0.20)-MgO composites showed the lowest tangent δ among the composites studied and reasonable dielectric tunability at 10 kHz and at room temperature, the composites based on the SPT (x = 0.20) have been selected to investigate further the potential of these materials for room temperature tunable microwave applications. Accordingly, the dielectric properties of the composites are characterized in a microwave frequency range. Various techniques exist depending on the geometries of samples and the values of relative permittivity, tangent δ, and measurement frequencies. Table 4.2.4.1 lists high and low frequency measurement methods [25-34].

This section will report factors which influence the dielectric properties of the SPT (x=0.20)-MgO composite samples measured over a wide frequency range using various techniques.
<table>
<thead>
<tr>
<th>Table 4.2.4.1 (a) Dielectric property characterization techniques (* Uniform field is assumed)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lumped impedance method</strong></td>
</tr>
<tr>
<td>Null-balance circuit method 2) Measurements: Unknown value is calculated based on the relationships of the other bridge elements, i.e., combination of L, C, and R 2) (Instrument: LCR meter)</td>
</tr>
<tr>
<td>I-V (current-voltage) method 2) Measurements: Unknown value is calculated based on I and V 2). (Instrument: Impedance analyzer)</td>
</tr>
<tr>
<td>Reflectometric method 2, 3) Measurements: The ratio of an incident signal to the reflected signal 2). (Instrument: Network analyzer)</td>
</tr>
<tr>
<td><strong>Resonant method</strong></td>
</tr>
<tr>
<td>Cavity resonator 1, 7) TE cavity resonator 5, 4)</td>
</tr>
<tr>
<td>TM cavity resonator 5)</td>
</tr>
<tr>
<td>Rectangular cavity resonator 5)</td>
</tr>
<tr>
<td>Split cavity resonator 4)</td>
</tr>
<tr>
<td>Re-entrant cavity* 5, 4)</td>
</tr>
<tr>
<td>Post dielectric resonator 1) Parallel plate dielectric post resonator 4, 7)</td>
</tr>
<tr>
<td>Courtney technique 5)</td>
</tr>
<tr>
<td>Split-cylinder resonator 5, 7)</td>
</tr>
<tr>
<td>Split-post dielectric resonator 5, 4)</td>
</tr>
<tr>
<td>Whispering gallery mode resonator</td>
</tr>
<tr>
<td>Perturbation method 1, 7) Stripline resonator 6)</td>
</tr>
<tr>
<td>Planar circuit method 1, 7)</td>
</tr>
<tr>
<td>Stripline resonator 6)</td>
</tr>
<tr>
<td>Microstrip resonator 6)</td>
</tr>
<tr>
<td>Coplanar-line resonator</td>
</tr>
<tr>
<td><strong>Open resonant method</strong></td>
</tr>
<tr>
<td>Open resonator 1, 7)</td>
</tr>
<tr>
<td>Near field microscope method 7)</td>
</tr>
<tr>
<td>Fabry-Perot resonator 5, 4)</td>
</tr>
<tr>
<td>**Transmission line method 1, 5, 7) 1) **</td>
</tr>
<tr>
<td>Coaxial line 1)</td>
</tr>
<tr>
<td>Transmission 1, 7)</td>
</tr>
<tr>
<td>Reflection 1, 7)</td>
</tr>
<tr>
<td>Waveguide 1, 7, 8)</td>
</tr>
<tr>
<td>Transmission</td>
</tr>
<tr>
<td>Reflection</td>
</tr>
<tr>
<td>Planar circuit 7)</td>
</tr>
<tr>
<td>Stripline</td>
</tr>
<tr>
<td>Microstrip</td>
</tr>
<tr>
<td>Coplanar-line method</td>
</tr>
<tr>
<td>**Free-space method 1, 6, 7)</td>
</tr>
<tr>
<td>Pure free space</td>
</tr>
<tr>
<td>Transmission 1)</td>
</tr>
<tr>
<td>Reflection 1)</td>
</tr>
<tr>
<td>Ellipsometry 1)</td>
</tr>
<tr>
<td>Beam-focusing</td>
</tr>
<tr>
<td>Lens 1)</td>
</tr>
<tr>
<td>Horn antenna 1)</td>
</tr>
<tr>
<td>**Calorimeter method 6)</td>
</tr>
<tr>
<td>L. inductance; C. capacitance: R. resistance, I. current; V. voltage.</td>
</tr>
</tbody>
</table>

Ref.
1) Hashimoto [25].
2) Agilent technologies impedance measurement handbook [26].
3) Santos et al. [27].
4) Baker-Jarvis et al. [28].
5) Baker-Jarvis et al. [29].
6) Helme [30].
7) Chen et al. [31].
8) Dube et al. [32].
Table 4.2.4.1 (b) Dielectric property characterization techniques based on external conditions

<table>
<thead>
<tr>
<th>Method</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time domain method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frequency domain method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature dependence</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Factor dependence (e.g., DC bias field, pressure)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

DC: Direct current.

Ref.
1) Zaengl [33].
2) Oyegoke [34].
3) Helme [30].
4.2.4.2 Experimental procedure

The processing of calcined (Sr, Pb)TiO₃ composition powders are described in Sect. 3.1 and an earlier paper [35]. The reactant powders were ball milled, magnesium oxide (99.998% purity MgO, Alfa Aesar) was added to the ball milled powders and then the powders were mixed. Pellets were formed from the mixed powders with uniaxial pressing and cold isostatic pressing (CIP) under a pressure of 3000 kg/cm². A low density plate sample was prepared without CIP. The formed samples were heated up to 300 °C to remove water which would be inside the samples. A typical heating cycle profile used for the water removal was as follows: heated to 110 °C at a rate of 0.1 °C per min; held at 110 °C for 12 h; heated to 300 °C at a rate of 0.1 °C per min; held at 300 °C for 6 h; cooled to room temperature at a rate of 2.5 °C per min. The samples were then sintered at 1350 °C for 3 h. Both heating and cooling rates were set as 5 °C per min and 2.5 °C/min, respectively. After surfaces of the samples were polished, these samples were annealed at 700 °C. In case electrodes were necessary for measurements, gold was evaporated or sputtered on the surfaces of the samples.

The densities of the samples were calculated based on their dimensions and weights.

Dielectric properties between 1 k and 1000 kHz were obtained as parallel components with an LCR meter (4284A, HP). The measurements were based on the null balanced circuit with the bridge [26] and the electrodes on the surfaces of the samples were required for these measurements. An alternating current (AC) field of 1 or 2 V/cm was applied, and the capacitances were obtained at an average of four values. Subsequently, relative permittivity, \( \varepsilon_r \), was calculated from the given equation

\[
\varepsilon_r = \frac{C_p}{C_o} = \frac{1}{\varepsilon_o} \frac{d}{A}
\]  

\[
C_o = \varepsilon_o \frac{A}{d}
\]  

where \( C_p \) is parallel capacitance, \( C_o \) is equivalent vacuum capacitance, \( \varepsilon_o \) is vacuum permittivity, \( d \) is the thickness of a sample parallel to a measurement direction, and \( A \) is the area of the sample [36-38]. The samples were measured with several different fixtures depending on the purpose of the measurements.

Dielectric properties between 5 M and 100 MHz were measured using an impedance analyzer (4291A, HP) as serial components based on the I-V (current-voltage) method [26] at 25 °C. The samples were coated with gold as electrodes. In order not to damage a probe, a spacer was used between a sample holder and the probe. The measurements were carried out at an AC
voltage of 125 mV, at an averaging number of 25 and at 25 °C. Relative permittivity, \( \varepsilon_r \), was calculated using the following equation

\[
\varepsilon_r = \frac{C_p}{C_o} = \frac{1}{1 + tan^2 \delta} \frac{C_S}{C_o} = \frac{1}{1 + tan^2 \delta} \frac{d}{\varepsilon_o A}
\]  

(4.2.4.3)

where \( C_S \) is serial capacitance [36]. Although the frequency range of the impedance analyzer (4291A, HP) is between 1 M and 1.8 GHz, a 3-pF standard capacitor showed lower capacitance values at ~1 MHz and an increase in capacitance above ~ 300 MHz after the calibration of the setup with a calibration kit (open, short, and load) at an averaging number of 8 for the only calibration. Additionally, the composite showed higher tangent \( \delta \) at ~1 MHz, and tangent \( \delta \) increased again above ~100 MHz even though the relative permittivity did not show a significant change. Thus values used were in the frequency range between 5 M and ~100 MHz.

In the frequency range between 60 M and ~ 3 GHz, dielectric properties were measured with a special holder using a network analyzer (8719 C, HP) at 27 °C based on the reflectometric method [27]. The procedure for the calculation of relative permittivity and tangent \( \delta \) are described in detail in the literature [27].

Dielectric properties at the microwave frequency range between 2.5 G and 4.5 GHz were calculated based on the Hakki-Coleman method or the parallel plate dielectric post resonator method [39-41] with the position of \( S_{21} \) peak of the TE\(_{011}\) mode or the resonant frequency, the width of the \( S_{21} \) peak (half power bandwidth) in the TE\(_{011}\) at –3 dB from the peak top (an insertion loss), the thickness and diameter of a sample, and the insertion loss. Because there were samples which showed asymmetric resonant peaks, the necessary widths for the tangent \( \delta \) calculation were calculated using twice the minimum values of a half width to achieve the reproducible results. The insertion loss was set to be around –30 dB. A network analyzer (8510C, HP) and an S-parameter detector (8515A, HP) were used to characterize the composites. Each datum point was an average of eight values and the results were an average of three consecutive measurements at 25 °C. Equations to calculate the dielectric constants and tangent \( \delta \) were described in the literature [42].

The split post dielectric resonator (resonant mode dielectric resonator: RMD-C with CAV-080 cavity, GDK) was also used to characterize the samples. Dielectric constants and tangent \( \delta \) were calculated from the position of the \( S_{21} \) peak (TE\(_{011}\)) and the width of the \( S_{21} \) peak at –3 dB using the network analyzer (8510C, HP) and the S-parameter detector (8515A, HP) with additional data such as the insertion loss and the thickness of a sample [43, 44]. The results
were acquired at an average of three runs. The results were obtained using one sample to thin and polish it.

The waveguide method was used to characterize the samples, and the system consisted of the network analyzer (8510 C, HP), the S-parameter detector (8515A, HP), and a rectangular wave guide (WR42TRL model K7007H14). Relative permittivity and tangent $\delta$ for the TE$_{10}$ mode were estimated using the program [42].

4.2.4.3 Results and discussion
4.2.4.3.1 Dielectric properties at low frequency

Table 4.2.4.2 lists the details of the samples used for the characterization of the dielectric properties at 10 kHz (low frequency). Fig. 4.2.4.1 shows dielectric properties at 10 kHz upon cooling using the samples which were uniaxially pressed under various pressures before cold isostatic pressing (CIP). The densities of the samples were 4.3 g/cm$^3$. Although the relative permittivities of the composites showed differences, the tangent $\delta$ values remained almost the same values. The samples pressed uniaxially under lower forming pressures than the CIP pressure showed higher dielectric constants. However, the samples did not show a significant difference of relative permittivity when the samples were pressed under a uniaxial pressure of more than 3000 kg/cm$^2$, which was the same as the cold isostatic pressure.

Fig. 4.2.4.2 shows the effect of measuring directions on dielectric properties using the same sample, S4-1~3. The sketches of the samples are shown in Fig. 4.2.4.3 (a)-(c). The sample was cut from the disk (S4: 18 mm in diameter; 6.5 mm in thickness, see Table 4.2.4.3) (Fig. 4.2.4.3 (d)). Because each sample was polished before each measurement to remove electrodes and to make the surfaces mutually parallel, each sample was not strictly the same. The S4-1 and S4-2 showed similar dielectric properties. Although the S4-3 showed lower dielectric constant values than S4-1 and S4-2, all three samples showed similar tangent $\delta$ behaviors. Fig. 4.2.4.1 showed the effect of the uniaxial forming pressure before CIP on dielectric constants, and the samples that were formed under lower pressures than the CIP pressure showed higher relative permittivity. The reason for the difference between S4-1 or S4-2 and S4-3 was similar to the reason for the difference of a uniaxial forming pressure, namely, the distribution of compression in the samples. The measurement directions of S4-1 and S4-2 were normal to the uniaxial pressing direction, while the measurement direction of S4-3 was parallel to the uniaxial pressing direction. Therefore, the S4-1 and S4-2 samples which could be pressed under lower uniaxial pressures than S4-3 sample showed higher relative permittivity. The direction dependence of the
Table 4.2.4.2 Description of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.2)-MgO (50:50 by weight) composites

<table>
<thead>
<tr>
<th>Description</th>
<th>Uniaxial pressure ($10^3$ kg/cm$^2$)</th>
<th>CIP</th>
<th>Note</th>
<th>Density (g/cm$^3$)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.32</td>
<td>Done</td>
<td>-----</td>
<td>4.3</td>
<td>2.2</td>
</tr>
<tr>
<td>B</td>
<td>1.27</td>
<td>Done</td>
<td>-----</td>
<td>4.3</td>
<td>2.1</td>
</tr>
<tr>
<td>C</td>
<td>3.19</td>
<td>Done</td>
<td>-----</td>
<td>4.3</td>
<td>2.1</td>
</tr>
<tr>
<td>D</td>
<td>6.37</td>
<td>Done</td>
<td>-----</td>
<td>4.3</td>
<td>2.0</td>
</tr>
<tr>
<td>BI</td>
<td>1.27</td>
<td>Done</td>
<td>Cut B</td>
<td>----</td>
<td>0.45</td>
</tr>
<tr>
<td>BII</td>
<td>1.27</td>
<td>Done</td>
<td>Thinned BI</td>
<td>----</td>
<td>0.23</td>
</tr>
<tr>
<td>EA</td>
<td>0.09</td>
<td>None</td>
<td>Cut</td>
<td>3.8</td>
<td>1.2</td>
</tr>
<tr>
<td>EB</td>
<td>0.09</td>
<td>None</td>
<td>Cut &amp; thinned</td>
<td>----</td>
<td>0.32</td>
</tr>
<tr>
<td>F1</td>
<td>1.27</td>
<td>Done</td>
<td>F1 &amp; F2 were</td>
<td>4.3</td>
<td>2.1</td>
</tr>
<tr>
<td>F2</td>
<td>1.27</td>
<td>Done</td>
<td>prepared at same time</td>
<td>4.3</td>
<td>2.1</td>
</tr>
<tr>
<td>G1</td>
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<td>Done</td>
<td>G1, G2, G3, &amp; G4</td>
<td>4.3</td>
<td>2.0</td>
</tr>
<tr>
<td>G2</td>
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<td>Done</td>
<td>were prepared</td>
<td>4.3</td>
<td>2.0</td>
</tr>
<tr>
<td>G3</td>
<td>1.27</td>
<td>Done</td>
<td>at the same time.</td>
<td>4.3</td>
<td>2.0</td>
</tr>
<tr>
<td>G4</td>
<td>1.27</td>
<td>Done</td>
<td></td>
<td>4.2</td>
<td>2.0</td>
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</table>

EA and EB were cut from a plate (37.5 × 37.5 × 1.2 mm).
CIP: cold isostatic pressing.
Figure 4.2.4.1 10 kHz dielectric properties of (Sr_{0.8}Pb_{0.2})TiO_3-MgO (50:50 by weight) composites as functions of temperature and uniaxial forming pressure before cold isostatic pressing.
Cold isostatic pressing pressure: 3000 kg/cm^2.
Uniaxial forming pressure; A: 300; B: 1300; C: 3200; D: 6400 kg/cm^2.
Figure 4.2.4.2 Dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites as a function of temperature at 10 kHz. Samples are described in Fig. 4.2.4.3.

S4-1: 6.45 mm(length), 4.32 mm(width), 3.89 mm(thickness).
S4-2: 6.34 mm(length), 3.78 mm(width), 4.29 mm(thickness).
S4-3: 4.27 mm(length), 3.74 mm(width), 6.30 mm(thickness).

Figure 4.2.4.3 (a), (b), and (c) the sketches of S4-1, S4-2, and S4-3 of which the results are shown in Fig. 4.2.4.2 and (d) and (e) the sketches of the samples in a disk.

S4-1, S4-2 and S4-3 were cut from the disk.
microstructure in the sample after CIP and sintering is not clear, but the microstructure could influence the magnitude of relative permittivity of the composites.

Fig. 4.2.4.4 shows the dielectric properties of the disk (B) and plate shaped samples (BI and BII) cut from disk B. Sample B, of which the thickness was 2.1 mm, was a disk prepared under the uniaxial pressure, 1300 kg/cm². Plate sample BI was cut from the middle part of disk B (thickness, 0.45 mm), and the measurement direction of BI was normal to the measurement direction of the disk B. Sample BII was further polished to thin BI, and the thickness of BII was 0.23 mm. Sample BI and BII showed higher relative permittivity than sample B, but the tangent δ of all three samples was in a similar range over the wide temperature range from 150 to −150 °C. The difference of relative permittivity between B and BI or BII could be due to the distribution of compactness in the samples, chemistry distribution, and/or structural difference. The tangent δ of sample BII were not stable under the measurement conditions in fluid in a cup fixture shown in Fig. 4.2.4.5 (a), and noisy spikes in tangent δ were observed. These spikes disappeared when a different measurement fixture was used (Fig. 4.2.4.5 (b)). The thin sample, of which the thickness was ~ 0.2 mm, did not avoid the spikes because of the interaction of AC fields with the sample in the setup.

Fig. 4.2.4.6 showed the reproducibility of dielectric properties of the SPT (x = 0.20)-MgO composites as a function of temperature at 10 kHz based on three different kinds of samples. These samples were prepared using the same mixture of calcined SPT and MgO powders but were pressed and sintered on different days (i) B, (ii) F1 and F2, and (iii) G1, G2, G3, and G4). Though small fluctuations in the relative permittivity were observed, tangent δ showed similar values.

Fig. 4.2.4.7 showed the effect of composite densities on the dielectric properties of the composites at 10 kHz upon cooling. The higher density sample (BI) cut from the disk (B) (density 4.3 g/cm³) was prepared with CIP (transition temperature, T_m, −63 °C). The lower density sample (EA) (density 3.8 g/cm³; T_m −56 °C) was prepared without the use of CIP. It is interesting to note that the lower density sample showed the ferroelectric transition (T_m ~ −56 °C), which was higher than the transition temperatures of the higher density samples (T_m ~ −63 °C). This suggests that the higher T_m observed in the lower density sample was not caused by the loss of lead oxide (PbO) during heating because the lead loss would decrease the T_m to lower lead titanate (PbTiO₃) content. It is suspected that the increase in transition temperature is
Figure 4.2.4.4 Dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites as a function of temperature at 10 kHz.
B: Disk (thickness: 2.14 mm, area: 44 mm$^2$).
BI: Plate prepared by cutting B (thickness: 0.45 mm, area: 6 mm$^2$).
BII: BI Polished (thickness: 0.23 mm, area: 6 mm$^2$).

Figure 4.2.4.5 Fixtures used for dielectric property measurements.
(a) Current measurement setup. The sample was placed in silicon (Si) oil. Noisy spikes were observed.
(b) New measurement setup. The sample was covered with Si rubber and copper (Cu) tape. The setup permitted stable and low fluctuation noise measurements.
Figure 4.2.4.6 Reproducibility of dielectric responses of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites as a function of temperature at 10 kHz. B, F1-2, and G1-4 were prepared on different days.

Figure 4.2.4.7 Effect of density on dielectric responses of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (50:50 by weight) composites as a function of temperature at 10 kHz. The densities of B and EA were 4.3 and 3.8 g/cm$^3$, respectively.
possibly due to the poor connectivity between the phases, namely, the changes in the microstructure.

The lower density sample (EA) showed lower relative permittivity and higher tangent \( \delta \). However, both the samples showed similar tangent \( \delta \) in the temperature range far from the transition temperatures, 100 ~ 20 °C \((T_{m} + 150 ~ 70 °C)\). The lower relative permittivity of the lower density samples could be due to the poor connectivity among grains. The tangent \( \delta \) of the low density sample increased at a temperature range above ~100 °C because of the conductivity rise due to the space charges in that range. The tangent \( \delta \) of the lower density sample showed higher values around the transition temperature than those of the higher density samples. There are various sources which contribute to tangent \( \delta \) in ferroelectric regions and close to phase transition temperatures. One source is domain wall motion. The domain walls in the lower density sample could move more easily and hence they might contribute more to tangent \( \delta \) in the lower density samples.

The effect of the uniaxial pressing before the cold isostatic pressing on the magnitude of relative permittivity could be explained by the microstructure in a way similar to that based on the effect of densities on the relative permittivity. The samples pressed under a lower uniaxial pressure than a cold isostatic pressure could have the structure in which grains (or powders) were more compressive after sintering (or CIP) and thus show higher relative permittivity. On the contrary, the samples pressed under higher uniaxial pressures before cold isostatic pressing might have relatively loose grains and thus show lower relative permittivity. In other words, samples pressed under lower uniaxial pressure could have more compressive structure after the CIP or sintering.

### 4.2.4.3.2 High frequency dielectric properties and issues on high frequency measurements

Table 4.2.4.3 lists the results of dielectric properties of the composites measured over a wide frequency range. Fig. 4.2.4.8 (a), (b), (c), and (d) show relative permittivity, tangent \( \delta \) (on a log-scale and a linear-scale), and Q (= 1/tangent \( \delta \) × frequency) on the samples as a function of frequency.

Though the difference in relative permittivities measured using the various instruments was apparent, relative permittivity did not show an obvious frequency dependence. Large disk samples (S5: 30.2 mm in diameter \((D_i)\), 6 mm in thickness \((T)\), \(D_i/T = 5.0\); S9: 18.2 mm in diameter, 3.7 mm in thickness, \(D_i/T = 4.9\)) showed lower relative permittivity ~ 100 using the
Table 4.2.4.3 (a) $\varepsilon_r$ and tangent $\delta$ of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) ($x = 0.2$)-MgO (50:50) composites at room temperature (cylinder samples after annealing)

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<th>Thickness (mm)</th>
<th>Di/T</th>
<th>Freq (Hz)</th>
<th>$\varepsilon_r$</th>
<th>tan $\delta$</th>
<th>Q</th>
<th>Q x F</th>
</tr>
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<td>10k</td>
<td>121</td>
<td>0.0005</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100k</td>
<td>121</td>
<td>0.0005</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 M</td>
<td>121</td>
<td>0.0006</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.498 M</td>
<td>112</td>
<td>0.0002</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>113</td>
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<td>-----</td>
<td>-----</td>
</tr>
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<td></td>
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<td></td>
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Samples with no marks and *** were measured at 25 °C. Samples with * and ** were measured at 27 °C and 23 °C, respectively. *** Non-annealed, but polished only. RT, room temperature.

1k-100k Hz: Null-balance circuit (HP 4284A LCR meter).
5M-100MHz: I-V method (HP 4291A impedance analyzer).
50M-2.9 GHz: Reflectometric method (HP 8719C network analyzer).
2.6G-4.5GHz: Post resonant method (HP 8510 C network analyzer and HP 8515A S-parameter detector).
5.5G-6.6GHz: Split cavity resonator (GDK (RMD-C, CAV-080), HP 8510 C network analyzer and HP 8515A S-parameter detector).
Table 4.2.4.3 (b) $\varepsilon_r$ and tangent $\delta$ of ($\text{Sr}_{1-x}\text{Pb}_x\text{TiO}_3$ (SPT) ($x = 0.2$)-MgO composites at room temperature (rectangular plate samples after annealing)

<table>
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<th>Description</th>
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<th>width (mm)</th>
<th>thickness (mm)</th>
<th>freq (Hz)</th>
<th>$\varepsilon_r$</th>
<th>$\tan \delta$</th>
<th>Q</th>
<th>$Q x f$</th>
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<td>25</td>
<td>640</td>
</tr>
</tbody>
</table>

Samples except those with ** were measured at 25 °C; samples with ** were measured at 23 °C.

RT, room temperature; Q, the reciprocal of tangent $\delta$; f or freq, frequency.

1k-100k Hz: Null-balance circuit (HP 4284A LCR meter).
5M-100MHz: I-V method (HP 4291A impedance analyzer).
50M-2.9 GHz: Reflectometric method (HP 8719C network analyzer).
2.6G-4.5GHz: Post resonant method (HP 8510 C network analyzer and HP 8515A S-parameter detector).
5.5G-6.6GHz: Split cavity resonator (GDK (RMD-C, CAV-080), HP 8510 C network analyzer, and HP 8515A S-parameter detector.
18-26.5GHz: Wave guide method(WR42TRL model K7007H14, HP 8510 C network analyzer, and HP8515A S-parameter detector.)
Figure 4.2.4.8 (a) Relative permittivity of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) ($x = 0.20$)-MgO (50:50 by weight) composites at room temperature as a function of frequency.

Sample: S1 through S13.

LCR: Measured using an LCR meter; Impedance: Measured using an impedance analyzer; Post R: Measured by the parallel plate dielectric post resonator method; GDK: Measured by the split post dielectric resonator method; WG: Measured by the waveguide method (transmission); Ref: Measured by the reflectometric method.

Di and T, diameter and thickness of a disk sample, respectively; W, D, and T, width, distance, and thickness of a rectangular sample, respectively.
Figure 4.2.4.8 (b) Tangent $\delta$ of $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ (SPT) ($x = 0.20$)-MgO (50:50 by weight) composites at room temperature as a function of frequency. X-axis scale: Logarithmic. Sample: S1 through S13.

LCR: Measured using an LCR meter; Impedance: Measured using an impedance analyzer; Post R: Measured by the parallel plate dielectric post resonator method; GDK: Measured by the split post dielectric resonator method; WG: Measured by the waveguide method (transmission); Ref: Measured by the reflectometric method; Di and T, diameter and thickness of a disk sample, respectively; W, D, and T, width, distance, and thickness of a rectangular sample, respectively.
Figure 4.2.4.8 (c) Tangent $\delta$ of $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ (SPT) ($x = 0.20$)-MgO (50:50 by weight) composites at room temperature as a function of frequency. X-axis scale: Linear. Sample: S1 through S13.

- **LCR**: Measured using an LCR meter
- **Impedence**: Measured using an impedance analyzer
- **Post R**: Measured by the parallel plate dielectric post resonator method
- **GDK**: Measured by the split post dielectric resonator method
- **WG**: Measured by the waveguide method (transmission)
- **Ref**: Measured by the reflectometric method

Di and T, diameter and thickness of a disk sample, respectively; W, D, and T, width, distance, and thickness of a rectangular sample, respectively.
Figure 4.2.4.8 (d) $Q (= 1/\text{tangent } \delta) \times \text{frequency of } (\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3 \text{ (SPT) } (x = 0.20)-\text{MgO (50:50 by weight)} \text{ composites at room temperature as a function of frequency.}$

Sample: S1 through S13.

LCR: Measured using an LCR meter; Impedence: Measured using an impedance analyzer; Post R: Measured by the parallel plate dielectric post resonator method; GDK: Measured by the split post dielectric resonator method; WG: Measured by the waveguide method (transmission); Ref: Measured by the reflectometric method.

Di and T, diameter and thickness of a disk sample, respectively; W, D, and T, width, distance, and thickness of a rectangular sample, respectively.
parallel plate dielectric post resonator method than ~120 of the other disk samples. S4 (18.1 mm in diameter, 6.5 mm in thickness, $Di/T = 2.8$) showed ~120 as relative permittivity. This resonant method would be suitable for the characterization of rods of which $Di/T$ is three or less than three [45]. In addition, $Di/T$ should be in a specific range to achieve a good separation of the TE$_{0ml}$ mode from adjacent high tangent $\delta$ leaky state modes even though $Di/T$ satisfies a value of three and less than three [41]. Furthermore, $Di/T$ would be preferable to be around two in order to characterize the TE$_{0ml}$ mode which is not disturbed by the adjacent modes [46]. Moreover, there is experimentally suitable range of a diameter for the characterization using this resonant method between 0.7 cm and 2.5 cm [47]. Therefore, lower relative permittivity observed using the resonant method could be explained by the effect of the huge ratio of $Di/T$, 5, which low relative permittivity samples possessed.

S13-1, measured by the reflectometric method, showed the tendency to decrease dielectric constant between ~50 M and 3 GHz. There are ways to assume uniform AC fields over the measurements (Table 4.2.4.4). The longest length of the sample for the reflectometric method was 2 mm as a diameter. If the square root of a wavelength in the sample at 3 GHz (3.2 mm) is assumed to be a short enough length to achieve the uniform field, then the dimensions of the sample would be valid. However, if a tenth of the wavelength in the sample at 3 GHz (1 mm) is necessary for the assumption of the uniform AC fields, then the sample could be too large. Consequently, observed reflection coefficients could be different from the reflection coefficients of the sample. Subsequently, the correction of the dielectric properties [e.g., 48] might be necessary to obtain values with lower errors. Besides the importance of AC fields, the impedance of a sample must be in the range in which the instrument is able to characterize the sample.

There are other possibilities to add errors to the dielectric properties measured using the reflectometric method: i) calibration errors of the setup, for example, the mismatch of a load impedance to the characteristic impedance [42], ii) measurement errors, for example, reflection coefficients with errors, iii) the effect of self inductance [49, 42], iv) the effect of fringing field [42], and v) the effect of higher order propagating modes [42].

Fig. 4.2.4.8 (b) shows the tangent $\delta$ of the composites as a function of frequency on the log-scale. Below 100 MHz, tangent $\delta$ showed close to or less than 0.001. Tangent $\delta$ measured using the impedance analyzer was not stable. Santos et al. demonstrated that the special fixture was necessary to avoid fluctuations because of the setup for the reflectometric measurements [27]. Similar consideration for the fixture and/or a further increase in the number of collected data to reduce the fluctuations is required to prevent the fluctuation of tangent $\delta$. The
Table 4.2.4.4 Maximum dimensions (1 and 2) of a sample ($\varepsilon_r = 100$) in which uniform AC fields are supposed to be applied

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Wavelength in a dielectric, $\varepsilon_r = 100$</th>
<th>Dimension 1 (Maximum)</th>
<th>Dimension 2 (Maximum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 GHz</td>
<td>$\lambda = 10$ cm</td>
<td>$\lambda_{\lambda} = 1$ cm</td>
<td>3.16 mm</td>
</tr>
<tr>
<td>300 MHz</td>
<td>$\lambda = 100$ cm</td>
<td>$\lambda_{\lambda} = 10$ cm</td>
<td>3.16 cm</td>
</tr>
</tbody>
</table>
reflectometric method showed consistency with the tangent $\delta$ values measured at low frequencies using the LCR meter and impedance analyzer. However, the parallel plate dielectric post resonator method, the split post dielectric resonator method, and the transmission waveguide method showed higher tangent $\delta$ compared with the lower frequency tangent $\delta$ values and the values obtained using the reflectometric method.

Resonators with cracks tend to show higher tangent $\delta$ measured using resonant modes than resonators without cracks. A main source of this discrepancy could be impurities in cracks, for example, water. In addition, the discontinuity of the signal propagation at the cracks could be a source. Although the cracks could be smaller compared with wavelengths in the dielectric resonators, changes in the electromagnetic field distribution at the cracks could have a possibility of the sources [50]. A pore (an example of a free surface) is also noted with the source of the relaxation [51 and reference in it]. The interaction of AC fields with the samples could be important. Additionally, the asymmetrical peaks of the TE$_{011}$ mode were observed when the samples were measured using the parallel plate dielectric post resonator method. This observation could be explained by a low background lever or low insertion level and/or the coupling of other modes to the TE$_{011}$ mode. In addition to these possibilities, there are factors related to setup conditions: i) the surface resistance of the conducting plates of the setup, ii) environments around the setup such as humidity, and iii) radiation losses [52, 42]. It is generally recognized that the parallel plate dielectric post resonator method gives reliable values for relative permittivity but often has more difficulty with tangent $\delta$ particularly for low loss tangent high dielectric permittivity samples.

The results of relative permittivity show consistency over the wide frequency range. However, the results of tangent $\delta$ show discrepancies. The discrepancy between the GHz frequency range and lower frequency tangent $\delta$ could be the differences of measurement principles and assumptions. There are differences among various measurement methods such as the assumption of the AC field distribution: i) low frequency and reflectometric methods assume that AC fields are applied to samples uniformly, but ii) AC fields are assumed to be distributed through samples over the higher frequency measurements. These kinds of differences could give different tangent $\delta$ values. Each technique has advantages and disadvantages, and actual values could be lower or higher than the measured values because the techniques add positive or negative errors to the real values.
4.2.4.3.3 Issues on tangent $\delta$

There are two contributions to tangent $\delta$ [53 and references in it]: i) intrinsic and ii) extrinsic. Both mechanisms contribute comparably to tunable ferroelectrics at microwave frequencies depending on the quality of the materials.

According to the phonon transport theory [53], fundamental losses occur due to the interaction of an AC field with the phonons of a crystal. There are three intrinsic loss mechanisms to compensate for the difference of energies after the interaction: i) three quantum, ii) four quantum, and iii) quasi-Debye mechanisms. The three quantum process includes an energy quantum and two phonons, and this process is sensitive to the symmetry of a material. The four quantum mechanism occurs by the quantum and three phonons. The quasi-Debye process is due to the relaxation of a phonon distribution function of a crystal. The crystal system of (Sr$_{1-x}$Pb$_x$)TiO$_3$ ($x = 0.2$) at room temperature is cubic [35] and centrosymmetric. The composites, (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO are also expected to be centrosymmetric because the samples should be in a paraelectric state at room temperature which is far above (more than 80 °C above) the transition temperatures. In the centrosymmetric materials, the three quantum and four quantum mechanisms contribute to the losses, but the three quantum process has the major contribution between the two mechanisms. Under DC bias fields, the quasi-Debye process is activated [53].

Regarding extrinsic losses [53], three extrinsic losses for the tunable ferroelectrics are as follows: i) charged defects, ii) universal relaxation law, and iii) quasi-Debye contribution induced by defects. The motion of the charged defects by the AC field generates acoustic waves at the AC field frequency. At lower than the microwave frequency, the weak frequency dependence of tangent $\delta$ is observed and is called the universal relaxation law. This is explained due to the variation in charge transport barriers, for example, at the grain boundaries or creep of the boundary of the depletion layer near the electrode. The quasi-Debye mechanism is activated in local polar-regions by various defects and structural imperfections such as grain boundaries and random field defects [53].

There are a number of reports on the improvement of tangent $\delta$ (i.e., $Q = 1/\tan \delta$) values and/or the investigation of factors which influence the tangent $\delta$ values. One of the reviews described the microwave properties of various materials such as Al$_2$O$_3$, TiO$_2$, BaTiO$_3$ and its derivatives, (Zr, Sn, Ti)O$_4$ ($Zr + Sn + Ti = 2$), Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$, and Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$. In addition, the review described different factors which would influence tangent $\delta$, for example,
purity, porosity, grain size, grain boundary, defects, dopants, composition, and ordering of specific ions [51]. Besides these parameters, the importance of the crystal symmetry [54, 53, 55] has also been pointed out [54]. In the Ba(Zn\textsubscript{1/3}Ta\textsubscript{2/3})O\textsubscript{3} system, Kawashima et al. showed processing conditions, for example, sintering for a longer time, improved Q values due to the change in superlattice ordering instead of the effects of pores and grain boundaries [56]. Additionally, Koga and Moriwake showed that liner relationships between Q values and both grain size and density rather than the ordering effect [50]. Wakino and Tamura demonstrated that (Zr, Sn)TiO\textsubscript{4} systems prepared from high purity raw chemicals showed high Q values [57]. Templeton et al. showed that specific dopants such as Al\textsubscript{2}O\textsubscript{3} and MgO improved the Q values of TiO\textsubscript{2} due to the prevention of Ti\textsuperscript{4+} reduction to Ti\textsuperscript{3+} [58].

In addition to the description of the intrinsic losses based on the phonon transport theory, there are two models which are often used and which are different from the model based on the phonon transport theory: The Vendik model originated from the four quantum mechanism and the damped oscillator model [59, 60] based on the classical dispersion theory [53]. Table 4.2.4.5 lists equations for intrinsic losses of cubic incipient ferroelectrics. All three models predict that tangent $\delta$ is linearly proportional with frequencies at a fixed temperature. In other words, $Q \times \text{frequency}$ values show a constant at a certain temperature. Because the damped oscillation model has restrictions in use, loss tangents based on the phonon transport theory covers a wider range of temperatures as a function of frequency, temperature, and relative permittivity than those based on the damped oscillation model [53]. Meanwhile, the Vendik model predicts the temperature, frequency, and relative permittivity dependence of loss tangents more correct than the damped oscillator model because the Vendik model is based on the four quantum mechanism [53].

Fig. 4.2.4.8 (c) shows the tangent $\delta$ of the SPT ($x = 0.20$)-MgO composites as a function of frequency on the linear-scale. The results obtained using the waveguide technique and reflectometric method showed relatively constant tangent $\delta$ as a function of frequency. At this moment, the effect of the setups and materials on the contributions to the tangent $\delta$ are not clearly separated. Fig. 4.2.4.8 (d) shows $Q \times \text{frequency}$ as a function of frequency. The results of tangent $\delta$ values also reflected $Q \times \text{frequency}$. The reflectometric method and waveguide method showed the increase in $Q \times \text{frequency}$, but the other resonant methods showed constant values, $\sim 700$ GHz. Further investigation is necessary to understand the behavior of tangent $\delta$. 282
Table 4.2.4.5 Tangent δ or intrinsic losses in cubic incipient ferroelectrics

<table>
<thead>
<tr>
<th>Frequency range</th>
<th>Phonon transport theory</th>
<th>Vendik model</th>
<th>Damped oscillator</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega \leq \Gamma )</td>
<td>[ \tan \delta \propto \omega T^2 \varepsilon^2 \left[ 1 + b \ln \left( \frac{\omega_{T}}{\Gamma} \right) \right] ]</td>
<td>[ \tan \delta \propto \omega T^2 \varepsilon^2 ]</td>
<td>[ \tan \delta \propto \omega T \varepsilon ]</td>
</tr>
</tbody>
</table>

\( \omega \) = Frequency; \( \Gamma \) = Damping phonon frequency (average frequency of the inter-phonon collisions); \( T \) = temperature; \( \varepsilon \) = relative permittivity.

Taken from Tagantsev et al. [53].
4.2.4.4 Summary

(Sr$_{1-x}$Pb$_x$)$_2$TiO$_3$ (x = 0.2)-MgO composites were prepared, and their dielectric properties were investigated. A uniaxial pressing pressure to a sample before a cold isostatic pressing might influence the relative permittivity of the sample. The samples pressed under a lower uniaxial pressure than a cold isostatic pressure showed higher relative permittivity. Lower density composites showed lower relative permittivity over a wide temperature range and higher tangent $\delta$ near the phase transition.

Well prepared samples showed that the transition temperatures were $\sim -60 \, ^\circ$C and relative permittivity was more than $\sim 100$. Additionally, these composites showed that tangent $\delta$ at room temperature was $\sim 0.0005$ between 10 k and 1 MHz, close to or less than 0.001 between 5 M and 100 MHz, and $\sim 0.005$ by the parallel plate dielectric post resonator measurement technique at $\sim 4$ GHz. The differences in tangent $\delta$ measured using the various techniques were noted. $Q \times f$ ($Q$: 1/ tangent $\delta$, f: Frequency) was $\sim 700$ GHz measured by the resonant methods, but the different $Q \times f$ values were obtained using the reflectrometric method and waveguide techniques.
4.2.5 Validity of mixing ratio in the (Sr<sub>1-x</sub>Pb<sub>x</sub>)TiO<sub>3</sub> (SPT) (x = 0.2)-magnesium oxide (MgO) composites

4.2.5.1 Introduction

Sect. 4.2.3 and Sect. 4.2.4 discuss the direct current (DC) dependence of relative permittivity and microwave dielectric properties of (Sr<sub>1-x</sub>Pb<sub>x</sub>)TiO<sub>3</sub> (SPT) (x = 0.2)-magnesium oxide (MgO) composites (SPT-MgO (50:50 by weight)). In order to seek the best composition of composites prepared from SPT and MgO, composites with various ratios between SPT and MgO are prepared. Consequently, dielectric properties are measured and analyzed. The application of the mixing rules is useful to analyze the relative permittivity of composites. Therefore, this section will review some of the mixing rules. After the review, the following sections will discuss how to estimate the volume fraction of a component in the composites, experimental results, and the application of the mixing rules to the room temperature relative permittivity of the composites at 10 kHz.

4.2.5.1.1 Background of mixing rules

Single phase ceramics are often unintentional composites incorporating pores as a second phase. The composites are more deliberate two or more phase systems in which again the individual phases may have very different properties. It is thus natural that many studies have been focused upon trying to develop the theoretical understanding of the behaviors and trying to predict the properties of the composites from those of the individual components in the composites [61-77].

Even for the weak-field linear dielectric properties, this task is not simple because single-phase relative permittivity values, $\varepsilon_r$, can cover a very wide range from $\varepsilon_r \sim 1$ to $\varepsilon_r > 100,000$. The electric field distribution in a dielectric composite depends markedly upon the shape and the random or regular distribution of the individual components and especially upon the manner in which the individual phases are self inter-connected (connectivity).

An objective of this section is to introduce several mixing rules for the estimation of the dielectric constant of two-component mixtures. The properties of the mixed components are dependent on their shapes, distribution, and connectivity (self and external), assuming that no reactions occur while mixing the components. Among various factors that affect the properties, the self connectivity of each component in three-dimensions is an important factor. Firstly, the classification of connectivity and its concept [78] will be described before introducing the
mixing rules. Secondly, the more widely known mixing rules will be described: i) the parallel mixing model, ii) the serial mixing model, and iii) the logarithmic mixing rule. Some other formulas derived theoretically and based on numerical methods will be also described. Finally, approaches which are useful to estimate the shape of a phase in the composites will be introduced in the introduction section.

4.2.5.1.2 Classification of composites with respect to their connectivity

Newnham et al. [78] introduced the concept of self internal connectivity to classify two-component mixtures and showed ten possible connectivity patterns using a cube as a building unit. When the components are not self interconnected in any of three dimensions, their states are called 0. In addition, when the components are self connected in n-dimensions (n = 1, 2, or 3), their connectivity becomes n. Thus the combinations of the two components resulted in ten possible patterns. Fig. 4.2.5.1 shows the models proposed by Newnham et al. The second digit is the connectivity of the host or matrix component, and the first number is the connectivity of the guest or active component. There are other representative models proposed later based on this classification [79, 80]. The Newnham model is based on only a very simple conceptual idea for classifying connectivity in two-phase composites.

4.2.5.1.3 Mixing rules

Mixing rules are used to estimate the properties of mixtures, composites, or materials which have at least two components, from the properties of each component in the mixtures. Various formulas have been proposed, and several relations are widely known among them for the determination or boundary of the dielectric constant of the mixture. The following sections will discuss these known and useful models and then some other formulas.

4.2.5.1.3.1 Widely known and useful equations [61]

This section will discuss three equations in detail: i) parallel model, ii) serial model, and iii) logarithmic mixing rule (Lichtenecker’s equation). In addition, this section will describe some other equations briefly. The equations based on the parallel and serial connected models determine the upper and lower limits of the relative permittivity of the mixture, respectively. The logarithmic mixing rule is not based on a theory with a sufficient background, but it would be sometimes practical.
Figure 4.2.5.1 Ten self-internal connectivity patterns for a diphasic solid. Each phase has zero-, one-, two-, or three-dimensional self-internal connectivity to itself. Arrows are used to indicate the connected directions. Two views of the 3-3 and 3-2 patterns are related by 90° counterclockwise rotation on Z-axis. Ref.: Newnham et al. [78].
Wiener [81] considered two-layer composites as shown in Fig. 4.2.5.2. $\varepsilon_\perp$ is dielectric permittivity, which is measured at an applied field perpendicular to the layers, and $\varepsilon_\parallel$ is dielectric permittivity, measured at an electric field applied parallel to the layers.

The dielectric constant of composites which are described as parallelly connected model (Fig. 4.2.5.2 (a)) is given by

$$\varepsilon_i = \delta_i \varepsilon_1 + \delta_2 \varepsilon_2 \quad (4.2.5.1)$$

where $\delta_i$ is the volume fraction of the $i$th component, $\varepsilon_i$ is the dielectric permittivity of the $i$th component, $i$ is 1 or 2 and $\delta_1 + \delta_2 = 1$.

In the case of the serially connected model shown in Fig.4.2.5.2 (b), the dielectric constant is given by

$$\frac{1}{\varepsilon_\perp} = \delta_i \frac{1}{\varepsilon_1} + \delta_2 \frac{1}{\varepsilon_2} \quad (4.2.5.2)$$

Furthermore, Wiener [82] demonstrated that Eqs. (4.2.5.1 and 4.2.5.2) show the upper and lower limits of dielectric permittivities of the mixtures, respectively, using Eqs. (4.2.5.3 and 4.2.5.4)

$$\frac{1}{\varepsilon_m + u} = \frac{\delta_i}{\varepsilon_1 + u} + \frac{\delta_2}{\varepsilon_2 + u} \quad (4.2.5.3)$$

$$\frac{\varepsilon_m + u}{\varepsilon_m} = \frac{\delta_i \varepsilon_1}{\varepsilon_1 + u} + \frac{\delta_2 \varepsilon_2}{\varepsilon_2 + u} \quad (4.2.5.4)$$

where $\varepsilon_m$ is the relative permittivity of the mixture, and $u$ is a variable number related to the shape, the volume fraction, and the distribution of the components. Eq. (4.2.5.4) is modified to multiply $u$ to both sides.

$$\frac{\varepsilon_m}{u} = \frac{\delta_i \varepsilon_1}{u} + \frac{\delta_2 \varepsilon_2}{u} \quad (4.2.5.5)$$

If $u$ is infinity, then Eq. (4.2.5.5 (or 4.2.5.4)) reduces to Eq. (4.2.5.1) for the parallel connectivity model. Meanwhile, if $u$ is zero, then Eq. (4.2.5.3) reduces to Eq. (4.2.5.2) for the serial connectivity model.

Lichtenecker [83] obtained Eqs. (4.2.5.6 and 4.2.5.7) for particles dispersed in a matrix in two-dimensions

$$\varepsilon_m = \varepsilon_1^{\delta_1} \varepsilon_2^{\delta_2} \quad (4.2.5.6)$$

$$\log \varepsilon_m = \delta_1 \log \varepsilon_1 + \delta_2 \log \varepsilon_2 \quad (4.2.5.7)$$
Figure 4.2.5.2 (a) Parallel and (b) serial mixing models.

1 and 2 are phase 1 and 2, respectively.

$\varepsilon$, dielectric permittivity. $\parallel$ or $\perp$, measurement direction with respect to the field.
where $\varepsilon_m$ and $\varepsilon_i$ are the dielectric constants of the mixture, and the $i$th component, respectively, and $\delta_i$ is the volume fraction of the $i$th component. Eq. (4.2.5.7) is called the logarithmic mixing rule. Lichtenecker and Rother [84] proposed the following equation for the mixture of two kinds of particles.

$$\varepsilon^k = \delta_1 \varepsilon_1^k + \delta_2 \varepsilon_2^k \quad (\delta_1 + \delta_2 = 1) \quad 1 \geq k \geq -1$$

(4.2.5.8)

If $k$ is 1, then Eq. (4.2.5.8) is the same as Eq. (4.2.5.1) for the parallel connectivity. When $k$ is –1, Eq. (4.2.5.8) becomes Eq. (4.2.5.2) for the serial connectivity. Eq. (4.2.5.8) is the same as Eq. (4.2.5.7) when $k$ is approaching 0 because $\varepsilon^k$ approximates $1 + k \log \varepsilon$.

Because Lichtenecker and Rother assumed that the final relative permittivity of the mixture was not influenced by the condition of the individual components in the mixture, the background of their theory was not sufficient [85]. However, this logarithmic mixing rule could be useful to predict the dielectric constant of the mixture when each component in the composites stayed in the same condition of the component before forming the mixture; that is, the interactions among these components were negligible.

Eq. (4.2.5.8) is generalized for the multi-components [63]

$$\varepsilon_m^n = \sum_{i} \delta_i \varepsilon_i^n \quad -1 \leq n \leq 1$$

(4.2.5.9)

where $\varepsilon_m$ and $\varepsilon_i$ are the dielectric constant of the mixture and the $i$th component of the mixture, respectively, $\delta_i$ is the volume fraction of the $i$th component, and $n$ is a constant which lies from –1 to 1. $n$ would mean connectivity among the components. When $n$ is –1, Eq. (4.2.5.9) reduces to the serial connectivity model (Eq. (4.2.5.2)). When $n$ is 1, Eq. (4.2.5.9) reduces to the parallel connectivity model (Eq. (4.2.5.1)). When $n$ approaches 0, Eq. (4.2.5.9) reduces to the logarithmic mixing rule shown in Eq. (4.2.5.7).

Besides the three formulas, there are mixing models such as the Maxwell formula [63], the Maxwell-Wagner formula [86, 66, 87, 88], the Maxwell-Garnett formula [74, 89, 90], the Bruggeman formula (the symmetric Bruggeman formula and the non-symmetric formula) [76, 91, 66, 92], and the modified general effective media equation [91]. The Hashin-Shtrikman formulas determine narrower bounds of the mixture than the parallel and serial mixing models [74, 73, 91, 93]

$$\varepsilon_m = \frac{\delta_1 \varepsilon_1 \left( \frac{2}{3} + \frac{\varepsilon_2}{3 \varepsilon_1} \right) + \delta_2 \varepsilon_2}{\delta_1 \left( \frac{2}{3} + \frac{\varepsilon_1}{3 \varepsilon_1} \right) + \delta_2}$$

(Maxwell)

(4.2.5.10)
\[ \varepsilon_m = \varepsilon_2 + \frac{\delta_1}{\varepsilon_1 - \varepsilon_2} + \frac{\delta_2}{n \varepsilon_2} \]  
\( \text{Maxwell-Wagner)  \hspace{1cm} (4.2.5.11) } \\
\[ \varepsilon_m = \varepsilon_1 + \frac{3\delta_1 (\varepsilon_1 - \varepsilon_2)}{\varepsilon_1 + 2\varepsilon_2 - \delta_1 (\varepsilon_1 - \varepsilon_2)} \]  
\( \text{Maxwell-Garnett)  \hspace{1cm} (4.2.5.12) } \\
\[ \delta_1 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + A \varepsilon_m} + \delta_2 \frac{\varepsilon_2 - \varepsilon_m}{\varepsilon_2 + A \varepsilon_m} = 0 \]  
\( \text{symmetrical Bruggeman)  \hspace{1cm} (4.2.5.13) } \\
\frac{\varepsilon_2 - \varepsilon_m}{\varepsilon_2 - \varepsilon_1} \left( \frac{\varepsilon_1}{\varepsilon_m} \right)^a = \delta_1 \]  
\( \text{non-symmetrical Bruggeman)  \hspace{1cm} (4.2.5.14) } \\
\[ \delta_1 \frac{1}{\varepsilon_1^s + A \varepsilon_m^s} + \delta_2 \frac{1}{\varepsilon_2^t + A \varepsilon_m^t} \]  
\( \text{modified general effective media)  \hspace{1cm} (4.2.5.15) } \\
\[ \varepsilon_m = \varepsilon_2 + \frac{\delta_1}{\varepsilon_1 - \varepsilon_2} \]  
\( \varepsilon_1 > \varepsilon_2 \)  
\( \text{(Hashin-Shtrikman, upper bound)  \hspace{1cm} (4.2.5.16) } \\
\[ \varepsilon_m = \varepsilon_1 + \frac{\delta_2}{\varepsilon_2 - \varepsilon_1} \]  
\( \varepsilon_2 > \varepsilon_1 \)  
\( \text{(Hashin-Shtrikman, lower bound)  \hspace{1cm} (4.2.5.17) } \\
\]  
\( \text{if the component 2 (minor phase) is three-dimensionally isotropic, then n = 3; } \\
\text{if the component 2 is two-dimensionally isotropic, then n = 2) } \\
\]  
where \( \varepsilon \) is relative permittivity, \( \delta \) is volume fraction, A (defined in Eq. 4.2.5.13), \( \eta \), and n (e.g., 3 for three-dimensionally isotropic components) are shape factors, s and t are exponent parameters, subscript m, 1, 2, or c is the mixture, component 1, component 2, or the critical condition of component 1 (and \( \delta_1 + \delta_2 = 1 \)). \( \varepsilon_1 \) is larger than \( \varepsilon_2 \) except for the notification if necessary.

4.2.5.1.3.2 Some other models than formulas in Sect. 4.2.5.1.3.1

This section will discuss some formulas based on theory and simulation.

4.2.5.1.3.2.1 Formulas based on the theory proposed by Reynolds and Hough

Reynolds and Hough [85] theoretically derived general formulas and demonstrated that these equations satisfied the relations proposed in the literature published earlier than their paper.
They considered that the composite which consisted of two phases and averaged electric displacement, \( \vec{D} \), over all volume, \( V \), is given by

\[
\vec{D} = \frac{1}{V} \int_{V_1} \vec{D} dv = \frac{1}{V} \left[ \int_{V_1} \vec{D}_1 dv + \int_{V_2} \vec{D}_2 dv \right] = \delta_1 \vec{D}_1 + \delta_2 \vec{D}_2 \tag{4.2.5.18}
\]

where \( D \) is electric displacement, \( \vec{D} \) is average displacement, \( V \) is volume, \( \delta \) is volume fraction, and the subscript 1 and 2 are component 1 and 2, respectively. Additionally, \( V_1 + V_2 = V \) and \( \delta_1 + \delta_2 = 1 \). The average electric field, \( \vec{E} \), is described as

\[
\vec{E} = \delta_1 \vec{E}_1 + \delta_2 \vec{E}_2 \tag{4.2.5.19}
\]

where \( \vec{E}_i \) is the average electric field of component \( i \). Dielectric permittivity is given by \( \vec{D} = \varepsilon \vec{E} \) and \( \vec{D}_i = \varepsilon_i \vec{E}_i \) for the component \( i \). Supposing \( f_i = \frac{\vec{E}_i}{\vec{E}} \) (field ratio) and using Eqs. (4.2.5.18 and 4.2.5.19), the equations below are obtained.

\[
\varepsilon = \varepsilon_2 + (\varepsilon_1 - \varepsilon_2) \delta_1 f_1 \tag{4.2.5.20}
\]

\[
(\varepsilon - \varepsilon_1) \delta_1 f_1 + (\varepsilon - \varepsilon_2) \delta_2 f_2 = 0 \tag{4.2.5.21}
\]

Eqs. (4.2.5.20 and 4.2.5.21) are theoretically equivalent, but empirically there is a difference between these equations. Eq. (4.2.5.20) is suitable for a mixture in which particles are dispersed in a continuous medium, while Eq. (4.2.5.21) is appropriate for the case in which the particle sizes of the two components are of the same order of magnitude.

The field ratio, \( f \), must be known to use Eqs. (4.2.5.20 and 4.2.5.21). \( f \) can be calculated for special mixtures, for example, parallel plates or infinitely diluted dispersions of ellipsoid shaped particles (the spheroids) but, in other cases, approximate values are estimated.

An induced field inside the spheroid in a homogeneous field is given by Eq. (4.2.5.22)

\[
f_i = \sum_{i=1}^{3} \frac{\cos^2 \alpha_i}{1 + A_i \left( \frac{\varepsilon_i}{\varepsilon} \right)^2 - 1} \tag{4.2.5.22}
\]

where \( \alpha_i \) is the angle made by the spheroid axes and the applied field, \( A_i \) depends on the axial ratio of the spheroid, and \( A_1 + A_2 + A_3 = 1 \). Randomly oriented spheroids demonstrate that \( \cos^2 \alpha_1 = \cos^2 \alpha_2 = \cos^2 \alpha_3 = \frac{1}{3} \), while \( \cos^2 \alpha_1 = \cos^2 \alpha_2 = \frac{1}{2} \) and \( \cos^2 \alpha_3 = 0 \) for long particles aligned with the long axes parallel but randomly oriented in other directions. Thus the spheroids have the relation that \( A_2 = A_3 = A \), that is, \( A_1 = 1 - 2A \). Fig. 4.2.5.3 shows the value of the shape factor, \( A \), especially for spheroids. Reynolds and Hough [85] summarized previously proposed formulas before their paper in Table 4.2.5.1 (a) and (b).
Figure 4.2.5.3 Shape factor value, A, of spheroids.
Ref.: Reynolds and Hough [85].
Table 4.2.5.1 (a) Formulas for randomly oriented particles in three-dimensions
\[
\cos^2 \alpha_1 = \cos^2 \alpha_2 = \cos^2 \alpha_3 = \frac{1}{3}
\] (After Reynolds and Hough [85])

<table>
<thead>
<tr>
<th>Particle Shape</th>
<th>Formula</th>
<th>References</th>
<th>Equation Used</th>
<th>Factors in Eq (iii)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spheres</td>
<td>( \frac{\varepsilon - \varepsilon_2}{\varepsilon + 2\varepsilon_2} = \delta_1 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} )</td>
<td>1~6</td>
<td>(ii)</td>
<td>( \frac{1}{3} ) ( \varepsilon_2 )</td>
</tr>
<tr>
<td>Spheres</td>
<td>( \frac{\varepsilon - \varepsilon_2}{3\varepsilon_2} = \delta_1 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} )</td>
<td>7</td>
<td>(i)</td>
<td>( \frac{1}{3} ) ( \varepsilon_2 )</td>
</tr>
<tr>
<td>Spheres</td>
<td>( \delta_1 \frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 + 2\varepsilon} + \delta_2 \frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 + 2\varepsilon} = 0 )</td>
<td>8</td>
<td>(ii)</td>
<td>( \frac{1}{3} ) ( \varepsilon )</td>
</tr>
<tr>
<td>Spheres</td>
<td>( \frac{\varepsilon - \varepsilon_2}{3\varepsilon} = \delta_1 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon} )</td>
<td>9</td>
<td>(i)</td>
<td>( \frac{1}{3} ) ( \varepsilon )</td>
</tr>
<tr>
<td>Spheroids</td>
<td>( \varepsilon = \varepsilon_2 + \frac{\delta_1}{3(1-\delta_1)} \sum_{i=1}^{3} \frac{\varepsilon_1 - \varepsilon}{1 + A_i \left( \frac{\varepsilon_1}{\varepsilon_2} - 1 \right)} )</td>
<td>10</td>
<td>(ii)</td>
<td>( A ) ( \varepsilon_2 )</td>
</tr>
<tr>
<td>Spheroids</td>
<td>( \varepsilon = \varepsilon_2 + \frac{\delta_1}{3} \sum_{i=1}^{3} \frac{\varepsilon_1 - \varepsilon_2}{1 + A_i \left( \frac{\varepsilon_1}{\varepsilon_2} - 1 \right)} )</td>
<td>11</td>
<td>(i)</td>
<td>( A ) ( \varepsilon )</td>
</tr>
<tr>
<td>Lamellae</td>
<td>( \varepsilon^2 = \frac{2(\delta_1 \varepsilon_1 + \delta_2 \varepsilon_2) - \varepsilon}{\delta_1 + \delta_2} )</td>
<td>8</td>
<td>(ii)</td>
<td>0 ( \varepsilon )</td>
</tr>
<tr>
<td>Lamellae</td>
<td>( 5\varepsilon^3 + \left( 5\varepsilon_p' - 4\varepsilon_p \right) \varepsilon^2 )</td>
<td>12</td>
<td>(i)</td>
<td>( \frac{1}{2} ) ( \varepsilon )</td>
</tr>
<tr>
<td>Rods</td>
<td>-( \left( \delta_1 \varepsilon_1^2 + 4\varepsilon_1 \varepsilon_2 + \delta_2 \varepsilon_2^2 \right) = \varepsilon_1 \varepsilon_2 ) ( x_p = 0 )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( \varepsilon^* \), dielectric constant of homogeneous medium; \( \varepsilon \), dielectric constant; \( \delta \), volume fraction; \( \alpha \), angle.

Eq(i): \( \varepsilon = \varepsilon_2 + (\varepsilon_1 - \varepsilon_2) \delta_1 f_1 \).
Eq(ii): \( (\varepsilon - \varepsilon_1) \delta_1 f_1 + (\varepsilon - \varepsilon_2) \delta_2 f_2 = 0 \).
Eq(iii): \( f_i = \frac{1}{1 + A_i \left( \varepsilon_1 \varepsilon^* - 1 \right)} \).

1) O. F. Mossotti, Mem. de mathem et di fisica in Modena II, 24, 49(1850).
2) R. Clausius, Die Moch, Warme Theorie, II (Braunschweig) (1879).
4) L. Lorentz, Ann. Phys., 11, 70(1880).
5) Rayleigh, Phil. Mag., 34, 481-502(1892).
6) V. I. Odelevskii, Zhurnal Technicheskai, 6, 667, 678(1951).
7) K. W. Wagner, Arch. Elektrotech., 2(9), 371-87(1914); K. W. Wagner, Arch. Elektrotech., 3, 68-106(1914)(in German).
Table 4.2.5.1 (b) Formulas for particles with the degree of orientation
(After Reynolds and Hough [85])

<table>
<thead>
<tr>
<th>Particle Shape</th>
<th>Formula</th>
<th>Ref.</th>
<th>Gen. Eq.</th>
<th>Factors in Eq (iii)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel cylinders</td>
<td>$\varepsilon_1 - \varepsilon_2 = \frac{\delta_1}{\varepsilon_1 + \varepsilon_2} (\varepsilon_1 - \varepsilon_2)$</td>
<td>5, 6</td>
<td>(ii)</td>
<td>$\frac{1}{2} \varepsilon_2 \frac{1}{2} \cos \alpha_4 \cos \alpha_3$</td>
</tr>
<tr>
<td>Parallel cylinders</td>
<td>$\delta_1 \frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 + \varepsilon} + \delta_2 \frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 + \varepsilon} = 0$</td>
<td>8</td>
<td>(ii)</td>
<td>$\frac{1}{2} \varepsilon_2 \frac{1}{2} \cos \alpha_4 \cos \alpha_3$</td>
</tr>
<tr>
<td>Parallel lamellae</td>
<td>$\varepsilon = \frac{\delta_1 \varepsilon_1 + \delta_2 \varepsilon_2}{\delta_1 + \delta_2}$</td>
<td>8</td>
<td>(ii)</td>
<td>$\varepsilon_2 \frac{1}{2}$</td>
</tr>
<tr>
<td>Lamellae with all axes aligned (field perpendicular to the lamellae planes)</td>
<td>$\varepsilon = \frac{\delta_1}{\varepsilon_1} + \frac{\delta_2}{\varepsilon_2}$</td>
<td>13</td>
<td>(ii)</td>
<td>$\varepsilon_2 \frac{1}{2} \cos \alpha_4 \cos \alpha_3$</td>
</tr>
<tr>
<td>Lamellae with all axes aligned (field parallel to the lamellae planes)</td>
<td>$\varepsilon = \delta_1 \varepsilon_1 + \delta_2 \varepsilon_2$</td>
<td>13, 14</td>
<td>(ii)</td>
<td>$\varepsilon_2 \frac{1}{2} \cos \alpha_4 \cos \alpha_3$</td>
</tr>
<tr>
<td>Spheroids with all axes aligned (field parallel to one of the axes)</td>
<td>$\varepsilon = \varepsilon_2 + \frac{\delta_1 \left( \varepsilon_1 - \varepsilon_2 \right)}{1 + \delta_1 \left( \frac{\varepsilon_1}{\varepsilon_2} - 1 \right)}$</td>
<td>15</td>
<td>(i)</td>
<td>$\varepsilon_2 \frac{1}{2} \cos \alpha_4 \cos \alpha_3$</td>
</tr>
<tr>
<td>Spheroids with all axes aligned (field parallel to one of the axes)</td>
<td>$\varepsilon = 1 + \frac{\delta_1 \left( \frac{\varepsilon_1}{\varepsilon_2} - 1 \right)}{\frac{1}{1 + \delta_1 \left( \frac{\varepsilon_1}{\varepsilon_2} - 1 \right)}}$</td>
<td>16</td>
<td>(ii)</td>
<td>$\varepsilon_2 \frac{1}{2} \cos \alpha_4 \cos \alpha_3$</td>
</tr>
</tbody>
</table>

A, shape factor; $\varepsilon^*$, dielectric constant of homogeneous medium; $\varepsilon$, dielectric constant; $\delta$, volume fraction; $\alpha$, angle.

Eq(i): $\varepsilon = \varepsilon_2 + (\varepsilon_1 - \varepsilon_2) \delta_1 f_1$.
Eq(ii): $(\varepsilon - \varepsilon_1) \delta_1 f_1 + (\varepsilon - \varepsilon_2) \delta_2 f_2 = 0$.
Eq(iii): $f_i = \sum_{i=1}^{3} \frac{\cos^2 \alpha_i}{1 + A_i \left( \varepsilon_1 \varepsilon^* - 1 \right)}$.

5) Rayleigh, Phil. Mag., 34, 481-502(1892).
6) V. I. Odelevskii, Zhurnal Technicheski, 6, 667, 678(1951).
4.2.5.1.3.2.2 Formulas based on numerical methods

There are equations proposed by Wakino et al. [86, 94] based on the Monte Carlo and finite element methods, and these equations predict that the dielectric constant of a compound consisting of two components with different dielectric constants

\[
\varepsilon_m^{(\delta_1 - \delta_2)} = \delta_1 \varepsilon_1^{(\delta_1 - \delta_c)} + \delta_2 \varepsilon_2^{(\delta_2 - \delta_c)} \tag{4.2.5.23}
\]

\[
\varepsilon_m = \exp \left[ \frac{\ln \{ \delta_1 \varepsilon_1^{(\delta_1 - \delta_c)} + \delta_2 \varepsilon_2^{(\delta_2 - \delta_c)} \}}{\delta_1 - \delta_c} \right] \tag{4.2.5.24}
\]

where \( \varepsilon_m, \varepsilon_1, \) and \( \varepsilon_2, (\varepsilon_1 > \varepsilon_2) \) are the relative dielectric permittivity of the mixture, component 1 and component 2, respectively, and \( \delta_1, \delta_2, \) and \( \delta_c \) are the volume fractions of component 1 and component 2, and the critical volume fraction of component 1. The critical volume fraction is obtained by the intersection between the proposed equation and the logarithmic mixing equation. According to the authors, \( \delta_c \) is approximately 0.35.

The procedure by Wakino et al. is as follows: i) the unit size square in two-dimensions is divided in 625 \((25 \times 25)\) cells; component 1 randomly occupies the cells in order to fit the volume fraction of component 1 by the Monte Carlo method; the other cells are assigned to component 2, ii) the apparent relative permittivity is calculated based on the two-dimensional finite element method, and iii) the mean value is obtained by averaging simulated and calculated data 1000 times. The equation includes the effects of dielectric polarization and infringing of the electric flux at the boundary region of the two components in two-dimensions.

Equations to calculate the dielectric properties of a mixture based on the finite element methods have been reported in the literature [95, 96]. Dielectric properties obtained using the Monte Carlo and finite element method have been reported in the literature [97, 98], and the three-dimensional model is described [91, 99]. There is literature which reviews the numerical methods [76, 77].

4.2.5.1.3.2.3 Formulas used for structural analysis of a component in the mixture

There are equations used to estimate the shape of a component in a diphase mixture based on the derivatives of the cube model. These models are based on finding an equivalent solid (e.g., rectangular solid) which represents a minor phase. The cube model depends on finding an equivalent cube (i.e., the length, width, and height are the same) for a minor phase of 0-3 composites [100], and the modified cube model needs to find an equivalent rectangular solid (i.e., a length and width are same, but the height is not necessary to be the same as the length and
The shapes of the minor phase in 0-3 composites were explained by the modified cube model. For example, the pores of normally sintered lead zirconate (PZT) doped with niobium (Nb) would be cube or sphere, but the pores for hot-pressed PZT doped with manganese (Mn) would be flat-tetragonal or flat-ellipsoidal [101].

If the height of the equivalent cube is approaching unity, then it is more difficult to find the equivalent rectangular solid since the slight increment changes the dielectric property substantially. Accordingly, Dias and Das-Gupta [75, 102] proposed the mixed connectivity model shown in Fig. 4.2.5.4. The dielectric permittivity is given by

\[
\varepsilon_m = \delta_1 \varepsilon_1 + \delta_2 \varepsilon_2 + \delta_s \varepsilon_s - \frac{\left( d_{33}^1 - d_{33}^2 \right)^2 s_{33} \delta_1 \delta_2}{s_{33}^1 s_{33}^2} - \frac{\left( d_{33}^1 - d_{33}^s \right)^2 s_{33} \delta_1 \delta_s}{s_{33}^1 s_{33}^s} - \frac{\left( d_{33}^2 - d_{33}^s \right)^2 s_{33} \delta_s \delta_2}{s_{33}^2 s_{33}^s} \tag{4.2.5.25}
\]

where \( \varepsilon \) is dielectric constant, \( \delta \) is volume fraction, \( d_{33} \) is piezoelectric constant which is measured in the direction perpendicular to an applied field (3 or z axis), \( s_{33} \) is elastic compliance which is measured in the direction perpendicular to the applied field, and suffix m, 1, 2, and s are the properties of the mixture, component 1, component 2, and series branch, respectively. Dias and Das-Gupta had assumptions to obtain the equation: i) the strain and the electric field in the direction 3 as well as the stress in the transverse directions 1 and 2 were equal in both phases and ii) the stress and the charge in the direction 3 as well as the strain in the transverse directions 1 and 2 were distributed between the two phases depending on their volume fractions. The authors demonstrated that the ratio of the serial and parallel connectivity of calcium modified lead titanate to poly (vinylidene fluoride-trifluorethylene) in the composites [75].

### 4.2.5.1.4 Summary

The mixing rules are used to predict the properties of a mixture based on the properties of each component and would estimate the structure of a component in the mixture. A number of researchers have proposed formulas for the mixing rules of dielectric relative permittivity based on theoretical and/or empirical results. The upper limit is determined by the parallel model, and the lower limit is determined by the serial model. A general equation may be given by

\[
\varepsilon_m^n = \sum_i \delta_i \varepsilon_i^n (-1 \leq n \leq 1) \text{ where } \varepsilon \text{ is relative dielectric permittivity, } \delta_i, \text{ and } \varepsilon_i \text{ are volume fraction and dielectric relative permittivity of the } i \text{ th component, respectively, and } n \text{ is a constant which would be related to the connectivity among the components. When } n \text{ are 1 and } -1, \text{ the formulas are for the parallel and serial models, respectively. When } n \text{ approaches 0, the equation is for the logarithmic mixing rule which is often used to check experimental results,}
\]

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Figure 4.2.5.4 Schematic diagram of cube based models.
(a) modified cube model and (b) mixed connectivity cube model.
Ref: Dias and Das-Gupta [75].
Das-Gupta [102].
even though it is sometimes difficult to fit the experimental data. Wakino et al. proposed the
equations using the Monte Carlo and finite element methods to estimate the dielectric relative
permittivity of the composites consisting two different non-aspect materials. The formula is
given by \( \varepsilon_m = \exp \left[ \frac{\ln \left( \delta_1 \varepsilon_1^{(\delta_1-\delta_c)} + \delta_2 \varepsilon_2^{(\delta_1-\delta_c)} \right)}{\delta_1 - \delta_c} \right] \) where \( \varepsilon_m, \varepsilon_1, \) and \( \varepsilon_2, (\varepsilon_1 > \varepsilon_2) \) are the relative
dielectric permittivity of the mixture, component 1, and component 2, respectively, and \( \delta_1, \delta_2, \) and \( \delta_c \) are the volume fractions of component 1 and component 2, and the critical volume
fraction of component 1, respectively. The critical volume fraction is obtained based on the
intersection between the above equation and logarithmic mixing equation (\( \delta_c \) is \( \sim 0.35 \) according
to their experiments). There are models which have been used to estimate the microstructure of a
component in the mixture.

4.2.5.2 Experimental

The processing of calcined (Sr, Pb)TiO\(_3\) composition powders were described in the
literature [36] and Sect. 3.1. The calcined powders were ball milled for 20 h, and sieved.
Magnesium oxide (99.998% purity MgO, Alfa Aesar) was added to the sieved powders with
specific ratios. They were ball milled with 3/8-in yttrium-stabilized zirconium oxide cylinders
for 4 h. The pure SPT powders were also ball milled for 4 h. Pellets were formed from the
powders with uniaxial and cold isostatic pressing (CIP) with a pressure of 2500 kg/cm\(^2\). The
samples were then sintered at 1350 °C for 3 h. After the surfaces of the samples were polished,
these samples were annealed at 700 °C for 3 h. When electrodes were necessary for low
frequency measurements such as 10 kHz, gold was evaporated or sputtered on the surfaces of the
samples. Two kinds of disk samples were prepared to enable the composites to be characterized
at low and high frequencies (~ 2-mm thickness samples for low frequency measurements and ~
5-mm thickness samples for high frequency measurements).

The structural phases within the samples were identified by their X-ray diffraction
(XRD)-patterns using Cu K\(_\alpha\) as an X-ray source (PDIV, SCINTAG, Inc.). The peak positions
were determined in the range between 20 and 130 degrees two-theta using the program, “PRO-
FIT” [1], and lattice parameters were obtained using the external reference, silicon powders, and
the program, “UNITCELL” [103].

The densities of the samples were obtained using the Archimedes method.
Low frequency dielectric properties were obtained as parallel components with an LCR meter (4284A, HP), and high frequency measurements were carried out using samples without electrodes using the parallel plate dielectric post resonator method [39, 42].

**4.2.5.3 Estimation of volume fractions of components in composites**

The volume fraction of a component in the composite was calculated based on a weight ratio between two components, the density of the composite, and several assumptions. The assumptions were as follows:

i) The chemical formula of each component, (Sr_{1-x}Pb_{x})TiO_{3} (SPT) (x = 0.2) or MgO was stoichiometry,

ii) No reactions between the SPT and MgO occurred during heating,

iii) The density of a composite was the sum of SPT and MgO densities (i.e., the sum of density of the SPT with pores and that of the MgO with pores),

iv) The weight ratio of the MgO to the SPT was not changed after mixing,

v) The theoretical (maximum) SPT density was 5.75 g/cm³ and a minimum MgO density was 2.0 g/cm³ for the calculation; the lattice parameter of the SPT (x = 0.2) was 3.913 Å [35] to calculate the theoretical density of the SPT at room temperature; the maximum density of MgO was 3.58 g/cm³ [104].

The volume fraction was determined by the following process:

i) The density of the composite was obtained using the Archimedes method,

ii) The range of the density for the SPT (x = 0.2) was the measured density ± 0.05 g/cm³ (± 0.05 was an error). The density of the composites was determined by the following equation

\[
density(\text{composite}) = \frac{1}{\frac{\text{weight fraction}(\text{SPT})}{\density(\text{SPT})} + \frac{\text{weight fraction}(\text{MgO})}{\density(\text{MgO})}} \tag{4.2.5.26}
\]

iii) The range of the volume fraction of SPT was determined by the equation below

\[
\text{volume fraction}(\text{SPT}) = \frac{\text{weight fraction}(\text{SPT})}{\frac{\text{density(SPT)}}{\text{weight fraction}(\text{SPT})} + \frac{\text{weight fraction}(\text{MgO})}{\density(\text{MgO})}} \tag{4.2.5.27}
\]

iv) The volume fraction was determined to divide the sum of the maximum and minimum volume fractions by two.
Table 4.2.5.2 (a) and (b) list examples. Table 4.2.5.3 lists the measured densities of the composites, and the weight fraction, volume fraction, and mole fraction of each component, the SPT or the MgO, in the composites.

4.2.5.4 Results

Fig. 4.2.5.5 shows the X-ray diffraction (XRD) patterns of calcined (Sr0.8Pb0.2)TiO3 (SPT) or the mixture of calcined SPT and MgO in the range between 20 and 70 degrees two-theta and Fig. 4.2.5.6 shows the XRD patterns of sintered products over the same range. When the weight fraction of the MgO is 0.005 (“1” in Fig. 4.2.5.5), then the MgO was not detected. With an increase in the MgO content, the MgO was apparently detected. Fig. 4.2.5.7 shows the lattice parameter of the SPT or MgO of the sintered products obtained in the range between 20 and 130 degrees two-theta with the value of MgO in the literature [105]. The composites with a low concentration of the MgO (2.5 wt % or less than that) showed an increase in SPT lattice parameter and the composites with the higher concentration MgO showed a decrease in SPT lattice parameter. The MgO lattice parameter decreased as the content of the MgO increased in the composites.

Fig. 4.2.5.8 shows the relative permittivity and tangent δ of the composites at 25 oC and at a frequency of 10 kHz after the samples were thermally stabilized at the temperature. Although the pure SPT system showed low tangent δ, the tangent δ became higher by the addition of the MgO. The pure SPT could be dense, and it could lead to low tangent δ. As the MgO content of the composites increased, the tangent δ was reduced.

Fig. 4.2.5.9 shows the application of the mixing rules to the relative permittivity of the SPT and the composites at 10 kHz and at 25 oC. Four models were used to calculate the relative permittivity of the composites, i) the parallel mixing model, ii) the serial mixing model, iii) the logarithmic mixing rule, and iv) the Wakino model. These equations used are described below. The room temperature relative permittivity of the SPT [35] and MgO [106; the value of single crystal at 27 oC and at 10 GHz was 9 ] used are 1200 and 10, respectively.

\[
\varepsilon_{SPT} \times \delta_{SPT} + \varepsilon_{MgO} \times \delta_{MgO} = \varepsilon_{SPT} \times \delta_{SPT} + \varepsilon_{MgO} \times (1 - \delta_{SPT}) \tag{4.2.5.28}
\]

\[
\varepsilon_{SPT} \times \ln \varepsilon_{SPT} + (1 - \delta_{SPT}) \times \ln \varepsilon_{MgO} \tag{4.2.5.29}
\]

\[
\frac{1}{\varepsilon_{SPT}} + \frac{\delta_{MgO}}{\varepsilon_{MgO}} = \frac{\varepsilon_{SPT} \times \varepsilon_{MgO}}{\varepsilon_{MgO} \times \delta_{SPT} + \varepsilon_{SPT} \times (1 - \delta_{SPT})} \tag{4.2.5.30}
\]
Table 4.2.5.2 (a) Expected density of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT)-MgO (95:5 by weight) composite based on the densities of SPT and MgO components

Measured density of the composite: 5.14 g/cm\(^3\)

<table>
<thead>
<tr>
<th>MgO density (g/cm(^3))</th>
<th>3.58</th>
<th>3.55</th>
<th>3.50</th>
<th>3.45</th>
<th>3.40</th>
<th>3.35</th>
<th>3.30</th>
<th>3.25</th>
<th>3.20</th>
<th>3.15</th>
<th>3.10</th>
<th>3.05</th>
<th>3.00</th>
<th>2.95</th>
<th>2.90</th>
<th>2.85</th>
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</tr>
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<tbody>
<tr>
<td>5.75</td>
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<td>5.571</td>
<td>5.565</td>
<td>5.558</td>
<td>5.551</td>
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<td>5.498</td>
<td>5.489</td>
<td>5.481</td>
<td>5.472</td>
<td>5.462</td>
<td></td>
</tr>
<tr>
<td>5.70</td>
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<td>5.532</td>
<td>5.526</td>
<td>5.520</td>
<td>5.514</td>
<td>5.507</td>
<td>5.500</td>
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<td>5.486</td>
<td>5.478</td>
<td>5.471</td>
<td>5.463</td>
<td>5.455</td>
<td>5.446</td>
<td>5.438</td>
<td>5.429</td>
<td>5.419</td>
<td></td>
</tr>
<tr>
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<td>5.488</td>
<td>5.482</td>
<td>5.475</td>
<td>5.469</td>
<td>5.462</td>
<td>5.456</td>
<td>5.449</td>
<td>5.442</td>
<td>5.434</td>
<td>5.427</td>
<td>5.419</td>
<td>5.411</td>
<td>5.403</td>
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Colored area: density, 5.14 ± 0.05 g/cm\(^3\).
Table 4.2.5.2 (b) Expected volume fraction of (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) component in SPT- MgO (95:5 by weight) composite based on the densities of SPT and MgO components.  
Measured density of the composite: 5.14 g/cm$^3$.

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Colored area: density, 5.14 ± 0.05 g/cm$^3$. 

Table 4.2.5.3 (a) Thin (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT)-MgO composite samples used for low frequency measurements

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Table 4.2.5.3 (b) Thick (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT)-MgO composite samples used for high frequency measurements

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<td>0.25:0.75</td>
<td>3.89</td>
<td>0.18:0.82</td>
<td>0.19</td>
<td>0.17</td>
<td>0.061:0.939</td>
</tr>
<tr>
<td>9L</td>
<td>0.05:0.95</td>
<td>3.43</td>
<td>0.035:0.965</td>
<td>0.04</td>
<td>0.03</td>
<td>0.010:0.990</td>
</tr>
</tbody>
</table>
Figure 4.2.5.5 Room temperature X-ray diffraction patterns of calcined $(Sr_{0.8}Pb_{0.2})TiO_3$ (SPT) and mixtures of calcined SPT and MgO. X-ray source: Cu $K\alpha$.

Note: 0-9 is a number which specifies the sample.

0: 1.00 (SPT weight fraction), pure SPT.
1: 0.995 (SPT weight fraction), [MgO was not detected].
2: 0.975 (SPT weight fraction), [MgO was detected].
3: 0.95 (SPT weight fraction).
4: 0.75 (SPT weight fraction).
5: 0.60 (SPT weight fraction).
6: 0.50 (SPT weight fraction).
7: 0.40 (SPT weight fraction).
8: 0.25 (SPT weight fraction).
9: 0.05 (SPT weight fraction).
Figure 4.2.5.6 Room temperature X-ray diffraction patterns of sintered (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ (SPT) and composites prepared from SPT and MgO.

X-ray source: Cu K$_\alpha$.

Note: 0-9 is a number which specifies the sample.
- 0: 1.00 (SPT weight fraction), pure SPT.
- 1: 0.995 (SPT weight fraction), [MgO was not detected].
- 2: 0.975 (SPT weight fraction), [MgO was detected].
- 3: 0.95 (SPT weight fraction).
- 4: 0.75 (SPT weight fraction).
- 5: 0.60 (SPT weight fraction).
- 6: 0.50 (SPT weight fraction).
- 7: 0.40 (SPT weight fraction).
- 8: 0.25 (SPT weight fraction).
Figure 4.2.5.7 Lattice parameters of (Sr<sub>0.8</sub>Pb<sub>0.2</sub>)TiO<sub>3</sub> (SPT) and composites prepared from SPT and MgO.

Fit range for SPT component, from sample “0” to “2” or from “3” to “6.”
Fit range for MgO component, from sample “3” to “9.”
0: 1.00 (SPT weight fraction); 1: 0.995; 2: 0.975; 3: 0.95; 4: 0.75; 5: 0.60; 6: 0.50; 7: 0.40; 8: 0.25; 9: 0.05
Ref: [105]. (MgO, 4.2112 Å).

Figure 4.2.5.8 Dielectric properties of (Sr<sub>0.8</sub>Pb<sub>0.2</sub>)TiO<sub>3</sub> (SPT) and composites prepared from SPT and MgO at 10 kHz and at 25 °C.
Values are at an average of 50 results.
Bars indicate maximum and minimum values among 50 results.
Measurement conditions: HP 4284A, 1 V<sub>AC</sub>/cm, Averaging number of 16.
Figure 4.2.5.9 Application of the mixing rules to the relative permittivity of (Sr_{0.8}Pb_{0.2})TiO_3 (SPT) and composites prepared from SPT and MgO measured at 10 kHz and at 25 °C.

- Parallel: calculated based on the parallel model.
- Logarithm: calculated based on the logarithmic mixing model.
- Serial: calculated based on the serial model.
- Wakino eq. at $\delta_c = 0.10$: calculated based on the Wakino model with $\delta_c = 0.10$.

\[ \varepsilon_{SPT} = 1200, \quad \varepsilon_{MgO} = 10, \quad \delta_{SPT} = \text{Volume fraction of SPT}, \quad \delta_{MgO} = 1 - \delta_{SPT}: \]

Volume fraction of MgO.

Phases in parallel

\[ \varepsilon_{SPT} \times \delta_{SPT} + \varepsilon_{MgO} \times (\delta_{MgO}) = \varepsilon_{SPT} \times \delta_{SPT} + \varepsilon_{MgO} \times (1 - \delta_{SPT}) \]

Logarithmic mixing model

\[ e^{\varepsilon_{SPT} \ln \delta_{SPT} + (1 - \delta_{SPT}) \ln \varepsilon_{MgO}} \]

Wakino model

\[ \ln \left[ \frac{\delta_{SPT} \times \varepsilon_{SPT}^{\delta_{SPT}} \times (1 - \delta_{SPT}) \times \varepsilon_{MgO}^{\delta_{MgO}}}{\delta_{SPT} - \delta_c} \right] = e^{\varepsilon_{SPT} \times \delta_{SPT} - \varepsilon_{MgO} \times (1 - \delta_{SPT})} \]

Note: $\delta_c = 0.1$; $\delta_c$ is the volume fraction of SPT which is the intersection between the fitting curve of samples and the logarithmic model.

Phases in serial

\[ \frac{1}{\frac{\delta_{SPT}}{\varepsilon_{SPT}} + \frac{\delta_{MgO}}{\varepsilon_{MgO}}} = \frac{\varepsilon_{SPT} \times \varepsilon_{MgO}}{\varepsilon_{MgO} \times \delta_{SPT} + \varepsilon_{SPT} \times (1 - \delta_{SPT})} \]
\[
\frac{\ln \left( \frac{\delta_{\text{SPT}} \varepsilon_{\text{SPT}} \delta_{\text{MgO}} \varepsilon_{\text{MgO}}}{\delta_{\text{SPT}} - \delta_c} \right)}{\delta_{\text{SPT}} - \delta_c} = (4.2.5.31)
\]

where \(\varepsilon_{\text{SPT}}\) (1200) and \(\varepsilon_{\text{MgO}}\) (10) are the relative permittivity of the SPT and MgO, respectively, \(\delta_{\text{SPT}}\) and \(\delta_{\text{MgO}}\) are the volume fraction of SPT and MgO in the composites, respectively, and the sum of the two values is 1. \(\delta_c\) is the critical volume fraction of the SPT, which is the intersection between the fitted curve and the logarithmic mixing equation. Among four models, the Wakino model showed reasonably good fitting.

Fig. 4.2.5.10 shows the dielectric properties of the SPT and the composites measured at low frequencies (e.g., 10 kHz) as a function of temperature and frequency. By the addition of MgO, the dielectric constant of the SPT component was suppressed. In the paraelectric states at a temperature not close to that of the phase transition, the relative permittivity as a function of temperature did not show an obvious frequency dependence. Tangent \(\delta\) as a function of temperature at lower frequency in the paraelectric state far from the phase transition stayed higher values due to the contribution of conductivity. Around the transition temperatures, dielectric constants as a function of temperature showed a frequency dependence, and lower frequency values were higher. On the contrary, lower frequency tangent \(\delta\) values were smaller around the phase transitions and in the ferroelectric states. The SPT- MgO (0.05:0.95 by weight) composites showed the lowest temperature dependence of relative permittivity among the composites studied.

Each plot in Fig. 4.2.5.11 shows the Curie-Weiss behavior of the SPT or each composite sample at 10 kHz in a cooling cycle. Fig. 4.2.5.12 shows the Curie-Weiss behaviors of the composites in one plot. When the composites, of which the MgO contents were up to 5 wt%, the Curie-Weiss constant decreased but the Curie-Weiss temperature was almost similar. Fig. 4.2.5.13 shows the Curie-Weiss constant of the composites as a function of SPT volume fraction in the SPT-MgO composites. The composites showed a gradual reduction in Curie-Weiss constant.

According to Fig. 4.2.5.9, the composites showed a parallel-like model at a low concentration of MgO. The Curie-Weiss behavior of the composite and SPT and the relative permittivity of the composite may be given by the following equations

\[
\frac{1}{\varepsilon_m - 1} = \frac{T - \theta_m}{C_m} \quad \text{or} \quad \frac{1}{\varepsilon_m} \approx \frac{T - \theta_m}{C_m} \quad \text{(if} \ \varepsilon_m \gg 1) \quad (4.2.5.32)
\]
Figure 4.2.5.10 (a) Dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ (SPT) and composites prepared from SPT and MgO as a function of temperature and frequency.

(0) (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$.
(1) Composite: (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (0.995:0.005 by weight).
(2) Composite: (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (0.975:0.025 by weight).
Figure 4.2.5.10 (b) Dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ (SPT) and composites prepared from SPT and MgO as a function of temperature and frequency.

(3) Composite: (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (0.95:0.05 by weight).

(4) Composite: (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (0.75:0.25 by weight).

(5) Composite: (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (0.60:0.40 by weight).
Figure 4.2.5.10 (c) Dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ (SPT) and composites prepared from SPT and MgO as a function of temperature and frequency.

(6) Composite: (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (0.50:0.50 by weight).
(7) Composite: (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (0.40:0.60 by weight).
(8) Composite: (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$-MgO (0.25:0.75 by weight).
Figure 4.2.5.10 (d) Dielectric properties of \((\text{Sr}_{0.8}\text{Pb}_{0.2})\text{TiO}_3\) and composites prepared from SPT and MgO as a function of temperature and frequency.

(9) Composite: \((\text{Sr}_{0.8}\text{Pb}_{0.2})\text{TiO}_3\)-MgO (0.05:0.95 by weight).
Figure 4.2.5.11 (a) Relative permittivity and Curie-Weiss behaviors of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ (SPT) and composites prepared from SPT and MgO at 10 kHz as a function of temperature.

$\varepsilon_r$: relative permittivity, Fit: Curie-Weiss behavior.

(0): SPT-MgO (1:0 by weight); (1): (0.995:0.005 by weight); (2): (0.975:0.025 by weight); (3): (0.95:0.05 by weight); (4): (0.75:0.25 by weight); (5): (0.60:0.40 by weight); (6): (0.50:0.50 by weight); (7): (0.40:0.60 by weight).
Figure 4.2.5.11(b) Relative permittivity and Curie-Weiss behaviors of (Sr0.8Pb0.2)\text{TiO}_3 (SPT) and composites prepared from SPT and MgO at 10 kHz as a function of temperature. $\varepsilon_r$: relative permittivity, Fit: Curie-Weiss behavior.

(8): (Sr0.8Pb0.2)\text{TiO}_3-MgO (0.30:0.70 by weight).

Figure 4.2.5.12 Relative permittivity and Curie-Weiss behaviors of (Sr0.8Pb0.2)\text{TiO}_3 (SPT) and composites prepared from SPT and MgO at 10 kHz as a function of temperature.

(0): SPT-MgO (1.00 :0 ); 115>T>−35; $T_m$=−56; $\theta$=−48; $C$=89100 °C; $r$=0.99990.
(1): SPT-MgO (0.995:0.005); 180>T>−7.5; $T_m$=−52; $\theta$=−47; $C$=81700 °C; $r$=0.99991.
(2): SPT-MgO (0.975:0.025); 180>T>5; $T_m$=−49; $\theta$=−48; $C$=76300 °C; $r$=0.99990.
(3): SPT-MgO (0.95 :0.05 ); 180>T>5; $T_m$=−50; $\theta$=−51; $C$=72900 °C; $r$=0.99992.
(4): SPT-MgO (0.75 :0.25 ); 180>T>−10; $T_m$=−53; $\theta$=−74; $C$=44300 °C; $r$=0.99990.
(5): SPT-MgO (0.60 :0.40 ); 135>T>−10; $T_m$=−61; $\theta$=−92; $C$=27300 °C; $r$=0.99990.
(6): SPT-MgO (0.50 :0.50 ); 95>T>−10; $T_m$=−70; $\theta$=−108; $C$=18200 °C; $r$=0.99990.
(7): SPT-MgO (0.40 :0.60 ); 55>T>−20; $T_m$=−77; $\theta$=−136; $C$=12300 °C; $r$=0.99990.
(8): SPT-MgO (0.25 :0.75 ); 27.5>T>−25; $T_m$=−8; $\theta$=−273; $C$=8500 °C; $r$=0.99990.

((8) is not shown in the figures.). Ratio between SPT and MgO is based on weight fraction.

T, Temperature; $T_m$, Transition temperature at 10 kHz; $\theta$, Curie-Weiss temperature; $C$, Curie-Weiss constant.
Figure 4.2.5.13 Curie-Weiss constants of \((\text{Sr}_{0.8}\text{Pb}_{0.2})\text{TiO}_3\) (SPT) and composites prepared from SPT and MgO at 10 kHz.

Figure 4.2.5.14 Reciprocal dielectric susceptibility of composites with parallel diphase mixtures.

\[ \varepsilon_1 \times \delta_1 \gg \varepsilon_2 \times \delta_2 = \varepsilon_2 \times (1 - \delta_1). \]

\(\varepsilon_n\), relative permittivity of phase \(n\).

\(\delta_n\), volume fraction of phase \(n\).

\(n\), 1 (major phase) or 2 (minor phase).

\[ C_{\delta_1=0.99} = 0.99 C_{\delta_1=1.00}, \quad C_{\delta_1=0.95} = 0.95 C_{\delta_1=1.00}, \quad C_{\delta_1=0.90} = 0.90 C_{\delta_1=1.00}. \]
\[
\frac{1}{\varepsilon_{\text{SPT}} - 1} = \frac{T - \theta_{\text{SPT}}}{C_{\text{SPT}}} \quad \text{or} \quad \frac{1}{\varepsilon_{\text{SPT}}} = \frac{T - \theta_{\text{SPT}}}{C_{\text{SPT}}} \quad \text{(if } \varepsilon_{\text{SPT}} \gg 1) \quad (4.2.5.33)
\]

\[
\varepsilon_{\text{m}} = \delta_{\text{SPT}} \times \varepsilon_{\text{SPT}} + \delta_{\text{MgO}} \times \varepsilon_{\text{MgO}} \quad \text{or} \quad \varepsilon_{\text{m}} = \delta_{\text{SPT}} \times \varepsilon_{\text{SPT}} \quad \text{(if } \delta_{\text{SPT}} \times \varepsilon_{\text{SPT}} \gg \delta_{\text{MgO}} \times \varepsilon_{\text{MgO}}) \quad (4.2.5.34)
\]

where \(\varepsilon, C, \theta, \text{ and } T\) are relative permittivity, Curie-Weiss constant, Curie-Weiss temperature, and temperature, respectively, and subscript \(m, \text{SPT, and MgO}\) are the property of the mixture, SPT and MgO, respectively.

From Eqs. (4.2.5.32, 4.2.5.33, and 4.2.5.34), the Curie-Weiss constant is reduced to Eq. (4.2.5.36) through Eq. (4.2.5.35).

\[
\frac{1}{\varepsilon_{\text{m}}} = \frac{1}{\delta_{\text{SPT}} \times \varepsilon_{\text{SPT}}} = \frac{T - \theta_{\text{SPT}}}{C_{\text{SPT}}} \quad \text{or} \quad \frac{T - \theta_{\text{m}}}{C_{\text{m}}} \quad (4.2.5.35)
\]

\[
C_{\text{m}} = \delta_{\text{SPT}} \times C_{\text{SPT}} \times \frac{T - \theta_{\text{m}}}{T - \theta_{\text{SPT}}} \quad (4.2.5.36)
\]

If \(\theta_{\text{m}} \text{ is nearly } \theta_{\text{SPT}}\), then Eq. (4.2.5.36) leads to

\[
C_{\text{m}} = \delta_{\text{SPT}} \times C_{\text{SPT}} \quad (\theta_{\text{m}} = \theta_{\text{SPT}}) \quad (4.2.5.37)
\]

Fig. 4.2.5.14 shows the effect of volume fraction of component 1 in the parallel model composites on the Curie-Weiss behavior (SPT-MgO (0.99:0.01, 0.945:0.055, and 0.90:0.10 by volume)). Assumptions for the plots are as follows: Relative permittivity is larger than 1 and the relative permittivity of component 1 times volume fraction of component 1 is larger than that of component 2. These plots showed the Curie-Weiss temperatures of the composites were similar, while the Curie-Weiss constants decreased as the volume fractions reduced.

Table 4.2.5.4 lists the Curie-Weiss behaviors of the composites. The parallel model explains the observed behavior well. Payne [107] showed the Curie-Weiss constant of barium titanate (BaTiO_3) sintered in oxygen (O_2) atmosphere was lower than that of BaTiO_3 sintered in air. However, a huge change in Curie-Weiss constat was not observed in SPT sintered in O_2 (Table 4.2.5.5; the results were based on samples prepared from high purity raw chemicals) (see Sect. 3.4). Therefore, the microstructure or the connectivity of the MgO to the SPT would be the major reason for the observation.

Falter demonstrated that systems with (Sr_1-xPb_x)TiO_3 (SPT) (x = 0.30) and Bi_5TiO_14 (BT) (SPT:BT = 1:0, 0.98:0.02, 0.95:0.05, and 0.90:0.10 by volume) and with SPT and infiltrated phase (IP) (SPT:IP = 1:0, 0.994:0.006, 0.989:0.011, 0.984:0.016, and 0.965:0.035 by volume) showed similar Curie-Weiss constants, but the systems showed lower Curie-Weiss temperature as the content of the minor phases increased [108]. Payne demonstrated that the Curie-Weiss
<table>
<thead>
<tr>
<th>Description</th>
<th>Volume fraction $\delta_{\text{SPT}}:\delta_{\text{MgO}}$</th>
<th>CW constant $\delta_{\text{SPT}}$ ($^\circ$C)</th>
<th>CW temperature $\delta_{\text{SPT}}$ ($^\circ$C)</th>
<th>Volume fraction ratio $\delta_{\text{SPT}} / \delta_{\text{SPT}(0.99)}$</th>
<th>CW constant ratio $C/C_{\text{SPT}(0.99)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.99:0.01</td>
<td>$8.2 \times 10^4$</td>
<td>-47</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.945:0.055</td>
<td>$7.6 \times 10^4$</td>
<td>-48</td>
<td>0.95</td>
<td>0.93</td>
</tr>
<tr>
<td>3</td>
<td>0.90:0.10</td>
<td>$7.3 \times 10^4$</td>
<td>-51</td>
<td>0.91</td>
<td>0.89</td>
</tr>
</tbody>
</table>

CW, Curie-Weiss; C, Curie-Weiss constant; $\delta_{\text{SPT}(0.99)}$, Volume fraction of SPT (= 0.99); $C_{\text{SPT}(0.99)}$, Curie-Weiss constant of SPT ($\delta_{\text{SPT}} = 0.99$).
Table 4.2.5.5 Description of samples sintered in air and flowing oxygen (O₂) and dielectric properties at 10 kHz

<table>
<thead>
<tr>
<th>Description (Sintering condition)</th>
<th>Shape</th>
<th>Thickness (mm)</th>
<th>Area (mm²)</th>
<th>Density (g/cm³)</th>
<th>ε_r at T_m</th>
<th>T_m (°C)</th>
<th>C (°C)</th>
<th>θ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>Part of a disk</td>
<td>1.21</td>
<td>28.6</td>
<td>5.50</td>
<td>36700</td>
<td>-58</td>
<td>8.8 x 10^4</td>
<td>-50</td>
</tr>
<tr>
<td>flowing O₂</td>
<td>Disk</td>
<td>1.20</td>
<td>47.5</td>
<td>5.60</td>
<td>20000</td>
<td>-59</td>
<td>9.4 x 10^4</td>
<td>-53</td>
</tr>
</tbody>
</table>

Samples: (Sr₀.₈Pb₀.₂)TiO₃  
Area: Calculated from diameters of a sample measured by a scaler or obtained with a computer program after taking a picture of a sample on a scaled graph.  
Density: Obtained using the Archimedes method at an average of three results.  
ε_r, Relative permittivity; T_m, Transition temperature at 10 kHz upon cooling; C, Curie-Weiss constant; θ, Curie-Weiss temperature.

Table 4.2.5.6 Description of samples sintered at various temperatures and dielectric properties at 10 kHz

<table>
<thead>
<tr>
<th>Description (Sintering temperature (°C))</th>
<th>Shape</th>
<th>Thickness (mm)</th>
<th>Area (mm²)</th>
<th>Density (g/cm³)</th>
<th>ε_r at T_m</th>
<th>T_m (°C)</th>
<th>C (°C)</th>
<th>θ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1375</td>
<td>Part of a disk</td>
<td>1.15</td>
<td>43.2</td>
<td>5.67</td>
<td>41100</td>
<td>-58</td>
<td>9.1 x 10^4</td>
<td>-51</td>
</tr>
<tr>
<td>1350</td>
<td>Part of a disk</td>
<td>1.30</td>
<td>20.0</td>
<td>5.62</td>
<td>36100</td>
<td>-58</td>
<td>9.0 x 10^4</td>
<td>-50</td>
</tr>
<tr>
<td>1300</td>
<td>Disk</td>
<td>1.11</td>
<td>50.2</td>
<td>5.39</td>
<td>20600</td>
<td>-58</td>
<td>8.0 x 10^4</td>
<td>-50</td>
</tr>
<tr>
<td>1250</td>
<td>Part of a disk</td>
<td>0.96</td>
<td>28.2</td>
<td>5.43</td>
<td>9300</td>
<td>-48</td>
<td>7.4 x 10^4</td>
<td>-48</td>
</tr>
</tbody>
</table>

Samples: (Sr₀.₈Pb₀.₂)TiO₃  
Area: Calculated from diameters of a sample measured by a scaler or obtained with a computer program after taking a picture of a sample on a scaled graph.  
Density: Obtained using the Archimedes method at an average of three results.  
ε_r, Relative permittivity; T_m, Transition temperature at 10 kHz upon cooling; C, Curie-Weiss constant; θ, Curie-Weiss temperature.
constant of the system with BaTiO₃ (BTO) and NaNbO₃ (NN) (BTO:NN = 1.000:0.000, 0.995:0.005, 0.990:0.010, 0.970:0.030, 0.950:0.050, 0.925:0.075, and 0.900:0.100 by mole) decreased, and the Curie-Weiss temperature became lower as the contents of the NaNbO₃ increased [107]. Frey et al. observed a similar manner in the Curie-Weiss behavior of BaTiO₃ with fine grains [109]. These systems were interpreted by the simple serial diphasic model. Reasons are that the boundary layers of the major phase (component 1) would be covered with the minor phase (component 2) and that the field would be interrupted by the boundary layer between components 1 along the field. Furthermore, the contribution of the parallel component of the phase 2 would be low. Therefore, these systems were modeled as the serial mixing structure (Fig. 4.2.5.15). On the contrary, the boundary layers of the SPT in the composites (with SPT (x = 0.2) and MgO) might not be covered with the MgO. Thus the parallel model was suitable to explain the observed results (Fig. 4.2.5.15). SPT ceramics sintered at various temperature showed similar behaviors. (Sr₁₋ₓPbx)TiO₃ (SPT) (x = 0.20) sintered at a lower sintering temperature showed a lower Curie-Weiss constant, but the SPT showed similar Curie-Weiss temperature and transition temperature (Table 4.2.5.6) (see Sect. 3.4). The composites of which the MgO amount was 25 wt% or more than this value demonstrated that the influence of MgO more, and a lower Curie-Weiss constant and Curie-Weiss temperature might be due to this influence.

Table 4.2.5.7 lists the dimensions of the samples used for the parallel plate post dielectric resonator technique and the results of microwave dielectric properties. Although the samples measured at high frequencies were different from those measured at 10 kHz, both kinds of samples showed similar dielectric constants at low and high frequencies. Fig. 4.2.5.16 shows Q × frequency of the SPT and the composites. The characteristics of tangent δ behaviors at high frequency were similar to those at low frequency.

4.2.5.5 Additional work

The important objective of this study is to develop tunable materials at room temperature. Therefore, the DC bias dependence of relative permittivity at room temperature is preferable. In addition, dielectric properties at cryogenic temperature will add information to the tangent δ behavior around −200 °C.
Figure 4.2.5.15 Schematic diagram of serial and parallel mixing models.
(a) Component 1 is covered with component 2.
(b) Serial and parallel mixing sketch which represents (a).
(c) Serial mixing sketch which represent (a) and (b).
   In case, volume fraction $\times$ relative permittivity of component 2
   is negligible compared with that of component 1.
(d) Component 1 is not covered with component 2.
   Component 2 occupies a specific space.
(e) Parallel mixing sketch which relatively represents (c).
Component 1: major phase; Component 2: minor phase.
Table 4.2.5.7 Dielectric properties of (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ (SPT) and composites prepared from SPT and MgO measured using the parallel dielectric post resonator method

<table>
<thead>
<tr>
<th>Description</th>
<th>Weight ratio SPT:MgO</th>
<th>Diameter (Di) (mm)</th>
<th>Thickness (T)(mm)</th>
<th>Di/T</th>
<th>Freq (GHz)</th>
<th>$\varepsilon_r$</th>
<th>tan $\delta$</th>
<th>Q</th>
<th>Q × F (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1:0</td>
<td>1.041</td>
<td>0.511</td>
<td>2.04</td>
<td>1.17</td>
<td>1220</td>
<td>0.0031</td>
<td>320</td>
<td>370</td>
</tr>
<tr>
<td>1</td>
<td>0.995:0.005</td>
<td>1.069</td>
<td>0.540</td>
<td>1.98</td>
<td>1.19</td>
<td>1080</td>
<td>0.0192</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
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<td>1.060</td>
<td>0.539</td>
<td>1.97</td>
<td>1.23</td>
<td>1010</td>
<td>0.0192</td>
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</tr>
<tr>
<td>3</td>
<td>0.95:0.05</td>
<td>1.051</td>
<td>0.524</td>
<td>2.01</td>
<td>1.30</td>
<td>950</td>
<td>0.0179</td>
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<td>70</td>
</tr>
<tr>
<td>4</td>
<td>0.75:0.25</td>
<td>0.998</td>
<td>0.490</td>
<td>2.04</td>
<td>1.98</td>
<td>460</td>
<td>0.0101</td>
<td>100</td>
<td>200</td>
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<tr>
<td>5</td>
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<td>0.961</td>
<td>0.470</td>
<td>2.04</td>
<td>2.80</td>
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<td>0.0085</td>
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<tr>
<td>6</td>
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<td>0.947</td>
<td>0.470</td>
<td>2.01</td>
<td>3.60</td>
<td>150</td>
<td>0.0097</td>
<td>100</td>
<td>370</td>
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<tr>
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<td>0.0081</td>
<td>120</td>
<td>600</td>
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<tr>
<td>8</td>
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<td>0.910</td>
<td>0.465</td>
<td>1.96</td>
<td>7.90</td>
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<td>0.0070</td>
<td>140</td>
<td>1120</td>
</tr>
<tr>
<td>9</td>
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<td>0.896</td>
<td>0.448</td>
<td>2.00</td>
<td>14.33</td>
<td>11</td>
<td>0.0004</td>
<td>2830</td>
<td>40610</td>
</tr>
</tbody>
</table>
Figure 4.2.5.16 $Q \times$ frequency of $(\text{Sr}_{0.8}\text{Pb}_{0.2})\text{TiO}_3$ (SPT) ceramics and composites prepared from SPT and MgO measured using the parallel plate dielectric post resonator method.
4.3 Composite prepared from (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) and aluminum oxide (Al$_2$O$_3$) and their temperature independent dielectric properties

4.3.1 Introduction

As mentioned in Sect. 1.1, conventional microwave dielectrics are required to possess the following typical properties: i) reasonable relative permittivity, ii) low tangent $\delta$, namely, high $Q$ and iii) low temperature coefficient of resonant frequency, that is, low temperature dependence of relative permittivity [18]. However, tunable ferroelectrics are not usually considered to have the low temperature coefficient of relative permittivity. It is because that dielectric tunability depends on the relative permittivity of a sample and that it is preferable to select candidate materials which have sharp peaks in dielectric permittivity vs. temperature behaviors. In other words, the potential materials have high temperature coefficients of relative permittivity. In order to use the materials under a low tangent $\delta$ condition, the ferroelectrics are generally operated in the paraelectric regions. There are thin films which show tunability at high E-fields and also have reasonable temperature coefficients of capacitance, for example, Bi$_2$O$_3$-ZnO-Nb$_2$O$_5$ (BZN) pyrochlore films [110].

(Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) is a potential material for the tunable ferroelectrics (Sect. 3.2) and it has advantages over other perovskites, for example, most commonly used (Ba, Sr)TiO$_3$ system: i) easy processing of a homogeneous solid solution system with a specific transition temperature, ii) low tangent $\delta$, and iii) comparatively high DC bias field dependence of the dielectric constant at a low frequency in a paraelectric state. As described in the earlier section (Sect. 3.2), the pure phase SPT has very high relative permittivity in the desirable application temperature range. Therefore, the relative permittivity of SPT needs to be diluted to the range suitable for the device requirement, the impedance matching. In this section, aluminum oxide (Al$_2$O$_3$) is used as the second possible component to form composites to tailor the relative permittivity of the SPT. The reason is that Al$_2$O$_3$ is expected to have low reactivity with SPT since high density Al$_2$O$_3$ crucibles are often used for the preparation of lead containing ceramics. However, unlike magnesium oxide (MgO), the Al$_2$O$_3$ reacts with the SPT and the composites result in a multiphase tunable material. However, the composites show low tangent $\delta$ values in the paraelectric states, reasonable tunability, and the low temperature coefficients of relative permittivity over a $\sim$ 100 °C temperature range. This section will describe the characteristics of the composites prepared from SPT and Al$_2$O$_3$ such as their temperature independent dielectric behaviors.
4.3.2 Experimental

(Sr, Pb)TiO3 (SPT) compositions were prepared from strontium carbonate (99.9 %+ purity SrCO3; Aldrich), lead oxide (99.9% purity PbO; Aldrich) and titanium oxide (99.5% purity TiO2; Alfa Aesar) by mixing suitable ratios of Sr:Pb:Ti (0.7:0.3:1) with extra 0.02 mole lead oxide. The raw materials were ball milled for eight hours, and then calcined in a platinum dish which was in a saggar at 1100 °C for three hours. The reactant powders were ball milled again for 20 hours, and aluminum oxide (99.997% purity Al2O3, Alfa Aesar) was added and mixed with the calcined powders (SPT-Al2O3 (50:50 by weight)) for 4 h. After these procedures, an acrylic resin was added to the mixed powders as a binder. Pellets were formed under a uniaxial pressure and then pressed further under a cold isostatic pressure of 3000 kg/cm². The pellets were burned out up to 550 °C and sintered at 1350 °C for 3 h.

4.3.3 Results and discussion

The structural phases within samples were identified by their X-ray diffraction patterns (PDIV, SCINTAG, Inc). Fig. 4.3.1 (a) shows the X-ray diffraction pattern for the mixture of calcined (Sr1-xPbx)TiO3-SPT (x = 0.3) and Al2O3 powders, and Fig. 4.3.1 (b) shows the pattern on the sintered samples. X-ray diffraction pattern peaks were determined using the program, “PRO-FIT” [1]. In Fig. 4.3.1 (a), only two phases were observed distinctly and identified as the SPT and Al2O3. After sintering, X-ray diffraction peaks of Al2O3 could not be clearly identified and new unidentified peaks and possibly pure SPT peaks were observed. This suggests a new phase formation resulted in the composite samples. Candidate components reacted between Al2O3 and Pb (lead), Sr (strontium) and/or Ti (titanium) oxides are PbAl2O4, PbAl2O5, PbAl12O19, Pb5Al8O21, SrAl2O4, SrAl4O7, SrAl12O19, Sr3Al2O6, Sr3Al2O51, Sr4Al14O25, Sr5Al2O8, Sr7Al12O25, Sr9Al6O18, Sr1.33Pb0.67Al6O11, Pb8.6Sr0.4Al8O21, and SrTi3Al8O19 based on PDF files [111, 111a]. Among the chemicals, SrAl12O19, PbAl2O19, and/or Sr3Al32O51 would be the possible candidate composites (Table 4.3.1), and the possibility of forming hexaaluminate family compounds such as SrAl12O19 is high (Fig. 4.3.2). A possible reaction could be as follows:

(Sr1-xPbx)TiO3+6y Al2O3 = (1-y) (Sr1-xPbx)TiO3+(1-x)y SrAl12O19+xy PbAl12O19

(4.3.1)

Another possibility of a minor material in the new phase is PbO (some of PbO in PDF files did not match the results), PbO2, Pb3O4, TiO2 (some of TiO2 in PDF files did not match the results), SrAl4O7, Sr3Al2O6, Sr4Al14O25, Sr9Al6O18, SrTi3Al8O19, SrTiO3 among various candidate chemicals, namely, PbO, PbO4 (x = 1.57, 1.55, 1.44, and 1.37), PbO2, Pb3O2 (x = 0.98, 0.986,
Figure 4.3.1 Room temperature Cu Kα X-ray diffraction patterns of (a) the mixture of calcined (Sr₀.7Pb₀.3)TiO₃ (SPT) and aluminum oxide (Al₂O₃ (A)) and (b) sintered pellet prepared from SPT and Al₂O₃.
Table 4.3.1 Comparison of a new phase resulted from the reaction between (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) ($x = 0.3$) and aluminum oxide (Al$_2$O$_3$) (measurement conditions: Cu K$_{\alpha}$, 20-70° 2θ)  
Al$_2$O$_3$ max intensity of the new phase/max intensity of the SPT phase = 0.22

<table>
<thead>
<tr>
<th>Description</th>
<th>Peak position (deg in 2θ) and relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>New phase</td>
<td>60.0 (100) 34.0 (90) 36.2(78) 42.7 (57) 58.5 (56)</td>
</tr>
<tr>
<td>New phase</td>
<td>(22) (20) (17) (13) (12)</td>
</tr>
<tr>
<td>[SPT based]</td>
<td></td>
</tr>
<tr>
<td>SPT phase</td>
<td>32.3 (100) 57.6 (51) 46.4(40) 39.8 (23) 22.7 (11)</td>
</tr>
</tbody>
</table>

SrAl$_{12}$O$_{19}$  
26-976, i  
70-947, C  
80-1195, C  

PbAl$_{12}$O$_{19}$  
20-558, i or ★  
80-1174, C  

Sr$_3$Al$_{32}$O$_{51}$  
2-964  

<table>
<thead>
<tr>
<th>Description</th>
<th>Peak position (deg in 2θ) and relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrAl$<em>{12}$O$</em>{19}$</td>
<td>36.04 (100)* 33.86 (95) * 42.61 (70)* 32.00(50)** 59.94(55)*</td>
</tr>
<tr>
<td>70-947, C</td>
<td>36.17 (99.9)* 42.78 (73.5)* 34.07 (71.6)* 67.28(69.5)** 32.16(66.2)**</td>
</tr>
<tr>
<td>80-1195, C</td>
<td>36.14 (99.9)* 34.02 (89.1)* 42.74 (67.9)* 60.06 (57.2)* 32.14 (48.7)**</td>
</tr>
<tr>
<td>PbAl$<em>{12}$O$</em>{19}$</td>
<td>34.10 (100)* 36.21 (85)* 18.87 (90) * 32.20 (70)** 42.78 (55)**</td>
</tr>
<tr>
<td>20-558, i or ★</td>
<td>36.10 (99.9)* 18.81 (90.7)* 33.97 (89.1)* 42.69 (58.8)* 32.11 (56.5)**</td>
</tr>
<tr>
<td>80-1174, C</td>
<td>36.10 (99.9)* 18.81 (90.7)* 33.97 (89.1)* 42.69 (58.8)* 32.11 (56.5)**</td>
</tr>
<tr>
<td>Sr$<em>3$Al$</em>{32}$O$_{51}$</td>
<td>33.93 (100)* 36.19 (100)* 42.82 (100)* 45.07 (100)* 58.56 (100)*</td>
</tr>
</tbody>
</table>

Note: * Observed in the new phase, ** Observed in the new phase, but unclear due to higher intensity peak of SPT next to the new phase peaks.

New phase and SPT phase were analyzed using “PRO-FIT.” ref.: Toraya [1].

( ) : %relative intensity based on the maximum intensity of a specimen.  
[SPT based]; Relative intensity based on the maximum intensity of the SPT phase.  
Relative intensity of New phase and SPT phase were based on an area of each peak.

A number below a chemical formula is PDF number. ⋆, i, C, or no mark (blank) is the qualities of data. ⋆: indexed and measured intensity objectively. i: Indexed; required quality is lower than that for a specimen marked as ⋆. No mark or blank: not indexed; quality could be good, but not confirmed. C: calculated data; required quality is the same as that for a specimen with ⋆.  
ref: PDF [111].

PbAl$_{12}$O$_{19}$, 20-558; ⋆ was noted in the literature (Powder diffraction: file Set3 19-20, JCPDS, USA(1979)) and i was noted in the literature (Powder diffraction file PDF: Alphabetical indexes for experimental patterns: Inorganic phases sets I-51, ICDD, USA(2001)).
Figure 4.3.2 Comparison of room temperature Cu Kα X-ray diffraction (XRD) patterns of (a) the sintered pellet prepared from (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.3) and Al$_2$O$_3$, (b) a number of SPT peaks refined using PRO-FIT*, (c) SPT calculated based on the lattice parameter, 3.917 Å, with CaRIne Crystallography 3.1 (developed by C. Boudias and D. Monceau), (d) selected peaks in the new phase refined using PRO-FIT*, (e) SrAl$_{12}$O$_{19}$ (PDF#, 26-976, i), (f) SrAl$_{12}$O$_{19}$ (PDF#, 80-1195, C), (g) PbAl$_{12}$O$_{19}$ (PDF#, 20-558, i)**, (h) PbAl$_{12}$O$_{19}$ (PDF#, 80-1174, C), and (i) Sr$_3$Al$_{32}$O$_{51}$ (PDF#, 2-964, i).

★, i, C, or no mark (blank) is the quality of data. ★: indexed and measured intensity objectively. i: Indexed; required quality is lower than that for a specimen marked as ★. No mark or blank: not indexed; quality could be good, but not confirmed; C: calculated data; required quality is the same as that for a specimen with ★. ref: PDF [111].

*Toraya [1].

**[111]. ★ was noted in the literature (Powder diffraction: file Set 3, 19-20, JCPDS, USA(1979)) and i was noted in the literature (Powder diffraction file PDF: Alphabetical indexes for experimental patterns: Inorganic phases sets 1-51, ICDD, USA(2001)).
0.97, and 0.958), Pb₂O, Pb₂O₃, Pb₂O₃.₃₃, Pb₃O₄, Pb₅O₈, SrO, SrO₂, TiO, TiO₂, Ti₂O, Ti₂O₃, Ti₃O₅, Ti₆O₁₁, Ti₇O₁₁, Ti₈O₁₅, PbTiO₃, PbTi₃O₇, and the chemicals described the above [111b].

The dielectric properties of a suitably cut and polished sample were measured using an LCR meter (4284A, Hewlett Packard) with or without the electric DC bias upon cooling. The thermal hysteresis measurements were carried out in both cooling and heating cycles. The LCR meter and an oven were controlled by computer interfaces. Fig. 4.3.3 shows dielectric properties of the sintered composites at 10 k, 100 k, and 1 MHz. In the ferroelectric and paraelectric regions near the transition temperature, the dielectric permittivity showed a frequency dependence, but a dispersion behavior was not apparent in a region far from the transition temperature. The tangent δ values were around 0.005 and less than 0.005 in the temperature range between 150 and 40 °C. The temperature coefficients of relative permittivity were ~ 700 ppm at 10 kHz over the same temperature range. Fig. 4.3.4 shows the dielectric behaviors of the composites as a function of temperature at 10 kHz in cooling and heating cycles, and very small differences in the dielectric values in the paraelectric region were observed. It could be due to the complex interaction between the SPT and the new phases in the composite samples. In the earlier studies on the SPT and MgO composites, this hysteresis characteristic, in paraelectric regions far from the transition temperatures, was not observed (Sect. 4.2). Because the dielectric losses in the samples were small and reproducible, the good quality of the samples would be suggested.

Figs. 4.3.5 and 4.3.6 show the effect of applied DC bias fields on the relative permittivity and the calculated dielectric tunability as a function of an applied DC bias field at various temperatures, respectively. Dielectric tunability was calculated by Eq. (4.3.2)

\[
\% \text{dielectric tunability} = \frac{\varepsilon(E_o) - \varepsilon(E)}{\varepsilon(E_o)} \times 100
\]

(4.3.2)

where \(\varepsilon(E_o)\) is dielectric constant at the zero field (of the last run) and \(\varepsilon(E)\) is dielectric constant at a DC bias field of E.

Typically, 5 % dielectric tunability was obtained at 20 kV/cm over the wide temperature range from 150 to 40 °C. Reference zero field dielectric constants (of the last runs) were chosen for the calculation of tunability. At higher fields ~ 40 kV/cm, the tunability values increased to 10 % between 150 and 90 °C (Fig. 4.3.7 (a)), and tangent δ remained the same under applied DC bias fields (Fig. 4.3.7 (b)). Below ~ 90 °C, the sample could not stand high fields of 40 kV/cm.

Above ~ 100 °C, initial tunabilities showed negative values since the dielectric constants of initial runs were higher than those of the last runs. Because initial dielectric constant values
Figure 4.3.3 Dielectric properties of composites prepared from \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) (SPT) and aluminum oxide \((\text{Al}_2\text{O}_3)\) as a function of temperature and frequency.

Figure 4.3.4 Dielectric properties of composites prepared from \((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) (SPT) and aluminum oxide \((\text{Al}_2\text{O}_3)\) as a function of temperature at 10 kHz in both cooling and heating cycles.
Figure 4.3.5 Dielectric properties of composites prepared from (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) and aluminum oxide (Al$_2$O$_3$) as a function of temperature and applied DC bias field at 10kHz.
Temperature range: from 150 to 40 $^\circ$C.
Shown data were at $-20$, $-15$, $-10$, $-5$, and 0 kV/cm in all applied fields (0 - 20 - $-20$ - 0 kV/cm, 5kV/cm as a step field).
Figure 4.3.6 Dielectric tunability of composites prepared from (Sr$_{0.7}$Pb$_{0.3}$)TiO$_3$ (SPT) and aluminum oxide (Al$_2$O$_3$) as a function of applied DC bias field and temperature. (0, 5, 10, 15, 20, 15, 10, 5, 0, -5, -10, -15, -20, -15, -10, -5, and 0 kV/cm). (a) from 150 to 100 °C and (b) from ~90 to 40 °C.
Figure 4.3.7 (a) Dielectric tunability and (b) relative permittivity and tangent δ of composites prepared from (Sr0.7Pb0.3)TiO3 (SPT) and aluminum oxide (Al2O3) as a function of applied DC bias field and temperature. DC fields applied: 0, 10, 20, 30, 40, 30, 20, 10, 0, -10, -20, -30, -40, -30, -20, -10, and 0 kV/cm.
were smaller than final values below ~ 100 °C, positive tunabilities were noted. This could be because the main phase became ferroelectric below ~ 100 °C. In addition, the hysteresis was apparently observed. D-E hysteresis measurement could help to understand these behaviors.

Microstructural analysis was carried out with gold-coated fracture surfaces of sintered composites by scanning electron microscope, SEM (S-3500N, Hitachi). Fig. 4.3.8 shows SEM micrographs obtained to detect secondary electrons with three notable features: i) image (a) consists of particles, ii) image (b) has particles and continuous phases, and iii) image (c) shows continuous phases.

As shown in Fig. 4.3.1 the reactions of the SPT with the Al₂O₃ during the sintering resulted in new phases. This feature could influence the stoichiometry of the SPT (x = 0.3 before sintering) and also give the varying amount of magnetoplumbite family compounds. Apparently, the new phases fabricated from the SPT and Al₂O₃ might not contribute to the loss tangents. Hexaaluminate compositions in general are not ferroelectric, and there is a family which shows low tangent δ, for example, LaMgAl₁₁O₁₉ (relative permittivity, \( \varepsilon_r = 14 \), tangent δ = 0.00015 at 90 K and at 10 kHz [112]; \( \varepsilon_r = 11 \), tangent δ = the order of 10⁻³ at room temperature (RT) and at radio frequencies (rf) [113, 114]; \( \varepsilon_r = 14 \), tangent δ = 0.00025 at 300 K and at 7 GHz [115]), NdGaMgAl₁₀O₁₉ (\( \varepsilon_r = 16 \), tangent δ = 0.00018 at 90 K and at 10 kHz [112]; \( \varepsilon_r = 15 \), tangent δ = the order of 10⁻³ at RT and at rf [113, 114]), CaGa₆Al₆O₁₉ (\( \varepsilon_r = 16 \), tangent δ = 0.00018 at 90 K and at 10 kHz [112]; \( \varepsilon_r = 15 \), tangent δ = the order of 10⁻³ at RT and at rf [113, 114]). Thus the new magnetoplumbite phase is expected to have low tangent δ. Moreover, the remaining fraction of the SPT did dominate the dielectric tunability of the composites. Overall, the variations of the SPT compositions and the negative temperature coefficients of dielectric constant of the SPT and with a positive (or small negative) temperature coefficient of dielectric permittivity of the new hexaaluminate phases have balanced the resulted low temperature coefficients in the composite.

Similar composites containing the SPT and MgO showed the values of dielectric constant, more than 200 at around the transition temperatures (Sect. 4.2) and high temperature coefficients of relative permittivity. The composites prepared from the SPT and Al₂O₃ showed low dielectric constant ~ 100 around the dielectric constant maximum, low tangent δ, and low tunability. The interesting features of these composites are temperature independence of both relative permittivity and dielectric tunability over the wide temperature range of 150 ~ 40 °C.

This system did not show reproducible dielectric behavior such as low temperature coefficients of relative permittivity among samples prepared under similar conditions. Therefore,
Figure 4.3.8 Scanning electron microscope (SEM) study: micrographs of the typical fracture surfaces of composites prepared from (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) ($x = 0.3$) and aluminum oxide (Al$_2$O$_3$) obtained to detect secondary electrons.
critical processing conditions will be required to achieve reproducible results. Additionally, (Sr_{0.8}Pb_{0.2})TiO_3 was also tried to make transition temperatures of the composites below room temperature, but the composites still showed the transition temperatures above room temperature. Additional studies will be needed to develop practical composites with low temperature coefficient of relative permittivity and reasonable tunability over a wide temperature range.

4.3.4 Conclusions

Partially reacted (Sr_{1-x}Pb_{x})TiO_3, SPT with Al_2O_3 composites showed dielectric permittivity ~ 100, tangent δ ~ 0.005, dielectric tunability ~ 5 % at 20 kV/cm over the temperature range from 150 to 40 °C along with the low temperature coefficients of relative permittivity of ~ 700 ppm at 10 kHz. Dielectric tunability increased 10 % under 40 kV/cm. The x-ray diffraction pattern showed the presence of the SPT and reacted materials, possibly hexaaluminate compounds.
4.4 (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) based composites with oxides besides magnesium oxide (MgO)

4.4.1 Introduction

Tunable ferroelectrics have been attractive due to the vast possibility of their applications. Composites with (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.2) and magnesium oxide (MgO) did not show obvious reactions between two components. The composites showed reasonable tunability and relatively low tangent $\delta$ at a low frequency such as 10 kHz. Although composites prepared from SPT (x = 0.3) and aluminum oxide (Al$_2$O$_3$) showed the reaction between two components, the composites showed the low temperature coefficients of relative permittivity and almost constant tunability over a wide temperature range. Objectives to prepare composite systems are as follows: i) to tailor the dielectric constant of the pure SPT system and ii) to develop low tangent $\delta$ systems by the addition of oxides. Consequently, the possible oxides to tailor the relative permittivity of the SPT system should be selected among microwave dielectric oxides because these oxides would show low dielectric constant and low tangent $\delta$. Table 4.4.1 lists the dielectric properties of candidate oxides [106, 116-119]. In this section, the studies to develop tunable ferroelectrics based on SPT will be further extended to explore the effects of other oxides such as magnesium aluminum oxide (MgAl$_2$O$_4$), tin oxide (SnO$_2$), or zirconium oxide (ZrO$_2$).

4.4.2 Experimental

(Sr, Pb)TiO$_3$ (SPT) compositions were prepared from strontium carbonate (99.9% purity SrCO$_3$, Aldrich), lead oxide (99.9% purity PbO, Aldrich), and titanium oxide (99.5% purity TiO$_2$, Alfa Aesar) by mixing suitable ratios of Sr-Pb-Ti (0.8:0.2:1) with extra 0.02 mol% PbO. The raw materials were ball milled for 8 h, and then calcined in a platinum dish placed in a saggar at 1100 °C for 3 h. The reactant powders were ball milled again for 20 h. Al$_2$O$_3$ (99.997% purity, Alfa Aesar), MgAl$_2$O$_4$ (i: 99% purity, Alfa Aesar; ii: 99.985% purity, Alfa Aesar), SnO$_2$ (99.996% purity, Alfa Aesar), ZrO$_2$ (99.978% purity, Alfa Aesar), or the mixture of MgO and ZrO$_2$ (MgO-ZrO$_2$ (90:10 by weight) was added and mixed with the calcined SPT powders (SPT-Oxide(s) (50:50 by weight)) for 4 h. After these procedures, pellets were formed using a cold isostatic pressure of 2000 kg/cm$^2$ except for the composites prepared from the mixture of MgO and ZrO$_2$ (2500 kg/cm$^2$). The samples were heated to remove water up to 300 °C and then sintered at 1350 °C for 3 h.

Approximate chemistries of the composites were estimated by their X-ray diffraction (XRD)-patterns using Cu $K_\alpha$ as an X-ray source (PDIV, SCINTAG, Inc.).
Table 4.4.1 Dielectric properties of oxides used for the preparation of composite samples

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Form</th>
<th>Relative permittivity</th>
<th>Tangent $\delta$ ($= 1/Q$)</th>
<th>Q</th>
<th>Frequency (GHz)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}<em>{2}\text{O}</em>{3}$&lt;sup&gt;1)&lt;/sup&gt;</td>
<td>Single crystal</td>
<td>10</td>
<td>$1 \times 10^{-5}$</td>
<td>100000</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>$\text{Al}<em>{2}\text{O}</em>{3}$&lt;sup&gt;2)&lt;/sup&gt;</td>
<td>Polycrystalline</td>
<td>10</td>
<td>$2 \times 10^{-5}$</td>
<td>50000</td>
<td>10</td>
<td>----</td>
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<tr>
<td>$\text{MgAl}<em>{2}\text{O}</em>{4}$&lt;sup&gt;3)&lt;/sup&gt;</td>
<td>Polycrystalline</td>
<td>8.3</td>
<td>$1 \times 10^{-4}$</td>
<td>10000</td>
<td>35</td>
<td>----</td>
</tr>
<tr>
<td>$\text{SnO}<em>{2}$·$\text{TiO}</em>{2}$&lt;sup&gt;4)&lt;/sup&gt;</td>
<td></td>
<td>43</td>
<td>$2.22 \times 10^{-4}$</td>
<td>4500</td>
<td>7</td>
<td>----</td>
</tr>
<tr>
<td>$\text{TiO}_{2}$&lt;sup&gt;2)&lt;/sup&gt;</td>
<td>Polycrystalline</td>
<td>100</td>
<td>$6.25 \times 10^{-5}$</td>
<td>16000</td>
<td>3</td>
<td>----</td>
</tr>
<tr>
<td>$\text{ZrO}_{2}$&lt;sup&gt;5)&lt;/sup&gt;</td>
<td>Polycrystalline (Monoclinic)</td>
<td>17.9</td>
<td>$7 \times 10^{-4}$</td>
<td>1429</td>
<td>X-band</td>
<td>----</td>
</tr>
<tr>
<td>$\text{MgO}$&lt;sup&gt;1)&lt;/sup&gt;</td>
<td>Single crystal</td>
<td>9</td>
<td>$1 \times 10^{-5}$</td>
<td>100000</td>
<td>10</td>
<td>300</td>
</tr>
</tbody>
</table>

1) Alford et al. [106].
2) Alford et al. [116].
3) Nazaré et al. [117].
4) Wakino et al. [118].
5) Lanagan et al. [119].
Lower frequency dielectric properties were obtained to measure gold-coated samples using an LCR meter (HP 4284A), and higher frequency measurements were carried out with samples which did not have electrodes on the samples using the parallel plate dielectric post resonator method [39, 42].

4.4.3 Results

Fig. 4.4.1 shows X-ray diffraction (XRD) patterns of composites prepared from (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) (x = 0.2) and the oxides, Al$_2$O$_3$, MgAl$_2$O$_4$, SnO$_2$, ZrO$_2$, or the mixture of MgO and ZrO$_2$ [104]. Table 4.4.2 summarizes the XRD results on the composites. The composites prepared from MgAl$_2$O$_4$ remained the SPT in the sintered composites. However, the composites prepared from the other oxides might not have the same SPT compositions in the sintered composites. The composites prepared from SnO$_2$ or ZrO$_2$ showed the shift of SPT peak positions.

Fig. 4.4.2 shows the dielectric properties of composites prepared from various oxides, namely, Al$_2$O$_3$, MgAl$_2$O$_4$ (99% purity), SnO$_2$, or ZrO$_2$. Table 4.4.3 summarizes the room temperature dielectric properties of the composites at 10 kHz and at high frequencies. Fig. 4.4.3 shows the dielectric tunability of the composites prepared with SnO$_2$ or ZrO$_2$. The composites prepared from (Sr$_{1-x}$Pb$_x$)TiO$_3$ (x = 0.2) and Al$_2$O$_3$ became somewhat conductive, and the DC bias measurements failed. Although MgAl$_2$O$_4$ based composites were in the paraelectric state at room temperature, DC bias measurements did not succeed because these composites would be conductive. Composites prepared from higher purity MgAl$_2$O$_4$ (99.9% purity) showed lower tangent $\delta$ at room temperature. Impurity would be the source of tangent $\delta$ values. DC bias dependent dielectric properties have not been carried out due to the lack of funding and time.

The composites based on SnO$_2$ or ZrO$_2$ showed tunability $\sim$ 0.02 at 25 °C as a frequency of 10 kHz with a DC field of 20 kV/cm. The SnO$_2$ based composites showed hysteresis over the applied DC bias field range used. The lower density SPT-MgO composites tended to show this type of behavior. Therefore, the connectivity between two phases could contribute to this hysteresis behavior (Sect. 4.2.3). The ZrO$_2$ based composites also showed hysteresis at low DC bias fields. However, this hysteresis behavior was not observed in the well prepared SPT-MgO composites. Thus further investigation on processing to prepare high quality samples (e.g., high density samples) will reduce this hysteresis behavior.

In conclusion, it is possible to prepare low relative permittivity composites of SPT with various oxides such as Al$_2$O$_3$, MgAl$_2$O$_4$, SnO$_2$, and ZrO$_2$. From the X-ray powder diffraction
Figure 4.4.1 (a) X-ray diffraction patterns of composites prepared from (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ (SPT) and various oxides.

(i) Sintered composites from SPT and Al$_2$O$_3$ (A), Sintered SPT, and Al$_2$O$_3$ chemicals.
(ii) Sintered composites from SPT and MgAl$_2$O$_4$ (MA), Sintered SPT, and MgAl$_2$O$_4$ chemicals.
(iii) Sintered composites from SPT and SnO$_2$ (S), Sintered SPT, and SnO$_2$ chemicals.
(iv) Sintered composites from SPT and ZrO$_2$ (Z), Sintered SPT, and ZrO$_2$ chemicals.

SPT* : SPT which showed changes in peak positions.
*: peaks which indicated materials resulted from reactions.
sh: shoulder peak.
Figure 4.4.1 (b) X-ray diffraction patterns of composites prepared from (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ (SPT) and various oxides.
(i) Sintered composites from SPT, MgO (M), and ZrO$_2$ (Z)  (ii) Sintered pure SPT, (iii) MgO chemicals, and (iv) ZrO$_2$ chemicals.
SPT:M:Z were in 10:9:1 formulation by weight before sintering.
SPT*: SPT which might show peak position changes.
*: peaks which indicated materials resulted from reactions.
<table>
<thead>
<tr>
<th>Oxide used</th>
<th>Purity$^1)$ (%)</th>
<th>Size$^1)$ (µm)</th>
<th>Observation of peaks</th>
<th>Additional peaks</th>
<th>Expected chemicals in the composites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>99.997</td>
<td>110</td>
<td>Observed (Could be)</td>
<td>Not observed</td>
<td>(SPT) + Reacted one</td>
</tr>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>99</td>
<td>-325 mesh</td>
<td>Observed</td>
<td>Observed</td>
<td>SPT+MgAl$_2$O$_4$+Reacted one</td>
</tr>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>99.985</td>
<td>&lt; 1</td>
<td>Observed</td>
<td>Observed</td>
<td>SPT+MgAl$_2$O$_4$+Reacted one</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>99.996</td>
<td>-22 mesh</td>
<td>Unclear$^2)$</td>
<td>Observed</td>
<td>(Reacted)SPT + SnO$_2$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>99.978</td>
<td>--------------</td>
<td>Unclear$^2)$</td>
<td>Observed</td>
<td>(Reacted)SPT + ZrO$_2$</td>
</tr>
<tr>
<td>MgO+ZrO$_2$</td>
<td>-------</td>
<td>--------------</td>
<td>Unclear$^2)$</td>
<td>Observed (MgO)</td>
<td>(Reacted) SPT +MgO +Reacted one</td>
</tr>
<tr>
<td>MgO</td>
<td>99.998</td>
<td>-22 mesh</td>
<td>Observed</td>
<td>Not observed</td>
<td>SPT+MgO</td>
</tr>
</tbody>
</table>

$^1)$ Alfa Aesar catalog [104].
$^2)$ The shifts of SPT peak positions were observed. Otherwise, additional peaks were not observed.
Figure 4.4.2 Relative permittivity and tangent δ of composites fabricated from (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ (SPT) and various oxides as a function of temperature and frequency. (a) Al$_2$O$_3$, (b) MgAl$_2$O$_4$, (99% purity), (c) SnO$_2$, and (d) ZrO$_2$ as the oxide which was added to SPT to make composites. SPT:Oxide in all the composites were in 50:50 formulation by weight before sintering.

Figure 4.4.3 Dielectric tunability of composites fabricated from (Sr$_{0.8}$Pb$_{0.2}$)TiO$_3$ (SPT) and (a) SnO$_2$ and (b) ZrO$_2$ as a function of temperature and DC bias field at 10 kHz upon cooling.
<table>
<thead>
<tr>
<th>Oxide used</th>
<th>purity (%)</th>
<th>size (µm)</th>
<th>10kHz &amp; 24°C</th>
<th>high frequency &amp; 24°C</th>
<th>freq. (GHz)</th>
<th>Q × freq (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>relative permittivity</td>
<td>tan δ</td>
<td>relative permittivity</td>
<td>tan δ</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>99.997</td>
<td>110</td>
<td>~70</td>
<td>~0.005</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>MgAl₂O₄</td>
<td>99</td>
<td>-325 mesh</td>
<td>~80</td>
<td>~0.017</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>MgAl₂O₄</td>
<td>99.9</td>
<td>&lt; 1</td>
<td>~75</td>
<td>~0.002</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>~160</td>
<td>~0.001</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>SnO₂</td>
<td>99.996</td>
<td>-22 mesh</td>
<td>~110</td>
<td>~0.0008</td>
<td>~100</td>
<td>0.007</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>99.978</td>
<td>----------</td>
<td>~50</td>
<td>~0.0005</td>
<td>~40</td>
<td>0.006</td>
</tr>
<tr>
<td>MgO+ZrO₂</td>
<td>----------</td>
<td>----------</td>
<td>-----</td>
<td>~20*</td>
<td>0.003*</td>
<td>10.14*</td>
</tr>
</tbody>
</table>

Low and high frequency dielectric measurements were carried out using different samples.

* : Measurement at 22 °C.
patterns, the reactions between the oxide and SPT were inferred. The SnO$_2$ or ZrO$_2$ based composites showed ~ 0.02 as tunability at 25 °C and a frequency of 10 kHz with a DC field of 20 kV/cm (i.e., the reference field to compare various materials). These values were similar to those of the SPT-MgO composites under the same conditions. In the microwave measurements using the parallel plate dielectric post resonator (Sect. 4.2.4), the SnO$_2$ and ZrO$_2$ based composites showed Q × frequency values of ~ 500 GHz and ~1300 GHz, respectively.

4.4.4 Additional studies

DC bias measurements of the composites with SPT and MgAl$_2$O$_4$ (99.9% purity) and composites prepared with SPT, MgO, and ZrO$_2$ will be preferable to be carried out in the future.
4.5 References


[38] ASTM D150-98: Standard test methods for AC loss characteristics and permittivity (dielectric constant) of solid electrical insulation.
[43] G. Kent, Instruction manual resonant mode dielectricmeter Model RMD-C-080;100;150 software RMDSFT V7.5, revised 7/98.


[105] PDF# 45-0946, ICDD, PA, USA.
[111] PDF Alphabetical indexes for experimental patterns, Inorganic phases, Sets 1-53, ICDD, PA, USA.

PbAl2O4 (PDF number, PDF quality mark: 19-673, i and 83-1016, C); PbAl2O5 (19-672, i); PbAl2O19 (20-558, i, and 80-1174, C); Pb9Al8O21 (73-1875, C); SrAl2O4 (34-379, ★, 74-794, C); SrAl2O7 (25-1289, i; 72-1252, C; 76-...
839, C); SrAl12O19 (26-976, i; 70-947, C; 80-1195, C); Sr3Al2O6 (24-1187, ★; 28-1203; 81-506, C); Sr3Al32O51 (2-
964); Sr4Al14O25 (52-1876, C; 74-1810, C; 89-8206, C); Sr5Al2O8 (10-65); Sr7Al12O25 (76-497, C; 83-2427, C);
Sr9Al6O18 (79-1094, C); Sr1.33Pb0.67Al6O11 (76-1202, C); Pb8.6Sr0.4Al8O21 (75-2009, C); SrTi3Al8O19 (37-1231, i; 81-
1652)

Possible minor chemicals: PbO (PDF number, PDF quality mark: 65-2826, C); PbO2 (41-1492, ★; 73-851,C; 76-
564, C; 89-1947); Pb3O4 (89-1947, C); TiO2 (21-1272, ★); SrAl4O7 (76-839, C); Sr3Al2O6 (24-1187, ★; 28-1203, B;
81-506, C); Sr4Al14O25 (52-1876, ★;74-1810, C); Sr9Al6O18 (79-1094, C); SrTi3Al8O19 (37-1231, i; 81-1652); SrTiO3 (35-734, ★).

Chemicals checked: PbO (38-1477, ★; 65-129,C; 65-399, C; 65-1471, C; 65-2809, C; 72-93, C; 72-94, C; 72-151,
C; 77-1971, C; 78-1663–6, C; 85-711, C; 85-1278, C; 85-1288, C–2, C; 85-1414, C; 85-1739, C; 88-1589, C );
PbOx (x=1.57, 26-577, i; x=1.55, 27-1200, i; x=1.44, 27-1201, i; x=1.37, 27-1202, i); PbO2 (37-517, C; 45-1416, I;
72-2102, C; 72-2440, C; 89-7387, C); Pb3O4 (41-1493, ★; 65-2851, C; 71-561, C; 73-532, C; 76-1799, C); Pb3O5 (52-772, ★); SrO (6-520,
★; 43-1031, C; 48-1477, C; 74-1277, C; 75-263, C); Sr2O3 (1-1113, i; 7-234, I;65-2652, C; 73-1740, C); TiO (23-1078, i; TiO2
(21-1272, ★; 21-1276, ★; 29-1360, ★; 53-619, ★; 65-190, C); Ti2O (11-218, i); Ti2O3 (10-63, ★); Ti3O5 (40-806, ★);
Ti6O11(18-1401, i); Ti7O13 (18-1403, i); Ti8O15 (18-1404); PbTiO3 (6-452, ★; 48-105, ★; 78-299, C); PbTi3O7
(45-533, C).

(PDF quality mark: ★, Quality data: i, Indexed; required quality is lower than that for a ★ marked specimen; No
mark or blank, Not indexed; quality could be good; O, Doubtful quality; D, Deleted; C, Calculated data; required
quality is the same as a ★ marked specimen)

[112] L. E. Cross, R. Roy, and A. S. Bhalla, Low loss substrates for microwave applications and sol-gel processing
[113] M. Yao, A study on magnetoplumbite structural materials as potential substrates for high Tc superconducting
Japanese).
Chapter 5
SUMMARY

5.1 Introduction
This section will summarize the development of tunable materials and composites based on \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT). It will also summarize the basic studies of SPT and doped SPT. The basic studies will cover the sources of relative permittivity of the relative permittivity vs. temperature behaviors and tangent \(\delta\) of the tangent \(\delta\) vs. temperature behaviors, a deviation from the Curie-Weiss law observed in the pure SPT ceramics, and the relaxation behavior of the doped SPT ceramics.

5.2 Development of tunable materials based on \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT) ferroelectrics
In order to develop direct current (DC) bias field dependant materials for microwave tunable applications, the solid solutions between lead titanate and strontium titanate, SPT, was selected as a source component. The SPT solid solutions were prepared using the conventional mixed oxide method.

5.2.1 Properties of SPT \((x = 0.2, 0.25, \text{ and } 0.3)\) at low frequency
The SPT \((x = 0.2, 0.25, \text{ and } 0.3)\) ceramics showed similar Curie-Weiss constant values \(1 \times 10^5\) \(^\circ\text{C}\) and thermal expansion coefficients \(1 \times 10^{-5}\) \(^\circ\text{C}^{-1}\). The transition temperatures of the SPT, –59, –24, and 10 \(^\circ\text{C}\), were measured on the compositions with \(x = 0.2, 0.25, \text{ and } 0.3\), respectively, and transition temperatures were linearly proportional to the mole fraction of lead (Pb), \(x\) in \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\). Room temperature dielectric tunability (DC field dependence of relative permittivity) of 3, 15, and 70 %, respectively, was measured on samples with \(x = 0.2, 0.25, \text{ and } 0.3\) at a frequency of 10 kHz with a DC bias field of 20 kV/cm (the reference field to compare various candidate materials). The tangent \(\delta\) values, less than 0.001, were measured at 25 \(^\circ\text{C}\) and at 10 kHz on all these samples. Furthermore, the SPT \((x = 0.2, 0.25, \text{ and } 0.3)\) showed similar dielectric behaviors in the paraelectric states. The study suggested the potentiality of the \((\text{Sr}, \text{Pb})\text{TiO}_3\) system for the field tunable devices. It was noted that the \((\text{Sr}, \text{Pb})\text{TiO}_3\) in bulk forms was easier to prepare compared to \((\text{Ba}, \text{Sr})\text{TiO}_3\).
5.2.2 Properties of SPT (x = 0.2 and 0.3) at high frequency

The dielectric properties of the SPT (x = 0.2 and 0.3) at high frequencies were measured based on the parallel plate dielectric post resonator method, the Hakki-Coleman method. The tangent $\delta$ of the SPT showed a discrepancy between high and low frequency data (e.g., SPT (x = 0.2): tangent $\delta = 0.001$ at 1.2 GHz, tangent $\delta < 0.0005$ at 10 kHz; SPT (x = 0.3): tangent $\delta = 0.009$ at 0.45 GHz, tangent $\delta = 0.0005$ at 10 kHz), but relative permittivity showed similar values at high and low frequencies (e.g., SPT (x = 0.2): relative permittivity, $\varepsilon_r = 1170$ at 1.2 GHz, $\varepsilon_r = 1160$ at 10 kHz; SPT (x = 0.3): $\varepsilon_r = 8550$ at 0.45 GHz, $\varepsilon_r = 8670$ at 10 kHz). Thus dielectric tunability at 10 kHz would be valid in a microwave frequency range.

5.2.3 Importance of process route for SPT-MgO composites

Because the relative permittivity of the SPT system was high for room temperature microwave applications, non-ferroelectric low tangent $\delta$ oxides, such as magnesium oxide (MgO), were added to the SPT system to tailor the dielectric constants of the SPT system. It was noted that the preparation routes of the composites had outstanding effects on the properties of the final products. It was necessary for raw chemicals to be calcined in a platinum dish (in a sagger) instead of a conventional ceramic container in order to achieve the transition temperatures of the SPT-MgO composites similar to those of the sintered pure SPT ceramics prepared from the SPT sources of the composites.

5.2.4 Selection of SPT (x = 0.2) as the source of composites

SPT (x = 0.2, 0.25, and 0.3)-MgO composites were prepared to investigate their properties and to select materials for room temperature tunable applications. The transition temperatures of the compositions, −61, −27, and 7 °C were measured on the composites with SPT (x = 0.2, 0.25, and 0.3), respectively, and the transition temperatures were linearly proportional to the x of SPT composition of the composites. The loss tangent values, 0.005, 0.001, and 0.002, were measured at 25 °C and at 10 kHz on the composites with the SPT (x = 0.2, 0.25, and 0.3), respectively. Room temperature dielectric tunability of 3, 7, and 18 % was measured for the composites with SPT compositions on x = 0.2, 0.25, and 0.3 at a 20 kV/cm DC bias field and at 10 kHz.

The composition, Sr-Pb (0.8:0.2 by mole), was selected as the source of the composites to study their properties in detail because the SPT (x = 0.2)-MgO composites showed the lowest
tangent $\delta$ at room temperature among the three compositions studied and the composites showed tunability at room temperature.

**5.2.5 DC bias dependant properties of SPT (x = 0.2)-MgO composites at low frequency**

The SPT (x = 0.2)-MgO composites showed tunability, 0.02, K-factor (dielectric tunability over tangent $\delta$), less than 100, with a DC field of 20 kV/cm at room temperature and at 10 kHz. The room temperature values increased 0.19 as tunability and 400 (tangent $\delta$ measured without DC bias, i.e., tangent $\delta$ measured at a different time from that of the DC bias measurements) or 700 (tangent $\delta$ measured at a DC bias field during the DC bias measurements) as K-factor at a frequency of 10 kHz with a DC field of 90 kV/cm. Additionally, the composites withstood DC fields up to 175 kV/cm. The tunability was 0.30, and the K-factor calculated from tangent $\delta$ measured without DC bias fields was ~800 at 10 kHz with a DC field of 175 kV/cm and at room temperature. The results suggested the high electric DC field tolerance of the samples.

**5.2.6 Room temperature dielectric properties of SPT (x = 0.2)-MgO composites over a wide frequency range**

The investigation of the composites focused on wide frequency dielectric property measurements at room temperature. Relative permittivity was more than 100. Tangent $\delta$ were approximately 0.0005 between 10 kHz and 1 MHz and close to or less than 0.001 between 5 MHz and 100 MHz. A high frequency (~ 4 GHz) loss tangent was obtained as 0.005 based on the parallel plate dielectric post resonator technique. Differences in tangent $\delta$ were observed depending on the measurement methods. $Q \times f$ ($Q, 1/\text{tangent } \delta; f$, frequency) was 700 GHz measured using the resonant methods, but there were differences in $Q \times f$ values measured using the reflectrometric method or waveguide technique. However, the dielectric constants of the composites showed consistency. This consistency also supported that low frequency tunability was valid at high frequencies.

**5.2.7 Application of mixing rules to SPT (x = 0.2)-MgO composites**

Mixing rules are analyzed for the best estimate relative permittivity of the composites. The relative permittivity of the SPT (x = 0.2)-MgO composites at room temperature and at 10 kHz showed a reasonable agreement with the Wakino model.
5.2.8 Summary of SPT (x = 0.2)-MgO composites for tunable microwave ferroelectrics

Observed properties made the SPT (x = 0.2)-MgO composites most suitable tunable microwave ferroelectrics reported so far. Further measurements of practical devices with the composites will establish their usefulness for ferroelectric tunable devices, such as filters.

The SPT and MgO composites (for which the ratio of MgO to SPT was various) were prepared, and further exploration of properties will determine the specific composition as a useful tunable material.

5.2.9 Tunable composites with low temperature coefficient of capacitance: Composites prepared from SPT (x = 0.3) and Al₂O₃

Although the SPT-MgO composites showed high temperature coefficients of capacitance, the composites prepared from SPT (Sr-Pb (0.7:0.3 by mole)) and Al₂O₃ showed relatively low temperature coefficients of capacitance. The composites showed dielectric permittivity ~ 100, tangent δ ~ 0.005 along with the low temperature coefficients of relative permittivity ~ 700 ppm at 10 kHz over the temperature range from 150 to 40 °C. 10 kHz dielectric tunability was ~ 5 % at 20 kV/cm over the same temperature range and ~ 10 % at 40 kV/cm in the temperature range from 150 to 90 °C along with almost constant tunability. The X-ray diffraction pattern showed the presence of SPT and reacted materials, possibly hexaaluminate compounds.

5.2.10 Composites prepared from SPT (x = 0.2) and various oxides other than MgO

Oxides other than MgO were explored to seek the possibility to dilute the relative permittivity of the SPT system and the composites were prepared by the addition of various oxides such as Al₂O₃, magnesium aluminum oxide (MgAl₂O₄), tin oxide (SnO₂), or zirconium oxide (ZrO₂). From the X-ray diffraction patterns, the reactions between the oxide and SPT (x = 0.2) were inferred. The SnO₂ or ZrO₂ based composites showed 0.02 as tunability at 10 kHz and at 25 °C with a DC field of 20 kV/cm. These values were similar to the tunability of the SPT-MgO composites under the same conditions. The SnO₂ based composites showed a Q × frequency value of 400 GHz and the ZrO₂ based composites showed 1300 GHz using the parallel plate dielectric post resonator technique.
5.3 Additional studies on \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) (SPT)

This section will discuss detailed studies of the SPT \((x = 0.3)\) with the additional data of SPT with different compositions and the enhancements of relative dielectric permittivity of SPT based on chemical inhomogeneity or doping.

5.3.1 Observations on relative permittivity and tangent \(\delta\) of SPT at low frequency

\((\text{Sr}_{0.7}\text{Pb}_{0.3})\text{TiO}_3\) (SPT) ceramics were prepared using the conventional mixed oxide method, and the ceramics showed one relative permittivity maximum at 10 °C in the relative permittivity vs. temperature plots at 10 kHz in the temperature range from 190 to –260 °C. Upon cooling, the thermal expansion coefficient data revealed the transition temperatures of the SPT \((x = 0.3)\) ceramics around 10 °C. The analysis of X-ray diffraction data extracted at various temperatures also suggested the phase transformation of the SPT \((x = 0.3)\) around 10 °C. 10 kHz tangent \(\delta\) of the SPT \((x = 0.3)\) as a function of temperature showed two distinct anomalies, at –95 °C and –210 °C.

The SPT \((x = 0.05, 0.1, \text{and } 0.15)\) ceramics were also prepared using the mixed oxide method, and their dielectric properties were measured at 10 kHz upon cooling. The SPT \((x = 0.05)\) showed one relative permittivity maximum in the relative permittivity vs. temperature plots at –190 °C and one major tangent \(\delta\) peak in the tangent \(\delta\) vs. temperature plots at –195 °C. The SPT \((x = 0.1)\) had the main relative permittivity peak at –145 °C and the second peak at –190 °C as a function of temperature. When the x of the SPT is 0.1, the SPT showed the first tangent \(\delta\) peak at –150 °C and the major second peak at –200 °C accompanying a shoulder peak around –230 °C in the tangent \(\delta\) vs. temperature plots. The major dielectric constant peak of the SPT \((x = 0.15)\) occurred at –100 °C, and the second peak was at –230 °C in the dielectric constant vs. temperature plots. The SPT \((x = 0.15)\) also showed the two tangent \(\delta\) peaks, at –110 °C and at –200 °C, as a function of temperature.

5.3.2 Sources of relative permittivity of SPT in relative permittivity vs. temperature plots

The first and major dielectric constant peaks observed in all the samples studied would be associated with the phase transitions from paraelectric to ferroelectric phases upon cooling. However, it was not fully understood that the secondary peaks were observed in the SPT \((x = 0.1 \text{ and } 0.15)\) because sufficient data were lacking.
5.3.3 Sources of tangent $\delta$ of SPT in tangent $\delta$ vs. temperature plots

The tangent $\delta$ of the SPT ($x = 0.3$) as a function of temperature showed two distinct anomalies at 10 kHz and the SPT ($x = 0.1$ and 0.15) ceramics also showed two tangent $\delta$ peaks. The tangent $\delta$ peaks which were closer to the major relative permittivity as a function of temperature would be associated with the domain wall motion because the dielectric constant and thermal expansion of the SPT ($x = 0.3$) did not show a corresponding anomaly in that temperature range, and the X-ray diffraction patterns of the SPT ($x = 0.3$) did not indicate any structural change. Although precise measurements of X-ray diffraction patterns are required, the preliminary results of the SPT ($x = 0.3$) would show a dynamic change in coherent crystal domains based on the X-ray diffraction pattern analyses. Furthermore, neither the SPT ($x = 0.3$)-MgO composites nor the SPT ($x = 0.1$ and 0.15) showed the anomaly in the relative permittivity vs. temperature plots in the temperature range in which the SPT ($x = 0.3$) showed the tangent $\delta$ anomaly. Therefore, it is suggested strongly that the anomaly would be due to the domain wall motion.

The anomaly in the tangent $\delta$ of the SPT ($x = 0.3$) vs. temperature plots at a lower temperature, $-210 \, ^{\circ}C$ which was observed in most SPT samples, could be related to the following factors: i) a different type of domain wall motion from that observed in higher temperature near the relative permittivity maximum peaks, ii) an antiferrodistortive phase transition similar to that observed in strontium titanate (SrTiO$_3$), and/or iii) behaviors due to the presence of polar and/or dipolar defects. Even though a clear dielectric constant anomaly was not apparent in that temperature range, the reciprocal dielectric susceptibility (or dielectric stiffness) of the SPT ($x = 0.3$) as a function of temperature showed a change in the slope around $-190 \, ^{\circ}C$. This tangent $\delta$ anomaly was also presented in the SPT ($x = 0.1$ and 0.15) and the SPT ($x = 0.3$)-MgO composites around $-200$, $-200$, and $-190 \, ^{\circ}C$, respectively. The SPT ($x = 0.2$) sintered at a lower temperature such as 1250 $^{\circ}C$ showed higher values than the SPT ($x = 0.2$) sintered at 1350 $^{\circ}C$. The SPT ($x = 0.2$) sintered in a tube furnace flowing oxygen showed higher values than the SPT ($x = 0.2$) sintered in a conventional box-type oven (in air). The anomaly, thus, could be more closely associated with the ferroelastic phase transition of SrTiO$_3$ rather than the domain wall motion or the defects in the SPT. The main tangent $\delta$ peaks as a function of temperature in the SPT with $x = 0.05$ might be the combined effects of the domain wall motion and the ferrodistortive phase transition similar to that observed in strontium titanate.

Due to the formation of the main relative permittivity peak as a function of temperature, a shoulder peak, tangent $\delta$, was observed around the dielectric constant maximum temperature. In
paraelectric states, the tangent $\delta$ of SPT ($x = 0.3$) ceramics started increasing at $\sim 30^\circ$C above the transition temperature at 10 kHz upon cooling. A source of tangent $\delta$ in the paraelectric states was not clear. The following could be possible: i) the breathing motion of micro-polar regions (expanding and shrinking of the regions) and ii) the motion of ferroelectric domains.

5.3.4 Deviation from the ideal Curie-Weiss law: Relative permittivity of SPT ($x = 0.3$)

When the samples were cooled, the deviation from the Curie-Weiss law was observed in the SPT ($x = 0.3$) almost up to $20^\circ$C above the dielectric maximum, $T_m$, of $10^\circ$C. Upon cooling, thermal expansion coefficients started showing the deviation nature from $90^\circ$C above the $T_m$ and the main anomaly at $5^\circ$C above the $T_m$. Lattice parameters measured in the cubic region (from $T_m + 50^\circ$C) empirically followed a similar temperature dependence and did not show a strong deviation from the temperature dependence, when the samples were cooled. Hysteresis loop plots showed an s-type shape (non-linearity) at $30^\circ$C above the $T_m$, and remnant polarization was clearly detectable at $15^\circ$C above the $T_m$ in cooling cycles.

The deviation from the Curie-Weiss behavior could be caused by some of the several regions associated with the physical state of the material, a component in the material and/or atoms (e.g., Pb$^{2+}$) in the system and hence by the micro polarization. The SPT ($x = 0.05, 0.1, 0.15, 0.2, 0.25$) also showed the departure from the ideal Curie-Weiss law. The Curie-Weiss constant increased as the lead content in the composition increased, and the values were nearly constant for the SPT ($x = 0.25$ and $0.3$).

5.3.5 Room temperature lattice parameter as a function of $x$ in (Sr$_{1-x}$Pb$_x$)TiO$_3$

Room temperature lattice parameters were obtained based on the X-ray diffraction pattern results. The plot of the room temperature lattice parameters vs. the mole fraction of lead, $x$ ($x = 0.05, 0.1, 0.15, 0.2, 0.25$, and $0.3$), showed a linear relationship. The phase transition temperatures based on the relative permittivity measurements as a function of temperature at 10 kHz upon cooling also showed a linear relationship with $x$.

5.3.6 Factors influencing the relative permittivity maximum of SPT in relative permittivity vs. temperature plots

The SPT ($x = 0.3$) showed the reasonable reproducibility of relative permittivity maximum values as a function of temperature and reproducible transition temperatures. However, the SPT ($x = 0.2$) showed various dielectric constant maxima as a function of temperature even
though the SPT (x = 0.2) showed similar transition temperatures. X-ray diffraction pattern analyses suggested that a chemical inhomogeneity might have an important role.

5.3.7 Doped SPT: Unusual relaxation behavior of Sm$_2$O$_3$ doped SPT

In order to decrease the tangent $\delta$ of SPT, cerium oxide (CeO$_2$) or samarium oxide (Sm$_2$O$_3$) was added (or doped) to the raw chemicals of the SPT (x = 0.3). However, both systems showed an increase in tangent $\delta$ as a function of temperature. Thus a further study is required to improve the tangent $\delta$ of the SPT system by the addition of chemicals.

The Sm$_2$O$_3$ doped SPT showed the enhancement of relative permittivity at a lower frequency, such as 100 Hz, compared with a higher frequency, such as 10 kHz, over the wide temperature range from 190 °C to –180 °C, and the Sm$_2$O$_3$ doped SPT showed unusual relaxation behaviors. The Cole-Cole plots did not show conventional closed circles or arcs and showed a temperature dependence. A widely known mechanism for the enhancement is due to the Maxwell-Wagner-Sillars or Maxwell-Wagner model and according to the model, the effective geometry of an insulating substance would be changing as a function of frequency (e.g., in diphase system: insulator and conductor). Although this model was not completely able to explain the observations, the frequency dependence of relative permittivity could be related to the effective geometry of less conductive species in the doped SPT ceramics. In addition, the analysis of incorporation of the Sm$_2$O$_3$ in the SPT matrix will be useful for understanding the enhancement of relative permittivity because conductive species would contribute to the observed relaxation.
Chapter 6
FUTURE WORK

6.1 Pure (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) solid solution system

An exciting feature of the development of the pure (Sr$_{1-x}$Pb$_x$)TiO$_3$ (SPT) solid solution system has been the manner in which the magnitude of the weak alternating current (AC) field dielectric maximum, $\varepsilon_{\text{rw-max}}$, at the Curie Point, $T_c$, has increased with developing experience in processing the system. Initially, it was rather naturally assumed that this evolution marked a developing capability to make more perfect solid solutions. Two facets of the behavior, however, now call this naive explanation into question and, hence, it is suggested that a future work on this dielectric behavior will be very rewarding.

Firstly, from the dielectric stiffness (the reciprocal dielectric susceptibility: the Curie-Weiss behavior) (Fig. 6.1), it is expected that for a perfect ferroelectric with the second-order change at $T_c$, very high values of $\varepsilon_{\text{rw-max}}$ are achieved by following the linearly decreasing $1/\varepsilon_{\text{rw}}$ ($\varepsilon_{\text{rw}}$: weak field relative permittivity) dictated by the soft mode behavior down to very low values (i.e., $1/\varepsilon_{\text{rw-max}} \rightarrow 0$ or $\varepsilon_{\text{rw-max}} \rightarrow \infty$). Clearly, however, in the “best” SPT (with highest $\varepsilon_{\text{rw}}$), this is not the case. Whilst still decreasing, the rate of decrease in $1/\varepsilon_{\text{rw}}$ slows (i.e., the Curie-Weiss constant, $C$, increases) in the vicinity of transition temperatures based on relative permittivity, $T_m$ (ideally $T_c$), and even continues to a temperature lower than $T_c$, where the perfect system would be in the ferroelectric state. This then gives rise to the impossible situation for the perfect ferroelectric: the ferroelectric transition, $T_c$, is below the Curie-Weiss temperature, $\theta$.

The second feature which calls the model of increasing perfection to achieve higher relative permittivity ferroelectrics into question is the clear evidence from X-ray diffraction measurements that an X-ray line broadening is in fact larger for the solid solution with higher $\varepsilon_{\text{rw-max}}$ as compared to a similarly processed composition with a linear dielectric behavior. In the X-ray diffraction spectrum, the causes of the line broadening due to specimens are two major factors which would be able to be separated: i) the small coherent length perpendicular to the incident X-rays and ii) the imperfection of local scattering regions along the incident X-rays. The preliminary data suggest that the broadening is due to the imperfection, but more work is needed for the complete confirmation.

It is well known that in the very large family of relaxor ferroelectric solid solutions, a strong departure from the Curie Weiss law occurs well above the transition temperatures. In
Figure 6.1 Relative dielectric permittivity and reciprocal dielectric susceptibility of \((\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3\) \((x = 0.2)\) ceramics as a function of temperature at 10 kHz upon cooling.
these systems, however, the permittivity becomes strongly dispersive at radio frequencies, RFs, due to the local field induced by the reorientation of polar micro-regions, which inhibits the normal ferroelectric transitions. In SPT, the results suggest that a measure and scale of heterogeneity can be introduced. The heterogeneity allows a slower but still increasing polarizability at temperatures even below $\theta$, but which also inhibits the system falling into a classical ferroelectric domain structure with the consequent catastrophic loss of a weak field response. This system, however, unlike the polar regions in the relaxor, does not induce the RF dispersion. Such a mechanism for raising $\varepsilon_{rw}$ will be particularly important, and an additional study on this topic will be certainly suggested.

Another interesting feature is to improve the reproducibility of SPT which shows similar $\varepsilon_{rw}$ using lower lead composition (e.g., $x = 0.2$). There were researchers who followed the preparation method in the processing section (Sect. 3.1) and prepared SPT ($x = 0.3$) with the weak AC field relative permittivity maxima similar to those of the samples described in this dissertation [1]. However, the SPT ($x = 0.2$) ceramics which were prepared at a different time did not show similar relative permittivity maximum. Calcination and ball milling conditions could influence the properties. A further investigation will be helpful to understand the materials better.

Tangent $\delta$ measurements over a wide frequency range lack general consistency. Low frequency techniques agree that tangent $\delta$ is very low, but in the microwave regions, there is disagreement between the parallel plate dielectric post resonator and the reflectometer measurements. The data taken using the reflectometric method suggest that low tangent $\delta$ is similar to those at low frequencies, but suggest that relative permittivity could be damped. The data taken using the post resonator method agrees closely with low frequency relative permittivity, but it shows significantly enhanced tangent $\delta$.

For the post resonator method, it is important to have a pure resonance. However, in the SPT based composites, the observed resonant peaks were often asymmetric, suggesting perturbation from a different mode. Since the field distribution is critical, perturbation from cracks and pores could also be a problem. A second difficulty concerns the power loss, $p$, in the samples given by $p = 2\pi f \varepsilon_{o} \varepsilon_{r} \tan \delta |E|^2$ (f is frequency, $\varepsilon_{o}$ is vacuum permittivity, $\varepsilon_{r}$ is relative permittivity, and $E$ is electric field). Because of very high relative permittivity, the power loss is very large, reducing available signal levels and enhancing dielectric loss from extraneous mechanisms.
It is generally agreed that the parallel plate dielectric post resonator method gives very good relative permittivity values but that tangent δ is difficult particularly in high dielectric permittivity low dielectric loss samples. Therefore, it is important to develop a tangent δ characterization method for low tangent δ ferroelectric materials in a microwave frequency range. In addition, this technique should show a correlation between values measured using the method and properties in a device. A possible technique could be based on the wave guide technique even though this technique currently measures dielectric properties accurately for tangent δ values in the 0.01 - 1 range. Additionally, investigation on extrinsic contribution to low tangent δ samples will be an interesting feature.

6.2 Composite systems

One of the exciting features is the aging effect of well prepared SPT-MgO composites. The degradation of dielectric properties after applying direct current (DC) bias depends on the conditions under which the samples are carried out. It will be important to comprehend the aging behavior of the composites in order to keep using composite systems in practical devices.

6.3 Miscellaneous studies

Various studies are in progress based on pure SPT with or without a dopant and/or composites systems. Microwave characterization, elastic characterization, TEM analysis, Raman analysis, the use of fine powders, and the flexo-electric behavior are ongoing. These measurements should be extended in order to understand the potentialities of the SPT system.

6.4 References
Appendix A  Studies on lead strontium titanate

The literature is categorized based on bulks (ceramics and single crystals) and films. Bulk materials are separated between pure systems and doped or composite systems. The literature is sorted yearly, and then alphabetically.

A.1 Bulks (pure systems; some articles reported composite systems or films)


A.2 Bulks (doped or composite systems)


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A.3 Films

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