# The Pennsylvania State University 

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## HIGH PERMITTIVITY RELAXOR-LEAD TITANATE PIEZOELECTRICS FOR HIGH FREQUENCY ULTRASONIC TRANSDUCERS

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## Abstract

Relaxor $\mathrm{Pb}\left(\mathrm{Mg}_{1 / 3} \mathrm{Nb}_{2 / 3}\right) \mathrm{O}_{3}-\mathrm{PbTiO}_{3}$ (PMN-PT) based ferroelectric materials have been significant interest for active transducer materials because of their superior dielectric and electromechanical properties. However, there are some limitations for these kinds of materials to implement into high frequency $(20-100 \mathrm{MHz})$ ultrasound transducers, arising from the inability to fabricate fine scale features and degraded electrical properties with increasing frequency. Therefore, this thesis deals with two important topics. One is the improvement of the mechanical properties of relaxor-PTs to enable the fabrication of high frequency transducers using these materials. The second is to understand the mechanism of degraded electrical properties of these materials with increasing frequency.

This thesis first presents the synthesis and characterization of fine ( $\sim 1$ microns) grained PMN-PT polycrystalline ceramics. Fine grain versions of piezoelectric materials have proven to be a great promise for high frequency transducers because of their benefits, such as improved mechanical strength and property stability at high frequency range. This thesis also includes the investigation of size and/or frequency dependent properties of various relaxor-PTs to study their applicability to high frequency ultrasound transducers. The compositions studied in this work include binary PMN-PT polycrystalline ceramics and single crystals, as well as modified ternary based PMN-PT single crystals.

The characterization of electrical properties of relaxor-PTs as a function of thickness and/or frequency showed that fine-grained PMN-PT ceramics provide greater mechanical strength and improved property stability at small thicknesses less than 50 mi crons, which correspond to $>40 \mathrm{MHz}$ ultrasound frequencies. For single crystals, binary PMN-PTs were found to exhibit significant property degradation in terms of dielectric and piezoelectric properties with decreasing sample thicknesses. In contrast, modified ternary based PMN-PT single crystals showed promise for a use in high frequency ultra-
sound transducers, with no performance degradation with decreasing sample thicknesses down to 40 microns. Analyses for thickness dependent permittivity at high temperatures and domain observations revealed that the thickness dependent properties of relaxor-PTs are closely related to the domain size with respect to the associated macroscopic scale of the samples.

The influence of dicing damage on the properties was further studied and discussed through the investigations of 1-3 relaxor-PT composites, which were fabricated by dicingfill technique. It was found that 1-3 composites showed further property degradation compared to monolithic relaxor-PTs at the same thickness level. X-ray diffraction pattern revealed that diced surface was covered with heavily stressed and damaged surface layer, which implies that surface damage created by dicing could be the origin of property degradation of 1-3 composites.

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## Introduction

### 1.1 Statement of the Problem and Motivation

Ultrasound imaging is a well-established medical imaging modality that provides non-invasive diagnostic information of living tissue and organs. Traditionally, ultrasonic imaging has been used in the area of cardiology, obstetrics, and abdominal diagnosis. In these applications, the ultrasound frequency is below 10 MHz allowing deeper penetration at the expense of resolution. Recently, there is growing need for higher resolution, particularly in the areas of dermatology, ophthalmology and, intravascular imaging (IVUS).[1-6]

In the ophthalmic eye imaging, for example, high frequency ultrasound can accurately distinguish or determine various types of glaucoma, such as pupillary block glaucoma and plateau iris syndrome. 50 MHz ultrasound eye images are shown in Figure 1.1, which clearly displays the anterior region of the eye, allowing the analysis of the anterior chamber depth (ACD) in patients with pupillary block and plateau iris syndrome.[7, 8]

For the case of dermatology, commercial ultrasound imaging system has been developed in the frequency range between 2 and 20 MHz . At these frequencies, however,
the resolution was limited to approximately $200 \mu \mathrm{~m}$ at best. Attempts have been made to develop high frequency ultrasound. Hoess et al.[9] and later Turnbull et al.[10] developed high frequency ultrasound operating over 50 MHz frequency, enabling clear visualization of cutaneous structures. In addition to providing basic measures of the skin thickness, high frequency ( $>50 \mathrm{MHz}$ ) ultrasound imaging has allowed the assessment of malignant melanoma and melanomas progression in mouse skin.[11-14]

High frequency ultrasound has also been successfully implemented in intravascular imaging (IVUS) for the assessment of vascular plaque and stenosis. It has been reported that ultrasound imaging system operating at 45 MHz can clearly distinguish the vessel structures such as the coronary intima and stent struts, identifying the initiation of plaque.[15] These examples clearly demonstrate that high frequency ultrasound ( $>20 \mathrm{MHz}$ ) offers unique advantage for medical diagnosis, though several limitations have been noted for high frequency ultrasound imaging.

One of limitations of high frequency imaging systems arises from a limited depth of field (DOF) because of the short wavelength and fixed-focused transducers. The pene-


Figure 1.1. Ultrasound biomicroscopy images of pupillary block (left) and plateau iris syndrome (right). $\mathrm{CP}=$ ciliary process. The resolution is approximately $40 \mu \mathrm{~m} .[7]$
tration depth is also limited as a result of increased attenuation in tissues with increasing ultrasound frequency. Improvement in signal-to-noise ratio (SNR) and transducer bandwidth is one way to improve shallow penetration depth of high frequency ultrasound imaging, which can be achieved with the improvement in transducer design and transducer properties.

A number of transducer materials have been emerged and investigated to strive for better performance of ultrasound transducers. The figure of merit of a piezoelectric transducer is electromechanical coupling factor. High coupling piezoelectric materials allow effective energy conversion in both transmitting and receiving energy, improving bandwidth and sensitivity of the transducer response. The dielectric permittivity of piezoelectric material is also an important consideration for the design of a transducer. In order to obtain the maximum transmit and receive sensitivity, the electrical impedance of the transducer should be close to the 50 Ohm imaging electronics. For ultrasound single element and array transducers operating at high frequencies ( $>20 \mathrm{MHz}$ ), such as IVUS, very small aperture sizes ( $<1 \mathrm{~mm}$ diameter) are generally used, resulting in mismatched electrical impedance to the imaging electronics. Therefore, it is desirable to use piezoelectric materials with high dielectric permittivity and high electromechanical coupling factor.

Currently, soft PZT materials, such as PZT-5H, have been the mainstay for low frequency ( $<10 \mathrm{MHz}$ ) ultrasound transducers due to their high electromechanical properties ( $\mathrm{k}_{t} \sim 0.50, \mathrm{k}_{33} \sim 0.72$ ). With reducing grain size, PZT ceramics showed higher mechanical strength and better dicing performance, enabling the fabrication of fine pitch and high aspect-ratio piezoelectric elements. Furthermore, in contrast to conventional PZT ceramics, fine-grained PZT ceramics retained their electromechanical properties at high frequencies ( $>50 \mathrm{MHz}$ ), making them suitable for use as high frequency ultrasound transducers.[16-18]

Recently, relaxor-PT piezoelectrics, such as $\mathrm{Pb}\left(\mathrm{Mg}_{1 / 3} \mathrm{Nb}_{2 / 3}\right) \mathrm{O}_{3}-\mathrm{PbTiO}_{3}$ (PMN-PT), have received attention because they can provide relatively higher dielectric permittivities $\left(\varepsilon_{33}^{T} / \varepsilon_{0} \sim 6000\right.$ ), nearly twice than that of conventional PZT ceramics, while possessing comparable electromechanical coupling factors. Of significant contrast to PZT ceramics, relaxor-PT piezoelectrics can grow a large size of single crystals, offering extremely a large piezoelectric coefficient ( $\mathrm{d}_{33}>2000 \mathrm{pC} / \mathrm{N}$ ) and electromechanical coupling factor ( $\mathrm{k}_{33}>90 \%$ ).[19-24] (see Figure 1.2) A second generation of crystal compositions in the ternary $\mathrm{Pb}\left(\mathrm{In}_{1 / 2} \mathrm{Nb}_{1 / 2}\right) \mathrm{O}_{3}-\mathrm{Pb}\left(\mathrm{Mg}_{1 / 3} \mathrm{Nb}_{2 / 3}\right) \mathrm{O}_{3}-\mathrm{PbTiO}_{3}$ (PIN-PMNPT) system, have been found to possess expanded temperature usage range ( $>120^{\circ} \mathrm{C}$ ), with higher coercive fields ( $\sim 5 \mathrm{kV} / \mathrm{cm}$ ) than binary PMN-PT crystals, making them more promising candidates for high frequency ultrasound transducers.[25]

Consequently, ultrasound transducers incorporating relaxor-PT single crystals showed


Figure 1.2. Dielectric permittivities of various piezoelectric materials as a function of electromechanical coupling.
almost double bandwidth and sensitivity of the transducers compared to the conventional ceramic transducers, resulting in significant improvements in ultrasound imaging in terms of resolution and penetration depth, an example of which is demonstrated in Figure 1.3.[22, 26]

However, as the transducer becomes very small, usually on the order of micrometers, with increasing ultrasound frequency ( $>20 \mathrm{MHz}$ ), several issues, such as the reduction of piezoelectric and electromechanical properties, have been addressed in several ferroelectric systems, and it was proposed that the reduced extrinsic contributions resulting from relatively large grain size are the main mechanism responsible for a decrease in the electrical properties of ferroelectric systems.[16-18, 27, 28]

To date, however, little work has been done to provide sufficient understanding of the size dependent properties of relaxor ferroelectric systems, including polycrystalline ceramics and single crystals. Recent experimental data for PMN-PT crystal/epoxy 1-3


Figure 1.3. 40 MHz Phantom ultrasound images. (Left: a standard 40 MHz PZT transducer; right: 1-3 composite relaxor-ferroelectric crystal (PMN-PT) transducer.[26])
composites operating at frequencies $>40 \mathrm{MHz}$ have revealed a large decrease in electromechanical coupling, leading to the question of the origin of property degradation of this system.[26, 29-33] Since the materials used in 1-3 composites were single crystals, the degraded properties of 1-3 piezocrystal composites are not because of grain size effects, remaining the question for the origin of the property degradation of relaxor-PT system.

### 1.2 Thesis Objectives and Outline

The purpose of this thesis is to investigate the performance of relaxor-PT piezoelectric systems for high frequency ultrasound transducers by measuring their dielectric, piezoelectric and electromechanical properties at high frequency range ( $>20 \mathrm{MHz}$ ). The brief outline of this thesis is as follows. Chapter 2 provides relevant background information of ultrasound imaging, with particular focus on the influence of the transducer characteristics on the imaging performance. It also discusses the basic concepts of ferroelectric materials, with emphasis on perovskite type ferroelectric materials. Chapter 3 presents the synthesis of fine grained PMN-PT ceramics and the characterization of synthesized ceramics with other relaxor-PT systems, including coarse grained PMN-PT ceramics, PMN-PT single crystals and PIN-PMN-PT single crystals. Chapter 4 provides the detail results of size dependent properties of monolithic relaxor-PT materials with a discussion of the mechanism of property degradation of this system. Chapter 5 describes the fabrication and characterization of low and high frequency 1-3 composites, and the presence and effect of surface damage from machining on active piezoelectric elements. Chapter 6 provides a final summary and the conclusions drawn from this research. It also provides suggestions about possible future research directions.


## Literature Review and Background

This chapter describes the basic concepts of the ultrasound imaging and the principle of transducer operation. After discussing the general background of an ultrasound imaging, this chapter will discuss the characteristics of the ultrasound transducer that affect the performance of ultrasound imaging, such as transducer design and transducer properties. The final section discusses the piezoelectric materials, focusing on the ferroelectric materials. The basic definition and characteristics of ferroelectric materials are discussed first, such as ferroelectric hysteresis and dielectric and piezoelectric properties of this class of materials. Lead zirconate titanate, one of the technologically important materials, is then discussed, focusing on the mechanisms of enhanced piezoelectric properties at morphotropic phase boundary. Background on the complex $A\left(B_{1} B_{2}\right) O_{3}$ type perovskites, referred to as relaxor-ferroelectrics, is then discussed, and the relevant interest of this system is emphasised.

### 2.1 Basic Ultrasound Imaging

### 2.1.1 Principle of Ultrasound Imaging

Ultrasound imaging is the most widely used imaging technique in the field of medical diagnosis. There are several advantages of ultrasound imaging compared to other imaging modalities, such as X-ray, computed tomography (CT) and magnetic resonance imaging (MRI), and they can be summarized as follows: (a) it is non-invasive so it does not utilize harmful electromagnetic radiation. (b) the spatial resolution of a high frequency ultrasound image is higher than that of other imaging modalities. (c) Doppler effect can be used to make quantitative measurements of blood velocity and to map blood flow. (d) the equipments are comparatively small, so it is portable and hand-held units. (e) ultrasound equipment is inexpensive, and the operating cost of an ultrasound system is also relatively low, compared to computed tomography (CT) and magnetic resonance imaging (MRI). (f) it is capable of real time observations of living tissues such as the movements of heart and muscles.[4, 34, 35]

Diagnostic ultrasound imaging is based on the phenomenon of scattering of ultrasound waves at the interface of two media with different acoustic impedances. The backscattered echo from acoustic interface is used to measure the distance of objects by the analysis of time duration (A-mode) or generate image from the amplitude of reflected signal (echo) (B-mode). Frequency shift in the reflected ultrasound signal is used to display flow information (Doppler).

A mode (amplitude mode) display is the earliest display mode, and was used to measure the distance from the transducer to the reflecting surface. The general principle of A mode display is the result of piezoelectric effects, which can be defined as the linear coupling between mechanical stress, X and polarization, P , or between electric field, E and strain, x. For example, a piezoelectric transducer can be excited from electrical
source, which induce the mechanical vibration as a result of the converse piezoelectric effects $\left(\mathrm{x}=\mathrm{d} \cdot \mathrm{E}\right.$, where d is piezoelectric coefficients, which is a third rank tensor $\left(\mathrm{d}_{j k l}\right)$, but d is frequently expressed using reduced matrix notation $\left(\mathrm{d}_{i j}\right)$ ). When the mechanical vibration is coupled to the medium, elastic waves are generated. These elastic waves are called ultrasonic waves because their frequencies are above the audible range ( $>20$ $\mathrm{kHz})$. When generated elastic waves encounter the changes in a tissue property along the path, some of the energy is reflected and/or scattered, and the remaining is transmitted ahead. The reflected waves travel back to the same transducer, then the ultrasound transducer converts the vibrations to an electrical signal as a result of direct piezoelectric effects $(\mathrm{P}=\mathrm{d} \cdot \mathrm{X})$. By analysis of the time of flight required for an echo to return from reflector, a particular depth (d) can be obtained (i.e., $1 / 2 \times$ time $\times$ ultrasound speed). The speed of ultrasound (c) in tissue can be determined by the tissue characteristics according to the following equation 2.1.

$$
\begin{equation*}
c=\sqrt{\frac{k}{\rho}} \tag{2.1}
\end{equation*}
$$

where k and $\rho$ are the stiffness and density of tissue, respectively. In general, a speed of ultrasound of $1540 \mathrm{~m} / \mathrm{s}$ is typically used in soft tissues. Ultrasound speeds in various tissues are listed in Table 2.1.

Table 2.1. Speed of ultrasound in soft tissues. [36]

| Tissue | Air | Fat | Urine | Liver | Blood | Muscle |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Speed (m/s) | 330 | 1450 | 1490 | 1540 | 1570 | 1580 |

Due to the limitation of one dimensional representation for A-mode, most ultrasound devices in modern medical imaging use B-mode (brightness mode) imaging. B-mode images can be created by rapidly back and forth sweeping of a transducer over the
region of interest. The image is, then, formed by a series of successive scan lines on a black background, and the brightness level changes depending on the amplitude of echo signals, allowing gray scale image on the image display.

### 2.1.2 Ultrasound Transducer

An ultrasound transducer is the most important component in an ultrasound imaging system. The overall performance of an ultrasound imaging is mainly determined by the transducer characteristics, since ultrasound transducers act as both a transmitter and a receiver in the ultrasound imaging system. The quality of ultrasound images have been greatly improved with improvements of transducer design.

There are various types of transducers used in ultrasound imaging. The simplest type of a ultrasound transducer is a single element transducer, as schematically depicted in Figure 2.1. The majority of uses for single element transducers is for non-imaging applications where only one line of information is necessary, such as the measurements of eyeball length and skin thickness. B-mode imaging is also realized with single element transducers by moving the transducer across the skin manually or mechanically. Most of the high frequency ( $>20 \mathrm{MHz}$ ) ultrasound imaging is based on the single element transducer because it is relatively easy to fabricate compared to array transducers.

There are several disadvantages for uses of single element transducers in ultrasound imaging systems. First, since focusing of single element transducers is utilized by mechanical lens, focal distance is fixed during manufacturing, resulting in limited the depth of focus (DOF). Second, the frame rate is also limited because ultrasound beam must be swept manually or mechanically, as opposed to the electronic scanning of an array system. This makes it difficult or impossible to produce real time imaging because for real time applications, each individual image must be generated as rapidly as possible,

Single element


Focusing is utilized by lens

Arrays

Beam pattern is narrow at all depths


Phased arrays can electrically steer beam


Figure 2.1. Schematic representation of a typical single element and array ultrasound transducer.
for instance, 30 to 60 complete images per second.
The development of array transducers, which are composed of a group of closely spaced multiple elements, provides the possibility of electronic focusing adjustable for depth and electronic beam steering, enabling a variety of image display formats, such as rectangular or fan shaped format, and real time imaging (see Figure 2.1). The common types of automated real-time scanners are linear or curved arrays, and phased arrays.

Linear array transducers consist of groups of rectangularly shaped piezoelectric elements arranged side by side, while a curved array is a modified linear array whose elements are arranged in an convex curve shape. Due to the geometry of these arrays, the resultant views from linear and curved arrays are rectangular and fan shape image, respectively.

The number of separate piezoelectric elements (channel) for linear and curved arrays are typically 128-512 channels. The importance of number of channels in transducer is closely linked to the lateral resolution. Since beam width is inversely proportional to the aperture size, the increased number of channels result in improved lateral resolution, but the number of channels are often limited by the cost and fabrication difficulties.

The radiating ultrasound beam from the linear and curved transducers is formed by a finite number of neighbouring elements (active aperture). Imaging of both linear and curved arrays is achieved by sequentially transmitting and receiving ultrasound beam starting from one end to the other end of the array. Electronic focusing is obtained by controlling the number of elements and the sequence that the elements are excited. This allows for the control of focal point at different depths (see Figure 2.1).[34, 36-40]

Like the two types of arrays, phased (or sector) arrays contain multiple piezoelectric elements (channels). However, all elements for phase arrays are involved in producing ultrasound beam, as shown in Figure 2.2; thus, the separate elements of phased arrays,

(a)

(b)

Figure 2.2. Comparison of a typical a linear (a) and phased (b) array transducer operation (not to scale).[41]
typically 64 to 256 channels, are usually smaller than linear and curved arrays.
Since all elements of the phased array are used for the formation of ultrasound beam, phased arrays can electrically steer the ultrasound beam in different directions with time delay method, as well as they can focus electronically (dynamic focusing). Due to the capability of beam steering, the phased array transducer is capable of producing the widest field of view from a small aperture. Thus, they are particularly useful for applications where the size of the arrays is limited by the entrance window, such as the examination of heart, liver, or in other areas where access is limited.[38, 39]

One of the important considerations in the design of array transducers is the formation of grating lobes due to the constructive interference between elements. Therefore, in order to avoid grating lobes, narrow closely spaced elements are required for phased array transducers. In general, linear array transducers require 1.5 wavelength element spacing or less, while phased array transducers require smaller element spacing, 1/2 wavelength or less, due to the requirement of beam steering. For instance, the wavelength of 40 MHz frequency is approximately 40 micrometer $(\lambda=\mathrm{c} / \mathrm{f}$, where c is 1540 $\mathrm{m} / \mathrm{s}$ ). Therefore, the required element spacing of 40 MHz phased array transducer is less than 20 micrometer, leading to the challenge for the fabrication of high frequency array transducers.

Annular array transducer consists of several concentric circular ring elements, and each element is electrically isolated from others, as shown in Figure 2.3. This design allows for dynamic focusing at different points along the axis through element-to-element time delay, similar to linear and phased array transducers. Therefore, annular arrays have improved depth of field (DOF) in comparison with single element transducers. In addition, required elements of annular arrays are far fewer than that of a linear or phased arrays, which reduces fabrication difficulties associated with high frequency arrays.


Figure 2.3. Schematic representation of an annular array transducer.[35, 42]

One of the disadvantages of annular array transducer compared to linear and phased array transducers is the transducer must be mechanically scanned along the scanning direction to form an image, which limit the frame-rate of the imaging system. Therefore, most of modern ultrasound transducers have been replaced by linear or phased array transducers, but annular arrays has proven to be useful for high frequency ultrasound transducer applications.[42-44]

### 2.2 Characteristics of Ultrasound Transducer

### 2.2.1 Ultrasound Frequency

One important aspect to determine the quality of ultrasound image is the spatial resolution, which can be defined as the ability of an ultrasound transducer to differentiate two independent objects. The spatial resolution of ultrasound transducer can be divided in axial and lateral resolution depending on the direction in which the ultrasonic wave propagates.

Axial resolution refers to the minimum spacing between reflectors in the direction that the ultrasound wave propagates, which is mainly determined by the time response of the transducer (pulse duration). Lateral resolution is the ability of a transducer to distinguish two closely separated reflectors in the direction perpendicular to the axis that ultrasound wave propagates, and is directly related to the beam width. Both axial and lateral resolution are closely related to the ultrasound frequency. In general, high ultrasound frequency provides better axial and lateral resolution.

The importance of a use of high frequency is apparent from the analysis of the ultrasound characteristics associated with spatial resolution. To produce an image, an ultrasound beam is swept across the region of interest, and the image is obtained by the
analysis of the time for an echo to return from reflectors. If echo pulse durations are larger than the time gap ( $\Delta t$ ) required for echo signals reflecting from two reflectors, the echo pulses overlap and two reflectors can not be resolved, limiting the axial resolution. However, if echo pulse durations are smaller than the time gap of echo signals, they will arrive separately and to be resolved. Therefore, an improved axial resolution can be obtained by generating pulse duration as short as possible.

Short pulses can be obtained either by damping the vibration (ringing) of transducer or by increasing ultrasound frequency. Damping the ultrasound transducer can be achieved with the insertion of the high impedance backing material, whose impedance is close to the impedance of an active material (piezoelectrics). However, undesirable loss in sensitivity is, in general, accompanied with this method.[45] The relationship between pulse duration and frequency can be easily understood by the definition of pulse duration, which is the time required for the ultrasound ringing. It is expressed as the number of cycles ( N ) in the pulse divided by the ultrasound frequency (f). Thus, higher ultrasound frequency results in shorter pulse duration, leading to improved axial resolution.

The dependence of lateral resolution on frequency is also apparent from the investigation of ultrasound beam characteristics. Figure 2.4 illustrates the ultrasound beam pattern when a focusing lens is attached to the transducer. This illustration depicts the relationship between lateral resolution and beam width. When the beam focus width is larger than the scatter diameter, a transducer receive echos from the scatterer even when it is off axis, giving stretched image. However, a transducer with a narrow beam width will receive echoes from the scatterer only when that object is directly in front of it, resulting in improved lateral resolution. Since higher frequency ultrasound generate narrower beam in the focal zone with less divergence, high frequency ultrasound can improve lateral resolution dramatically.



However, it should be noted that a significant drawback associated with high frequency ultrasound is the increased signal loss in tissue at high frequencies, limiting imaging depth and image quality. The cause of signal loss with increasing frequency is related to the frequency dependent attenuation in biological tissue.

In general, when ultrasound wave travels through tissue, its amplitude and intensity (energy associated with wave) are gradually reduced with increasing distance travelled, whose effect is termed as attenuation. The sources of attenuation in body tissue are mainly associated with the reflection or scattering and absorption at interfaces of impedance discontinuity (tissue). An important contribution of attenuation is absorption, where acoustic energy is converted to heat energy, meaning that the ultrasound energy is lost and cannot be recovered. Therefore, when the attenuation of tissue is large, the echoes returned from deep tissues are too weak to be detected.

Unfortunately, the attenuation in tissue is strongly dependent on ultrasound frequency. The relationship between ultrasound frequency and attenuation in various tissues is demonstrated in Figure 2.5. It is evident from this figure that in most cases, the attenuation coefficient in tissue increases linearly with frequency, and frequency dependence of attenuation shows variations depending on tissue type. This means that the implementation of high frequency ultrasound requires detailed knowledge of the ultrasonic properties of target tissues.

### 2.2.2 Piezoelectric Properties

The operation of an ultrasound transducer is a direct consequence of piezoelectric effects. The direct piezoelectric effect is used in the ultrasonic receiver, while the converse piezoelectric effect is used in the ultrasonic transmitter. The principle of piezoelectricity was discovered by Pierre and Jacques Curie brothers in 1880. They discovered that
certain crystals, such as quartz, tourmaline, cane sugar, and rochelle salt, develop surface charges proportional to a mechanical stress. Soon after they also found that the same crystals also exhibit mechanical strain with the application of electric field. The two effects define piezoelectricity. The former is called direct piezoelectric effect, and the latter is called converse piezoelectric effect.[46-48] Although a large number of piezoelectric properties are involved with the performance of ultrasound transducer applications, the electromechanical coupling factor $\left(\mathrm{k}_{i j}\right)$, dielectric permittivity $\left(\varepsilon_{r}\right)$, and acoustic impedance $(\mathrm{Z})$ are the key parameters that are directly associated with the performance of ultrasound transducer applications. In the following, the definitions of terms ( $\mathrm{k}_{i j}, \varepsilon_{r}$, and Z ) and their relevance to the properties of ultrasound transducers will be discussed.


Figure 2.5. Frequency dependence of attenuation for several types of tissues.[37]

## Coupling Factor

The material parameter, electromechanical coupling coefficient (or coupling factor) is a measure of performance of a piezoelectric material as a transducer since electromechanical coupling coefficient reflects the capability of the material to convert from one energy to another. The physical meaning of electromechanical coupling coefficient can be understood from the definition of electromechanical coupling coefficient, which is the energy conversion rate between electrical energy and mechanical energy, as shown below;

$$
\begin{align*}
& k^{2}=\text { Stored mechanical energy/Input electrical energy }  \tag{2.2}\\
& k^{2}=\text { Stored electrical energy/Input mechanical energy }
\end{align*}
$$

Alternatively, electromechanical coupling coefficient can be expressed as a mathematical form using piezoelectric relations. Constitutive equations of piezoelectric effects can be expressed as follows:

$$
\begin{align*}
& D=\varepsilon^{T} E+d T  \tag{2.3}\\
& S=s^{E} T+d E \tag{2.4}
\end{align*}
$$

where D is the dielectric displacement $\left(\mathrm{Coulomb} / \mathrm{m}^{2}\right), \mathrm{E}$ is the electric field, T the stress and S the strain. $\varepsilon^{T}$ is the dielectric permittivity under constant stress, $\mathrm{s}^{E}$ is the compliance when the electric field is constant and $d$ is the piezoelectric coefficient of the material.

When an electric field is applied under the condition $\mathrm{T}=0$, the input electrical energy is equal to the $0.5 \mathrm{D} \cdot \mathrm{E}$. Since there is no mechanical stress $(\mathrm{T}=0)$ on the system, D is
equal to $\varepsilon^{T} \cdot \mathrm{E}$ from the equation 2.3. Thus, input electrical energy is $0.5 \varepsilon^{T} \mathrm{E}^{2}$. The stored mechanical energy can be expressed as $0.5 \mathrm{~S} \cdot \mathrm{~T}$. Due to the absence of stress in the initial stage, $S$ is equal to $\mathrm{d} \cdot \mathrm{E}$ from the equation 2.4 , and the generated stress ( T ) after electric field is removed is equal to $\mathrm{S} / \mathrm{s}^{E}$, which gives $0.5(\mathrm{dE})^{2} / \mathrm{s}^{E}$ for stored mechanical energy. Therefore, from definition 2.2, the square of electromechanical coupling coefficient can be expressed as follows:

$$
\begin{equation*}
k^{2}=\frac{0.5(d E)^{2} / s^{E}}{0.5 \varepsilon^{T} E^{2}}=\frac{d^{2}}{\varepsilon^{T} s^{E}} \tag{2.5}
\end{equation*}
$$

The equations 2.6-2.7 show the relationship between coupling factor and transducer efficiency. This indicates that high coupling factor of an ultrasound transducer allows effective energy conversion in both transmitting and receiving an ultrasound wave. Therefore, improved sensitivity and broad bandwidth of an ultrasound transducer can be expected from high electromechanical coupling coefficient of a piezoelectric material.

$$
\begin{gather*}
\text { Transmit Efficiency }=\frac{k_{t}}{1-k_{t}^{2}} \frac{\varepsilon_{33}^{S}}{c_{33}^{D}}  \tag{2.6}\\
\text { Receiver Efficiency }=\frac{k_{t} t}{c_{33}^{D} \varepsilon_{33}^{S}} \tag{2.7}
\end{gather*}
$$

## Electrical Impedance

Generally, the transducer is connected to the imaging electronics by a coaxial cable, whose impedance is around $50 \Omega$. When the electrical impedance of piezoelectric materials is not matched to that of coaxial cable, the energy transfer is limited, resulting in reduced sensitivity or signal to noise ratio (SNR).[49] In order to maximize energy transfer in the frequency range of operation, the electrical impedance of a piezoelectric material should be close to that of the coaxial cable.

The electrical impedance of the transducer can get a rough estimation by calculating the element of capacitance, C , and operating center frequency, $\mathrm{f}_{c}$ according to the equation 2.8 .

$$
\begin{equation*}
Z=\frac{1}{j \omega C} \tag{2.8}
\end{equation*}
$$

where C and $\omega$ are capacitance and angular center frequency $\left(2 \pi \mathrm{f}_{c}\right)$, respectively. The capacitance, C is can be computed by the equation 2.9 .

$$
\begin{equation*}
C=\frac{\varepsilon_{0} \varepsilon_{r} A}{t} \tag{2.9}
\end{equation*}
$$

where A is the area, t is thickness, $\varepsilon_{0}$ and $\varepsilon_{r}$ are the free space and relative dielectric permittivity.

The equations indicate that the dielectric permittivity of transducer materials has a major influence on the electrical impedance $(\mathrm{Z})$ of a transducer. Thus, in order to improve the electrical impedance matching between the transducer and imaging electronics, the permittivities and the geometries of the piezoelectric elements in transducers should be considered. In general, high frequency single element transducers require low permittivity materials, while high frequency array transducers require high permittivity materials.

## Acoustic Impedance

Analogous to electrical impedance matching, the acoustic impedance of a piezoelectric material should be matched to that of body tissue for an efficient transfer of acoustic energy from the transducer to the tissue. Acoustic impedance (Z) can be computed by the stiffness ( k ) and the density ( $\rho$ ), or ultrasound speed (c) and the density ( $\rho$ ), as shown in equation 2.10 .

$$
\begin{equation*}
Z=\sqrt{k \times \rho}=c \times \rho \tag{2.10}
\end{equation*}
$$

The strength of the reflection at the interface can be computed with the difference in acoustic impedance between the tissue and the piezoelectric transducer. When the difference between the impedances is greater, the reflection of the incident ultrasound wave becomes larger according to the equation in Figure 2.6. Thus, the best acoustic impedance matching between the transducer and the tissue in body can be achieved by using a piezoelectric material whose impedance is similar to the tissue impedance.


Figure 2.6. Schematic representation of ultrasound reflection at the interface between a transducer and a tissue.

Unfortunately, ferroelectric materials generally have high density, and thus, high acoustic impedance (greater than 30 MRayl ) according to the equation 2.10. Since the acoustic impedance of most soft tissues in body is around 1.5 MRaly, as shown in Table 2.2, a large impedance mismatch between soft tissues and a piezoelectric transducer is expected, resulting in a large reflection at the interface.

This problem can be overcome by using one or two impedance matching layers.[50,

51] In general, the optimum thickness of matching layer is one fourth of the ultrasound wavelength in the layer, and the acoustic impedance of matching layer is intermediate between the piezoelectric and the tissue impedance according to the following equations:

Single matching layer,

$$
\begin{equation*}
Z_{m}=\sqrt{Z_{p} Z_{a}} \tag{2.11}
\end{equation*}
$$

Double matching layer,

$$
\begin{align*}
Z_{m 1} & =Z_{a}^{3 / 7} Z_{p}^{4 / 7}  \tag{2.12}\\
Z_{m 2} & =Z_{a}^{6 / 7} Z_{p}^{1 / 7}
\end{align*}
$$

where subscipts $\mathrm{p}, \mathrm{m}$, and a, denote the piezoelectric element, the matching layer, and the acoustic media, respectively, and $\mathrm{Z}_{m 1}, \mathrm{Z}_{m 2}$ denote the acoustic impedance of the first and second matching layer, respectively.

The role of backing layer is similar to that of matching layer. With the application of an electrical signal to the transducer, the piezoelectric element vibrate or ring on at its resonance frequency, and the induced pulse of sound propagates both in the front and back directions. Without damping the vibration of the transducer, the pulses will ring on for many cycles (long pulse duration) than those with damping, causing reduced axial resolution.

Backing materials of ultrasound transducers provide damping the transducer's vibra-

Table 2.2. Acoustic impedance of various tissues. (MRayl $=10^{6} \times \mathrm{kg}\left(\mathrm{m}^{2} \mathrm{~s}\right)$ )[36]

| Tissue | Air | Fat | Urine | Liver | Blood | Muscle | Bone |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Impedance <br> (MRayl) | 0.0004 | 1.38 | 1.49 | 1.64 | 1.62 | 1.7 | 7.8 |

tions by removing or absorbing vibration energy from the ultrasound transducer. In order to fabricate a damped transducer, the backing materials should have an impedance close to the piezoelectric materials, as well as sufficient attenuation coefficient and thickness. This allows the energy to flow or to be absorbed by the rear face, reducing the reflections at the interface between piezoelectric and backing layer.[45] In addition to damping the transducer, backing layer also serves a mechanical support for the brittle piezoelectric materials.

### 2.3 Piezoelectric Materials

As discussed previously, a piezoelectric material is the material that develop electric polarization through an applied stress, or conversely the development of a strain upon the application of an electric field. Currently, many types of piezoelectric materials are available for ultrasound transducers. These include wurtzite-structured compounds ( ZnO and AiN ), quartz, and ferroelectric materials. Each material has its own advantages and disadvantages in terms of either electrical or mechanical properties, but ferroelectric materials are of interest for ultrasound transducer applications since exceptionally high dielectric properties can be found in this crystal structure. Ultrasound transducers would greatly benefit from the presence of high dielectric permittivity of ferroelectric materials since high dielectric permittivity value allows the materials with large piezoelectric properties according to the following equation 2.13.[52]

$$
\begin{equation*}
d_{i j} \sim 2 Q_{i j} \varepsilon_{0} \varepsilon_{r} P_{i} \tag{2.13}
\end{equation*}
$$

where $\mathrm{Q}_{i j}$ is electrostrictive constant, $\varepsilon_{0}$ is the permittivity of free space, $\varepsilon_{r}$ is the relative permittivity, and $\mathrm{P}_{i}$ is the remnant polarization.

Table 2.3 summarizes property comparison of non-ferroelectrics and ferroelectric materials. It is evident from Table 2.3 that ferroelectric families generally possess high dielectric and piezoelectric properties, and among them, perovskite-type ferroelectric materials are of interest, offering much higher dielectric and piezoelectric properties.

Table 2.3. Room temperature dielectric and piezoelectric properties of various piezoelectric materials.[53-58]

| Material | Structure | $\mathrm{T}_{c}\left({ }^{\circ} \mathrm{C}\right)$ | $\varepsilon_{33}^{T} / \varepsilon_{0}$ | $\begin{gathered} \mathrm{d}_{33} \\ (\mathrm{pC} / \mathrm{N}) \end{gathered}$ | $\mathrm{k}_{33}$ | $\mathrm{Q}_{m}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Quartz (Single crystal) | $\alpha$-Quartz | $\begin{gathered} 573 \\ (\alpha-\beta) \end{gathered}$ | $\begin{gathered} 4.5 \\ \left(\varepsilon_{11}^{T} / \varepsilon_{0}\right) \end{gathered}$ | $2\left(\mathrm{~d}_{11}\right)$ | $0.09 \quad 1$ | 100,000 |
| PVDF-TrFE[59] (Polymer) |  |  | 7.9 | 33 | 0.3 |  |
| $\mathrm{LiNbO}_{3} \text { (Single }$ crystal) | Corundum | 1150 | 27.8 | 6 | $0.49\left(\mathrm{Y} / 36^{\circ}-\right.$ <br> cut) | $10,000$ |
| $\mathrm{Na}_{0.5} \mathrm{Bi}_{0.5} \mathrm{Ti}_{4} \mathrm{O}_{15}$ | Aurivillius | 600 | $\sim 140$ | 18 | 0.15 | 100 |
| $(\mathrm{Pb}, \mathrm{Ba}) \mathrm{Nb}_{2} \mathrm{O}_{6}$ | Tungsten Bronze | 400 | 300 | 85 | 0.3 | 15 |
| $\mathrm{BaTiO}_{3}$ | Perovskite | 120 | 1500 | 190 | 0.49 | 100 |
| Undoped PZT[52] | Perovskite | 386 | 730 | 223 | 0.67 | 500 |
| PZT 5H | Perovskite | 193 | 3500 | 590 | 0.73 | 65 |
| PMN-33PT | Perovskite | 160 | 5000 | 690 | 0.73 | 75 |
| PMN-PT (Single crystal) | Perovskite | 150 | $\begin{aligned} & 5500- \\ & 7500 \end{aligned}$ | $\begin{aligned} & 1700- \\ & 2200 \end{aligned}$ | >0.9 |  |

### 2.3.1 Ferroelectric Materials

Ferroelectric materials can be defined as the materials that can display a spontaneous polarization $\left(\mathrm{P}_{s}\right)$ at least in two equilibrium states in the absence of an external electric field. Spontaneous polarization $\left(\mathrm{P}_{s}\right)$ are, in general, temperature dependent, thus, ferroelectric materials is a subgroup of pyroelectric materials. When $\mathrm{P}_{s}$ can be
switched at least in two equilibrium states by electric field, pyroelectric materials are called ferroelectric materials.[52, 60-62] Therefore, all ferroelectrics are pyroelectric and all pyroelectrics are also piezoelectric, but not vice versa, as schematically shown in Figure 2.7.

There are a wide range of ferroelectric materials, such as tungsten bronze, aurivillius compounds (bismuth layer structured), illmenite ferroelectrics $\left(\mathrm{LiNbO}_{3}\right.$ and $\left.\mathrm{LiTaO}_{3}\right)$ and perovskite structures.[47, 61, 63] Among them, perovskite ferroelectric oxides are the most technologically important class of ferroelectric materials due to high dielectric and piezoelectric materials.

The composition of perovksite is generally described by the chemical formula $\mathrm{ABO}_{3}$. Barium titanate and lead zirconate titanate are common examples for this $\mathrm{ABO}_{3}$ formula. One of key characteristics for this class of materials is that they can undergo a phase transition from a high temperature non-ferroelectric phase to a low temperature ferroelectric phase as the cation ion (B) in the oxygen octahedra shift off the center. This leads to a spontaneous polarization of a crystal even in the absence of


Figure 2.7. Venn diagram showing the relationship between different classes of dielectric materials.
electric field, as illustrated in Figure 2.8, and the materials whose structures possess non-centrosymmetric exhibit the phenomenon of piezoelectricity. At high temperature, however, the perovskite structure is a centre of symmetry (cubic phase); thus, spontaneous polarization cannot be a unique direction, resulting in no spontaneous polarization and piezoelectricity. The temperature at which the material transforms from ferroelectric to non-ferroelectric phase is called Curie temperature $\left(\mathrm{T}_{C}\right)$. At this temperature ( $\mathrm{T}_{C}$ ), the dielectric permittivity exhibits sharp first or second order phase transition, and follows Curie Weiss law above $\mathrm{T}_{C}$ [62, 64-66]

Ferroelectricity is often determined by the measurement of the dielectric displacement (D) as a function of electric field. Since ferroelectric materials have ferroelectric domains, they exhibit dielectric hysteresis with the application of electric field. The relationship between the polarization and the dielectric displacement is given by

$$
\begin{equation*}
D=\varepsilon_{0} E+P \tag{2.14}
\end{equation*}
$$

Due to their high dielectric permittivity ( $\varepsilon$ ) for most ferroelectric materials, polarization $\left(\mathrm{P} \approx \varepsilon_{0} \varepsilon E\right)$ is much larger than $\varepsilon_{0} E$. Therefore, in ferroelectric materials, dielectric displacement (D) is simply regarded to as the polarization (P). For non-ferroelectric materials, the dielectric displacement is directly proportional to the applied electric field according to the equation ( $\mathrm{P} \approx \varepsilon_{0} \varepsilon E$ ), leading to a linear response as a function of electric field. However, ferroelectric materials contain multiple domains that can be switched by applying electric field, as schematically illustrated in Figure 2.9. When electric field is applied to the ferroelectric material, the domains start to switch along the direction of the electric field at the expense of other domains, and the polarization shows strongly non-linear behavior (hysteresis). As the field is increased beyond the point where no further polarization can develop, all of the domains are aligned in the direction of the


## $T\left({ }^{0} \mathrm{C}\right)>$ Curie temperature $\left(\mathrm{T}_{\mathrm{c}}\right)$

No spontaneous polarization ( $\mathbf{P}_{\mathrm{s}}$ )
$\mathbf{a}=\mathbf{b}=\mathbf{c}$
$\alpha=\beta=\gamma=90^{\circ}$
$T\left({ }^{0} \mathrm{C}\right)<$ Curie temperature $\left(\mathrm{T}_{\mathrm{c}}\right)$

Rhombohedrally distorted unit cell

$$
\mathbf{a}=\mathbf{b}=\mathbf{c}
$$

$$
\alpha=\boldsymbol{\beta}=\gamma \neq 90^{\circ}
$$


[111]
Tetragonally distorted unit cell


Figure 2.8. Perovskite unit cell in the symmetric cubic state above Curie temperature, and tetragonally or rhombohedrally distorted unit cell below the Curie temperature.
electric field. This is corresponding to the region B in Figure 2.9. At this stage, the ferroelectric behaves as a linear dielectric with further increasing electric field, and the polarization is said to be saturated $\left(\mathrm{P}_{s}\right)$.

When the electric field is removed, the polarization does not go to zero but possesses macroscopic polarization called a remnant polarization, $\mathrm{P}_{r}$. If the material is a ideal single domain crystal, $\mathrm{P}_{r}$ and $\mathrm{P}_{s}$ would be identical, but in polycrystalline materials or multi-domain crystals, $\mathrm{P}_{s}$ is, in general, larger than $\mathrm{P}_{r}$ due to the complex domain configurations resulting from the presence of boundary conditions and some elastic and charged defects in the material. These mechanical boundary conditions may nucleate new reverse domains and some domains will back-switch as the electric field is removed, leading to lower macroscopic polarization $\left(\mathrm{P}_{r}\right)$ compared to saturation polarization $\left(\mathrm{P}_{s}\right)$. To reach the zero polarization, reverse electric field need to be applied, and the electric field to bring the polarization to zero is called the coercive field, $\mathrm{E}_{c}$. Application of an oppositely directed electric field larger than coercive field will, thus, cause the material


Figure 2.9. Schematic representation of a hysteresis loop of a ferroelectric material.[65]
to saturate in the opposite direction. Therefore, in an ideal situation, the hysteresis loop induced by electric field is symmetrical, displaying the equal quantities of coercive field, remnant polarization in the positive and negative directions.

## Lead zirconate titanate

The perovskite structure is tolerant of a wide range of substitution on both A-site and B-site, allowing for the synthesis of a large number of complex compounds. Currently, there are a large number of ferroelectric solid solutions. Among them, lead zirconate titanate (PZT), the compound of $\mathrm{PbZrO}_{3}$ and $\mathrm{PbTiO}_{3}$, is of great importance since they are the most widely used piezoelectric materials for electromechanical devices owing to their superior piezoelectric and electromechanical properties.

At room temperature, $\mathrm{PbZrO}_{3}$ belongs to an anti-ferroelectric material with orthorhombic crystal structure; thus there are no piezoelectricity. $\mathrm{PbTiO}_{3}$ belongs to the ferroelectric material with tetragonal phase, but $\mathrm{PbTiO}_{3}$ possess low piezoelectric activities. However, the solid solution of these two compositions (PZT) exhibits the excellent dielectric and piezoelectric properties near a morphotropic phase boundary (MPB), as indicated in phase diagram of PZT (Figure 2.10). Since the phase transition is induced by chemical composition, the coexistence of two phases is not sensitive to the temperature, which results in stable composition over a wide range of temperatures.

The origin of the maximum dielectric and piezoelectric response for MPB composition has been a topic of research studies. The most widely accepted explanation for enhanced properties in the MPB composition has been attributed to the increased number of possible directions for spontaneous polarization, $\mathrm{P}_{s .}$.[67, 68] For instance, PZT was believed to have 14 possible directions for $\mathrm{P}_{s}$ in the phase coexistence region (MPB) since the tetragonal phase $\left(\mathrm{PbTiO}_{3}\right)$ has six possible direction of $\mathrm{P}_{s}$ along $<100>$ directions, and rhomboehdral phase $\left(\mathrm{PbZrO}_{3}\right)$ has eight possible direction of $\mathrm{P}_{s}$ along


Figure 2.10. Structural phase diagram for the (1-x) $\mathrm{PbZrO}_{3}-\mathrm{xPbTiO}_{3}$ ( $\mathrm{P}_{C}$-paraelectric cubic phase, $\mathrm{F}_{R}$ ferroelectric rhombohedral phase, $\mathrm{F}_{T}$-ferroelectric tetragonal phase)[52]
$<111>$ directions. This can substantially enhance the alignment of randomly oriented ferroelectric domains, allowing optimum polarization under an applied electric field.

Polarization rotation is another theory for the mechanism of high dielectric and piezoelectric properties near MPB. As for PZT systems, due to the absence of PZT single crystals, the intrinsic properties of PZT have been obtained by using theoretical analysis based on Landau-Ginzburg-Devonshire (LGD) approach.[69-72] According to the theoretical calculations, a large increase in dielectric softening occurs along the direction of incipient crystal structure as the crystal transforms from one phase to another near MPB. For example, when tetragonal phase transforms to rhombohedral phase, dielectric softening occurs $<111\rangle$ directions, while rhombohedral phase transforms to tetragonal phase, dielectric softening occurs $<001>$ directions. Consequently, this leads to the maximum dielectric and piezoelectric response at the boundary through averaging of the anisotropy properties (see Figure 2.11).


Figure 2.11. Dielectric permittivity perpendicular and parallel to polar axis as a function of concentration in systems.[73]

## Relaxor-ferroelectrics

$A\left(B_{1} B_{2}\right) O_{3}$ type perovskites, referred to as relaxors or relaxor-ferroelectrics, are another very important class of oxides, and are distinguished from normal $\mathrm{ABO}_{3}$ type ferroelectric materials due to different characteristics from normal ferroelectrics. For instance, as can be seen in chemical formula, $\mathrm{A}\left(\mathrm{B}_{1} \mathrm{~B}_{2}\right) \mathrm{O}_{3}$, the B site of relaxors is occupied by a mixture of cations, such as a low-valence cation $\left(\mathrm{Mg}^{2}+, \mathrm{Fe}^{3}+, \mathrm{Sc}^{3}+\right.$ or $\left.\mathrm{Zn}^{2}+\ldots\right)$ and a high valence cation $\left(\mathrm{Ta}^{5}+, \mathrm{Nb}^{5}+\right.$ or $\left.\mathrm{W}^{6}+\ldots\right)$. These random occupations of the B-site in same crystallographic sites lead to the onset of relaxor behaviors, such as a diffuse phase transition over a Curie temperature range, and strong frequency dependent dielectric permittivity.[74, 75]

The usefulness of relaxors for ultrasound transducer applications is from the discovery of the piezoelectric properties when $B$ site ions of relaxors, such as $\mathrm{Pb}\left(\mathrm{Mg}_{1 / 3} \mathrm{Nb}_{2 / 3}\right) \mathrm{O}_{3}$ ( PMN ) or $\mathrm{Pb}\left(\mathrm{Zn}_{1 / 3} \mathrm{Nb}_{2 / 3}\right) \mathrm{O}_{3}(\mathrm{PZN})$, are substituted with normal ferroelectrics, such as $\mathrm{PbTiO}_{3}(\mathrm{PT})$. The incorporation of PT into PMN or PZN system leads to MPB solid solutions, subsequently exhibiting the enhanced dielectric and piezoelectric properties, analogous to PZT system. Figure 2.12 shows the phase diagram of PMN-PT. MPB in PMN-PT is situated at approximately $33 \%$ PT, but in contrast to PZT, MPB in these materials displays strongly curved near Curie temperature, resulting in phase transition below Curie temperature. This indicates that high piezoelectric response of MPB composition of PMN-PT can be achieved with the expense of more temperature dependent properties. In addition, the Curie temperature of these materials is quite low $\left(\sim 150^{\circ} \mathrm{C}\right)$, compared to PZT system, whose Curie temperature is approximately $350^{\circ}$ C. Since all piezoelectric properties are lost when the piezoelectric material is heated above Curie temperature, a low Curie temperature of relaxor ferroelectric materials is one of disadvantages for piezoelectric applications operating at high temperatures.


Figure 2.12. Phase diagram of PMN-PT solid solution system.[76]

The advantages of relaxor-ferroelectric solid solutions over normal ferroelectric materials can be attributed to their higher dielectric permittivity and comparable piezoelectric properties to PZT system. Most importantly, relaxor-ferroelectrics can be grown as large single crystals by variety of methods, which can offer significantly high electromechanical coupling factor, exceeding $90 \%$ of $\mathrm{k}_{33}$, resulting in a large improvement in overall performance of ultrasound transducers.

The mechanism of such a high piezoelectric response of relaxor-PT single crystals has been explained with polarization rotation effect. Park et al.[19-24] investigated the properties of rhomobohedral compositions of PZN-4.5PT as a function of the crystallographic orientations, and found that $<001>$ oriented relaxor single crystals exhibited extremely high piezoelectric responses, strain over $1.7 \%$, piezoelectric constant $\mathrm{d}_{33}$ over $2000 \mathrm{pC} / \mathrm{N}$, electromechanical coupling factor $\mathrm{k}_{33}$ over $90 \%$, with almost anhysteretic strain-field behavior. However, with increased deviation from $<001>$ direction, an increase in strain hysteresis and a decrease in piezoelectric response were observed from the same crystal materials. The results indicate that $<001>$ oriented rhombohedral relaxor-PT crystal creates four degenerate domain variants, which can be aligned along any one of the four equivalent $<111\rangle$ directions. This leads to the stable multi-domain configurations; therefore, poling with small external electric field has little effect on domain reorientation, resulting in low strain hysteresis. However, the application of large electric field rotates polarization vector from the $<111\rangle$ toward $<001\rangle$, leading to the phase instability in this crystal, contributing to the large dielectric and piezoelectric properties, similar to the mechanism of enhanced properties of PZT in the MPB region.


## Ceramic Processing and

## Characterization of Relaxor-PTs

### 3.1 Introduction

Ferroelectric ceramics, represented by PZT ceramics, have been the material of choice in many ultrasound transducers due to their high electromechanical coupling factors and a wide range of dielectric permittivities. Unfortunately, typical ferroelectric ceramics have grain size in the range of 4 to 10 microns. Such a large grain size of ferroelectric ceramics is too coarse to allow accurate machining of small feature size, making them unsuitable for high frequency ultrasound transducers.

Fine grained ( $\leq 1$ microns) ferroelectric ceramics have been an enabling technology for high frequency ultrasound transducer applications. The effects of grain size on mechanical properties of PZT ceramics have been studied over the years, and experimentally found that fine grained ferroelectric ceramics have higher mechanical strength with high Weibull modulus (m) and better dicing performance than coarse grained counterparts.[77, 78] One of examples is demonstrated in Figure 3.1. From the fig-
ure, the element width of these materials is approximately $70 \mu \mathrm{~m}$, and the operating frequency for this design is less than 10 MHz . Even at this low frequency surface damage of commercial PZT (Motorola 3203 HD ) are evident, exhibiting a number of grain pull-outs in the kerf wall. It can be easily imagined that for high frequency ( 40 to 50 MHz ) ultrasound transducer, whose element width is only 10-20 microns, coarse grained PZT ceramics have very few grains across the width with a large portion of damaged surfaces, degrading the performance and reliability of the materials.

One issue associated with fine grained piezoelectrics is, however, a reduction in grain size ( $<1$ micron) can suppress extrinsic contributions to piezoelectricity, e,g., clamping of domain wall motion, and the consequence is reduced piezoelectric activities. Several studies regarding the effects of grain size on piezoelectric properties have been reported, showing that fine grained piezoelectric materials, whose grain sizes are less than $1 \mathrm{mi}-$ crons, generally possess reduced piezoelectric properties compared to normal grain size of ferroelectric ceramics.[27, 28, 79-81]

As the size of aperture becomes very small with increasing ultrasound frequencies, there is increasing concern about electrical impedance mismatch between the transduc-


Figure 3.1. Cross section of a diced array of fine grained PZT and commercial PZT (Motorola $3203 \mathrm{HD})$.[35]
ers and imaging electronics. This leads to a demand of piezoelectric materials with a high dielectric permittivity because the electrical impedance inversely proportional to the dielectric permittivity of the piezoelectric element. Among various piezoelectric materials, PMN-PT based piezoelectrics are of interest, offering superior dielectric permittivity than other piezoelectric materials, with comparable electromechanical coupling factors to PZT ceramics.

The objective of this work is to develop fine-grained ( $\leq 1$ micron) PMN-PT ceramics without compromise of dielectric, piezoelectric and electromechanical properties. This chapter describes the synthesis and processing of fine grained PMN-PT ceramics, followed by the characterization of synthesized materials. In addition to the characterization of polycrystalline PMM-PT ceramics, the dielectric, piezoelectric and electromechanical properties of bulk binary and ternary PMN based single crystals were also characterized, and quantitatively compared with those of polycrystalline ceramics.

### 3.2 Experimental Methods and Materials Preparation

### 3.2.1 Preparation of Powders and Ceramic Specimens

Fine-grained ( $\leq 1$ micron) PMN-PT polycrystalline ceramics were fabricated using PMN-PT powder obtained from TRS technologies Inc. Sub-micron particles prepared from attrition milling for 8 hours to break into sub-micron particles. Commercial dispersant, Darvan 821A (R.T.Vanderbilt Company Inc., CT), which was $40 \mathrm{wt} \%$ ammonium polyacrylate in solution was used for the preparation of the well-dispersed slurry. The pH was adjusted with ammonium hydroxide solutions $\left(\mathrm{NH}_{4} \mathrm{OH}\right)$ to $9-10$. To minimize contamination, high purity and high strength zirconia media balls were used during milling process. The characteristic size of particles of the milled powder was performed
by scanning electron microscope (S-3500N, Hitachi, Tokyo, Japan), and a Zetasizer instrument (Malvern Instruments, Malvern, UK). In order to provide the strength to the green body, the milled powder was mixed with binder (Rhoplex), as rotating a plastic bottle containing powder, ethanol and binder for $3 \sim 4$ hours. The powder was then sieved through a 80 mesh screen to obtain desirable powder flowability as well as to maintain strength for pressing. The granulated powders were uniaxially pressed into pellets of 20 mm in diameter and $2 \sim 3 \mathrm{~mm}$ thickness. Once the desired shape is formed by pressing, thermal debinding method was used to remove the organic phase of binder. In order to prevent defects during debinding, burn out processs was performed by slow heating at $325^{\circ} \mathrm{C}$ for 1 hour and then $550^{\circ} \mathrm{C}$ for 2 hours. The burn out samples were then pressed by cold isostatic pressing (CIP) in order to increase the green body densities.

The green samples were placed on platinum foil in a closed alumina crucible to prevent a reaction between the samples and the alumina crucible. Because of the volatile nature of PbO , a PbO rich atmosphere was maintained with the self source powder (TRS-HK1 powder) during sintering process. Dense ceramic samples were produced by conventional sintering using various temperatures $\left(1160 \sim 1250^{\circ} \mathrm{C}\right)$ for 2 hours in air. Since the porosity leads to a problem in processing very thin samples, as the electrodes can short across a pore if it is large enough, the pellets were hot isostatically pressed (H.I.P) at $1080^{\circ} \mathrm{C}$ for 2 hours in an $\mathrm{O}_{2} / \mathrm{Ar}$ atmosphere to eliminate any porosity. Figure 3.2 summarizes the steps to prepare fine grained PMN-PT ceramics.

The prepared samples were coated with gold using a sputtering machine for electrical measurements, and poled in silicone oil at room temperature at an electric field two times the coercive field of each material. After poling, the samples were aged at room temperature overnight prior to the electrical measurements.


Figure 3.2. Schematic flow chart of fine grained PMN-PT ceramics

### 3.2.2 Characterization of Physical and Electrical Properties

## Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM, S-3500N, Hitachi, Tokyo, Japan) was used with an accelerating voltage of 20 kV for imaging of the particle and grain sizes of PMNPT materials. For sample preparation, the powders and fractured piece of bulk materials were put on the carbon tape, and mounted on the sample holder. To prevent them from charging during scans, powders and the surfaces of prepared samples were coated with a thin layer of gold using sputtering prior to load them into vacuum chamber.

## Electrical Properties Measurements

Free and clamped dielectric permittivity were determined using an HP4284 multifrequency LCR meter (Hewlett-Packard) and/or HP4294A impedance analyzer (HewlettPackard). The free and clamped dielectric permittivity were calculated from capacitance measurements according to the following equation 3.1.

$$
\begin{equation*}
\varepsilon_{33} / \varepsilon_{0}=\frac{C \cdot t}{A \cdot \varepsilon_{0}} \tag{3.1}
\end{equation*}
$$

where $\varepsilon_{33}$ and $\varepsilon_{0}$ are the relative and free space dielectric permittivities, A is the area of the sample, C is the capacitance measured at 1 kHz frequency (for $\varepsilon_{33}^{T}$ ) and at the frequency above 2 times anti-resonance frequency, $\mathrm{f}_{a}$ (for $\varepsilon_{33}^{S}$ ), where the sample is essentially clamped. A typical plot of dielectric permittivity of piezoelectric materials as a function of frequency is shown in Figure 3.3, exhibiting the regions of free and clamped dielectric permittivity of the samples.

The dielectric-temperature measurements were performed to determine the temperature related dielectric parameters such as transition temperatures $\left(\mathrm{T}_{C}\right.$ or $\left.\mathrm{T}_{O-T}\right)$ and


Figure 3.3. Measurements of dielectric permittivity. $\varepsilon_{33}^{S}$ is determined in the constant region between the first and third resonances, whereas $\varepsilon_{33}^{T}$ is calculated in the indicated region below the first harmonic $(1 \mathrm{kHz})$.
maximum dielectric constant. The dielectric measurements were carried out with an automated system consisting of an HP multiple frequency LCR meter interfaced with an HP desk top computer, which also controlled the Kanthal-wound resistance furnace. Capacitance and dissipation factor of the samples were measured pseudo-continuously at frequencies of $0.1,1,10 \mathrm{kHz}$ as the sample heated from 30 to $300^{\circ} \mathrm{C}$ at a rate of $5^{\circ} \mathrm{C}$ per minute.

To determine electromechanical properties, the samples were prepared in the different geometric shapes based on IEEE standard, which are described in Figure 3.4.[82] The magnitudes of electromechanical coupling factors ( $\mathrm{k}_{p}, \mathrm{k}_{t}$ and $\mathrm{k}_{33}$ ) were calculated from the measured $\mathrm{f}_{r}$ and $\mathrm{f}_{a}$ using an HP4294A impedance-phase gain analyzer, based on the equations in Figure 3.4.

Polarization hysteresis and unipolar strain hysteresis were measured at 1 Hz frequency using a modified Sawyer-Tower circuit and linear variable differential transducer


Figure 3.4. Schematic representation of the measurements and equations for electromechanical properties.[82]
(LVDT) driven by a lock-in amplifier (Stanford Research Systems, Model SR830). The remnant polarization $\mathrm{P}_{r}$ and coercive field $\mathrm{E}_{c}$ were determined from the hysteresis loops at a driving field of $20 \mathrm{kV} / \mathrm{cm}$. High field piezoelectric coefficient $\left(\mathrm{d}_{33}\right)$ were measured from the slope of strain / field curves driven with a unipolar signal at the driving field of $10 \mathrm{kV} / \mathrm{cm}$, and strain hysteresis were calculated from the equation in Figure 3.5.


Figure 3.5. Schematic representation of unipolar strain hysteresis. $x_{\text {max }}$ is the maximum strain and $\Delta x$ is the strain deviation during the rise and fall of the field at half of the maximum electric field

### 3.3 Results and Discussion

### 3.3.1 Characterization of Powders and Sintered Ceramics

SEM images of received powders (TRS-HK1) are shown in Figure 3.6. From figures, agglomerates in received powders are apparent, and the particle size varied widely, which can cause the problems for the synthesis of uniform fine grain microstructures. Figure 3.7 shows the particle size distribution and SEM image of the milled powders. After attrition milling, particle aggregates were ground and crushed by the media, resulting in a narrow particle size distribution with smaller particle sizes compared to as-received powder. The average particle size of the milled powder was found to be $\sim 300 \mathrm{~nm}$.

An optimized sintering temperature was determined from the highest density as well as the analysis of microstructure. Densities were measured by Archimedes method. Densities of more than $95 \%$ of theoretical value were achieved above $1180{ }^{\circ} \mathrm{C}$. With further increasing sintering temperature, weight loss and grain size were increased. Table 3.1 summarizes the obtained results from the sintering process.

Based on the physical properties of sintered samples, the samples were fired at 1180 ${ }^{\circ} \mathrm{C}$ for 120 minutes. The microstructures of PMN-PT ceramics sintered at $1180^{\circ} \mathrm{C}$ were investigated using SEM, and shown in Figure 3.8. For comparison, the microstructures of the commercial TRS-HK1 ceramics (hereafter designated, coarse grained PMN-PT) were also investigated using the same method, and shown in Figure 3.8. The average grain size of synthesized PMN-PT at $1180^{\circ} \mathrm{C}$ was found to be on the order of $1 \mu \mathrm{~m}$, whereas that of coarse grained PMN-PT was approximately from 5 to $7 \mu \mathrm{~m}$.


Figure 3.6. SEM images of as-received PMN-PT powder.


Figure 3.7. SEM image and particle size distributions of milled PMN-PT powder. The distributions were obtained using Zetasizer instrument.

Table 3.1. Sintering conditions and properties of PMN-PT ceramics depending on sintering temperature.

| Sintering conditions |  |  | Weight loss | Density $^{a}$ | ${\text { Average grain size }{ }^{b}}^{2}$Temperature <br> $\left({ }^{\circ} \mathrm{C}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Heaing rate <br> $\left({ }^{\circ} \mathrm{C} / \mathrm{min}\right)$ | Times <br> $($ min. $)$ | $(\%)$ | $\left(\mathrm{g} / \mathrm{cm}^{3}\right)$ | $(\mu \mathrm{m})$ |  |
| 1150 | 5 | 120 | 0.5 | 6.8 | 0.8 |
| 1180 | 5 | 120 | 1 | 7.7 | 1 |
| 1200 | 5 | 120 | 2 | 8 | 2 |
| 1250 | 5 | 120 | 2.2 | 7.9 | 5 |

[^0]

Figure 3.8. SEM images for (a) fine and (b) coarse grained PMN-PT ceramics.

### 3.3.2 Characterization of Electrical Properties

## Dielectric Properties

At room temperature, the dielectric properties of synthesized fine-grained PMNPT ceramics were found to be comparable values to those of coarse grained PMN-PT, approximately 4500 for dielectric permittivity and 0.03 for dielectric loss $(\tan \delta)$ at 1 kHz . After poling, both samples exhibited an increase in dielectric permittivity $\left(\varepsilon_{33}^{T} / \varepsilon_{0}\right)$ and a decrease in $\tan \delta$. Poled $\varepsilon_{33}^{T} / \varepsilon_{0}$ and $\tan \delta$ of fine and coarse grained PMN-PT samples were found to be on the order of $\sim 6000$ and $\sim 2 \%$, respectively. The clamped dielectric permittivity ( $\varepsilon_{33}^{S} / \varepsilon_{0}$ ) of fine-grained PMN-PT samples were found to be on the order of 2500 , which are also comparable to that of coarse grained PMN-PT.

For PMN-PT and PIN-PMN-PT single crystals, the magnitude of permittivities were found to be smaller than those of polycrystalline ceramics before poling. $\varepsilon_{33}^{T} / \varepsilon_{0}$ of $<001>$-poled PMN-PT crystals was found to be $\sim 3200$, while that of $<001>$-poled PIN-PMN-PT crystals was $\sim 2700$.

Upon poing, similar to the polycrystalline ceramics, increases in $\varepsilon_{33}^{T} / \varepsilon_{0}$ were observed in both PMN-PT and PIN-PMN-PT crystals, exhibiting $\sim 6000$ of $\varepsilon_{33}^{T} / \varepsilon_{0}$. As expected, $<001>$-poled single crystals exhibited low dielectric losses ( $<1 \%$ ), which are much lower than those of polycrystalline materials as a result of the optimum domain engineering. For clamped dielectric permittivity $\left(\varepsilon_{33}^{S} / \varepsilon_{0}\right)$, single crystals exhibited lower values than polycrystalline PMN-PT ceramics, on the order of $\sim 900$ for both PMN-PT and PIN-PMN-PT samples. The obtained dielectric properties of relaxor-PT materials are summarized in Table 3.2.

The increased dielectric permittivity after poling can be account for the result of a large dielectric anisotropy of the relaxor-PT crystals. It is well known that lead $(\mathrm{Pb})$-based ferroelectric materials, such as PZT and PMN-PT, possess large dielectric

Table 3.2. Dielectric properties of relaxor-PT polycrystalline ceramics and single crystals. Free dielectric permittivity and dielectric loss were measured at $1 \mathrm{kHz} .{ }^{*}$ refers to unpoled dielectric properties at 1 kHz .

| Materials | Cut | Grain Size ( $\mu \mathrm{m}$ ) | $\varepsilon_{33}^{T} / \varepsilon_{0}$ | $\varepsilon_{33}^{S} / \varepsilon_{0}$ | $\tan \delta$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| PMN-PT ceramics |  | 1 | 5800 | 2500 | 0.025 |
|  |  |  | *4500 |  | ${ }^{*} 0.031$ |
|  |  | 5-7 | 6100 | 2700 | 0.016 |
|  |  |  | *4800 |  | *0.022 |
| PMN-PT crystals | 001 |  | 6000 | 900 | 0.004 |
|  |  |  | *3250 |  | ${ }^{*} 0.02$ |
|  | 110 |  | 4500 | 730 | 0.008 |
|  |  |  | *3239 |  | *0.025 |
| PIN-PMN-PT crystals | 001 |  | 5600 | 900 | 0.006 |
|  |  |  | *2760 |  | *0.03 |
|  | 110 |  | 3300 | 650 | 0.01 |
|  |  |  | ${ }^{*} 1620$ |  | *0.04 |

anisotropy near morphotropic phase boundary (MPB), and generally exhibit highest value along the perpendicular to the polar axis, i.e., $\varepsilon_{\perp}>\varepsilon_{\|}$.[73] Therefore, when the crystals are unpoled states, the crystals are macroscopically cubic (m3m); thus, have an intermediate value between the maximum and minimum of dielectric permittivity of the crystals.[83] However, with poling along non-polar directions (e.g., $<100>$ ), optimized domain configurations are occurred in crystals, leading to an increase in dielectric permittivity.

Similarly, a change in dielectric permittivity of polycrystalline materials after poling can also be explained by the domain reorientations. Turik et al.[84] states that when $180^{\circ}$ domain reorientations are dominant over non- $180^{\circ}$ domain rotations during the poling process, the dielectric permittivity is, in general, increased since the presence of $180^{\circ}$ domains causes domain clamping, leading to a decrease in dielectric permittivity. Therefore, an increase in dielectric permittivity of PMN-PT ceramics after poling indicates that there are a large fraction of the $180^{\circ}$ domains in relaxor-PT ceramics before poling, and most of $180^{\circ}$ domains are realigned after poling. This process also results
in a decrease in dielectric loss since the dielectric loss is mainly originated from domain wall motions.

Figure 3.9 shows temperature dependence of dielectric properties of relaxor-PT samples at three different frequencies $(0.1 \mathrm{kHz}, 1 \mathrm{kHz}$, and 10 kHz$)$. From the figures, it can be observed that coarse grained PMN-PT ceramics exhibited sharp, high dielectric maximum, while fine grained PMN-PT ceramics exhibited a little broader and lower dielectric maximum at Curie temperature $\left(\mathrm{T}_{C}\right)$, indicating clamping of domain wall motion of fine-grained ceramics due to the conditions of more neighbouring grains and grain boundaries. However, the $\mathrm{T}_{C} \mathrm{~s}$ of both fine and coarse grained PMN-PT materials were found to be similar, around $\sim 150{ }^{\circ} \mathrm{C}$.

In contrast to polycrystalline PMN-PT materials, PMN-PT and PIN-PMN-PT single crystals showed dielectric anomalies below the $\mathrm{T}_{c}$, which indicates the ferroelectricferroelectric (F-F) phase transition temperature, where the crystal transforms to the tetragonal phase from rhombohedral phase $\left(\mathrm{T}_{R-T}\right)$. It has been reported that piezoelectric properties of single crystals significantly decreased above the F-F phase transition temperature.[25, 85-88] Thus, the phase transition temperature, $\mathrm{T}_{R-T}$, often indicates the maximum usage temperature of relaxor-PT single crystals. Higher Curie temperature $\left(\mathrm{T}_{c}\right)$ and F-F phase transition temperature $\left(\mathrm{T}_{R-T}\right)$ were found on PIN-PMN-PT crystals, compared to PMN-PT crystals. The $\mathrm{T}_{R-T}$ and $\mathrm{T}_{C}$ of $<001>$ PMN-PT crystals were found to be $\sim 95^{\circ} \mathrm{C}$ and $\sim 135^{\circ} \mathrm{C}$, while those of $<001>$ PIN-PMN-PT crystals were $\sim 105^{\circ} \mathrm{C}$ and $\sim 178{ }^{\circ} \mathrm{C}$.

## Ferro- and Piezo- electric Properties

Ferroelectric polarization-electric field (P-E) hysteresis loops for each material are shown in Figure 3.10. All samples exhibited well saturated P-E hysteresis loops. Compared to coarse grained PMN-PT ceramics, fine grained PMN-PT exhibited higher co-


Figure 3.9. Dielectric permittivity and loss as a function of temperature for relaxor-PT materials. Solid and dash line represent dielectric permittivity and dielectric loss, respectively. With increasing frequency, dielectric permittivity and dielectric loss were decreased and increased, respectively.
ercive field $\left(\mathrm{E}_{c}\right)$ and lower remnant polarization $\left(\mathrm{P}_{r}\right)$. An increase in coercive field and a decrease in remnant polarization of fine grained PMN-PT are a consequence of domain wall clamping by neighbouring grains and grain boundaries.

For relaxor-PT single crystals, it was found that $<001\rangle$ oriented crystals exhibited lower $\mathrm{P}_{r}$, when compared to $\left.<110\right\rangle$ oriented crystals, which is the result of crystal anisotropy. Theoretically, the polar direction of spontaneous polarization $\left(\mathrm{P}_{s}\right)$ of rhombohedral crystals is along [111], and the magnitude of $\mathrm{P}_{s}^{*}$ along non-polar direction can be estimated according to the following equation 3.2.[83]

$$
\begin{equation*}
P_{s}^{*}=P_{s} \cos \theta \tag{3.2}
\end{equation*}
$$

Since the angles $(\theta)$ between [111] and [001] and between [111] and [110] are $54.7^{\circ}$ and $35.3^{\circ}$, respectively, $\mathrm{P}_{s}^{*}$ s of $<001>$ and $<110>$ oriented crystals are 0.58 and 0.82 of $\mathrm{P}_{s}$, respectively. Therefore, $\mathrm{P}_{r}$ of $<001>$ oriented crystals is lower than that of $\left.<110\right\rangle$ oriented crystals.

High field piezoelectric properties of relaxor-PT materials are also shown in Figure 3.10. High field piezoelectric coefficients $\left(\mathrm{d}_{33}^{*}\right)$ were calculated from the slopes of unipolar strain curves, and the properties were compared with the $\mathrm{d}_{33}$ values directly measured from Belincourt meter.

For polycrystalline ceramics, both fine and coarse grained PMN-PT ceramics were found to be comparable piezoelectric coefficients ( $\mathrm{d}_{33}$ ), being on the order of $800 \mathrm{pC} / \mathrm{N}$ with the error range of $\pm 50$. However, as can be seen in the figure, fine grained PMNPT ceramics exhibited higher strain levels than coarse grained PMN-PT samples. The calculated $\mathrm{d}_{33}^{*}$ s of fine grained PMN-PT samples are on the order of $\sim 900 \mathrm{pm} / \mathrm{V}$, while those of coarse grained PMN-PT were around $\sim 800 \mathrm{pm} / \mathrm{V}$.

As expected, the piezoelectric properties of single crystals were superior to those

## Polycrystalline materials (PMN-PT ceramics)




## Single crystals (PMN-PT crystals)



Electric Field (kV/cm)

## Single crystals (PIN-PMN-PT crystals)



Electric Field (kV/cm)


Electric Field (kV/cm)


Electric Field (kV/cm)

Figure 3.10. Polarization-electric field hysteresis loops and unipolar strain curve for relaxorferroelectric polycrystalline and single crystal materials at room temperature.
of polycrystalline ceramics as a result of optimum domain orientation. In particular, $<001>$ oriented single crystals including PMN-PT and PIN-PMN-PT crystals exhibited much higher piezoelectric coefficients, $\mathrm{d}_{33} \mathrm{~s}>1700 \mathrm{pC} / \mathrm{N}$, when measured by Belincourt meter. Similarly, high field piezoelectric coefficients, $\mathrm{d}_{33}^{*} \mathrm{~s}$ also exhibited over 1800 pm/V for both $<001>$ oriented PMN-PT and PIN-PMN-PT crystals. For $<110>$ oriented crystals, however, the piezoelectric coefficients including $\mathrm{d}_{33}$ and $\mathrm{d}_{33}^{*}$ exhibited lower values than those of $<001>$ oriented crystals, being on the order of $\sim 1100 \mathrm{pC} / \mathrm{N}$ for $<110\rangle$ oriented PMN-PT crystals and $\sim 900 \mathrm{pC} / \mathrm{N}$ for $<110\rangle$ oriented PIN-PMNPT crystals.

The strain hystereses of the single crystals including $<001>$ and $<110\rangle$ orientation were significantly lower than those of polycrystalline ceramics owing to the enhanced stability of the domain- engineered $4 \mathrm{R}(<001\rangle)$ and $2 \mathrm{R}(<110\rangle)$ structures, as illustrated in Figure 3.11. Those unique domain configurations of single crystals limit domain wall motions, resulting in the almost anhysteretic response.


Figure 3.11. Illustrations of multi-domains of rhombohedral crystals. (a) single domain state with electric field in $\langle 111\rangle$ direction (b) 4 -domain state with electric field in $\langle 001\rangle$ direction and (c) 2-domain state with electric field in $\langle 110\rangle$ direction.[89]

## Electromechancial Properties

The impedance-phase spectrum of fine grained PMN-PT ceramics were recorded using impedance analyzer and shown in Figure 3.12. The resonant frequency $\left(f_{r}\right)$ corresponds to minimum resistance component $(\mathrm{Z})$, while the anti-resonant frequency $\left(\mathrm{f}_{a}\right)$ corresponds to the maximum of resistance component in the impedance curve. High electromechanical coupling factor corresponds to a large value of the frequency gap from $\mathrm{f}_{a}$ to $\mathrm{f}_{r}$. The average values of $\mathrm{k}_{p}$ and $\mathrm{k}_{t}$ of fine grained PMN-PT ceramics were found to be 0.60 and 0.50 , respectively, which are the similar coupling factors as coarse grained PMN-PT ceramics. A longitudinal coupling factor $\left(\mathrm{k}_{33}\right)$ of fine-grained PMNPT ceramics also exhibited the similar $\mathrm{k}_{33}$ of coarse grained PMN-PT ceramics, being on the order of 0.72 .

For single crystals, the electromechanical coupling factors were found to be higher than those of polycrystalline PMN-PT ceramics. Thickness mode coupling factor, $\mathrm{k}_{t}$, was found to be 0.60 for PMN-PT crystals, and 0.56 for PIN-PMN-PT crystals. As expected, the longitudinal couplings ( $\mathrm{k}_{33}$ ) of $<001>$ oriented single crystals were significantly higher than polycrystalline PMN-PTs, being $>90 \%$ for both PMN-PT and PIN-PMN-PT single crystals, as shown in Figure 3.13.



Figure 3.12. Impedance and phase spectrum measured from a disk and a bar geometry of fine grained PMN-PT ceramics.


Figure 3.13. Impedance and phase spectrum of $<001>$ oriented PMN-PT single crystals.

### 3.4 Conclusion

Dense PMN-PT ceramics with fine grains were synthesized by reducing starting particle sizes. Sub-micron particle sizes ( $\sim 300 \mathrm{~nm}$ ) of PMN-PT powders, were obtained using attrition milling, as confirmed by SEM analysis and particle size measurements.

The resultant grain size of synthesized PMN-PT ceramics was found to be on the order of 1 microns, and their dielectric and electromechanical properties were found to be comparable to those of coarse grained PMN-PT ceramics. The dielectric and electromechanical properties of PMN-PT single crystals were also characterized and compared with polycrystalline PMN-PT ceramics. $<001>$ oriented PMN-PT single crystals exhibited higher piezoelectric and electromechanical properties ( $\mathrm{d}_{33}>1800 \mathrm{pC} / \mathrm{N}$, and $\mathrm{k}_{33}>0.9$ ) than polycrystalline PMN-PT ceramics ( $\mathrm{d}_{33} \sim 800 \mathrm{pC} / \mathrm{N}$, and $\mathrm{k}_{33}>0.72$ ). In particular, ternary PIN-PMN-PT single crystals showed higher temperature usage range ( $>120^{\circ} \mathrm{C}$ ) with higher coercive fields ( $\sim 4-5 \mathrm{kV} / \mathrm{cm}$ ) than binary PMN-PT crystals, while possessing comparable dielectric and electromechanical properties to the binary PMNPT crystals. The material properties obtained here are summarized in Appendix A.


## Size Effects and Electrical Properties of Relaxor-PTs

### 4.1 Introduction

For high frequency $>20 \mathrm{MHz}$ transducers, the selection of a suitable piezoelectric material is very important as the thickness of a piezoelectric material becomes very thin, typically on the order of a few microns. It was reported that the machining of such a fine scale resulted in the issues of domain instability of ferroelectric ceramics, consequently degrading the various electrical properties. PZT ceramics, as an example, have been demonstrated that several piezoelectric properties degraded with increasing frequency, as a result of domain clamping effects; however, they showed less scale/frequency dependent characteristics by reducing the grain size.[16-18]

To date, however, the frequency dependence of high permittivity relaxor-PT ferroelectric ceramics and single crystals have yet to be investigated. In this chapter, the detail results of scale/frequency dependent dielectric and electromechanical properties of polycrystalline and single crystal relaxor-PT ferroelectric materials were presented.

Special attention is devoted to demonstrating the origin of property degradation of these materials at high frequency range $(>20 \mathrm{MHz})$.

### 4.2 Experimental Methods and Materials Preparation

### 4.2.1 Sample Preparation

For the measurements of thickness dependent properties, various sample thicknesses were prepared by lapping and polishing. Initial lapping utilized $15 \mu \mathrm{~m} \mathrm{Al}_{2} \mathrm{O}_{3}$ powder suspended in a distilled water medium. Final lapping was done with a $0.05 \mu \mathrm{~m}$ diamond to minimize surface damage that can deteriorate the material properties. Gold sputtering was then used to deposit electrodes on both surfaces. The samples were then drilled or cut to the desired dimensions with diameter to thickness ratio of 20-30. This ensured that any lateral harmonic frequencies would not interfere with the fundamental thickness mode. All samples were then annealed at $400^{\circ} \mathrm{C}$ for 5 hours in order to alleviate mechanical stress from polishing and lapping. Samples were then poled at room temperature at an electric field two times the coercive field of each material.

### 4.2.2 Characterization of Physical and Electrical Properties

## Optical Microscope

The samples were prepared by polishing to the thicknesses of 50-100 microns using diamond paste ( 1 micron). The domain structure of poled single crystals were then examined using a polarizing light microscope (Olympus BX60) in transmission mode.

## Measurements of Electrical Properties

Various dielectric, piezoelectric, and electromechanical properties were measured by the techniques described in chapter 3 .

### 4.3 Results and Discussion

### 4.3.1 Dielectric Properties

The free $\varepsilon_{33}^{T} / \varepsilon_{0}$ and clamped $\varepsilon_{33}^{S} / \varepsilon_{0}$ dielectric permittivities of various polycrystalline and single crystal samples, with thicknesses ranging from 500 microns to 30 microns, are plotted in Figure 4.1. Each value is the average of 3-5 samples, and the error bar represents the standard deviation. The corresponding thickness mode resonance frequencies of the various crystals are also added on top of the X-axis of Figure 2, ranging from thickness resonance frequency of 2 MHz to 100 MHz .

For polycrystalline ceramics, fine grained PMN-PT ceramics were found to be no noticeable change in free and clamped dielectric permittivity even in the high frequency range ( $20-100 \mathrm{MHz}$ ). As reported previous studies of frequency dependent PZT samples,[16, 18, 35] fine grained PMN-PT also showed improved mechanical performance as a result of an enhanced mechanical integrity of fine grains, allowing the fabrication of much higher frequency ( $>100 \mathrm{MHz}$ ) compared to coarse grained PMN-PT ceramics.

In contrast, coarse grained PMN-PT ceramics were found to have reduced free dielectric permittivities below 100 microns of their thicknesses. Meanwhile, below 50 microns, the strength of coarse grained samples became problematic. They often crumbled apart during polishing and lapping, limiting the fabrication and investigation of coarse grained PMN-PT ceramics above 40 MHz frequency.

For single crystals, the clamped dielectric permittivity of both PMN-PT and PIN-



Figure 4.1. Clamped and free dielectric permittivities of relaxor-PT materials as a function of thickness and corresponding ultrasound frequency.

PMN-PT samples were found to maintain similar values as a function of thickness. However, the free dielectric permittivity of PMN-PT crystals was found to be degraded with decreasing thicknesses. At a thickness of 40 micron, only half the original value of the free dielectric permittivity was observed for PMN-PT crystals. Of particular significance, the free dielectric permittivity of PIN-PMN-PT samples exhibited minimal thickness dependence, even for the thicknesses less than 50 microns.

Figure 4.2 shows free dielectric permittivities of [001]- and [110]- poled crystals as a function of thickness/frequency. It can be seen that [110]-poled PMN-PT crystals exhibited a similar decrease with decreasing thicknesses. For [110]-poled PIN-PMN-PT crystals, no degradation was observed even the thicknesses were as thin as 30 microns, similar to [001]-poled PIN-PMN-PT crystals. This indicates that different domain configuration (i.e., 2-domain state for $<110\rangle$ and 4 -domain state for $<001\rangle$ ) does not help improving the stability of dielectric permittivity for PMN-PT crystals at high frequencies.

### 4.3.2 Electromechanical Properties

The laterally clamped thickness mode coupling factor $\left(\mathrm{k}_{t}\right)$ of relaxor-PT materials were evaluated using the resonance technique. The calculated thickness frequency constant $\left(\mathrm{N}_{t}\right)$ and $\mathrm{k}_{t}$ of each sample from resonance measurements were summarized in Figure 4.3 as a function of frequency/sample thickness. For comparison purpose, reported $\mathrm{k}_{t}$ of commercial PZT (EC-65) and fine grained ( $\sim 0.9 \mu \mathrm{~m}$ ) PZT were also plotted as a function of frequency in Figure 4.3.[17, 35]

For polycrystalline PMN-PT ceramics, although the magnitude of $\mathrm{k}_{t}$ was found to decrease slightly with increasing frequency, $\mathrm{k}_{t}$ of coarse grained PMN-PT at high frequencies ( $>20 \mathrm{MHz}$ ) were much higher than those of coarse grained $(\sim 0.9 \mu \mathrm{~m})$ PZT at


Figure 4.2. Free dielectric permittivities of [001] and [110] poled PMN-PT and PIN-PMN-PT crystals as a function of thickness.
the same frequency range. At 40 MHz of resonance frequency, $\mathrm{k}_{t} \mathrm{~s}$ of coarse grained PMN-PT ceramics were found to be in the range of $0.45-0.47$, while reported $\mathrm{k}_{t}$ of EC65 PZT was $\sim 0.4$. Similar to fine grained PZT, fine grained PMN-PT also exhibited stable $\mathrm{k}_{t} \mathrm{~s}$ in the frequency range studied, exhibiting no degraded $\mathrm{k}_{t} \mathrm{~s}(0.49-0.50)$ up to 80 MHz of resonance frequency.

For single crystals, $\mathrm{k}_{t} \mathrm{~s}$ of PMN-PT crystals were found to be slightly higher than those of PIN-PMN-PT crystals over the frequency range studied. $\mathrm{k}_{t} \mathrm{~S}$ of PMN-PT crystals exhibited in the range of 0.55 to 0.60 , while those of PIN-PMN-PT crystals were in the range of 0.54 to 0.58 .

It is somewhat surprising that PMN-PT crystals did not show thickness dependence of $\mathrm{k}_{t}$ since $\varepsilon_{33}^{T} / \varepsilon_{0}$ of PMN-PT crystals showed a large decrease with decreasing thickness. Considering the error in the measurement techniques, the $\mathrm{k}_{t} \mathrm{~s}$ of all samples at different frequencies were the same, indicating that $\mathrm{k}_{t}$ s of relaxor-PT materials were not affected by the sample size. The resonance characteristics of PMN-PT single crystal samples with different thickness are shown in Figure 4.4, observing a strong and clear resonance and anti-resonance peaks even in the high frequency range ( $>20 \mathrm{MHz}$ ) with no degraded $\mathrm{k}_{t} \mathrm{~s}$.

### 4.3.3 Ferro- and Piezo- electric Properties

Measurements of polarization versus electric field ( $\mathrm{P}-\mathrm{E}$ ) hysteresis loops were performed to examine the influence of the sample thickness on the domain swithcing behavior of each sample. Figure 4.5 shows P - E hysteresis loops for relaxor-PT ceramics and single crystals with different thicknesses.

For fine grained PMN-PT ceramics, the average remnant polarization, $\mathrm{P}_{r}$, was calculated to be $\sim 28 \mu \mathrm{C} / \mathrm{cm}^{2}$ for thin samples (thickness $<50$ microns) with a coercive field,


Figure 4.3. Frequency dependence of frequency constant $\left(\mathrm{N}_{t}\right)$ and electromechanical coupling factor $\left(\mathrm{k}_{t}\right)$ for fine and coarse grained PMN-PT ceramics, and $<001>$ oriented PMN-PT and PIN-PMN-PT crystals. For comparison, PZT data were also plotted in graph.[17, 35]


Figure 4.4. Measured electrical impedance (solid line) and phase (dashed line) of $<001>$-poled PMN-PT single crystals with different thickness.


Figure 4.5. Thickness dependent domain switching for relaxor-ferroelectric materials.
$\mathrm{E}_{C}$, of $\sim 6 \mathrm{kV} / \mathrm{cm}$, which are comparable to the bulk values ( $30 \mu \mathrm{C} / \mathrm{cm}^{2}$ and $5.5 \mathrm{kV} / \mathrm{cm}$, respectively, for thickness $>500$ microns). For coarse grained PMN-PT ceramics, tilt P - E loops were observed with decreasing thickness. When the thickness decreased from 500 microns to 50 microns, $\mathrm{P}_{r}$ decreased from $32 \mu \mathrm{C} / \mathrm{cm}^{2}$ to $27 \mu \mathrm{C} / \mathrm{cm}^{2}$, while $\mathrm{E}_{c}$ increased from $5 \mathrm{kV} / \mathrm{cm}$ to $6 \mathrm{kV} / \mathrm{cm}$, indicating the clamping/pinning of domain wall motion at small thicknesses ( $<100$ microns).

For PMN-PT single crystals, the clamping/pinning of domain wall motion is more evident, exhibiting a noticeable change in $\mathrm{E}_{C}$ and $\mathrm{P}_{r}$ with decreasing thickness. The $\mathrm{P}_{r}$ and $\mathrm{E}_{C}$ of thick PMN-PT crystals ( 500 microns) were initially $27 \mu \mathrm{C} / \mathrm{cm}^{2}$ and 2.5 $\mathrm{kV} / \mathrm{cm}$, respectively, changing to $20 \mu \mathrm{C} / \mathrm{cm}^{2}$ and $3.5 \mathrm{kV} / \mathrm{cm}$ when the thickness reduced to 50 microns. In contrast, similar to the fine grained PMN-PT ceramics, PIN-PMN-PT crystals showed subtle changes in hysteresis loops with decreasing thickness.

The high-field piezoelectric behavior for the polycrystalline and single crystals with different thicknesses are given in Figure 4.6 and 4.7, respectively. From the figure, it was observed that the strain levels of fine-grained PMN-PT ceramics were almost constant, exhibiting approximately $\sim 900 \mathrm{pm} / \mathrm{V}$ of high-field piezoelectric coefficients $\left(\mathrm{d}_{33}\right)$ with decreasing thicknesses. However, an increase in strain hysteresis was observed with decreasing thickness, reaching $30 \%$ for 20 micron samples from $12 \%$ for 500 micron samples.

For coarse-grained PMN-PT ceramics, the high-field $\mathrm{d}_{33}$ maintained similar values with decreasing thicknesses down to 100 microns with $10-15 \%$ of strain hysteresis. Then, a decrease in maximum strain level was observed when the sample thicknesses were less than 100 microns. At a thickness of 50 micron, the high-field $d_{33}$ were found to be $650 \mathrm{pm} / \mathrm{V}$ with $30 \%$ of strain hysteresis.

For PMN-PT single crystals, the high field $\mathrm{d}_{33}$ was found to degrade significantly, with the values being on the order of $1800 \mathrm{pm} / \mathrm{V}$ and $1000 \mathrm{pm} / \mathrm{V}$ for 500 micron and



Figure 4.6. Thickness dependence of unipolar strain as a function of electric field for fine and coarse grained PMN-PT ceramics. Arrow indicates decreasing thickness.


Figure 4.7. Thickness dependent unipolar strain hysteresis for (a) <001> PMN-PT crystals and (b) $<001>$ PIN-PMN-PT crystals.

40 micron samples, respectively, with increased strain hysteresis from 5\% to $15 \%$. In contrast, ternary PIN-PMN-PT single crystals maintained original strain levels down to 40 micron thicknesses. However, it should be noted that PIN-PMN-PT crystals also exhibited an increase in strain hysteresis from $7 \%$ to $25 \%$ with decreasing thicknesses.

### 4.3.4 Discussion

A reduction in dielectric and piezoelectric properties could be associated with the ferroelectric domains. In order to delineate the influence of ferroelectric domains on the observed degraded properties, the dielectric permittivity of PMN-PT single crystals with different thicknesses were investigated as a function of temperature. If the ferroelectric domain is a primary origin for degraded properties, it can be expected that the permittivities of thin PMN-PT crystals in the paraelectric state (above $\mathrm{T}_{C}$ ) exhibit similar values as those of normal size PMN-PT crystals, where no domains exist.

Figure 4.8 shows the dielectric permittivity and loss of PMN-PT crystals and PIN-PMN-PT crystals as a function of temperature. In the temperature range below the rhombohedral to tetragonal phase transition $\left(\mathrm{T}_{R-T}\right)$, the dielectric permittivity of PIN-PMN-PT crystals was found to show nearly thickness independent dielectric behavior, while for PMN-PT crystals, the permittivity of the 50 micron sample was found to be much lower than that of thick samples. The results are the same behavior as seen from thickness dependence of room temperature dielectric permittivity of PMN-PT and PIN-PMN-PT crystals (Figure 4.1).

However, in the region between $\mathrm{T}_{R-T}$ and $\mathrm{T}_{C}$, where the crystals are in the tetragonal phase region, the thickness dependent behavior was found to be opposite to those of rhombohedral phase crystals. It was found that both 50 micron thickness of PMN-PT and PIN-PMN-PT crystals exhibited higher permittivities compared to 500 micron thick


Figure 4.8. Dielectric permittivity and loss as a function of temperature for different thickness of PMN-PT and PIN-PMN-PT crystals.
samples, indicating that the single domain state in tetragonal phase became unstable at small thicknesses.[90]

As the temperature approached to $\mathrm{T}_{C}$, the dielectric permittivity of 50 micron thickness of PMN-PT samples exhibited broader peaks as well as depression of dielectric maximum, compared to thick PMN-PT samples. In contrast, 50 micron thickness of PIN-PMN-PT crystals exhibited comparable dielectric maxima to 500 micron thickness of PIN-PMN-PT crystals. The results suggest that there were severe domain clamping for PMN-PT crystal samples with decreasing thickness.

For temperatures well beyond $\mathrm{T}_{C}$, where no domains exist, the dielectric permittivities of both thin and thick PMN-PT and PIN-PMN-PT crystals showed similar dielectric properties with temperature. This indicates that the degraded properties of PMN-PT single crystals at room temperature are closely associated with the domain effects.

The above results demonstrate that ferroelectric domains are the primary origin of the degraded properties of PMN-PT crystals at small thicknesses. The fact that the origin of a large dielectric and piezoelectric response of $<001>$-poled relaxor-PT single crystals is closely related to the domain engineered 4 R structures and polarization rotation mechanism.[73, 91] For instance, on the microscopic scale, poling along [001] in rhombohedral relaxor-PT crystals creates four degenerate domain variants, and the dipoles in domains can be aligned along any one of the four equivalent $<111\rangle$ directions. Since four polarization directions are energetically equivalent, four types of domains will be equally populated under the small electric field, leading to the stable multidomain (4R) configuration. Due to a large transverse dielectric permittivity in single domain rhombohedral relaxor-PT crystals, the polarization can be freely rotated from $<111\rangle$ to $<001>$ under $<001>$ electric field, leading to the free energy instability and structural (phase) instability, resulting in a large longitudinal dielectric and piezoelectric properties of $<001\rangle$-poled relaxor-PT crystals. However, when the phys-
ical size of the samples becomes of the same order as the domain size, it is possible that the surface boundary conditions may disrupt the equilibrium 4R domain structures and impede polarization rotation effect. This might explain an increase in strain hysteresis of relaxor-PT crystals at small thicknesses, as seen from Figure 4.7 since anhysteretic strain-field behavior of $<001>$-poled relaxor-PT crystals is the consequence of stable 4R domain structures.

Therefore, the different thickness dependent properties of relaxor-PT materials at room temperature may be associated with their respective domain sizes. It was reported that compared to polycrystalline ceramics, the domain sizes of PMN-PT crystals are much larger, with sizes being reported on the order of 10-100 microns.[92] Consequently, due to the comparable sample sizes to domain sizes of PMN-PT crystals, both"extrinsic", i.e., contribution of the irreversible domain wall motion, and "intrinsic" from polarization rotation can be suppressed by surface boundary conditions, resulting in the degraded dielectric and piezoelectric properties when the sample thicknesses were less than 100 microns. For the case of PIN-PMN-PT crystals, since no degraded dielectric permittivity was observed in the thickness range from 500 to 30 microns, it can be believed that ternary PIN-PMN-PT single crystal possess much smaller domain size when compared to binary PMN-PT crystals.

Optical microscope was used to confirm the different domain sizes of poled PMNPT and PIN-PMN-PT single crystals. Figure 4.9 shows the optical micrographs taken through crossed polarizers. It is evident from these figures that the domain sizes of poled PIN-PMN-PT crystals are much smaller, being on the order of 1 micron, compared to those of poled PMN-PT crystals, being on the order of 10-20 micron, indicating that a large thickness dependence of PMN-PT crystals are associated with their domain size.


Figure 4.9. Domain structures for PMN-PT and PIN-PMN-PT single crystals using optical microscope.

### 4.4 Conclusion

The properties of fine-grained ( $\leq 1$ micron) PMN-PT ceramics were investigated as a function of thickness and/or frequency. Compared to coarse-grained materials, whose grain size is around 5-7 microns, fine-grained PMN-PT ceramics showed improved mechanical strength and performance at high frequency ( $>20 \mathrm{MHz}$ ) range, showing no degraded electrical properties with decreasing thickness.

For single crystals, it was found that domain size plays a dominant role in property degradation with decreasing thickness. Degradation in dielectric and piezoelectric properties was observed in PMN-PT crystals with decreasing thicknesses due to the increased surface boundary effects. In contrast to PMN-PT crystals, PIN-PMN-PT exhibited excellent property stability at high frequencies ( $>20 \mathrm{MHz}$ ), with minimal thickness dependence down to 40 microns, due to their relatively smaller domain sizes. The results suggest that fine-grained PMN-PT ceramics and ternary PIN-PMN-PT single crystals are promising candidates for high frequency ultrasound transducer applications.

\section*{| Chapter |
| :---: |}

## Piezoelectrics/Epoxy 1-3

## Composites

### 5.1 Introduction

The properties of relaxor-PT piezoelectric materials are of interest for ultrasound transducers, offering high dielectric and electromechanical properties. In particular, relaxor-PT piezoelectrics have excellent longitudinal coupling factors ( $\mathrm{k}_{33}$ ), for example, $\mathrm{k}_{33}>0.72$ for polycrystalline ceramics and $>0.90$ for single crystals. Composite technology enables the use of high electromechanical coupling factors of these materials in both single element and array transducers, contributing to the transducers with broad bandwidth and high sensitivity.

As ultrasound transducers become smaller with increasing frequency, there is increasing awareness of the effects of surface damage introduced during composite machining because the damage layer volume becomes increasing in relation to the active piezoelectrics. However, as yet little is known of the performance of high frequency relaxor-PT composites fabricated by dicing-fill technique.

This chapter begins with a brief review of composite materials, focusing on the advantages of composites, as well as issues of high frequency 1-3 composites. Following that is a description of the fabrication of low and high frequency relaxor-PT composites with 1-3 connectivity performed in this study. Measured properties from the fabricated 1-3 composites are presented as a function of scale/frequency with a discussion of degradation mechanism in relaxor-PT composites.

### 5.2 Piezoelectric/Polymer Composites

Piezoelectric/polymer composites have a number of distinct advantages over traditional piezoelectric ceramics, taking advantages from both piezoelectric ceramics and polymer. In general, the transducer performance is limited by trade-off between high piezoelectric activity and low density with mechanical flexibility. Although lead-based ferroelectric materials offer high electromechanical properties, such as high coupling factor and dielectric permittivity, a critical issue of this system for ultrasound transducers is its high acoustic impedance $(\mathrm{Z})$ as a result of its high density $\left(\sim 8.0 \mathrm{~g} / \mathrm{cm}^{3}\right)$, which impede the energy flow between transducer and tissue. Piezopolymers, on the other hand, have advantages of low density and mechanical flexibility, but their low piezoelectric properties have limited their implementation into ultrasound transducer applications.[93]

Piezoelectric composites, which consist of a matrix of piezoelectric elements and soft epoxy, are typically flexible and have lower density. This can reduce acoustic impedance of ferroelectric materials, alleviating acoustic impedance matching problems. Moreover, several electrical properties of piezoelectric materials can be tailored to specific device requirements by varying volume fraction of the portions of ferroelectric materials, offering a new range of material properties (see Table 5.1 and Figure
5.2).[59, 94-96]

The enhanced usefulness of composites for ultrasound transducers is related to optimized connectivity of the piezoelectrics and polymer phases. To date, the most widely used composite connectivities for ultrasound transducers are 1-3 and/or 2-2 connectivity. The composites with 1-3 connectivity are comprised of individual active phases (piezoelectrics) embedded in a passive (polymer) matrix, while 2-2 composites consist of alternating layers of the two phases, as illustrated in Figure 5.1.

The 1-3 composites have emerged as superior structures since they can effectively utilize the geometrical advantages of piezoelectric materials, as evident in Figure 5.1. The composite with 2-2 connectivity is also an important connectivity for ultrasound transducers since this pattern is often used in linear arrays, and also offers better electromechanical coupling value $\left(\mathrm{k}_{33}^{\prime}\right)$ compared to pure thickness mode $\left(\mathrm{k}_{t}\right)$ of a piezoelectric material (see Figure 5.1).

It is interesting to note that the electromechanical coupling factor of a composite material does not significantly vary with volume fraction of piezoelectric element compared

Table 5.1. Comparison of the material properties for piezoelectric ceramics, polymers, and composites. (Positive and negative sign indicate advantage and disadvantage for ultrasound transducer applications, respectively.) [59, 96]

| Parameter | Ceramic | Polymer | Composite |
| :---: | :---: | :---: | :---: |
| Coupling factor | 0.45-0.55 (+) | 0.1-0.3 (-) | 0.5-0.75 (+) |
| Acoustic impedance <br> (MRayl) | 30 (-) | 1.5-4 (+) | $10 \text { (can be tailored) }$ $(+)$ |
| Dielectric permittivity | 200-5000(+) | 6-10 (-) | Proportional to volume fracture |
| Spurious modes | Many (-) | Weak (+) | Weak (+) |

to other properties, such as dielectric permittivity and acoustic impedance, as shown in Figure 5.2. This means that high electromechanical coupling of an active piezoelectric material can be retained over a wide range of volume fractions.

Such a behavior can be attributed to the presence of soft polymer matrix because the elastically soft polymer phase provides the condition of the piezoelectric bars to freely expand or contract in the lateral direction, as evident in Figure 5.2, exhibiting that composite materials using a stiff polymer have lower values of electromechanical coupling factors than those with a soft polymer. [59]

One of difficulties for piezoelectric/polymer composites is associated with the machining capability, especially at high frequency range. In the case of 1-3 piezocomposites, for example, the most widely used method to fabricate piezocomposites is dice-fill method, where a mechanical dicing saw is used to machine kerfs into a piece of bulk piezoelectric material and subsequently filled with an polymer, usually epoxy. In order for the piezoelectric materials to vibrate over 20 MHz frequency, the required thickness of composite materials, such as PZT-polymer composites, is approximately less than 50


Figure 5.1. The geometrical dependence of electromechanical coupling factor for PZT-5H.[97]


Figure 5.2. Variation with PZT5 volume fraction of a composite's acoustic impedance, Z, longitudinal velocity, $\mathrm{v}_{l}$, and thickness mode electromechanical coupling constant, $\mathrm{k}_{t}$ for three different polymers: a soft, low density polymer (dotted lines), a firm, medium-density polymer (dashed lines), and a stiff, high-density polymer (solid lines).[59]
microns. The thickness-to-width aspect ratio for each piezoelectric elements should be high, more than 2, in order for the lateral mode frequency to push outside the operating frequency bandwidth. This condition requires less than 20 micron piezoelectric element width. Such a fine scale requirement is one of the challenges to fabricate high frequency 1-3 piezocomposites.[50, 51, 98-105]

### 5.3 Experimental Methods and Materials Preparation

### 5.3.1 Sample Preparation

For the fabrication of 1-3 piezocrystal/epoxy composites, the samples were diced using an automatic dicing machine, K\&S 982-6 (Kulicke \& Soffa Industries, Willow Grove, PA) with different sizes of blades depending on the frequency of interest. For transducers operating below $10 \mathrm{MHz}, 1-3$ composites were machined with a $50 \times 762$ $\mu m^{2}$ nickel bond dicing blade (Dicing Blade Technology, Inc.), and a $26 \times 586 \mu m^{2}$ nickel bond dicing blade (Asahi Diamond, Inc.). For transducers operating above 10 MHz , the samples were diced using 2-4 $\mu \mathrm{m}$ grit, $12 \times 343 \mu \mathrm{~m}^{2}$ nickel bonded diamond blade (Asahi Diamond, Inc.). The samples were first diced along one direction with a spindle speed of $30,000 \mathrm{rpm}$ and a feed rate of $1.5 \mathrm{~mm} / \mathrm{sec}$. The samples were then diced in the perpendicular direction using the same dicing conditions. A low viscosity epoxy (Epotek 301, Bellerica, MA) was then backfilled into the kerfs in vacuum for 30 min , and subsequently cured at room temperature for 24 hours. After the epoxy was cured, the fabricated composites were polished until the piezoelectric posts were exposed. Then, gold electrodes were sputtered on both surfaces. The composite samples were poled at room temperature at an electric field two times the coercive field of each material. Schematic representation of dice-and-fill method for this study is shown in Figure 5.3.


Figure 5.3. Schematic representation of 1-3 composite fabrication method (dice-fill method).[31]

### 5.3.2 Composite Characterization

## Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM, S-3500N, Hitachi, Tokyo, Japan) was used to obtain the dimension of 1-3 composites, such as the size of post and kerf width. For sample preparation, composites were polished using 1 micron $\mathrm{Al}_{2} \mathrm{O}_{3}$ powder suspended in a distilled water medium. The prepared composites were put on the carbon tape, and mounted on the sample holder. To prevent them from charging during scans, the surfaces of prepared samples were coated with a thin layer of gold using sputtering prior to load them into vacuum chamber.

## Field Emission Scanning Electron Microscope (FESEM)

For imaging of the diced surfaces of 1-3 composites, field emission scanning electron microscope (FESEM; JSM-5900LV, JEOL) was used in order to obtain higher resolution of damaged surface of 1-3 composites. Operating accelerating voltages of FESEM were varied between 1 and 5 kV . Conducting tape was used to adhere the samples on the sample holder as well as to minimize charging.

## X-ray Diffraction Measurement (XRD)

X-ray analysis was carried out using a X-ray diffractometer (PANalytical) and Cu $\mathrm{K}_{\alpha}$ radiation equipped with XPert Pro MPD. The operation voltage and current are 40 kV and 40 mA , respectively. Zero background holders were used to analyze the prepared samples. The measurement range of $2 \theta$ and step scanning rate were varied based on the purpose of analysis.

## Electrical Measurement

Dielectric properties of prepared 1-3 composites were determined using an multifrequency LCR meter (HP4284A). The permittivities of the piezoelectric elements can be obtained using the parallel mixing rule:

$$
\begin{equation*}
\varepsilon_{c}=V_{f} \varepsilon_{f}+V_{p} \varepsilon_{p} \tag{5.1}
\end{equation*}
$$

where $\varepsilon_{c}$ is the permittivity of composite, and $\mathrm{V}_{f}$ and $\mathrm{V}_{p}$ are the volume fractions of the ferroelectric and polymer dielectric phase, respectively $\left(\mathrm{V}_{f}+\mathrm{V}_{p}=1\right)$. In the case where $\varepsilon_{f} \gg \varepsilon_{p}$, the composite permittivity can be written as follows:

$$
\begin{equation*}
\varepsilon_{c}=V_{f}\left(\varepsilon_{f}-\varepsilon_{p}\right)+\varepsilon_{p} \simeq V_{f} \varepsilon_{f} \tag{5.2}
\end{equation*}
$$

Resonance characteristics were measured using an HP4294A impedance- phase gain analyzer. Electromechanical coupling properties were calculated by the standard resonance method (IEEE)[82]

### 5.4 Results and Discussion

### 5.4.1 Characterization of PMN-PT Ceramic 1-3 Composites

Dicing of polycrystalline PMN-PT ceramics was performed using 70 micron diamond blades for $<5 \mathrm{MHz}$ PMN-PT ceramic 1-3 composites. The post width was $\sim 200$ micron, and the cut depth was greater than 800 micron. To avoid lateral mode coupling within the operating frequency bandwidth, the final thicknesses of the composites were polished to $\sim 400$ microns. The representative ceramic 1-3 composite structures are shown in Figure 5.4. From the image, the kerf and post width of ceramics were found to
be 70-80 and 200 microns, respectively, and the volume fractions of the ceramics were approximately $40 \%$.

The average free and clamped permittivities of both fine and coarse grained PMNPT 1-3 composites were found to be on the order of 1800 and 800, respectively, which are lower than the values predicted from the equation 5.2. The electromechanical properties of PMN-PT ceramics 1-3 composites calculated from the resonance data revealed similar $\mathrm{k}_{t} \mathrm{~s}$, ranging from 0.68 to 0.70 , regardless of grain size and $\sim 1650 \mathrm{~Hz} . \mathrm{m}$ of thickness frequency constant $\left(\mathrm{N}_{t}\right)$. A decrease in $\mathrm{k}_{t}$ and an increase in $\mathrm{N}_{t}$ of 1-3 composite materials, compared to the values of monolithic piezoelectric elements ( $\mathrm{k}_{33} \sim 0.72$ and $\mathrm{N}_{33} \sim 1400$ ), can be attributed to the clamping of ceramics by the surrounding epoxy phase. Plots of impedance and phase spectrum for polycrystalline PMN-PT ceramic composites are shown in Figure 5.5.

### 5.4.2 Single crystal 1-3 Composites

Thickness frequency constant $\left(\mathrm{N}_{t}\right)$ of single crystal 1-3 composites were found to be lower than that of ceramic 1-3 composites. $\mathrm{N}_{t}$ s of both PMN-PT and PIN-PMN-PT single crystal 1-3 composites were found to be $\sim 1000 \mathrm{~Hz}$.m. This indicates that for the same frequency range, the required thickness of crystal composites should be smaller than ceramic 1-3 composites.

The different designs were applied on single crystal composites. The width of crystal element was designed with one half of that of ceramic element, $\sim 100$ micron, with $>600$ micron cut depth. The dicing was performed using $\sim 50$ micron diamond blades. The composites were polished to the thicknesses from 250 to 500 microns, which are corresponding to the frequency range of $2-4 \mathrm{MHz}$. The SEM image of the representative single crystal 1-3 composite structures is shown in Figure 5.6.


Figure 5.4. The picture of $1-3$ composites fabricated using the dice-and-fill technique..


Figure 5.5. Measured electrical impedance (solid line) and phase (dashed line) for PMN-PT ceramic 1-3 composites with different thickness.


Figure 5.6. SEM image of single crystal 1-3 composites fabricated using the dice-and-fill technique.

Dielectric properties of both PMN-PT and PIN-PMN-PT crystal 1-3 composites were found to be lower than ceramic 1-3 composites, being on the order of 1100 for free and 300 for clamped dielectric permittivity. Considering that free dielectric permittivity of monolithic PMN-PT ceramics and single crystals are similar, approximately 6000, a decrease in dielectric properties of crystal 1-3 composites might be associated with small lateral size of piezoelectric elements ( $\sim 100$ microns), with surface damage from dicing.

Figure 5.7 shows the plots of impedance and phase of 1-3 composite materials. The electromechanical coupling factors of both single crystal composites were found to be in the range of $0.79-0.84$. These values are higher than those of ceramic 1-3 composites, but lower than those of monolithic samples ( $\mathrm{k}_{33}>0.90$ for monolithic single crystals). The lower coupling values of single crystal 1-3 composites can also be attributed to the clamping of the single crystal elements by the polymer phase, as well as the influence of surface damage created by mechanical dicing.

High frequency ( $\sim 20 \mathrm{MHz}$ ) PMN-PT and PIN-PMN-PT 1-3 piezocomposites were fabricated using the same dicing-fill technique. The designs of both samples were 3035 micron wide of crystal elements by 130 micron deep using 17 micron blade. The thicknesses of finished composites were around 70-80 micron. The image of 1-3 single crystal composites is shown in Figure 5.8.

Both single crystal 1-3 composites showed a decrease in dielectric properties. PMNPT 1-3 composites showed $\sim 450$ of free dielectric permittivity and $\sim 200$ of clamped dielectric permittivity. For PIN-PMN-PT 1-3 composites, the free and clamped dielectric permittivity were found to be $\sim 900$ and $\sim 320$, respectively.

Figure 5.9 summarizes the results of obtained electromechanical coupling factors of PMN-PT and PIN-PMN-PT 1-3 composites as a function of frequency. For comparison purpose, the longitudinal coupling factors $\left(\mathrm{k}_{33}\right)$ of the monolithic samples, including


Figure 5.7. Measured electrical impedance (solid line) and phase (dashed line) for single crystal 1-3 composites with different thickness.


Figure 5.8. SEM images of single crystal 1-3 composites.

PMN-PT polycrystalline ceramics and single crystals and PIN-PMN-PT single crystals, were calculated from the permittivities using equation 5.3 and plotted as a function of frequency. In addition, reported experimental data of high frequency PMN-PT single crystal/epoxy 1-3 composites, fabricated by dry etching method, were also included in Figure 5.9.

$$
\begin{equation*}
k_{33}=\sqrt{1-\frac{\varepsilon_{33}^{S}}{\varepsilon_{33}^{T}}} \tag{5.3}
\end{equation*}
$$

From Figure 5.9, due to their respective thickness dependence of dielectric properties, monolithic fine-grained PMN-PT ceramics and PIN-PMN-PT crystals exhibited original $\mathrm{k}_{33}$ values at high frequencies ( $>20 \mathrm{MHz}$ ), while the monolithic PMN-PT crystals exhibited a notable decrease in $\mathrm{k}_{33}$ with increasing frequency, which caused by the domain size/surface boundary effect as discussed in previous chapter.

PMN-PT single crystal 1-3 composites were also found to decrease in couplings $\left(\mathrm{k}_{33}\right)$ with increasing frequency, however, it should be note that the level of the decrease in coupling of PMN-PT crystal composites in this work are larger than those of monolithic samples. This might be due to the result of surface damage on the piezoelectric elements during dicing, causing further property degradation.

As expected, PIN-PMN-PT/epoxy 1-3 composites were found to maintain higher electromechanical coupling factors, being on the order of $0.79-0.80$. The measured impedance and phase spectrum is shown in Figure 5.10. It is believed that less frequency dependent properties of PIN-PMN-PT 1-3 composites compared to PMN-PT 1-3 composites are due to the smaller domain sizes of PIN-PMN-PT single crystals, as discussed in the previous chapter.


Figure 5.9. Frequency dependence of electromechanical coupling factors ( $\mathrm{k}_{33}$ ) for relaxor-PT materials. Data for PMN-PT/epoxy composites fabricated by dry etching (PC-MUT) are obtained from Ref[31-33].


Figure 5.10. Measured electrical impedance (solid line) and phase (dashed line) for PIN-PMNPT single crystal 1-3 composites.

### 5.4.3 Surface Damage

As discussed previously, the dielectric and electromechanical properties of piezoelectrics can be degraded upon machining. Experimentally, the surface properties have been measured to be smaller than those of bulk materials, and a series capacitance model, in which non-ferroelectric layers exist in series with the normal ferroelectric layer, has been used to explain degraded various properties of ferroelectric materials at small dimensions.[106-118]

Figure 5.11 shows SEM images of diced edge microstructures for fine and coarse grained ceramics 1-3 composites without epoxy filling. For fine grain materials, the improvement in dicing performance was observed in terms of surface roughness, exhibiting much cleaner edges and minimal chipping. In contrast, surface damage on coarse grained PMN-PT ceramics is clearly evident, showing grain pull-outs on the edge of the diced cut.

Surface damage of 1-3 composites was further investigated using X-ray analysis. Experimentally, it has been reported that the properties of ferroelectric materials degraded with the formation of surface damage layers, and surface damage can be investigated using X-ray since the penetration depth of X-ray is on the order of a few microns.[119-122]

Figure 5.12 shows an X-ray profile of a fine-grained PMN-PT polycrystalline ceramic prepared by final surface finishing with 0.05 micron particles. For comparison, Figure 5.12 also includes an X-ray profile of the same ceramic prepared by dicing. Note that the X-ray profile of coarse-grained PMN-PT is not included here due to the same X-ray results as fine-grained PMN-PT.

As can be seen in Figure 5.12, after poling, the sample prepared by polishing showed a noticeable change in the intensity ratio of (200) and (002) X-ray reflections, while the


Figure 5.11. SEM images of diced fine and coarse grained PMN-PT ceramics.


Figure 5.12. X-ray diffraction of the surfaces of fine-grained PMN-PT ceramics.


Figure 5.13. X-ray diffraction of the surfaces of PMN-PT and PIN-PMN-PT single crystals.
samples prepared by dicing did not exhibit the change in intensity ratio after poling. The results suggest that mechanical dicing can change domain orientations in the surface regions. It is well known that poling process leads to the domain realignments parallel to the applied electric field, meaning that the switch of the intensity peak after poling is the result of domain realignments. For the case of diced surface, however, poling did not cause the change in domain orientations because mechanical dicing already induced domain rotation well beyond that attained by the electric field.

Figure 5.13 demonstrates the XRD profiles taken from the polished surface of PMNPT and PIN-PMN-PT single crystals. For comparison, the diced surfaces were also xrayed and included in Figure 5.13. Compared to the XRD profiles of polished surfaces of single crystals, those of diced surfaces of both samples exhibited broad peaks in the $2 \theta$ angles from 20 to $120^{\circ}$, indicating surface damage on the diced surfaces.

The above observations clearly demonstrate that mechanical dicing can induce surface damage on the samples, resulting in degraded electrical properties of piezoelectric materials when the sample thickness approaches the dimension associated with surface damage.

### 5.5 Conclusion

1-3 relaxor-PT piezocomposites were fabricated and their properties were investigated as a function of thickness/frequency. As expected, coarse grained PMN-PT ceramics showed the issues of fabrication of high frequency 1-3 composites, exhibiting chipping and grain pull-outs during machining, while fine grained PMN-PT ceramics showed improved machinability.

SEM investigation of relaxor-PT single crystal 1-3 composites revealed that there were no macroscopic damage, but high frequency (20MHz) PIN-PMN-PT 1-3 piezo-
composites were found to possess lower coupling factors when compared to their monolithic counterparts ( $\sim 84 \%$ at 2 MHz ), due to dicing induced surface damage and/or low polarizable surfaces, as confirmed by XRD. Of great potential is, however, their high couplings, being $80 \%$ at 20 MHz , much higher when compared to PMN-PT 1-3 piezocomposites, being only $72 \%$ at the same frequency, making PIN-PMN-PT single crystal system as a promising candidate for high frequency ultrasound transducers.
$\square$

## Conclusion and Future Work

### 6.1 Summary and Conclusion

Fine grained PMN-PT polycrystalline ceramics were synthesized using high energy milling with hot isostatic pressing. The optimum processing conditions were determined by investigating their density and microstructures. The dielectric and electromechanical properties of synthesized materials were found to decrease when the grain size was well below 1 micron. The detail property measurements revealed that fine grained ( $\sim 1$ micron) PMN-PT ceramics showed comparable electrical properties to those of commercially available TRS-HK1 ceramics (i.e., coarse grained PMN-PT ceramics). This makes fine grained PMN-PT ceramic a promising candidate for a use in high frequency ultrasound transducers that require fine scale features.

The properties of relaxor-PT single crystals, $<001\rangle$ oriented PMN-PT and PIN-PMN-PT, were also characterized. It was found that both PMN-PT and PIN-PMN-PT single crystals poled along the $<001>$ crystallographic direction offer similar piezoelectric and electromechanical properties; the piezoelectric coefficients, $\mathrm{d}_{33}$ were in the range of 1700-2000 $\mathrm{pC} / \mathrm{N}$, with electromechanical coupling factors, $\mathrm{k}_{t} \sim 0.6$ and $\mathrm{k}_{33}$
$\sim 0.9$.
The dielectric, piezoelectric and electromechanical properties of each material, whose thicknesses correspond to resonance frequencies in the range of 2 to 80 MHz , were investigated as a function of thickness/frequency to evaluate their applicability for high frequency ultrasound transducers. Various thicknesses of relaxor-PT materials including polycrystalline ceramics and single crystals were prepared by fine polishing in order to minimize or eliminate surface damage caused by polishing.

As expected, fine grained PMN-PT ceramics showed greater mechanical strength and improved machinability in comparison with coarse grained counterpart, allowing the fabrication and characterization of much thinner samples (less than 20 microns). Fine grained PMN-PT ceramics also exhibited the improved stability of dielectric and piezoelectric properties at small thicknesses, resulting in minimal property degradation at high frequencies. In contrast, coarse grained PMN-PT ceramics became problematic with decreasing thicknesses. When the thicknesses were less than 50 microns, cracks were initiated across grain boundaries, with the property degradation when the thicknesses were below 100 microns.

Binary PMN-PT and ternary PIN-PMN-PT single crystals were also investigated as a function of thickness/frequency. PMN-PT single crystals showed a large decrease in dielectric and piezoelectric properties with decreasing sample thicknesses, regardless of different crystal orientations. In contrast, ternary PIN-PMN-PT single crystals showed less thickness dependent dielectric, piezoelectric and electromechanical properties. Temperature dependent dielectric behavior and the domain size investigation using optical microscope suggest that the observed thickness dependence in PMN-PT single crystals is closely related to their large domain size, $>20$ microns.

High frequency 1-3 piezocomposites were fabricated and their properties were compared with those of low frequency 1-3 piezocomposites. Similar to the results of thick-
ness dependent properties from the monolithic samples, PMN-PT crystal 1-3 composites exhibited degraded properties at high frequency ( $\sim 20 \mathrm{MHz}$ ), while fine grained PMNPT ceramics and PIN-PMN-PT crystal 1-3 composites showed less degraded piezoelectric properties. However, the observed couplings of PIN-PMN-PT crystal 1-3 composites, being on the order of $80 \%$ at 20 MHz , were lower than expected values. Based on the x-ray diffraction results, showing peak switching and broadening on diced surfaces, it can be concluded that mechanical dicing can cause the surface damage on active piezoelectric elements, and this surface damage is believed to be the origin of further property degradation of 1-3 piezocomposites in the high frequency range, as the volume of surface damage increases with increasing frequency.

### 6.2 Future Work

This thesis is intended to investigate thickness dependent dielectric and piezoelectric properties of relaxor-PT materials for possible uses in high frequency ultrasound transducers. From this study, it was found that the domain sizes play an important role in the property variation. The degradation in dielectric and electromechanical properties of fine grained PMN-PT ceramics and PIN-PMN-PT crystals was significantly lower than that of other relaxor-PT materials (coarse-grained PMN-PT and PMN-PT crystals) with decreasing thickness due to their relatively smaller domain sizes with respect to their sample thickness.

However, as seen in the results of 1-3 composites, the level of couplings for PIN-PMN-PT 1-3 composites was found to decrease with decreasing thickness, in contrast to monolithic PIN-PMN-PT samples. This indicates that dicing can deteriorate the piezoelectric properties as a result of surface damage. Therefore, future studies should involve the investigation of the influence of surface damage on property degradation. X-ray
diffraction studies conducted in this study have limited the resolution and incapability of in-situ observation with electric field, which make it difficult to identify the extent of surface damage on each sample. High-energy, high-penetration neutron or X-ray diffraction data as a function of sample depth would be useful to reveal the extent of surface damage and internal domain populations of relaxor-PT materials. In addition, it would be interesting to investigate in-situ observations of domain evolution with electric field using optical microscope and/or SEM, which will greatly improve understanding of the role of domain sizes in the properties of piezoelectric materials.

Investigation on the properties of high frequency ( $>20 \mathrm{MHz}$ ) composites is also necessary to ensure the performance of ultrasound transducers at high frequencies. The present studies have limited to below 20 MHz due to the limitation of the width of current dicing saw ( 17 microns). A variety of methods have been emerged over the years in order to fabricate high frequency ( $>20 \mathrm{MHz}$ ) 1-3 or 2-2 composites. An overview of proposed fabrication methods and materials for ultrasound transducer is schematically shown in Figure 6.1. For 2-2 composites, tape-casting, stacked plates or lamination techniques and interdigital phase boding have been demonstrated to be effective fabrication techniques to create high frequency transducers (20-40MHz).[123-125] For 1-3 composites, micromolding technique has allowed for the fabrication of high frequency composite transducers above 20 MHz .[126, 127] Thick and thin film techniques[127] allow for the fabrications of very high frequency $(>100 \mathrm{MHz})$ ultrasound transducers.

Recently, the novel lithography based micromachining technology has been successfully used to fabricate high frequency 1-3 PMN-PT single crystal composites beyond 60 MHz.[26, 29-33] The advantage offered by this technique lies on the ability to realize narrow channels or kerfs less than 10 microns, enabling high aspect ratio of piezoelectric elements. In addition, lithography based micromachining technology uses dry etching method, which might result in less surface damage on the samples compared to the
composites using conventional dicing-fill method. This suggests that high frequency 13 composites fabricated by dry etching method could be achieved with minimal property degradation.


Figure 6.1. Enabling piezoelectric materials and/or fabrication methodologies as a function of ultrasound frequency and/or scale.


## Material Properties

The dielectric, piezoelectric, and electromechanical properties of investigated materials described in Chapter 3 are presented here.

Table A.1. Characterization of PMN-PT polycrystalline ceramics. Free $\left(\varepsilon_{33}^{T} / \varepsilon_{0}\right)$ dielectric permittivity was measured at 1 kHz , and clamped $\left(\varepsilon_{33}^{S} / \varepsilon_{0}\right)$ permittivity was measured at the frequency of $2 \mathrm{f}_{a}$ (thickness mode anti-resonance frequency). High field $\mathrm{d}_{33}^{*}$ was measured by unipolar strain at a driving field of $10 \mathrm{kV} / \mathrm{cm}$.

| Material | Grain Size | $\mathrm{T}_{C}$ | $\varepsilon_{33}^{T} / \varepsilon_{0}$ | $\varepsilon_{33}^{S} / \varepsilon_{0}$ | $\tan \delta$ | $\mathrm{~d}_{33}^{*}$ | $\mathrm{~d}_{33}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $(\mu \mathrm{~m})$ | $\left({ }^{\circ} \mathrm{C}\right)$ |  |  |  | $(\mathrm{pm} / \mathrm{V})$ | $(\mathrm{pC} / \mathrm{N})$ |
| Fine Grain PMN-PT | 1 | 150 | 5800 | 2500 | 0.025 | 920 | 820 |
| Coarse Grain PMN-PT | $5-7$ | 150 | 6100 | 2700 | 0.016 | 820 | 800 |
| Material | $\mathrm{k}_{p}$ | $\mathrm{k}_{t}$ | $\mathrm{k}_{33}$ | $\mathrm{P}_{r}$ | $\mathrm{E}_{C}$ |  |  |
| Fine Grain PMN-PT | 0.6 | 0.5 | 0.72 | 30 | 5.5 |  |  |
| Coarse Grain PMN-PT | 0.62 | 0.51 | 0.74 | 32 | 5 |  |  |

Table A.2. Characterization of PMN-PT and PIN-PMN-PT single crystals. Free $\left(\varepsilon_{33}^{T} / \varepsilon_{0}\right)$ dielectric permittivity was measured at 1 kHz , and clamped $\left(\varepsilon_{33}^{S} / \varepsilon_{0}\right)$ permittivity was measured at the frequency of $2 \mathrm{f}_{a}$ (thickness mode anti-resonance frequency). High field $\mathrm{d}_{33}^{*}$ was measured by unipolar strain at a driving field of $10 \mathrm{kV} / \mathrm{cm}$.

| Material | $\mathrm{T}_{R-T}$ | $\mathrm{~T}_{C}$ | $\varepsilon_{33}^{T} / \varepsilon_{0}$ | $\varepsilon_{33}^{S} / \varepsilon_{0}$ | $\tan \delta$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\left({ }^{\circ} \mathrm{C}\right)$ | $\left({ }^{\circ} \mathrm{C}\right)$ |  |  |  |  |
| $<001>$ PMN-PT | 95 | 135 | 6000 | 900 | 0.004 |  |
| $<110>$ PMN-PT | 90 | 135 | 4500 | 730 | 0.008 |  |
| $<001>$ PIN-PMN-PT | 105 | 178 | 5600 | 900 | 0.006 |  |
| $<110>$ PIN-PMN-PT | 115 | 171 | 3300 | 650 | 0.01 |  |
| Material | $\mathrm{d}_{33}^{*}$ | $\mathrm{~d}_{33}$ | $\mathrm{k}_{t}$ | $\mathrm{k}_{33}$ | $\mathrm{P}_{r}$ | $\mathrm{E}_{c}$ |
| $<001>$ PMN-PT | 1800 | 1800 | 0.6 | 0.90 | 27 | 2.5 |
| $<110>$ PMN-PT | 1130 | 1100 | 0.51 |  | 34 | 3.2 |
| $<001>$ PIN-PMN-PT | 1850 | 1700 | 0.58 | 0.91 | 27 | 4 |
| $<110>$ PIN-PMN-PT | 800 | 900 | 0.50 |  | 37 | 4.4 |



## List of Publications

- H.J. Lee, S. Zhang, J. Luo, F. Li, and T.R. Shrout, "Thickness-dependent properties of relaxor- $\mathrm{PbTiO}_{3}$ ferroelectrics for ultrasonic transducers," Adv. Funct. Mater., vol. 20, 3154-3162, 2010.
- H.J. Lee, S. Zhang, and T.R. Shrout, "Scaling effects of relaxor- $\mathrm{PbTiO}_{3}$ crystals and composites for high frequency ultrasound," J. Appl. Phys., vol. 107, 124107, 2010.


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[^0]:    ${ }^{a}$ Densities measured by Archimedes method
    ${ }^{b}$ Average grain size determined by intercept method from SEM images

