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CHARACTERIZATION OF BISMUTH TITANATE THICK FILMS FABRICATED USING A SPRAY-ON TECHNIQUE

FOR HIGH TEMPERATURE ULTRASONIC NON-DESTRUCTIVE EVALUATION

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by

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ABSTRACT

Recent shifts towards green power generation have led to renewed interest in nuclear energy. However, the recent incident with the Fukushima Dai-ichi power plant has been a grim reminder that safety is of utmost importance. Similarly, monitoring of jet engine turbine blades has seen a renewed interest because of incidents such as US Airways Flight 1549, which suffered turbine damage upon take off and a water landing in the Hudson river needed to be performed. As a result, both of these two major industries have set goals for developing and implementing new in-situ systems for damage detection. Inspection via ultrasonic non-destructive evaluation (UNDE) is one of the leading methods being considered for such systems due to the light weight, relatively low cost, and low system footprint required for UNDE. However, UNDE in such real world systems is a non-trivial task due in large to the high temperature environments involved with such systems.

Utilization of a spray-on deposition technique of ferroelectric bismuth titanate (Bi$_4$Ti$_3$O$_{12}$) is investigated. The spray-on technique has several advantages compared to more standard methods of transducer fabrication, particularly for high temperature systems. The primary advantage of this technique is that transducers can be deposited directly onto the structure requiring investigation. Eliminates the need to develop a means of maintaining reliable high temperature mechanical coupling between the transducer and structure under evaluation. Additionally, the ability to analyze structures with complicated geometries with greater ease can potentially be achieved. Moreover, this method allows for fabrication of thick film transducer and therefore transducers with center frequencies typical to industrial UNDE (1-20 MHz) can be realized. Bismuth titanate has been chosen as the material to be investigated due to its high Curie temperature (685 °C) and because it has already been shown that fabrication of bismuth titanate based ultrasonic transducers via the spray-on deposition method is possible.

Since initial results with conventional sintering methods were unsuccessful, microwave sintering was pursued and is capable of producing films with superior
quality. Industrial partners showed strong interest for on-site deposition transducers. However, with on-site deposition, microwave sintering may not be a viable option. As a result, a crude, but very successful, method of sintering with a blow torch was developed and transducers fabricated in this fashion showed equivalent electromechanical strength.

Moreover, the entire temperature range which bismuth titanate fabricated with the spray-on technique had yet to be explored. In this work it has been shown that spray-deposited bismuth titanate transducers are capable of generating ultrasonic signals with strengths equivalent to room temperature signals up to 650 °C for short periods of time. Above this temperature, thermal depoling of the sample occurs rapidly as temperature increases and signal strength diminishes. Furthermore, little has been done to date to characterize material properties bismuth titanate films deposited with the spray-on technique. Initial results indicated that higher electromechanical coupling could be achieved with films deposited in this fashion when compared to their bulk counterparts due to the fact larger field strengths can be employed during poling without breakdown. Typically, the electromechanical properties of substrate supported films are determined via curve fitting methods since the standards outlined by the Institute of Electrical and Electronic Engineers are not valid for the boundary conditions inherent to substrate supported films. However, as it is demonstrated in this work with the Mason model, due to the loading on the transducer from the substrate and the porosity of the films, these techniques cannot be employed as no electromechanical resonance is observed in the impedance spectrum of the transducer. Values for the $d_{33}$ of the films were approximated by using a commercial $d_{33}$ meter and suggest $d_{33}$ values within the range of 13-16 pC/N are being achieved. Extrapolation of field strengths applied to the films fabricated herein during poling to numbers reported for bulk bismuth titanate imply that these values for the $d_{33}$ are fairly accurate. Conductivity measurements were made of the bismuth titanate films and were found to be equivalent to bulk bismuth titanate, thus eliminating lower
conductivity as a possible reason as to why larger field strengths are attainable. It is well
known that if thermal breakdown is the mechanism responsible for breakdown within a
material, larger field strengths can be achieved in samples as thickness decrease due to
the fact that localized heating can be dissipated more quickly in thinner materials.
Therefore, thermal breakdown is posited here as the breakdown mechanism in bismuth
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Chapter 1

INTRODUCTION

1.1 THESIS SCOPE, OUTLINE, AND MOTIVATION

The goal of this work was to fabricate ultrasonic transducers for high temperature ultrasonic non-destructive evaluation (UNDE). The motivation for this work springs from a growing interest for harsh environment UNDE from two primary industries, namely, the aerospace and nuclear energy industries. The Energy Policy Act of 2005 included many new incentives for the construction of new commercial next generation nuclear reactors and as many as 31 reactor license applications have been announced, which some speculate is the beginning of a “nuclear renaissance” (Holt 2011). In his 2011 State of Union address, President Barack Obama called for a national goal of generating 80% of the United States’ Energy to be from clean energy, which includes nuclear power. In 2010, the Department of Energy’s Nuclear Energy Development and Roadmap report to Congress, the stated number one research and development objective is to “develop technologies and other solutions that can improve the reliability, sustain the safety, and extend life of current reactors”. In the aerospace industry, there has been a recent push to develop sensors for in-situ health monitoring of turbine blades in order to reduce downtime from schedule based maintenance. For instance, it was reported in 2003 that United States Air Force spends over one billion dollars a year on turbine maintenance (Schulz 2003). If in-situ sensors can be developed for real time monitoring of turbines, millions of dollar would be saved annually as well as increase fleet availability. Using piezoelectric media for high temperature NDE is particularly advantageous in these fields because of their light weight and the small footprint necessary for required electronic equipment.
The work contained in this thesis is part of a two pronged approach at developing ultrasonic transducers for high temperature environments. One approach was to try and develop high temperature sensors using single crystal piezoelectric materials and the other method chosen was by fabricating transducers using a spray-on technique. This thesis deals with the latter approach and details concerning the former can be found in other texts (Parks, 2011; Baba, 2010). The spray-on fabrication process originally developed by Kobyashi was chosen because it offered several clear advantages for high temperature UNDE (Kobayashi, 2000). The primary advantages are that transducers can be deposited directly onto structures, eliminating any need for high temperature ultrasonic couplant and that the material is permanently held to the structure on its own accord (does not need to be clamped). Bismuth titanate, Bi$_4$Ti$_3$O$_{12}$, was the first material chosen for fabrication because it has a reasonably high Curie temperature (~685 °C) and also because it had been previously shown that it can be fabricated using the spray-on technique (Kobayashi, 2004). Another reason this technique was chosen was that its potential for in-field deposition seemed appealing (as opposed to conventional thin film technology) and that it showed potential to make UNDE of structures with complex geometry (e.g. a pipe) without requiring to machine a bulk piezoelectric material.

Another goal of this work was to characterize the material properties of these films since, to date, very little has been performed on materials deposited using the spray-on technique. Typical $d_{33}$ values for undoped, conventionally poled, bismuth titanate are reported to be around 3.5 pC/N (Shulman, 1997). These low values of $d_{33}$ have been attributed to the fact that field strengths of only 20 kV/mm can be achieved during poling due to the high conductivity of bismuth titanate. However, previous works reported on bismuth titanate transducers fabricated with the spray-on technique suggested that these films have higher electromechanical strength since their apparent strength as ultrasonic transducers indicated a $d_{33}$ higher than only 3.5 pC/N. Although, this was only speculation since little characterization of spray deposited films had been
performed and details of the poling procedure are vague. Therefore, another goal of this work has been to characterize material properties of these films for the first time and to determine if this hypothesis was true. Initial results of the spray deposited films seemed to confirm this conjecture as it was observed that field strengths obtainable during the poling process were in the range of 50-70 kV/mm, as is discussed in Section 4.1.

Previous reports on bismuth titanate demonstrated that if the growth of anisotropic plate like grains can be suppressed during sintering then lower conductivities, and therefore higher breakdown strengths, are observed (Dhage 2004). Therefore, the initial hypothesis for the observed high field strengths was that lower conductivities were being obtained with these films since their porous nature and associated short sintering times inhibits plate like growth during sintering. It was also suggested that the electrical properties of these films may be different as there may be an excess of depletion/inversion layers within the films due to the porosity, as is discussed in Section 1.3. To evaluate this hypothesis, conductivity measurements were made on deposited films as presented in Section 3.4. However, the conductivity measurements showed that the films have conductivities roughly equal to their bulk counterparts, and thus the microstructure was determined to not be responsible for achieving larger field strengths. It was then posited that the larger field strengths can be obtained due to the breakdown mechanism in bismuth titanate being thermal breakdown. With thermal breakdown, localized heating within the material is the mechanism responsible for breakdown. However, in thinner samples heat can be dissipated more rapidly and the increasing achievable field strength is typically inversely proportional to the cube or square root of the material thickness. Calculations made in Section 4.1 support this hypothesis and the field strength in bismuth titanate appears to increase at a rate inversely proportional to the cube root of the thickness. It is also shown in this work that field strengths which can be achieved on fabricated thicker samples are typically lower, giving further support to this hypothesis.
For determining electromechanical properties of films supported by a substrate the methods for measuring material properties outlined in the IEEE standards do not apply because of the mechanical boundary conditions the substrate imposes on the film. A common method for determining material properties of substrate supported films is to curve fit the impedance spectrum of the film to the Mason model (Ritter, 1999). However, due to damping imposed on the film by the substrate as well as damping from the material porosity, electromechanical resonances cannot be observed in deposited films. To illustrate this, the Mason model was employed in this work and shows that values of $k_t$ can be as high as 0.07-0.09 and electromechanical resonances would still not be visible in the impedance spectrum.

To approximate the $d_{33}$ of the films a commercial $d_{33}$ meter was used on deposited films, and for optimized processing conditions approximate $d_{33}$ values between 13-16 pC/N are measured. One problem with using a $d_{33}$ meter, however, is that measured values can be skewed due to biaxial stresses induced in the film from uniaxial loading. However, in Section 4.1 it is shown that if one assumes a linear relationship between the poling field strength and $d_{33}$ induced during poling, then these measurements are likely accurate. The ultimate conclusion from this is that because the breakdown mechanism in bismuth titanate appears to be thermal breakdown, higher poling field strengths and therefore higher $d_{33}$ values can be obtained with these films than can be achieved in their bulk counterparts due to smaller thicknesses.

At the same time, it was realized a solution for quantifying transducer performance needed to be produced. Prior work on spray-on deposited films only showed the ultrasonic waveforms generated in “arbitrary units” and the details on the method of signal generation and detection were vague or not given at all. Of course, when reporting ultrasonic data, the use of arbitrary units is acceptable since typically it is the method of investigation that is of importance. However, now new materials are being fabricated in a fashion never before performed. Therefore, reporting material
performance as ultrasonic waveforms with arbitrary units is unacceptable, as no real comparison can be made between different materials fabricated in this way and thus it is not possible to judge which materials or processing conditions are best. As a result, as is derived in Section 3.7, a figure of merit has been developed in order to be able to quantify transducer performance. The figure of merit itself is purposefully quite simple and utilizes basic ultrasonic principles that most involved in the field are familiar with.

It was discovered early on in this work that sintering samples using conventional processes, such as a tube furnace, proved to be difficult as adhesion of the films was routinely poor. As a result, focus was giving to alternative methods of sintering, namely microwave sintering. Films fabricated using this method proved to be superior and thus became the primary method for fabricating films early on in this work (Section 2.2.1). Later, interest from industrial partners grew for in-field deposition of these transducers. As a result, a crude, but successful, technique using a blow torch was developed (Section 2.2.2). This result shows that in-field deposition of transducers can be achieved.

In addition to the conductivity being measured for these films for the first time, measurements of the density and elastic modulus also been made for the first time and are presented in Section 4.1. Furthermore, the effect of sintering technique, as well as the effect of sol gel solution to powder ratio used on material properties has been evaluated. As is presented in Section 4.1, films fabricated with microwave sintering exhibit higher elastic modulus and higher relative permittivities, but the piezoelectric strength between the two remains equal. These differences in material properties are attributed to microwave sintering achieving a more uniform microstructure, as well as suspected oxygen loss during blow torching. It has also been determined that films with a powder to sol gel solution ratio of 2 g : 1.2 mL displayed superior piezoelectric response and substrate adhesion.

Section 4.2 presents the high temperature performance of these samples as ultrasonic transducers. Prior work has only demonstrated that bismuth titanate
transducers fabricated with the spray-on method are capable of operating as transducers only to temperatures of 200 °C. In this work, it has been shown for the first time that bismuth titanate transducers fabricated in this manner are capable of operating as ultrasonic transducers, at least for short time periods, up until the material Curie temperature of 685 °C. Conductivity is always a concern when considering materials for high temperature UNDE, however, this result also shows that despite the fact that bismuth titanate has a conductivity relatively higher than most piezoelectrics, it does not affect its performance as a high temperature transducer.

Further applications of transducers deposited with the spray-on technique is explored in Section 5.1. The first application is testing whether inter-digitized electrode based Lamb wave transducers can be fabricated. It is shown here that Lamb wave transducers can be fabricated with this method and are capable of operating to temperatures of 675 °C. Another major appeal which started the investigation of this deposition technique is that transducers could theoretically be deposited onto complex geometries. In Section 5.2, the applicability of this deposition technique to deposit onto and investigate a curved surface was proven by successfully depositing a functional transducer on a pipe segment. This particular geometry was chosen since a potential major real world application of this technology is for fluid level measurements in piping in nuclear reactor facilities. It has been shown that these measurements can indeed be performed with transducers fabricated with the spray-on technique.

In summary, the goal of this work has been to develop bismuth titanate transducers using the recently established spray-on deposition technique and test their ability to function as high temperature ultrasonic transducers. Since to date there has been a lack of characterization of material properties of films fabricated in this fashion, another goal of this work has been to a clear a path for characterizing future materials deposited in this fashion.
### 1.2 Introductory Remarks On Ferroelectricity And Piezoelectricity

A material is said to be a dielectric if when upon application of an external electric field if it acquires a net charge without (ideally) any long range charge transport. Thus, an electric field induces a dipole moment within the material and it becomes polarized (Moulson and Herbert 1990). The induced polarization can be caused by one or any combination of several mechanisms, namely, displacements of the negatively charged electron cloud relative to the nucleus; relative displacement of cation and anion species; or reorientation of dipolar molecules; as well as development of space charge along potential barriers such as grain boundaries (Kinegry, Bowen and Uhlman 1960). This is a result of the insulating nature of dielectrics since there is a limited amount of free charge carriers. Dielectrics can exist in many forms, including gasses, liquids, and crystalline/non-crystalline solids; but the common property which they all share is the ability to store electrical energy in the form of potential energy (Hayt and Buck 2001). This is mechanically analogous to the stretching of a spring. In linear dielectrics, the polarization, $P$, and electric displacement, $D$, are expressed as

\[ P = \chi \varepsilon_0 E \]  \hspace{1cm} (1.1)

\[ D = \varepsilon_0 E + P = \varepsilon_0 \varepsilon_r E \]  \hspace{1cm} (1.2)

Where $\chi$ is the material’s electric susceptibility, and $\varepsilon_0$, $\varepsilon_r$ are the permittivity of free space and the relative permittivity of the material, respectively. $\chi$ and $\varepsilon_r$ are related by $\varepsilon_r = 1 + \chi$. Here, the relative permittivity and electric susceptibility are being treated as scalars, but in general they are second-order tensors.

In some materials, a polarization exists without an applied electric field and this is referred to as a spontaneous polarization. This phenomenon is a result of a lack
symmetry within the materials atomic structure. More specifically, these materials have a unique polar axis. Accordingly, these materials are therefore anisotropic (Berlincourt, Curran, and Jaffe, 1964). Commonly, materials of the perovskite crystal structure are referenced to illustrate this phenomenon. Figure 1.1 shows an illustration of tetragonal barium titanate, BaTiO$_3$, which crystallizes in the perovskite structure. In BaTiO$_3$ the smaller Ti$^{4+}$ cation is shifted towards one of the six oxygen atoms which make up an octahedron. Thus, the center of positive charge and negative charge within the unit cell no longer coincide thereby creating a dipole and a spontaneous polarization results (Richeter and Trolier-McKinstry 2005). It should be noted that while a lack of symmetry is necessary for spontaneous polarization, it does not necessarily guarantee it (Uchino 2000).

If the spontaneous polarization of the material can be reoriented with an electric field of a certain strength (known as the coercive field $E_c$), the material is said to be ferroelectric. The dipole moment associated with the unique polar axis required for ferroelectrics also changes as a function of temperature and therefore surface charges develop as temperature is varied—this is known as the pyroelectric effect (Xu 1991).
Ferroelectrics also exhibit the piezoelectric effect and the converse piezoelectric effect. A material is said to be piezoelectric if it develops a charge (electric field) that is linearly proportional to an applied mechanical stress. Materials which possess the piezoelectric effect also possess the converse piezoelectric effect and this is defined as the development of a stress which is linearly proportional to the strength of an applied electric field. It is worth mentioning that while all ferroelectric materials are pyroelectric and piezoelectric, not all materials which are piezoelectric are pyroelectric and not all pyroelectrics are ferroelectric (IEEE Std 180-1986; Ikeda, 1990). One can also rightfully conclude that equations (1.1) and (1.2), as well as relations governing a materials stress-strain behavior require some modification in order to accurately describe piezoelectric media.

The differentiation between piezoelectric materials which are ferroelectric and those which are not has practical implications that concern the fabrication of devices which utilize the piezoelectric effect. In fabrication of bulk ferroelectric ceramics, the following steps are typically followed: (1.) Weighing and mixing (usually by ball milling); (2.) calcination; (3.) regrinding; (4.) repressing into desired shape (6.) sintering. During the mixing and calcination stages, metal oxide precursors are mixed and react during calcination to produce the desired compound. For example, Bi$_2$O$_3$ and TiO$_2$ can be mixed in ratios of 2:3 and upon calcination react to produce bismuth titanate, Bi$_4$Ti$_3$O$_{12}$. After regrinding and pressing, sintering is performed in order to densify the material. The end result, however, is a polycrystalline sample with each grain having an atomic structure which has crystallized in a direction that is random relative to other grains. Therefore the vectors of local spontaneous polarizations in each grain throughout the material do not coincide. This results in no net piezoelectric effect over the sample as a whole despite the fact local regions of the sample may be strongly piezoelectric. However, since in ferroelectric materials their polarizations can be reoriented with an applied
FIGURE 1.2 Illustration of (a) banded and (b) simple lamellar twin formations in polycrystalline ceramics. Thicker lines represent grain boundaries and thinner lines represent directions of (as well as domain walls in (a)) of ferroelectric domains.

field, piezoelectricity can be induced if a suitable field is applied. This process is known as poling. The same cannot be said for a polycrystalline material that may be piezoelectric in single crystal form but is not ferroelectric.

Regions where a polarization exists and is uniform in a single direction is known as a ferroelectric domain and the region surrounding it is referred to as a domain wall. In fact, it is not unlikely that a single grain possesses multiple ferroelectric domains, especially in coarse grain ceramics, since defects such as vacancies, interstitials, and impurities, as well as clamping imposed on a grain by adjacent grains can cause twinning of the domains. This variation of ferroelectric domains within a samples’ microstructure is illustrated in Figure (1.2). Even in single crystals it is not common to find them spontaneously oriented and poling may be necessary to induce piezoelectricity (Jaffe, Cook and Jaffe 1971). The poling process attempts to align the spontaneous polarizations within a sample as much as possible. During this process the sample is typically heated to a certain temperature and placed under an electric field of a required strength for a certain amount of time—the temperature and time of course are material dependent. Raising the temperature during the poling process aids in domain alignment through several mechanisms. Increasing temperature reduces the local anisotropy
within the material and therefore the strain associated with the reorientation of a 90°
domain is lowered. Second, as the bulk resistivity of a material decreases, space charges
can move more freely and their effects on pinning domain walls are minimized (Xu
1991). To complete the poling process, the temperature is lowered then the applied
field is removed.

To better explain the poling process and the ferroelectric effect in general,
Figure 1.3 shows an illustration of a plot of polarization versus applied electric field. The
arrows drawn on the samples in the illustration represent the directions of local regions
of polarization. Point A in the plot is for a sample with no previous history of an applied
electric field, often referred to as the virgin state. Here, ferroelectric domains within the
sample are randomly oriented and the sample as a whole is isotropic. Once an electric
field is applied the domains begin to align with the direction of the field as field strength
increases. When the field strength exceeds that of the coercive field, \( E_c \), the domains
begin to fully align with the direction of the field. At point B, polarization within the
sample reaches a value where the polarization is saturated and the sample is aligned
with the electric field to its fullest extent. If the field is then lowered to zero, a remnant
polarization, \( P_r \), exists within the sample. At this point, with the domains aligned, the
original isotropy of the sample is now eradicated and for polycrystalline ceramics the
symmetry of the sample is \( \infty \text{mm} \), or cylindrical polar symmetry which is equivalent to
the hexagonal crystal class 6mm (Jaffe, Cook and Jaffe 1971). If the field is then
increased again, but with opposite polarity, the direction of the polarization reverses
once the field strength exceeds \(-E_c\) (point C). If the field was to then be lowered again to
zero and then raised again beyond \( E_c \), the sample would once again return to the state
found at point B. The plot in Figure 1.2 is referred to as a hysteresis loop, since a
samples state of polarization relies on its history of prior field exposure. It is convenient
to point out here that theoretically an applied field equal to that of the coercive should
be enough to reorient most domains, however, practice indicates that maximum
piezoelectricity is obtained with fields 3 or 4 times larger than \( E_c \) (Xu 1991).
It should be noted that the arrows representing the directions of electric domains at points B and C in Figure 1.2 are highly idealized. In reality, a polycrystalline sample cannot possess a polarization as large as it would in single crystal form. The amount of polarization a polycrystalline sample can achieve relative to its ideal single crystal form is dependent upon how many allowable polar directions its crystal symmetry (Jaffe, Cook and Jaffe 1971). For example, for tetragonal BaTiO$_3$ illustrated in Figure 1.1, the Ti$^{4+}$ ion shifts towards one of the oxygen ions, therefore, there are six possible polar directions (Richeter and Trolier-McKinstry 2005). Solid solutions of PbTiO$_3$-PbZrO$_3$ near the morphotropic phase boundary are highly polarizable and exhibit superior piezoelectric properties because both tetragonal and rhombohedral phases are present which results in up to 14 possible directions of polarization (Jaffe, Cook, & Jaffe, 1971; Richeter & Trolier-McKinstry, 2005; Park & Shrout, 1997). Other factors such as defects and internal stresses adversely affect the efficiency of the poling process by inhibiting domain wall motion (pinning).
1.2.1 **Coupled Field Interactions and the Piezoelectric Relations**

As the previous sections state, Equations (1.1) and (1.2) are not sufficient to fully describe behavior of piezoelectric materials. In this section a brief overview of basic relations used for describing piezoelectric behavior are presented. There are many excellent texts which discuss this topic in further detail (Ikeda, 1990; Berlincourt, Curran, & Jaffe 1964; Tiersten, 1969; Auld, 1973).

The relations which govern the properties of piezoelectric materials can be derived from thermodynamic principles, but this derivation is omitted here but can be found in several texts (Berlincourt, Curran, & Jaffe, 1964; Ikeda, 1990). For piezoelectric media, the electric displacement, \( D_i \), and strain, \( S_{ij} \), are given by:

\[
D_i = \varepsilon^T_{ij}E_j + d_{ijk}T_{jk} \quad \text{(1.3)}
\]

\[
S_{ij} = d^{*}_{ijk}E_k + s^E_{ijkl} \quad \text{(1.4)}
\]

Where \( \varepsilon^T \) and \( s^E \) are the materials’ permittivity and elastic compliance, respectively, and \( E \) and \( T \) are applied electric fields and stresses. \( d_{jk} \) is the piezoelectric charge coefficient (sometimes also referred to as the piezoelectric charge coefficient) and ‘\(*\)’ indicates the transpose of the \( d \) matrix. In general, the piezoelectric charge coefficient is a tensor of rank 3, however, using symmetry considerations the number of independent coefficients is reduced and matrix notation can be used. Since \( d_{ijk} \) \((i, j, k = 1,2,3)\) is symmetric in \( j \) and \( k \) it can be reduced to \( d_{ij} \) \((i=1,2,3 \text{ and } j = 1,2,3,4,5,6)\) (Uchino 2000). Convention has it that for poled ceramics the 3 axis indicates the direction of poling and the shear planes represented by the suffixes 4, 5, and 6; see Figure 1.4. Furthermore, for
the piezoelectric coefficient, the first subscript indicates the direction of field or
displacement while the second subscript indicates the direction of mechanical strain or
stress. For the symmetry of poled polycrystalline ceramics, $d_{24}=d_{15}$ and $d_{32}=d_{31}$ and
similar arguments can be made for electrical and elastic constants. For 6mm symmetry,
the compliance, dielectric and piezoelectric constants have the form (Jaffe, Cook and
Jaffe 1971):

**Elastic compliance**

\[
\begin{bmatrix}
  s_{11} & s_{12} & s_{13} & 0 & 0 & 0 \\
  s_{12} & s_{11} & s_{13} & 0 & 0 & 0 \\
  s_{13} & s_{13} & s_{33} & 0 & 0 & 0 \\
  0 & 0 & 0 & s_{44} & 0 & 0 \\
  0 & 0 & 0 & 0 & s_{44} & 0 \\
  0 & 0 & 0 & 0 & 0 & 2(s_{11}-s_{22})
\end{bmatrix}
\]

**Permittivity**

\[
\begin{bmatrix}
  \varepsilon_{11} & 0 & 0 \\
  0 & \varepsilon_{11} & 0 \\
  0 & 0 & \varepsilon_{33}
\end{bmatrix}
\]
Piezoelectric charge coefficient

<table>
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<tr>
<th></th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>d_{31}</th>
<th>0</th>
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<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>d_{31}</td>
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<td>d_{31}</td>
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<td>d_{33}</td>
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</tr>
</tbody>
</table>

And the piezoelectric equations of Equations (1.3) and (1.4) take on the following expanded form:

\[ D_1 = \varepsilon_{11}^T E_1 + d_{15} \]  \hspace{1cm} (1.5)
\[ D_2 = \varepsilon_{11}^T E_2 + d_{15} T_4 \]  \hspace{1cm} (1.5(b))
\[ D_3 = \varepsilon_{33}^T E_3 + d_{33} T_3 + d_{31} (T_1 + T_2) \]  \hspace{1cm} (1.5(c))
\[ S_1 = S_2 = s_{11}^E T_1 + s_{12}^E T_2 + s_{13}^E T_3 + d_{31} E_3 \]  \hspace{1cm} (1.6)
\[ S_3 = s_{13}^E (T_1 + T_2) + s_{33}^E T_3 + d_{33} E_3 \]  \hspace{1cm} (1.6(b))
\[ S_4 = s_{44}^E T_5 + d_{15} E_1 \]  \hspace{1cm} (1.6(c))
\[ S_5 = s_{44}^E T_5 + d_{15} E_1 \]  \hspace{1cm} (1.6(d))
\[ S_6 = s_{66}^E T_6 \]  \hspace{1cm} (1.6(e))

Since piezoelectric media have coupled field interactions, e.g. electromechanical responses, the values of their material properties depend more strongly on the electrical and mechanical boundary conditions the material is subjected when a measurement is taken. Convention has it that boundary conditions for which material constants such as permittivity (impermeability) or elastic compliance (elastic modulus) measured at are indicated by superscripts. In Equations 1.3-1.6 the superscript “T” on the permittivity indicates that it is valid for a material exposed to constant (typically zero) mechanical stress and the superscript “E” placed on the elastic compliance means it is valid for when the material is exposed to constant (typically zero) electric field. Further explanation of the specific boundary conditions just mentioned and others closely related follows below, but it is worth mentioning that constants may also be sensitive to whether or not the system is adiabatic, isothermal, or if magnetic fields are
present. Typically, magnetic field effects are ignored and differences between adiabatic and isothermal constants are negligible, or at the very least easily controlled since there is often little heat exchange and the piezoelectric relations derived for adiabatic conditions Equations 1.3 and 1.4 can simply be used (Berlincourt, Curran and Jaffe, Piezoelectric and Piezomagenetic Materials and Their Function in Materials 1964). Thus, no further attention will be devoted to such special situations here.

For further explanation of electrical and mechanical boundary conditions, consider an electroded piezoelectric element that is poled in the direction perpendicular to the electroded surfaces and that the electrodes are short circuited (Figure 1.5 (a)). If a compressive stress is applied in the direction of the poling, the sample will strain and a change in polarization will also occur within the material. The change in polarization will generate bound charges at the surface of the sample and free charges will gather to compensate the bound charge—this is illustrated in Figure 1.5 (b). An electric displacement field (indicated by blue lines in Figure 1.5 (b)) exists in the material, however, since the electrodes are short circuited there can be no electric field and this is said to be a constant, or zero, electric field condition. The ratio of the strain to stress is the elastic compliance and if the compliance were to be measured under the conditions being discussed this would be the compliance at constant electric field, $s^E$. This is the same elastic compliance in Equations 1.3-1.6. The strain curve for zero electric field boundary conditions is represented by the red arrow in Figure 1.6 whose slope is equal to the compliance.

If the electrodes are open circuited and followed by removal of the stress, a different elastic compliance will be measured and the sample will not return to the original state it was in prior to having a stress applied. The compensating charge from when the stress was originally applied is still present, however, now that electrodes have been disconnected from each other. Another accumulation of free charge of
FIGURE 1.5 Illustration of electric field and displacement behavior of piezoelectric subjected to different boundary conditions (see text for details).
opposite polarity will form in response to the original compensating charge. This is illustrated in Figure 1.5 (c). Due to this second accumulation of charge, an electric field now exists throughout the material. In response to this field, a second electric displacement field will form. This second electric displacement field has the same magnitude of the electric displacement which formed when stress was first applied under short circuit conditions, but is opposite in sign. This second field is known as a depolarizing field. The two fields cancel one another as is illustrated in Figure 1.5 (c). Hence, these boundary conditions set up a situation of constant electric displacement \((D=0)\). If the stress were to be removed to zero, an electric field would still exist within the material because of the open circuit condition and therefore a residual strain will exist in the material. The compliance measured under these conditions is the compliance at constant \(D\) and is indicated by a superscript \(D\) and is illustrated in Figure 1.6 by the green arrow. What this demonstrates is that a piezoelectric material at constant electric displacement is less compliant than one at constant electric field. To have the sample return to the original state prior to initial application of stress, the sample is connected to an ideal load. As work is delivered to the load the sample returns to its original strain state.

A relationship between \(s^D\) and \(s^E\) can be established by starting with Equation 1.3 for the open circuit condition, \(D=0\). This gives

\[
D_3 = 0 = d_{33} T_3 + e_{33}^T E_3
\]  

1.7

Solving for \(E_3\),

\[
E_3 = -\frac{d_{33} T_3}{e_{33}^T}
\]  

1.8

Substitution of \(E_3\) into Equation 1.4 gives the strain as
FIGURE 1.6 Stress-strain curve for a piezoelectric material at constant or zero electric field (red) and under constant or zero electric displacement (green).

\[ S_3 = T_3 \left( s_{33}^E - \frac{d_{33}^2}{\varepsilon_{33}} \right) \quad 1.9 \]

The current boundary conditions under consideration are those of zero electric displacement, and \( s_{33}^D \) can be solved for by taking the ratio of \( S_3/T_3 \) in Equation 1.9. This gives

\[ \left( \frac{S_3}{T_3} \right)_{D=0} = s_{33}^D = s_{33}^E \left( 1 - \frac{d_{33}^2}{s_{33}^E \varepsilon_{33}} \right) \quad 1.10 \]

Thus Equation 1.9 quantitatively relates the difference in values in \( s_{33}^D \) and \( s_{33}^E \). The last quantity within the parenthesis on the right hand side is the square of what is known as the electromechanical coupling coefficient, \( k_{33} \), and is expressed as

\[ \frac{s_{33}^D}{s_{33}^E} = 1 - k_{33}^2 \quad 1.11 \]

An interesting conclusion about the behavior of piezoelectric materials can be drawn from Equation 1.10. The coupling factor, \( k_{33} \), which is discussed in more detail below, is
always a value less than one, therefore, as is discussed before, piezoelectric media are less compliant under conditions of constant electric displacement than when they are under conditions of constant electric field.

As its name indicates the coupling factor can be used as a figure of merit for how efficiently electrical energy can be converted to mechanical energy and vice versa. \( k^2 \) can best be understood by realizing it is the ratio of stored electrical energy to input mechanical energy or the ratio of stored mechanical energy to input electrical energy. Quantitatively, for a piezoelectric material electrode and poled as mentioned before, this is expressed as (Uchino 2000)

\[
k_{33}^2 = \frac{\text{Stored Electrical Energy}}{\text{Input Mechanical Energy}}
\]

\[
= \left( \frac{1}{2} \right) \left( \frac{P_3^2/E_3}{s_{33}T_{33}^2} \right) = \frac{(d_{33}T_{33})^2/E_{33}}{(s_{33}T_{33})^2}
\]

\[
= \frac{d_{33}^2}{s_{33}E_{33}}
\]

This result is the same as that obtained in Equations 1.9 and 1.10.

To further elucidate this point consider again the example above. Again, under short circuit conditions, a stress is applied to the sample and a strain, \( S_3 \), occurs. The mechanical work done on the sample is given by

\[
W = \int T_3 dS_3 = W_1 + W_2
\]

Therefore, \( W \) is given by the area above the curve as shown in Figure 1.7. \( W_2 \) is the mechanical work supplied to the system but is not available when work is done on the
FIGURE 1.7 Stress-strain curve for a piezoelectric material under constant electric field and electric displacement boundary conditions.

electrical load after the stress is removed under open circuit conditions. The work that is done on the electrical load is given by $W_1$ (IEEE Std, 1978; Berlincourt, 1971). Again, by referencing Figure 1.7, it is evident that the larger the difference between the compliance at constant $D$ and at constant $E$, and therefore the larger $k_{33}$ as Equation 1.10 points out, the more energy is available to be delivered to the electrical load.

Similarly, electrical properties of a piezoelectric can have a strong dependence on the mechanical boundary conditions—namely the effect of zero stress and zero strain boundary conditions on the permittivity. To indicate permittivity at zero stress, a superscript $T$ is placed on the permittivity while zero strain is indicated by a superscript $S$. To briefly illustrate this, once again consider a piezoelectric element whose electrodes are perpendicular to its poling direction. If a voltage is then applied a strain will develop (consider in this case that the field is applied such that a negative strain develops). If the sample is then rigidly clamped followed by removal of the field, a stress will develop
in response to the originally induced strain state. Under this ideal circumstance, the strain, \( S_3 \), will be zero. Therefore, Equation 1.4 gives

\[
S_3 = 0 = d_{33}E_3 + s_{33}^E T_3
\]  

1.14

Solving for \( T_3 \) and inserting into equation 1.3 gives

\[
D_3 = E_3 (\varepsilon_3^T - \frac{d_{33}^2}{s_{33}^E})
\]  

1.15

From Equation 1.2 the permittivity is simply the ratio of \( D_3/E_3 \), and keeping in mind that this is a zero strain boundary condition the following is obtained

\[
\left( \frac{D_3}{E_3} \right)_{S_3=0} = \varepsilon_3^S = \varepsilon_3^T \left( 1 - \frac{d_{33}^2}{s_{33}^E\varepsilon_3} \right)
\]  

1.16

The cycle in question here is completed by replacing rigid clamping with a finite mechanical load. Noting that the last term in the brackets is \( k_{33}^2 \) the following relation can then be formulated

\[
\frac{\varepsilon_3^S}{\varepsilon_3^T} = 1 - k_{33}^2 = \frac{s_{33}^D}{s_{33}^E}
\]  

1.17

This result is a good representation of the coupled field behavior that is present in piezoelectrics. In these idealized examples, equivalent expressions for ratios of constants for electrical properties and mechanical properties are achieved; however the origins of these separate expressions are from considering situations where the electrical or mechanical boundary conditions are separately either passive or active. It is a very interesting result that helps to clarify some of the basic physics for this very unique family of materials.

Another piezoelectric coefficient commonly used as a figure of merit that is commonly used is the piezoelectric voltage coefficient, \( g \). The piezoelectric charge coefficient, \( d \), and piezoelectric voltage coefficient are related to one another in the following way
The piezoelectric charge coefficient is used to describe an induced strain for a given voltage, while the piezoelectric constant \( g_{ij} \) is commonly used when discussing sensing applications to determine an induced voltage when an element is subjected to a specific force. Equation 1.17 points out that with a low piezoelectric \( d \) coefficient and a low permittivity then a material will have a large piezoelectric \( g \) coefficient.

Other piezoelectric coefficients exist but will not be mentioned here. This is born out of the fact that Equations 1.3 and 1.4 are not the only constitutive equations governing piezoelectric materials. Depending on the mechanical, electrical, and geometrical circumstances for a specific situation one equation may be more convenient than another. For brevity, these other equations are omitted but can be found in the 1987 IEEE Standard for Piezoelectricity, as well as in other sources (Ikeda, 1990; Berlincourt et al., 1964).

\[
d_{ip} = \varepsilon_{ik}^T g_{kp} \quad 1.18
\]

1.3 **Conductivity in Ferroelectrics and Dielectric Breakdown**

In practice, dielectrics conduct small amounts of charge. Motion of charge through the material can have significant effects on the materials behavior, particularly in the magnitude of the dielectric loss and the degree of domain alignment that can be achieved during the poling process. Therefore, a piezoelectric materials conductivity will have a significant effect on its performance as an ultrasonic transducer, especially at elevated temperatures as the electronic, ionic and impurity mobilities increase (as is discussed in more detail in Section 1.4.1.). Therefore it is worth discussing mechanisms of charge motion.

Conductivity, \( \sigma \), is defined as
\[ \sigma = \frac{J}{E} \]

\( E \) is the applied electric field strength and \( J \) is the current density. Intrinsic conduction mechanisms are those that are present in a perfect, defect free, crystal of the material and are from the generation of electron-hole pairs from thermal vibrations in the lattice. Extrinsic conduction mechanisms are introduced from defects such as grain boundaries, dislocations, vacancies, interstitials, or impurity atoms. These defects introduce excess electrons or holes to a material and alter ion mobility in the lattice and have significant effects on material conductivity.

At the surface of a semiconductor bonds that are normally terminated are exposed, and oxides or nitrides form and can change the band structure (Hench & West, 1990). In a p-type semiconductor, surface states that are positive form because of ionized acceptors. The negative charge of the ionized acceptors will attract positive charge to the surface in order to insure charge neutrality. The valence and conduction bands will then rise by a potential, \( V_o \). This surface region forms what is known as a depletion layer. If \( V_o \) is large enough an inversion layer will form, as is illustrated in Figure 1.8. Due to the large concentration of positive charge adsorbed on the surface, a correspondingly large amount of negatively charge acceptors are formed and an electric field can form across the interface. In other words, an n-type semiconductor will form on the surface of a p-type bulk semiconductor and these regions can be as large as 1 \( \mu \)m (Hench & West, 1990; Kasap, 2002). These grain boundary depletion regions can form significant barriers for both the cross transport of ionic and electronic charge and near these boundaries there can be a significant drop in conductivity (Waser 1996). For porous ceramics, as this text will deal with, such boundaries exist in greater numbers.
than in dense ceramics and can potentially affect the conductivity as well as the dielectric constant and loss and therefore performance as an ultrasonic transducer. Similar effects occur at grain boundary interfaces and in intergranular layers. Conduction band electrons approaching the grain boundary will then have to overcome a potential barrier with height, $\varphi$, as is illustrated in Figure 1.9. This is especially prevalent in thin films and fine grained ceramics and can have significant effect on conductivity (Waser 1996). Such charge buildups at interfaces can lead to large polarizations and a subsequent higher dielectric constant. These effects are well documented and can be exploited for use as positive temperature coefficient resistors and gas sensors, for example. A classic example of this is with BaTiO$_3$ (Moulson & Herbert, 1990; Newnham, 1986).

1.3.1 Dielectric Breakdown

In the previous section background on conductivity within a dielectric material was considered. Understanding electronic nature is important for many reasons, however, in ferroelectrics it is important for two reasons: 1. The effects conductivity has
on sensor and actuator performance (see Section 1.4.2), and 2. Its effects on dielectric breakdown.

The conductivity of a material is strongly dependent on factors such as temperature, applied field strength, and defect concentration. Electrical failure can occur within a material when an electrical short occurs across the material—this is referred to as breakdown and can permanently damage a material (Hench and West 1990). Several mechanisms can be responsible for breakdown and are discussed briefly below, however, the phenomena can simply be regarded as a burst of current which occurs at a certain field strength and/or temperature that results in breakdown
channels or metal dendrites which extend throughout the material (Kinegry, Bowen and Uhlman 1960). The voltage gradient minimum at which dielectric breakdown occurs is known as the breakdown strength and can depend upon multiple parameters, including (but not limited to): thickness, temperature, atmosphere, electrode material and shape, field frequency, porosity, and defect composition (Hench & West, 1990; Moulson & Herbert, 1990).

The degree of domain alignment achieved during the poling process can be greatly limited by the breakdown strength, as well as the conductivity, of the material which requires poling. If a material’s conductivity is too high, it becomes difficult to establish a large electric field across the material during the poling process (Seth & Schulze, 1989; Ikegami & Ueda, 1974). Likewise, if a material’s breakdown strength is smaller than the coercive field required for poling, maximum, if any, alignment of domains becomes will not be possible.

Breakdown occurs when the thermal energy of the electrons and/or lattice reaches a particular value that causes the material conductivity to increase rapidly during the application of an applied field. During breakdown, the passage of high currents results in fusion and vaporization which in turn destroy the materials insulating properties (Kinegry, Bowen and Uhlman 1960). Generally, the mechanisms considered to be responsible for breakdown are intrinsic breakdown, thermal breakdown, and discharge breakdown (Moulson & Herbert, 1990; Hench & West 1990). There are also several pseudo-type mechanisms which are from combinations of the three basic mechanisms, including avalanche breakdown which essentially is a combination of intrinsic and thermal breakdown theories.

Intrinsic breakdown is primarily field dependent and is independent of electrode geometry and the waveform applied. Intrinsic breakdown is attributed to energy transfer between electrons and the lattice. If the applied field strength is greater than the intrinsic breakdown strength, then the energy given to the system by the applied
field is equal to or greater than the ionization energy and electrons are quickly promoted from the valence band to the conduction band. The number of conduction electrons quickly multiplies due to heat generated from electron-hole recombination events and lattice collisions. As the ionization rate eventually exceeds the recombination rate, the conduction electron density increases irreversibly. As these accelerated electrons exchange energy with the lattice via collisions the lattice within the material is eventually destroyed. Intrinsic breakdown can usually be measured with good reproducibility in single crystals, but since dielectric strength depends highly on material homogeneity it can be difficult to obtain reproducible values in polycrystalline materials.

In thermal breakdown, it is the temperature dependence of dielectric properties of the material that are responsible. Thus it is the temperature of the lattice and not the electrons which gives way to breakdown. It is based on the balance between heat dissipated in the material and heat generated from Joule heating, discharges within the material, and dielectric losses. Applied field strength plays a minor role as it only influences the heat generating mechanisms. If the heat generated in the material is not dissipated quickly enough, rises in conductivity and dielectric loss begin to runaway eventually leading to breakdown (Moulson & Herbert, 1990; Hench & West 1990).

Discharge breakdown is from inhomogeneities within the material, most notably porosity. As a DC field is applied to a porous dielectric, a field strength will eventually be reached where gas discharge occurs within a pore. This can lead to several mechanisms which can destroy the material. A stream of discharges traveling from pore to pore can result causing stresses in the material between discharging pores. Failure may also occur from the heat generating in the pore from discharge. Other mechanisms that lead to the failure of a material during discharge breakdown may exist, however, there is no doubt that higher breakdown strength is achieved with lower porosity (Moulson & Herbert, 1990; Kinery, Bowen, & Uhlman, 1960).
1.4 PIEZOELECTRIC MATERIALS FOR USE AS ULTRASONIC TRANSDUCERS

Until this point only some of the basic physics of ferroelectrics has been discussed with little focus given to their applications. Applications of ferroelectric materials are numerous and a few such applications include, but are not limited to, pyroelectric sensors, high permittivity capacitors, accelerometers, signal filters, ferroelectric memory (FRAM), transformers, and precision positioners (Uchino 2000). This thesis will be primarily concerned with the application of ferroelectrics as ultrasonic transducers designed specifically for high temperature (>500 °C) applications. Other means of detecting and generating ultrasound exist, such as magnetostrictive transducers, EMAT’s, and laser based techniques, for example; however piezoelectric materials are the most commonly used in practice.

The premise of using a piezoelectric material as an ultrasonic transducer is relatively simple. If being utilized to generate an ultrasonic wave (actuator), an electrical signal is applied to a piezoelectric material and via the converse piezoelectric effect a strain is induced. Likewise, a stress wave can be detected and converted into an electrical signal via the piezoelectric effect. The resonant frequency, \( f \), of an unloaded piezoelectric material is given by,

\[
f = \frac{v}{2t}
\]

Where \( v \) and \( t \) are the piezoelectrics’ acoustic wave velocity and thickness, respectively. Naturally, signals are generated and detected more efficiently if they are near the resonant frequency.

In UNDE, piezoelectric transducers can be used to find surface and sub-surface defects, as well as measure material properties such as the modulus of elasticity. Being
able to detect sub surface information without destructive investigation (e.g. cut it open) is UNDE’s greatest advantage. Other methods of obtaining subsurface information of a specimen exist, such as X-ray, microwave, and magnetic resonance (MRI) based technologies; however, UNDE has a major advantage over these techniques since the equipment required for typical UNDE is generally much cheaper and with a smaller required footprint (Shull and Tittmann, 2002).

Figure 1.10 illustrates the basic premise of a UNDE flaw detection system. A pulser generates a voltage spike (or tone-burst signal) which is sent to the piezoelectric transducer which is in contact with the specimen under evaluation. An oscilloscope, which measures voltage as a function of time, also receives this voltage spike and this is often referred to as the ‘main bang’ or ‘break through’ signal. When the voltage spike reaches the piezoelectric transducer, it is converted into an elastic wave which is launched into the specimen. If a flaw is present within the material which is on the order of or larger than the wavelength of the wave, it will reflect part of or the entire ultrasonic wave back towards the transducer. The reflected wave will then be converted into a voltage once it reaches the ultrasonic transducer. The same will happen from the portion of the wave reflected from the end of the specimen being examined, also referred to as the backwall reflection.

There are several key parameters for addressing the utility of an ultrasonic transducer. Two important parameters are the transducer center frequency, \( f_c \), and the transducers bandwidth (Shull and Tittmann, 2002, Krautkrämer, 1983). As mentioned above, the center frequency dictates the size of a flaw which can be detected. Center frequency also dictates the depth that an ultrasonic signal can penetrate since attenuation of the ultrasonic waves’ amplitude increases inversely with frequency.

Bandwidth describes the frequency response of a transducer. Narrowband transducers will respond efficiently only to a small range of frequencies; whereas broadband transducers will respond efficiently to a large range of frequencies. The as
Figure 1.10 Illustration of basic UNDE test set up (adapted from Shull and Tittmann, 2002).

Figure 1.11 Comparison of frequency spectrums of narrowband and broadband transducers.
The frequency response of a transducer is typically classified by the quality factor, $Q$ (Krautkrämer 1983). The 6 dB $Q$ of a transducer, or $Q_{6db}$, is quantitatively defined

$$Q_{6db} = \frac{f_c}{B}$$

1.21

Where $f_c$ is the transducer center frequency, and $B$ is the transducer bandwidth which is given as

$$B = f_a - f_b$$

1.22

Here, $f_a$ and $f_b$ represent the frequencies where the power distribution has fallen to 50% or, -6 dB, of its peak value in the frequency domain (Shull and Tittmann, 2002). There are several definitions for what percentage of the peak value the bandwidth should be measured at, but here the -6 dB down definition will be employed. Figure 1.11 shows a generic illustration comparing the frequency spectrum of broadband and narrowband transducers. Transducers are often made from fully dense ceramics or single crystals. Typically, these types of materials tend to have narrowband responses. Frequency response can be broadened, and this is typically achieved by adding a backing layer which will dampen the ringing that is associated with narrowband transducers. Backing layers are lossy materials, for instance an epoxy filled with tungsten spheres.

Another key parameter in transducer design is its acoustic impedance. The acoustic impedance of a transducer relative to the mechanical impedance of the specimen warranting investigation will dictate how efficiently elastic waves are transferred from the transducer to the specimen and vice versa. How well one material transmits an elastic wave into another material is described by the transmittance, $T$, and reflectance, $R$. These parameters are derived from the energy intensity of a wave and are given by (Shull & Tittmann, 2002)

$$T = \frac{4Z_1Z_2}{(Z_1 + Z_2)^2}$$

1.22

$$R = \left(\frac{Z_2 - Z_1}{Z_2 + Z_1}\right)^2$$

1.23
$Z_1$ is acoustic impedance of the material the acoustic wave is leaving and $Z_2$ is the acoustic impedances of the material that the wave is incident upon. For each material, $Z=\rho c$, where $\rho$ is the material density and $c$ is the wave velocity. Clearly, when the two bodies in contact are the same material, $T$ is one and $R$ is zero. From conservation of energy

$$R + T = 1$$

1.24

From this discussion it is clear that how well a transducer couples mechanical energy and how mechanical energy is delivered to a transducer depends on the relative acoustic impedances of the transducer and the material under investigation. If the transducer material is poorly matched acoustically to the specimen under investigation a quarter wave matching layer can be attached to the front end of the transducer to help couple mechanical energy (Krautkrämer 1983).

Similarly, the relative electrical impedances of the transducer and signal generator will govern how effectively electrical energy is transferred to and from a transducer. An analytical solution for the electrical impedance of a mounted piezoelectric transducer operating in thickness mode was derived by Lukacs, and is given by (Lukacs, 1999).

$$Z(\omega) = \frac{-id}{\omega \varepsilon_{33} A} + \frac{h_{33}}{\omega A} \left\{ G \sin \left( \frac{\omega d}{c} \right) - B \left[ \frac{G \rho \omega}{c} - h_{33} \right] \left[ \cos \left( \frac{\omega d}{c} \right) - 1 \right] \right\}$$

1.25

where $\omega$ is the angular frequency, $h_{33}$ is a piezoelectric coefficient similar to $d_{33}$, $A$ is the area of the transducer, and $d$ is the material thickness. The coefficients $G$ and $B$ are constants comprised of mechanical and electromechanical constants. The first term on the right is the effective capacitance of the piezoelectric, since

$$C_0 = \frac{\varepsilon A}{d}$$

1.26

The second term accounts for electromechanical effects, primarily stiffening of the material from the piezoelectric effect. From this one can conclude that for weakly
piezoelectric materials \((k_t \leq 0.15)\), the electrical impedance can be approximated as (see also, (Auld 1973))

\[
Z(\omega) = \frac{1}{i\omega C_o}
\]

Thus, for best electrical matching between a transducer and the driving unit the reactance must be tuned out. This can be achieved fairly easily by connecting an inductor in parallel with the transducer (O’Donnel et. al, 1981). The introduction of an inductor shunts the clamped capacitance, and produces a resonant frequency, \(f_t\) of

\[
f_t = \frac{1}{2\pi \sqrt{LC_o}}
\]

Introduction of an inductance does not always affect transducer performance. More precisely, electrical tuning benefits transducer signal strength when the mechanical branch of the transducer equivalent circuit is greater than that of the electrical branch. A rule of thumb for determining when electrical tuning is beneficial was given by Silk, and is (Silk, 1984),

\[
\frac{\pi(Z_B+Z_F)}{8k_t^2Z_c} > 1
\]

\(Z_c\) is the electrical impedance of the transducer at mechanical resonance, and \(Z_B\) and \(Z_F\) are the mechanical impedances of the front and back face of the transducer. For example, for the case of PZT, \(k_t^2 \approx 0.25\) and \(Z_c \approx 33 \text{ M\text{\ohm}}\), \(Z_f + Z_B > 2 \times 10^7\) and for quartz, \(Z_B + Z_f > 4 \times 10^5\) (Silk, 1984). Thus, the quartz transducer would benefit more from inductive tuning than say a lightly mechanically damped PZT sample. Of course, optimization of signal response via electrical tuning comes at the expense of decreasing the transducers bandwidth and this should be considered depending upon the application in question.
1.4.1 High Temperature UNDE

The most appealing advantage of UNDE is that it is one of the few techniques where in-situ evaluation is possible. This stems primarily from the fact that sensors to be used are small in size, low weight, and relatively inexpensive and the same can be said of the equipment necessary to drive them (such as a pulser-receiver). In-situ evaluation is ideal for harsh environments because system downtime for inspection of in-service parts is essentially eradicated. For instance, in order to use a dye penetrant technique on a turbine blade which operates at high temperatures would require the system to be shut down so the turbine blade can be removed in order to be inspected. Of course, there are several techniques for UNDE at elevated temperatures. These include electromagnetic acoustic transducers (EMATs) and magnetostrictive wire waveguide techniques, but this text will only deal with ultrasound generation/detection based on piezoelectric transducers (Hernandez-Valle & Dixon, 2010, Kropf & Tittmann, 2007). Conducting UNDE at high temperatures, however, is a non-trivial task.

1.4.2 Material Selection Considerations

The first major issue with piezoelectric based UNDE is the selection of the piezoelectric material. If the sample is ferroelectric, a material with a high enough \( T_c \) needs to be chosen. If the sample is a non-ferroelectric piezoelectric single crystal or oriented film piezoelectric, then a material must be selected where there is no phase transition where piezoelectricity is lost. For instance the \( \alpha-\beta \) phase transition in quartz is at 573 °C, but further complicating its use up to such a temperature is that above 350 °C twinning is prone to occur and thus destroy its piezoelectricity (Turner 1994). A few high temperature (for \( T > 500 °C \)) piezoelectric (non-ferroelectric) materials are aluminum
TABLE 1.1 T_c’s of several piezoelectric materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>T_c (°C)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi4Ti3O12</td>
<td>685</td>
<td>Cummins &amp; Cross, 1968</td>
</tr>
<tr>
<td>BiTi3NbO9</td>
<td>940</td>
<td>Subbarao, E.C., 1962</td>
</tr>
<tr>
<td>(1-x)BiScO3-xPbTiO3</td>
<td>~450</td>
<td>Eitel, 2001</td>
</tr>
<tr>
<td>LiNbO3</td>
<td>1200</td>
<td>Lynnworth, 1999 Baba, 2010</td>
</tr>
<tr>
<td>La2Ti2O7</td>
<td>1300</td>
<td>Nanamatsu, 1974</td>
</tr>
</tbody>
</table>

The choice of using polycrystalline ferroelectrics has the advantage that it is possible via composition modifications to control mechanisms that affect electromechanical behavior (Damjanovic 1998). Unfortunately, a typical trend in high temperature ferroelectrics is that the higher the transition temperature of the material, the lower the piezoelectric response (Shrout 2004). However, in that regard there are exciting new developments in tailoring materials existing near morphotropic phase boundaries, namely the (1-x)BiScO3-xPbTiO3 and Bi(Mg,Ti)O3-PbTiO3 families of materials, to have higher transition temperatures, (Eitel, 2001; Shrout, 2004). Since these materials exist near a morphotropic phase boundary they have exceptionally high piezoelectric strength ($d_{33} > 400$). Additionally, domain engineered ferroelectric single crystals of these materials are also being investigated (Shrout, 2004; Zhang, 2005). These materials have T_c’s generally around 450 °C.

Additionally, the working environment of the piezoelectric will also affect material, especially if long-term service is desired. For example, Baba and Lynnworth separately demonstrated that LiNbO3 can be used successfully as an ultrasonic transducer (at least for short term operation) at temperatures in excess of 1000 °C (Baba, 2010; Lynnworth, 1999). However, if a LiNbO3 transducer is operated in a reducing environment, it decomposes in the form of oxygen loss and the materials
piezoelectricity is lost (Seth and Schulze 1989). Oxygen loss in LiNbO$_3$ has been observed at temperatures as low as 300 °C (Hornsteiner, 1997). The pyroelectric effect may also pose a threat with regard to piezoelectric screening at high temperatures. In contrast to this, Shulman demonstrated that conductivity in bismuth titanate increased when annealed in O$_2$ atmospheres because of the reduced number of oxygen vacancies (H. T. Shulman 1996). Since the effect of atmosphere on conductivity is to a degree reversible, it could be posited that a bismuth titanate transducer could operate more efficiently in a reducing atmosphere as opposed to LiNbO$_3$ which would show a decline in efficiency.

Similar effects have been observed in AlN (Parks & Tittmann, 2011). Depending on the manufacturing process, various defects may be introduced during fabrication increasing the number of mobile charge carriers. This study compared several AlN single crystals fabricated using different methods and showed that defects assumed to be introduced during fabrication have a dramatic affect on transducer performance. A strong correlation between increasing dielectric loss and decreasing transducer efficiency as temperature increased was shown. The samples that showed increase in dielectric loss were assumed to have larger amounts of ionic defects in the material. The loss in transducer efficiency with temperature was attributed to the piezoelectric screening effect which is induced by the excess mobile charge carriers interfering with detection of piezoelectric induced charge (Zhang, 2008; McFee, 1966). In addition, piezoelectrically induced charge must be maintained long enough that it can be detected by the electrical circuit being used to detect it. This time is proportional to the sensors time constant, and a sensors minimum useful frequency is given by the lower limiting frequency, $f_{ll}$, and is expressed as (Turner, 1994; Shrout, 2002)

$$f_{ll} = \frac{1}{2\pi RC}$$

1.30

Below this frequency, charge will be reabsorbed into the lattice before being detected.
Another important aspect is that electromechanical properties are desired to be fairly constant across a broad temperature range. The same can be said as well for electrical properties, in particular dielectric loss as discussed above, but also mechanical properties such as $Q_m$ and attenuation. A materials microstructure will affect sensor properties, so microstructure evolution at elevated temperatures is another aspect which can be of concern in polycrystalline ceramics.

The literature available on high temperature piezoelectrics is fairly vast. The goal of this section is to simply address main issues of concern with material selection and therefore properties of specific materials will not be discussed further in detail with the exception of bismuth titanate which is the material of focus in this thesis. Interestingly, material properties of many materials are well characterized over large temperature ranges but the number of reports on their ability to function as ultrasonic transducers is much less. One of the goals of this work is to characterize the material properties of ferroelectric bismuth titanate films and to also characterize its performance as ultrasonic transducers at elevated temperatures.

1.4.3 Practical Considerations

Aside from choice of material to use as a transducer, there are many practical issues with high temperature UNDE that must be addressed. Operating at high temperatures poses several challenges and they will be discussed briefly here.

One of the first major obstacles to overcome is bonding of the transducer to a structure. In room temperature environments, transducers are traditionally coupled mechanically to a specimen with either a gel or glue. Clearly, at temperatures in excess of 200 °C such methods of mechanical coupling are unsatisfactory. There are several techniques which do exist, however. One method is to adhere the transducer to a surface using a high temperature adhesive, such as those supplied by Aremco, Inc.
These adhesives are satisfactory, but can be prone to flake off as they are ceramic based, especially if thermal expansion mismatch between sensor and structure is significant. The bond strength is also somewhat weak, so for sensors which to be adhered to rotating parts or systems which experience a significant amounts of vibration, these adhesives are not likely to be long term solutions. Another method is to place a soft metal foil between the transducer and the specimen. As temperature increases, the metal will further soften and coupling of ultrasonic metal to the structure is more efficient. For instance, aluminum foil is good for coupling ultrasound into structures in the 500 °C range. However, in order for this method to be most effective, a fairly substantial stress needs to be applied to the back of transducer element (for example by a spring or bolt) to ensure good contact. Since high temperature elements are ceramics cracking of the element from the pressure becomes an issue. Plus, as temperatures are increased, the mechanism forcing contact between the transducer and specimen could weaken or strengthen and therefore the potential of disbonding or cracking becomes larger. This method requires some careful additional design parameters.

Another method involves using glass solders (Mrasek 1996). When using glass solders, a material must be chosen that has comparable thermal expansion and softens at a reasonably low temperature. A few such materials are NaPoLi (composed of sodium oxide, phosphor oxide, and lithium oxide) and non-alkaline powdered glass solders known as LG-K1 and LG-K2. One drawback of this method is that at elevated temperatures the solders can become chemically reactive, resulting in damage to the sensor housing. Another method of bonding is brazing, however, the stresses induced on the transducer during brazing can be quite extreme and destruction of the transducer is a major issue.

Another practical issue is mismatch between the thermal expansion of coefficients between the transducer material and the structure under investigation.
Many structures requiring high temperature UNDE are metals, such as titanium alloy turbine blades or stainless steel pipes in nuclear reactors. Since high temperature piezoelectric transducers are ceramics thermal expansion mismatch between the piezoelectric and strucutre being investigated can result in cracking of the transducer element and/or disbonding of the sensor. The difficulties of thermal expansion mismatch becomes particularly troublesome when working with single crystals. Properties in single crystals can be extremely anisotropic when compared to polycrystalline ceramics. If a certain cut of a single crystal is used where thermal expansion coeffients in the plane of the crystal differ significantly, cracking of the crystal during heating is likely to happen. For instance, it s well know that 128-X cut lithium niobate is prone to shattering upon heating. However, some potential solutions to these problems do exist, such as a thermal expansion matching layer between the specimen and sensor.

Choice of electrode material must also be considered. First and foremost, the electrode material must have a melting temperature higher than the operating range. Second, the electrode must also be chemically stable at elevated temperatures to ensure that its conductivity does not decrease and nor does its mechanical strength. Another problem is that at elevated temperatures metallic ions of the electrode may migrate into the material and increase its conductivity. This is particularly prominent when silver is the material used as an electrode (Moulson and Herbert 1990). Although, materials such as platinum and Ag-Pd compounds are some known stable alternatives. Thin film deposited electrodes also exhibit some difficulties. For instance, it was shown by Bernhardt that Pt-Zr electrodes deposited onto langasite crystals experience dewetting at elevated temperatures (Bernhardt 2001). This challenge can be overcome by co-depositing alloys of metals in proper combinations that are stable at elevated temperatures. For example, it has been reported that a Pt-Rh alloy deposited onto a ZrO$_2$ layer on a langasite substrate can maintain stable surface acoustic wave operation at 800 °C for over 5 months--a truly impressive result (Pereira da Cunha 2008).
Cabling at high temperatures also needs consideration. For the frequencies often worked with in UNDE (<20 MHz), shielded coaxials are best for keeping signals low noise. There are some solutions, however; Omega® offers high temperature cables which are specified to operate at ~1200 °C which have been tested and successfully used on transducer to temperatures in excess of 1000 °C (Baba, 2010; Searfass, 2010).

1.5 Bismuth Titanate

Bismuth titanate (Bi₄Ti₃O₁₂) is a ferroelectric material and is a member of the family of bismuth layer structure ferroelectrics (BLSF) and was first discovered by Aurivilius in 1949 (Aurivillus 1949). The BLSF family of materials is composed of bismuth oxide layers, (Bi₂O₂)²⁺ interleaved in between layers of perovskite units which are infinite in two dimensions. Materials with an odd number of perovskite layers tend to have a single first order phase transition, whereas many with even number perovskite layers show two phase transitions with the high temperature transition considered to be the Curie point (Newnham 1971). Chemically, this family of materials can be represented by Bi₂Mₙ₋₁RₙO₃n+₃, where n =1, 2, 3, 4, 5, and n represents the number of perovskite groups separated by the bismuth oxide layer. Following the typical convention used to describe ABO₃ perovskites, the A site can accept Bi, Ba, Sr, K, Ca, Na, and Pb ions and the B site accepting T, Nb, Ta, Fe, W, Mo, Gr, and Cr ions. There exist over 70 compounds of these groups, 50 of which are known to be ferroelectric, and another 50 more may exist (Newnham, 1971; Subbarao, 1962). Recently, industrial interest in high temperature piezoelectrics has generated a renewed interest in members of the BLSF family since many of the bismuth based members of this group have high Curie points. Several materials are compared in Table 1.2. The high Curie temperatures and modest piezoelectricity make this family of materials appealing for


**TABLE 1.2** Comparison of some members of the bismuth layer Structure family.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c , (^\circ C)$</th>
<th>Resistivity ($\Omega \cdot m$)</th>
<th>$d_{33}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_4$Ti$<em>3$O$</em>{12}$</td>
<td>675</td>
<td>$10^3$</td>
<td>25</td>
<td>(Seth and Schulze 1989)</td>
</tr>
<tr>
<td>Na$<em>{0.5}$Bi$</em>{4.5}$Ti$<em>4$O$</em>{15}$</td>
<td>660</td>
<td>$10^{12}$</td>
<td>~17</td>
<td>(Takenaka 1984)</td>
</tr>
<tr>
<td>Bi$_3$TiNbO$_9$</td>
<td>~920</td>
<td>$10^{12}$</td>
<td>5</td>
<td>(Moure 2001)</td>
</tr>
<tr>
<td>CaBi$_4$Ti$<em>4$NbO$</em>{15}$</td>
<td>790</td>
<td>$10^{11}$</td>
<td>8</td>
<td>(H. Shulman 1997)</td>
</tr>
</tbody>
</table>

high temperature UNDE. However, their low resistivities, often combined with high coercive fields, coupled with large $T_c$’s, can make them difficult to pole.

Of the BLSF family, bismuth titanate is the most well researched material. Bismuth titanate has 3 perovskite units (A=Bi, B=Ti) between the bismuth oxide layers. Since there are an odd number of perovskite units, bismuth titanate has only one phase transition at its Curie point at 685 $^\circ$C. There have been some reports of dielectric anomalies in single crystal and ceramic samples at temperatures below the Curie point, and have been attributed to several mechanisms including a phase transition; however more recent research of the material seems to indicate that observed peaks are due to space charge or ion jump mechanisms and not a phase transition (Ehara, 1981; Ehara, 1986; Seth & Schulze, 1989; Shulman, 1997; Shulman, 1996). In grain oriented ceramics, $d_{33}$ values as high as 26 pC/N have been reported (with pulse poling) (Seth and Schulze 1989).

One of the primary issues with bismuth titanate is that it has a large coercive field (~100 kV/cm) combined with high conductivity (Cummins & Cross, 1968). Originally, there was a discrepancy in the electronic nature of bismuth titanate, but Shulman showed bismuth titanate is electronic p-type (Shulman, 1996). Through donor doping with Nb, it was demonstrated that the conductivity can be decreased by as much as 3 orders of magnitude. By decreasing the conductivity, larger field strengths could be used during poling and the value of $d_{33}$ was increased from 3.5 pC/N to 20 pC/N. There are a few bismuth titanate based piezoelectrics available commercially, such as Piezo
Technologies K-12 and K-15 products which are reported to have Tₜ’s of 820 °C and 600 °C, respectively (Custom Piezoelectrics 2010). It has also been shown that bismuth titanate is capable of operating as an ultrasonic transducer in pulse-echo mode up to 670 °C, at least for short time periods and has also been shown that it can be used as an ultrasonic drill at 500 °C (Searfass, 2010; Bao, 2010).

1.5.1 Fabrication of Transducers using a Sol Gel Spray-on Technique

Fabrication of bismuth titanate is well established in both bulk and thin film form. In mixed oxide methods a solid-state reaction between oxide powders occurs. This method is frequently used to make ceramics since it is cheap and reproducible. For bismuth titanate, mixed oxide precursors are Bi₂O₃ and TiO₂. Sol gel routes have also been formulated. A typical route for sol-gel processing involves dissolving bismuth nitrate pentahydrate (Bi(NO₃)₅·5H₂O) in acetic acid. Titanium isopropoxide is then added to the solution followed by addition of water (Fuierer 2002). Bismuth titanate has also been fabricated by various other techniques such as co-precipitation, molten salt synthesis, for bulk materials, there are also PVD and CVD techniques for thin film deposition. A good review of all these techniques has been presented by Lazarevic (Lazarević 2005).

A rather novel approach for developing high temperature ultrasonic transducers was developed by Kobayashi (Kobayashi 2000). In this approach, a sol gel based method is used to spray piezoelectric transducers, via an air gun, onto metallic substrates. This is particularly advantageous for high temperature UNDE since it can potentially eliminate the difficulties of finding a means of coupling and making contact with structures at elevated temperatures, as was mentioned in Section 1.4.3. The potential for in-field deposition may also be possible with this technique. This technique was adapted from the work of Barrow for making PZT 0-3 ceramic/ceramic composites (Barrow, 1996;
Barrow 1997). In this method, 0-3 composites are made by adding ceramic powders to sol gel solution and the films can be prepared via spin or spray coating, dipping, or screen printing. Sol gel films adhere well to oxide surfaces of the substrate as well as to those found on the crystallites dispersed in the solution, thus strong bonds form between sol gel, the powders and the substrate. A good analogy given is that “the sol gel makes up the mortar and the ceramic particles make up the bricks in a wall” (Barrow, 1996). This method has the advantages of sol gel fabrication such as cost effectiveness and ease of fabrication, but now thicker films can be achieved due to the addition of the ceramic powders. In many applications, such as wireless surface acoustic wave devices, the thickness of thin films is enough. However, for typical industrial (e.g. non-medical) UNDE where frequencies of 500 kHz-20 MHz are commonly desired, standard sol-gel deposition is not adequate as thick enough films are not easily achieved.

In the work by Barrow, films were made by spin coating. This technique was later adapted by the same group to spin coat several types of diphasic composite piezoelectrics. The first was a lithium niobate/lithium niobate composite were lithium niobate powders were dispersed into a lithium niobate sol gel solution which was spin coated onto stainless steel substrates. The objective here was being able to fabricate high temperature ultrasonic transducers (Zou 1997). These transducers’ thicknesses were 170 µm and had center frequencies around 10 MHz. Later, LiTaO₃-PZT composites were fabricated by dispersing LiTaO₃ powders into a PZT sol gel solution followed by spin coating onto stainless steel substrates. The objective of this work was once again to be able to obtain a high temperature ultrasonic transducer (Chen 1999). These films were 56 µm thick with center frequencies of 12 MHz. This transducer showed reasonable piezoelectric strength, with a $k_r$ that was determined to be 0.17. The parameters were determined by curve fitting the impedance spectrum using a method developed by Lukacs. Since these materials are on a substrate, the guidelines laid out by the IEEE standards for determining piezoelectric properties cannot be used due to the
mechanical boundary conditions imposed by the substrate (Lukacs, 1999). It was determined that the maximum operating temperature fabricated LiTaO$_3$-PZT composites was 368 °C. No X-ray diffraction patterns were reported, so the desired phases were assumed to have formed.

The first spray-on transducers fabricated were composed of LiTaO$_3$/PZT and PZT/Al$_2$O$_3$ composites (Kobayashi, 2000). These composites were fabricated with PZT and LiTaO$_3$ powders dispersed in Al$_2$O$_3$ and PZT sol gels, respectively, and were deposited onto stainless steel and aluminum substrates by using a spray gun similar to what one might find in arts and crafts store. Fabricated transducers had center frequencies between 4 and 15 MHz. Here, the high temperature LiTaO$_3$/PZT transducers were capable of operating to temperatures of 250 °C. It is difficult to tell the efficiency of these transducers since characterization of the piezoelectric properties was not performed and ultrasonic signal strengths were reported in arbitrary amplitudes. Again, no x-ray diffraction data was given so phase formation must have been assumed or not reported. It should also be noted that the composites are reported with a connectivity of (0-3), however, due to deposition process, the films are inherently quite porous. Thus, it is likely that the pores introduce a third inactive phase into the composite and, following the convention laid out by Newnham and Pilgrim, the connectivity of the material is likely to be more accurately classified with a connectivity of \{3(0-3)-0\} (Pilgrim 1987).

This spray-on technique was then utilized to deposit bismuth titanate/PZT composites and bismuth titanate/bismuth titanate composite transducers for high temperature applications (Kobayashi & Jen, 2004; Kobayashi, 2004). The bismuth titanate/PZT samples were fabricated by dispersing bismuth titanate powders into a PZT sol gel with a volume ratio of powder to solution being about 3:1. These transducers were deposited onto flat and curved stainless steel substrates and corona poling was used to pole the samples. X-ray diffraction was performed on the samples and only the
bismuth titanate phase was detected and the authors speculate as to whether the PZT was able to crystallize at the anneal temperature of 650 °C. For the samples deposited onto planar substrates, films were 200 µm thick with center frequencies of 4 MHz. These transducers were able to operate up to 440 °C with only a 2 dB loss in signal strength. In a later study it was shown that these transducers are not suitable for temperatures above 450 °C (Kobayashi, 2007). The bismuth titanate/bismuth titanate transducers were fabricated by dispersing bismuth titanate powders into a sol gel of bismuth titanate. The bismuth titanate slurry was then sprayed onto flat and curved steel substrates. Deposited films were 40 µm thick and had center frequencies of 10 MHz. The transducers ultrasonic wave velocity was determined to be 2.2 mm/µs. This is half the wave velocity of bulk bismuth titanate and this difference in wave velocities is attributed to the porosity in the films. The transducers were capable of operation to 200 °C. It was reported that the bismuth titanate/bismuth titanate composites were about 20 dB weaker than the bismuth titanate/PZT transducers. However, the substrates between the two papers through which the comparisons were claimed to have been made were of different thicknesses and the operating frequencies at which the transducers operated at were also different. This of course will skew the comparison between the two materials’ performance as ultrasonic transducers since the operating frequency and distance the ultrasonic signal traveled will greatly affect the detected signal amplitude (unless of course identical substrates and center frequencies are used, but this was not conveyed to be the case). Furthermore, for both the bismuth titanate/bismuth titanate and bismuth titanate/PZT transducers characterization of the piezoelectric properties was not performed (which is not a trivial procedure, especially for low k, highly damped materials as is discussed in Section 3.6). The ultrasonic signals were also reported with arbitrary units so no real conclusion can be made about the strength of the transducers nor can any real comparison be made between the two different materials. All that can be concluded is that the transducers are, to some degree, functional, given some unknown excitation source. Of course, one could argue
that a trained ultrasonic technician could guess at the signal amplitude by judging the number of backwalls seen in the reported wave trains; however this is by no means is a way to make a good quantitative comparison. Additionally, the fabrication process described is rather vague, in particular, the firing and annealing times and environments in which they are performed are not reported, although this is most likely for proprietary reasons. Nonetheless, transducers fabricated in this manner have been used successfully in industrial applications such as polymer injection molding (Kobayashi, 2006).

More piezoelectric composites were later reported using the same technique. These include manganese sodium doped bismuth titanate (NBT+Mn)/PZT and lithium niobate/PZT (Kobayashi, 2007). It was determined that NBT+Mn/PZT composites were not suitable for temperatures above 450 °C while the lithium niobate/PZT transducers showed good stability to 700 °C. Again, no X-ray diffraction studies were performed so the phases formed during fabrication are assumed as reported and all measured signals were provided in arbitrary units. Despite the arbitrary quantitative results, it seems that this method of fabricating ultrasonic transducers by mixing and matching multiple materials for specific applications is possible and is worthy of further investigation.

1.6 Microwave Sintering

For a dielectric with a capacitance, $C$, the current, $I$, passing through a capacitor for an applied voltage, $V$, is

$$ I = C \frac{dv}{dt} $$

For an ideal capacitor the electric charge will change instantaneously with any change in voltage and the current and voltage will be 90° out of phase with each other, according to Eqn. 1.30. In practice, this is not the case since the motion of charge has an
associated inertia. The result of this is that the current does not lead voltage by 90°, but rather it leads by some angle 90 - δ (Kinegry, Bowen and Uhlman 1960). Therefore, δ represents a polarization mechanisms’ inability to react with an applied field. For example, electronic polarization is the only process which is quick enough to follow applied fields into the visible range and this why a materials’ index of refraction is solely dependent upon this process. Figure 1.13 shows a generic plot of frequency dependence of various polarization mechanisms in dielectrics. If the permittivity of a material is defined as a complex quantity,

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$  \hspace{1cm} 1.32

Then the angle δ can be shown to be represented by the loss tangent, tanδ, as the ratio of energy dissipated per radian in the dielectric to the energy stored at peak polarization, or (Jonscher 1966)

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$  \hspace{1cm} 1.33

In fact, because of the Kramers-Kronig relations, it is impossible to have a loss free dielectric with a finite susceptibility and dispersion of the value of the dielectric constant is an essential trait of dielectrics (Jonscher 1966). The energy loss per unit volume in a dielectric can be expressed as (Newnham, 1991)

$$P = \omega (E_0^2 \varepsilon_0 \varepsilon'' + \mu_0 \mu'' H^2)$$  \hspace{1cm} 1.34

With $E_o$ being the internal electric field and $H_o$ being the magnetic field. The second term on the right is typically ignored with electroceramics as they tend to have low magnetic permeability. Energy losses in dielectrics are from three primary processes (several of these loss mechanisms are illustrated in Figure 1.12.) (Kinegry, Bowen and Uhlman 1960)

1. Ion migration losses
   a. DC conductivity losses
   b. Ion jump and dipole relaxation process
2. Ion vibration/deformation losses
3. Electron polarization losses

Maximum loss occurs when the period of a particular relaxation mechanism is the same of an applied field (see Figure 1.13).

Microwave processing of materials utilizes polarization and conduction losses to induce heating in materials. The microwave region of the electromagnetic spectrum corresponds to electromagnetic waves having frequencies between 0.3 and 300 GHz (1 m < λ < 1mm). Like lasers, microwaves can also be generated coherently (Clark 1991). Using microwaves for ceramic processing was known by the 1950’s and some investigation had been performed by a limited amount of reasearchers. In 1975, it was observed while trying to dry alumina castables that microwaves could also heat alumina to temperatures in excess of 1400 °C (Sutton 1993). Studies on microwave sintering of a wide range of materials have shown that not only can extreme heating rates be achieved, but that reaction kinetics can be expedited and may occur through different mechanisms. Many of these studies have also shown that material properties equal to or better than those conventionally sintered can be obtained. Sometimes this phenomenon is referred to as “the microwave effect”. Some materials in which these studies have been performed on include PZT, AlN, WC/Co composites, and bismuth titanate (Vaidhyanathan, 2001; Cheng, 2002; Breval, 2005; Kumar, 2003, Azurmendi, 2003; Searfass, 2009).

In conventional sintering, heating is performed by the transfer of energy. With microwave sintering, the sample is heated via energy conversion and thus can be much more rapid and heating rates greater than 400 °C/min have been achieved (Agrawal 1998). Since the sample is the heat source itself, an inverse temperature profile occurs,
FIGURE 1.12 Illustrations of (a) electronic, (b) atomic/ionic, (c) dipolar and (d) interfacial space charge polarization mechanisms in solids.
relative to conventional sintering (see Figure 1.14). In the case of reasonably sized samples, there is a volumetric heating of the sample. As discussed more generally above, the absorption of microwaves by metal oxide ceramics and their subsequent heating is attributed to several factors associated with absorption losses. In conductive processes, collisions from the motion of ionic and electronic charges generate heat within the material. With polarization processes heat is the by-product of the rotation of electric dipoles and short range charge displacement. Polarization losses are also generally attributed to effects associated to interfacial, ionic and electronic polarization. Similarly, as Newnham pointed out, for materials with spontaneous polarizations (piezoelectrics) millimeter size materials show resonances in the MHz range. Extrapolating this, piezoelectric materials with micron sized grains/domains will have resonances in the GHz range and electromechanical behavior will also contribute to losses in the microwave regime (Newnham, 1991). All these losses are generally summed up within the above effective relative dielectric loss, expressed as (Clark 1991)

\[ \varepsilon''_{\text{eff}} = \varepsilon''_c + \varepsilon''_s + \varepsilon''_d + \varepsilon''_i + \varepsilon''_e \]
The subscripts c, s, d, i, and e correspond to conductive, interfacial, dipolar, ionic, and electronic losses. Since $\tan\delta$ is a function of temperature and increases with temperature, as the dielectric heats, $\tan\delta$ will increase and thus the dielectric will heat more rapidly. This is the reason why such extreme heating rates are possible and can lead to thermal runaway within the sample if attention is not paid to the sample during the sintering process.

There are several theories as to why enhanced reaction kinetics are observed in some materials. One theory is a pondermotive force model investigated by Booske, Cooper, and Freeman (Booske 1997). This model attributes the enhanced reaction kinetics to microwaves serving as an additional mechanism for the driving force of ionic diffusion along the surface and grain boundaries. Experiments on crystals have had good agreement with this model. Another theory for porous materials was formulated by Willert-Porada (Willert-Porada 1997). This theory accounts for enhanced reaction kinetics due to micro-plasmas forming inside pores. These micro plasmas are thought to enhance surface diffusion or mass transport by evaporation. Another theory, set forth by Peelamedu, Roy and Agrawal, showed that anisothermal heating of a system is also
responsible for reaction kinetics not possible in conventional sintering (Peelamedu 2001). Experimentally it was shown that if a good absorber of microwave energy and a poor microwave absorber are mixed there is a unidirectional flux of the good absorber (high temperature) to the poor absorber (low temperature). Such a situation cannot be achieved using conventional techniques since the materials will be predominantly isothermal compared to multiphase materials heated in microwave fields. An example of this experiment is shown in Figure 1.15 in which bulk samples of Fe$_3$O$_4$, an excellent absorber of microwaves, and Y$_2$O$_3$, a poor microwave absorber, are placed on top of one another and exposed to microwave radiation. The experiment demonstrates how extreme thermal gradients are present in multiphase systems where one of the phases is a poor absorber and one phase is a good absorber. Other physical explanations for “microwave effects” may still remain elusive. However despite this, enough empirical results exist that it is indisputable that, at least in some materials, different reaction rates and routes occur during microwave processing. One of the titular examples of this is the complete decrystallization of titania without melting using microwave magnetic fields (Roy 2005).

Some dielectric materials absorb little microwave energy at room temperature so heating them with microwaves can be impractical. To overcome this, techniques known as hybrid heating have been developed to aid with microwave sintering. One method of hybrid heating involves either the heating of a material via conventional means, such as a furnace, to a temperature where the material has become lossy enough to absorb microwave energy. Another method is to add material into the sample that is a good absorber at lower temperatures. A third method is by using susceptors. Susceptors are materials, such as SiC or carbon, that absorb microwave energy well at low temperatures. The susceptors are placed in close proximity to the sample that is to be sintered. As the susceptors begin to heat the sample will be heated
by the energy radiated by the susceptors. This will heat the sample until it is lossy enough to be able to convert the microwave energy into heat.

Illustrations of a standard microwave heating system are shown in Figure 1.16. In Figure 1.16 (a) is the overall setup. A microwave generator generates the microwaves, typically with a magnetron. The waves are delivered to the chamber/cavity via waveguides. Reflected power is directed by a circulator to prevent too much power from being reflected back to the microwave source. In Figure 1.16(b) is a close up of the chamber itself. At the top of the chamber is a quartz window. Through this window one can use a pyromter or IR thermometer to make temperature measurements of the sample (using these methods only a measurement of the surface temperature is possible). The sample holder is placed at the proper position such that the sample will be in good position to absorb the incoming electromagnetic waves. The sample holder itself must be made of a microwave transparent material such that the microwaves will be not be attenuated before they reach the sample. One material commonly used is Fiberfrax® (aluino-silicate fibers). In Figure 1.16 (c) is a close up of the sample. Here the susceptors are shown, placed within close proximity of the sample such that it can be heated by the susceptors. The sample holder also serves as an insulator to help keep thermal equilibrium.
FIGURE 1.16 Illustrations of (a) entire microwave setup, (b) close up of the chamber and (c) close up of the sample holder.
FIGURE 1.17 Image of the microwave furnace used in this work.
2 FABRICATION PROCESS

This chapter outlines the procedure for fabricating bismuth titanate transducers via a spray-on technique in a similar manner that was presented originally by Kobayashi (Kobayashi, 2004). However, several steps within the process outlined by Kobayashi differ here in this work. In order to develop a process which gives the best ultrasonic transducer performance, several parameters of the fabrication process such as sintering time and sintering method, as well as solution-to-powder ratio, have been varied. Performance of the transducers fabricated under different conditions have been evaluated and compared to one another. A general outline of the fabrication procedure is first presented followed by more in-depth discussions of the individual steps.

2.1 OUTLINE OF FABRICATION PROCEDURE

The first step of the procedure is making a liquid solution of bismuth titanate metal oxide precursors. In this work bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O)) dissolved in glacial acetic acid mixed with titanium isopropoxide ((TiOC₃H₇)₄) are used to make the solution. For stability, water is added to the solution. Next, powders of bismuth titanate (325 mesh) are added to the liquid solution followed by mixing of the powder/liquid solution with a high intensity ultrasonic horn. Sonification with high intensity ultrasound serves to break up powder agglomerates and reduce particle size. Next, the solution/powder mixture is sprayed onto substrates using an air gun. Except when indicated otherwise, all substrates used in this work are 1 inch thick, 1 inch diameter stainless steel 316 cylinders. Spraying is followed by placing the sample on a hot plate at 400 °C for 10 minutes to pyrolyze any residual organics and water which are left over from the fabrication of the solution. Once the samples have cooled
they are sprayed again followed by heating on the hot plate. This is process is repeated until a desired thickness is achieved. During each spray, a layer of roughly 20 microns is deposited. Samples are then sintered, the conditions of which are discussed below in greater detail (technically speaking this part of the process is a combination of crystallization of the sol gel and sintering of the film but will simply be referred to as sintering throughout this text). Following sintering, a 150 nm layer of gold is deposited via sputtering. The sputtered gold layer is then coated with SPI high purity silver paint. After application of the silver paint, the samples are allowed to sit at room temperature followed by curing of the electrode by placing the sample on a hot plate at 400 °C for at least one hour. After the electrodes cure, samples are poled in an oil bath at 150 °C. All samples in this work were poled by breakdown. After poling, samples are placed on a hot plate again at 400 °C for an hour to burn out oil introduced into the sample during poling. A flow chart of the overall procedure is shown in Figure 2.2. Figure 2.3 shows an
image of a film deposited onto a stainless steel substrate ready for high temperature testing. X-ray diffraction analysis showed that films fabricated in this manner were phase pure Bi$_4$Ti$_3$O$_{12}$ (Figure 2.1).

2.1.1 Solution Preparation

Solutions were prepared following the same procedure outlined by Kobayashi and this method is similar to that reported by Fuierer (Kobayashi, 2004; Fuierer, 2002). First, bismuth nitrate pentahydrate (BNP) is dissolved with constant stirring at 80 °C in glacial acetic acid with the ratio 0.5 g BNP to 1 mL acetic acid and a clear solution is obtained. The solution is then allowed to cool to 30-33 °C. Then titanium isopropoxide (TiI) is added in a stoichiometric amount with constant stirring. Warm water (~30 ° C) is then added in a ratio of solution to water being 2:1 (volumetric ratio) to ensure solution stability. It has been found that if the temperature of water added is too low the solution destabilizes and large particulates can form in the solution. Solution destabilization with cold water is most likely due to the fact that titanium isopropoxides freezing temperature is ~ 17 °C. The clear solution is then allowed to sit for 45 minutes to an hour. Titanium isopropoxide used was ordered from Sigma Aldrich with an assay of 99.999% (Sigma Aldrich) and the bismuth nitrate pentahydrate, also from Sigma Aldrich, was reagent grade (≥ 98%). Solutions made following this procedure have low viscosities (water like viscosity) and are stable for about two weeks. After two weeks, the material starts to form a continuum and after roughly a month gelation is complete (when stored in typical ambient environments). Materials undergoing the transformation to gel start to develop a blue hue and when gelation is complete the gel is typically cloudy. No work has been done with the gelated solutions to date.
Dissolution of Bi(NO$_3$)$_3$·5H$_2$O in Acetic Acid

Addition of Ti(OC$_3$H$_7$)$_4$

Add water (solution to water 2:1 volumetric ratio)

Add Bi$_4$Ti$_3$O$_{12}$ powders to solution

Mixing with Ultrasound

Spray onto substrate

Heat on hot plate at 400°C for 10 minutes

Sinter

Poling/electroding of sample

**Figure 2.2** Flow chart for fabrication process of spray-on bismuth titanate spray-on transducers.
2.1.2 **Mixing of Powder and Solution**

Typically the properties of a bulk material and its sol gel equivalent are not the same. For example, it was shown with good agreement by Barrow that the dielectric constant of PZT powder- PZT sol gel 0-3 composite films can be modeled using the cube model originally put forward by Pauer (Barrow, 1996; Pauer, 1973). In this model, the dielectric constant is expressed as

\[
\varepsilon = \frac{\varepsilon_1 \varepsilon_2}{(\varepsilon_2 - \varepsilon_1)V_1^{-1/3} + \varepsilon_1 V_1^{2/3}} + \varepsilon_2 \left(1 - \frac{2}{V_1^{3/2}}\right)
\]

2.1

Where \( \varepsilon_1 \) and \( \varepsilon_2 \) are dielectric constants of the PZT powder and sol gel matrix, respectively, and \( V_1 \) is the volume fraction of the powder. With this model, the powder-sol gel is treated as a composite existing in both series and in parallel. This scenario is more likely than treating the system as either a purely parallel or series composite since in practice the powder does not have a truly zero connectivity. Thus, the cube model predicts values of the permittivity as an intermediate value between parallel and series model predictions which set the upper and lower bounds, respectively, for the materials.
permittivity. Figure 2.4 shows a comparison of these models using generic values for the permittivity. However, due to the presence of high porosity in spray deposited films the above equation would not be valid since the connectivity, assuming fully enclosed pores, is actually \(3(0-3)-0\), as is mentioned above.

Given this, it seemed likely that different ratios of sol gel and bulk powder would lead to differences in material properties. In this work two ratios of powder to sol gel were tested. These ratios were 3.2 g powder to every 1 mL of solution and 2 g powder to every 1.2 mL of solution. In order to be able to test these two cases and obtain a deposited layer of high quality two different types of air guns were necessary.

For the case of the 3.2 g of powder to 1 mL of solution a bottom feed air gun was used. For the 2 g powder to 1.2 mL of solution, a Kobalt gravity feed high velocity low pressure spray gun was used. In both cases, mixing was not performed until full gelation was achieved, unlike the work of Kobayashi where ball milling was performed until gelation occurred (Kobayashi, 2004). With the ratios reported above the powder-liquid is more like a inhomogenous solution. If ratios are used where the powder concentration is higher, a film with a sand-like texture is deposited and can be easily removed from the substrate. In contrast to this, if a ratio with the solution in higher concentration is used the sprayed solution has too low a viscosity and does not deposit evenly to the substrate.

In the previous works reported in this method, ball milling was the method of choice used to mix the sol gel and powders. In this work, this step was performed by using high intensity ultrasound. This would reduce any potential contamination from being introduced during ball milling and also reduced processing time. To perform this, an ultrasonic horn was built in-house. The horn consisted of 8 cylindrical PZT-5H elements stacked with alternating polarity. The elements were then screwed tightly into a titanium alloy horn tip. The operating frequency of the horn was 23.5 kHz.
2.2 SINTERING CONDITIONS AND METHODS

Initial attempts at sintering using conventional furnaces proved to be unsuccessful. A variety of sinter times, temperatures and environments (both reducing and oxygen environments) were attempted but the adhesion of films to substrates was almost always poor. Almost 90% of samples had some sort of serious delamination. As a result, different methods of sintering were pursued and are discussed below. It should be noted that it may be possible to achieve good adhesion if the substrate surface is treated such that a larger oxide layer forms. However, the methods discussed below were capable of sintering films with both good adhesion and performance and thus methods of surface treatments were not pursued.

2.2.1 MICROWAVE SINTERING

Samples fabricated with microwave sintering were sintered in a multimode microwave chamber with a Cober microwave source (6 kW maximum forward power). During microwave sintering, samples were placed in Fiberfrax holders. In order for the samples to heat from the microwave radiation susceptors had to be used. Both silicon
carbide and carbon powder were used with equal success. Samples were sintered at 850 °C with hold times of 10 minutes. Longer hold times were attempted but film delamination was prone to occur for hold times longer than 15 minutes. Several samples were also sintered by heating to 850 °C, holding for 10 minutes, letting the sample cool, and then reheating to 850 °C and holding again for 10 minutes. In these samples, delamination occurred in roughly 50% of the samples. Those which did survive the sintering process worked well as transducers but since adhesion was not always guaranteed further fabrication of samples with these conditions was abandoned. Unless specifically stated throughout the rest of this thesis all samples being considered that have been microwave sintered were processed at 850 °C with 10 minute hold times. Temperature measurements were made using an optical pyrometer.

Occasionally samples experienced thermal runaway. This is evident by a brilliant flash of white light. Runaway usually occurred if the forward power of the microwave was raised to quickly. Therefore runaway can be easily avoided if the forward power is raised slowly. A good recipe for the power ramp rate to avoid thermal runaway is as follows:

1.  Raise power to 1.2 kW. Wait 10 minutes
2.  Raise power 200 W. Wait 5 minutes.
3.  Repeat step 2 until desired temperature is achieved.

Usually a forward power of 1.8 kW is necessary to achieve a temperature of 850 °C and therefore the sintering procedure typically takes about 30 minutes (followed by an hour and a half of allowing the sample to cool). Thermal runaway is not detrimental to samples as long as the forward power is turned off quickly enough and the sintering process is resumed as per usual. However, for the sake of completeness no samples which experienced thermal runaway are discussed in this thesis. If the forward power is not turned off quickly enough melting of the films occur and they appear to have a glass-like appearance once they have cooled. Figure 2.5 shows SEM images of a region
of a sample which appeared to have melted as a result of thermal runaway. The microstructure which appears to form during melting is a very interesting one.

2.2.2 BLOW TORCH SINTERING

One of more appealing aspects of the spray on fabrication method is that on-site deposition of transducers may be possible, and as this work continued to evolve interest from industrial partners grew to investigate this. For instance, it may be possible to travel to a remote location of an oil pipe line and coat the pipe with a transducer such that it could be monitored non-destructively. Therefore, one of the goals of this work was to investigate the feasibility of this potential application. When considering in-field deposition, the immediate question of how sintering is performed comes to mind. A solution was proposed to simply use a blow torch. Indeed the method is crude, however, surprisingly it is capable of producing quality transducers. Scientifically, of course, this method is performed with less precision since obtaining accurate temperature measurements of the film surface is difficult.

Sintering films with the blow torch can be performed quickly and with relative ease, as long a few precautions are taken. The first precaution is to heat the substrate first before applying the flame directly to the film surface. If the flame is held directly over the film during the heating process the film will delaminate. This is likely from hydrocarbons introduced into the film from the burning of butane ruining the bond by reacting with the oxides responsible for the bond between the film and the substrate. Once the film is hot enough that the hydrocarbons do not remain within the film (i.e. when the film does not look charred after the flame is used directly on the sample surface) the blow torch should be used directly on the sample surface. Direct exposure to the flame for about 1 minute is sufficient time. Again, obtaining good temperature measurements of the film surface during blow torching is difficult, but thermocouple
FIGURE 2.5 (a) and (b) SEM images of a region of a sample which appeared to melt during thermal runaway.
measurements indicate the best temperature for the films surface to be somewhere in the range of 775 °C-825 °C. Samples sintered with the blow torch tend to have more of a brown color compared to those sintered in the microwave, which have more of an eggshell color. This is likely due to diffusion of oxygen out of the bismuth titanate because of the reducing environment created by the blow torch.
3 CHARACTERIZATION OF MATERIAL PROPERTIES AND QUANTIFICATION OF TRANSDUCER PERFORMANCE

3.1 THICKNESS AND DENSITY MEASUREMENTS

Thickness measurements were made on samples using an Olympus optical microscope. Quantifying a true thickness of the samples is difficult since film surface roughness is significant. The method which was established to measure film thickness is as follows and description of the procedure is supplemented by Figure 3.1. After the surface of the film has been leveled with respect to the lens, the top of the film is brought into focus on a region where the film has been removed to reveal the substrate surface. This is then set as the zero point for the film thickness measurement. Next, the microscope is then defocused to the very top surface of the film and the defocusing distance relative to the substrate surface is recorded ($t_1$ in the image). Next, the microscope is brought into focus on the bottom portion of the film surface and the defocusing distance relative to the substrate surface is recorded ($t_2$ in the image). An average of the numbers $t_1$ and $t_2$ is then taken and is used as the average film thickness. This process is then repeated several times until the average of all the averages converge (~5%). The z-stage for focusing has an accuracy of 0.5 µm. Surface roughness of the samples is somewhat extreme and $t_1$ and $t_2$ typically differ by about 30%.

Prior to spray coating substrates are carefully weighed using a Denver Instruments Company scale with 0.1 mg resolution. After spray coating the substrates and following sintering, samples are weighed. The difference in weight along with the thickness can then be used to calculate the samples density.

Typical thicknesses for samples fabricated with a solution to powder ratio of 3.2
FIGURE 3.1 Illustration of the procedure for obtaining film thickness.
g : 1 mL were around 300 µm but could be as large 400 µm. Samples made from this ratio were more dense; a typical density value being 4.2 g/cm$^3$. It should be noted however, densities of these samples could be quite erratic and values as high as 6 g/cm$^3$ were obtained. For samples made with ratios of powder to solution being 2 g : 1 mL, thicknesses were typically in the range of 80-120 µm. These samples were typically less dense with densities falling between the range of 2.6-3.2 g/cm$^3$.

3.2 MICROSTRUCTURE EVALUATION

Scanning electron microscope images were taken in order to discern the differences in microstructures for samples made under different process conditions. Samples which were microwave sintered tended to display a slightly finer and more uniform microstructure. Figure 3.2 shows images illustrating this for samples fabricated with a powder to solution ratio of 2 g : 1.2 mL (images taken with a Philips XL 30 Environmental Scanning Electron Microscope). Larger differences were observed between samples fabricated with powder to solution ratios of 3.2 g : 1 mL (Figure 3.3) and those with ratios of 2 g : 1.2 mL. The surfaces for samples fabricated with the larger solution to powder ratio are clearly much rougher. The samples with higher powder to solution ratios also appeared more dense in the sense that less amount of pores were visible. Figure 3.4 shows an image of a sample illustrating the large surface roughness as was discussed in the previous section.
FIGURE 3.2 Comparison of microstructure for samples made with powder to solution of 2 g : 1.2 mL. (a) and (b) are samples that were sintered with microwaves and (c) and (d) were blow torched.

FIGURE 3.3 SEM images of samples made a powder to solution ratio of 3.2 g : 1 mL.
3.3 **PERMITTIVITY MEASUREMENTS**

After waiting at least 24 hours after poling, the permittivity and $\tan\delta$ of samples were measured using a Stanford Research Systems SR715 LCR meter at frequencies between 0.1-10 kHz. At these frequencies, the measured permittivity would be closer to the free permittivity, $\varepsilon_{ji}^T$, of the material, however since the material is deposited onto a substrate this is not the true free permittivity (IEEE Standard on Piezoelectricity 1987). Since the materials are presumed to have low $k_r$ values and given Eqn. 1.16 it is safe assume that $\varepsilon^s$ and $\varepsilon^T$ do not vary from each other by a significant amount. Throughout this frequency range, changes in permittivity on all samples were typically less than a percent indicating a good electrode layer on the films.
3.4 Conductivity Measurements

It is well understood that in certain materials porosity can affect the conductivity of a material. A good example of this is Sb doped BaTiO$_3$ with 20% connected porosity which displays a large step in resistivity (Kuwabara 1981). In this case, the porosity is necessary such that oxygen can diffuse into the material in order to create insulating Schottky barriers between grains. Given the porous nature of films deposited using the spray-on technique it was hypothesized that these films may have a different conductivity than their bulk counterparts. Since low conductivity is desired in a material to be used as a high temperature ultrasonic transducer, and given that bismuth titanate is well known to have a high conductivity, characterizing the conductive nature of these films appeared essential since it has yet to be performed on bismuth titanate films deposited in this fashion.

The unit constructed to carry out these measurements consisted of a small box with walls made of ceramic tiles. The outside of the box was then wrapped in fiberglass insulation in order to ensure thermal equilibrium. In the top of the test holder were two holes; one for the electrical leads and one for a thermocouple. Samples would be placed into the holder and the thermocouple was placed on the sample surface as close as possible, but not touching, the electrode area of the film. An illustration is shown in Figure 3.5. This test bed was then placed on a hot plate such that the temperature could be raised and measurements taken. Current measurements were made using a National Instruments PXI 4071 7.5 Digit Flex digital multi meter (pA resolution) and a National Instruments PXI 5402 function generator was used to create DC voltages.

The method used to determine the conductivity was a charge-discharge method. When a DC voltage is applied to a dielectric, the initial current measured begins relatively high and then rapidly falls off and converges on a constant value. The value towards which the current converges upon is defined as the value used for
characterizing a dielectric resistivity. When working with ferroelectrics, one has to be wary that the polarization current which can form from the ferroelectric domains within the material does not affect the measured current. However, for field strengths $< 0.005 E_c$ this ferroelectric current is generally negligible (Bunget 1984). In the charge-discharge method, the discharge current which is produced upon removal of the applied field is subtracted from the charging current. It was found in this work that the discharge current was significantly smaller in magnitude than the charging current (by two orders of magnitude) and was neglected. It should also be noted that all measurements were made on unpoled samples.

At lower temperatures it was not possible to obtain good values of the conductivity. Large fluctuations in the current were always present due to electrical noise and potentially from small fluctuations in the applied voltage. Spontaneous jumps in current may also be from random electronic and ionic conduction from thermal fluctuations within the material. At $200 \, ^\circ C$, the material conductivity was sufficiently high that that these small fluctuations were negligible and a quality measurement could be made. Unfortunately, this was the temperature limit the apparatus could achieve; however, these measurements still provide useful information on the material. The
steady state leakage current was usually obtained after an hour. Figure 3.6 shows what a typical current measurement plot looks like. Both the charge and discharge currents are shown. It was found that samples displayed Ohmic behavior below 10 kV/m and matches measurements made by Shulman (Shulman, 1996). It was within this range measurements were made.

Interestingly, typical measured values of conductivity of the films prepared with solution to powder ratios 2 g : 1.2 mL did not differ much from measurements reported on bulk samples of bismuth titanate. Typical values for the conductivity at 200 °C were found to be in 1-3 x 10^{-7} (Ω·m)^{-1} range. For samples made from solutions with ratios of 3.2 g : 1 mL, the measured conductivity averaged within this range, but the variance from this average was much greater as conductivities were between the range of 10^{-6}-10^{-8} (Ω·m)^{-1}. However, as it is discussed later, transducers fabricated with the latter ratios were far more inferior as transducers so not much attention has been paid to this.

3.5 Calculation of the Elastic Modulus

It was found that the elastic modulus of poled films could be measured using their pulse echo response. With this method, transducers are operated in pulse echo
mode and the frequency domain of the first backwall echo is used to find the center frequency of the transducer. The center frequency of a loaded transducer, $f_c$, is given by (Berlincourt, 1964)

$$f_c \left( \frac{M_s}{M_t} + 1 \right) = f_t + f_s \left( \frac{M_s}{M_t} \right)$$  \hspace{1cm} (3.1)

Where $M_s$ and $M_t$ are the masses of the transducer and substrate, respectively, and $f_t$ and $f_s$ are the center frequencies of the substrate and the transducer if it were not loaded, respectively. Solving for $f_t$ and noting that the velocity, $v$, is given by

$$v = \lambda f = \sqrt{\frac{c}{\rho}}$$  \hspace{1cm} (3.2)

Then the elastic modulus of the film, $c$, can be solved for as,

$$c = 4\rho t^2 \left( f_c \frac{M_s}{M_t} + 1 \right) - f_s \frac{M_s}{M_t}$$  \hspace{1cm} (3.3)

Results are given in the following chapter.
3.6 Measuring Electromechanical Properties Films Supported By Substrates

As it was discussed in the introduction, one of the major problems with works concerning fabricating films using the spray-on technique is that there has been a lack of thorough characterization of material properties. Furthermore, reported performance of transducers has been, until this point, done so using waveforms which are reported with “arbitrary units.” Additional details regarding the experimental setup used in transducer excitation are typically also obscure. Thus, from the reports to date all that is really known is that the transducers fabricated are to some degree capable of generating ultrasound. Therefore, despite the fact that a variety of different materials have been successfully fabricated using the spray-on method, it is difficult to judge which materials operate the best. In light of this, one of the main focuses of this work was to characterize the properties of spray deposited thick films.

With thick and thin film materials, the typical resonance method outlined in the IEEE standards for free standing materials cannot be used due to the boundary conditions imposed on the film from the substrate (i.e. stress free mechanical boundary condition is non-existent) (IEEE Standard on Piezoelectricity 1987). However a few methods have been created to characterize films. One method is to determine the effective piezoelectric coefficients using laser interferometry (Trolier-McKinstry 2004). Relations exist relating the effective coefficients to the true coefficients. While an effective method, it cannot be employed to characterize films made with the spray-on method since the large surface roughness characteristic of spray deposited films makes obtaining interferometry measurements impossible.

Another common technique for obtaining material properties of supported films is curve fitting measured impedance data to equivalent circuits such as the Mason model or to closed form solutions obtained by solving the wave equation (Ritter, 2000;
FIGURE 3.8 Measured impedance spectrum of a bismuth titanate film. Lukacs, 1999). However, this method also cannot be employed, at least not for Bi$_4$Ti$_3$O$_{12}$ films. Due to the low coupling, as well as the damping induced on the transducer from the substrate, no resonance in the impedance spectrum is observed. Additionally, the porosity of the material will contribute to the mechanical dampening the film, further subduing the possibility of measuring a resonance. Figure 3.8 shows a measured impedance spectrum of a fabricated bismuth film. Again, no resonance is observed and therefore all that is really being measured are the electrical properties of the film.

To further explore the effect the substrate has on the impedance of the film a computer code of the Mason model was written in the Mathematica Software Package. The details of the model are in Appendix A. Figure 3.9 shows a comparison of the measured impedance spectrum of a bismuth titanate film and one modeled with the Mason model. The values used for permittivity and elastic modulus were determined as is outlined previously in this chapter, and an arbitrarily small value of $k_t$ was used ($<0.0001$). The model and measured values show very close agreement, thus validating the permittivity measurement. To illustrate how the substrate affects the impedance spectrum, models of samples with air backing and stainless steel substrates were compared and is shown in Figure 3.10 (value of $k_t=0.05$ was arbitrarily used). The results are what one would expect, that is, a decrease in the amplitude and resonance frequency due to loading from the substrate is clearly visible.
FIGURE 3.9 Comparison of measured impedance spectrum (blue dots) of a bismuth titanate film and the modeled spectrum (Red).

FIGURE 3.10 Comparison of transducer modeled with stainless steel substrate (red) and an air backed transducer (green).
Furthermore, the model can be used to demonstrate the effects that mechanical losses will have on the material. This can be done by setting the elastic modulus as a complex quantity with the imaginary portion representing the losses. The modulus is then defined as (Kwok 1997)

\[ c_{33}^{D^*} = c_{33}^{D} (1 + i \tan \delta_m) \]  

It has been shown mechanical losses in dense high frequency PZT transducers can be as high as almost 10 % (Ritter, 2000). Figure 3.11 compares modeled impedance spectrums of a transducer neglecting mechanical losses and one where a loss of 9% has been used \((k_t=0.05)\). The effect of mechanical losses on decreasing the magnitude of the resonance is clearly portrayed.

From this analysis it is clear that combination of the loading of the transducer as well as the porosity of the material are prohibiting measuring the electromechanical resonance in the impedance spectrum of the transducer. As a result, the common method of determining material parameters via curve fitting is not possible. If one assumes a mechanical loss of 9%, the Mason model predicts that a minimum value of \(k_t\) necessary to observe a resonance is about 0.025. However, if the frequency spectrum of the waveforms generated by fabricated transducers is analyzed, the half width Q values are typically around 1.7. This of course is a very broadband frequency spectrum for an unbacked piezoelectric transducer. Using the Q value measured from the pulse echo response and using it to estimate shows \(\tan \delta_m\) may be as high 0.8. However, this number is just an estimate since the broadband nature of the transducers can be a combination of the dielectric loss, mechanical loss and electromechanical losses. No treatment of the electromechanical losses will be given here since these numbers can be difficult to predict.
FIGURE 3.11 Comparison of a transducer impedance spectrum with (red) and without (green) mechanical losses accounted for.

Of course, a simple way to approximate the $d_{33}$ of a transducer is to use a commercial $d_{33}$ meter such as a Berlincourt $d_{33}$ meter. However, care must be taken, since even a small bend in the substrate from a uniaxially applied load can cause biaxial stress in the film which generates charge via the $d_{31}$ coefficient (Xu F. C.-M., 1999). The value of the measured $d_{33}$ (when measured via the direct piezoelectric effect) is related to the materials true $d_{33}$ by (Lefki 1994)

$$
\hat{d}_{33} = d_{33} \frac{2d_{31}(s_{11}^{E} + \nu)}{s_{11}^{E} + s_{12}^{E}}
$$

3.4

Where $s_{ij}^{E}$ are the elastic compliances of the piezoelectric film and $\nu$ and $C$ are Poisson’s ratio and the modulus of the substrate. Thus, as long as the $d_{31}$ of the material in question is low, measurement of the $d_{33}$ with a $d_{33}$ meter can be a reasonably good approximation and relative comparisons can be made between different transducers so long as the substrates are identical. As is discussed in further detail later, transducers fabricated under the conditions discovered to be optimal, typical values of the films’ $d_{33}$ made using a commercial $d_{33}$ meter are between 13-16 pC/N. Noting that the $d_{33}$ can be related to $k_t$ via the piezoelectric coefficient $e_{33}$ by (Berlincourt, 1971)
FIGURE 3.12 Modeled impedance response of a bismuth titanate transducer with a $k_t$ value of 0.09 and $\tan\delta_m$ of 0.8.

$$k_t = \frac{\epsilon_3}{\sqrt{\epsilon_3^S \epsilon_3^D}} = (1 - k_{33}^2)\frac{c_{33}^P}{\sqrt{\epsilon_3^D}}$$  \hspace{1cm} 3.5

Using the values measured for the permittivity and elastic modulus, and assuming a maximum value of 0.2 for $k_{33}^2$ gives a range between 0.07-0.09 for $k_t$. If the maximum value above for $k_t$, is used for modeling a transducer with the above estimated value for $\tan\delta_m$, a resonance still cannot be observed (Figure 3.12). Again, these numbers are only roughly approximate, however, this model demonstrates that it may be possible for films to have values of 0.07-0.09 for $k_t$ and still not observe a resonance. Despite the fact that the Mason model was unable to obtain the material properties some useful insight of the material behavior; namely, that the damping imposed by the substrate on the film and the inherent lossy mechanical behavior from the films porosity are prohibiting any measurement of a resonance thus restricting the ability to estimate material properties via curve fitting. It should also be noted that another method based on the works previously reported by Schmerr and Song was also attempted to try and back out material properties via curve fitting (Schmerr 2007). However, results which could be trusted could not be obtained due the complex nature of the model.
compounded with the lack of a continuum in the films. Although, this model was successfully applied to single crystals. This work is demonstrated in Appendix B.

3.7 Establishing A Figure of Merit For Transducers Supported By A Substrate

Despite the work of the previous section, the issue still remains that the performance of transducers still has yet to be quantified in a precise manner. The goal of this section is to establish a parameter which is capable of doing so. The method described herein is rather simple and is similar to work done in the 60's and 70's on reciprocity parameters (Bobber, 1965; Tittmann, 1976; Lakin, 1976). The formulation has been kept rather simple purposefully in the hopes that this method of characterizing transducers may take hold within the scientific community such that accurate comparisons between various materials loaded by substrates with low coupling can be made. If the technique were to become too complicated, the chances of other researchers to use it may decrease, especially if sophisticated instruments are required to make the measurements necessary for quantification. What is attempted here is the elimination of any substrate effects on the signal by factoring out acoustic impedance mismatches, attenuation, and scattering due to the backwall. For characterization it is suggested that the peak to peak voltage of the first backwall be measured and used to calculate the figure of merit (this will eliminate any effects of a DC bias may have on the signal). The figure of merit which is developed below is determined in terms of pressure. What this means is that all parameters introduced to the formulation such as reflection coefficients and scattering coefficients are defined in terms of their pressure formulations (as opposed to their formulations in terms of intensity).
FIGURE 3.13 Illustration demonstrating interpretation of notation.

To begin, consider a transducer being exciting in thickness mode which is mounted on a substrate. The ratio of the transmitted pressure \( P_{St} \) to the incident pressure \( P_{Si} \), is given by \( T \), and is expressed as (Shull & Tittmann, 1991)

\[
T_1 = \frac{P_{St}}{P_{Ti}} = \frac{2Z_s}{Z_t+Z_s} \tag{3.6}
\]

Where \( Z_s \) is the acoustic impedance of the substrate and \( Z_t \) is the acoustic impedance of the transducer. Here, capital letters indicate the material and lower case letters indicate direction of wave propagation, where \( S \) and \( T \) stand for substrate and transducer, respectively, and \( t \) and \( i \) represent transmitted and incident (see Figure 3.13). Therefore \( P_{St} \) means the pressure of the wave transmitted into the substrate. Strictly speaking this equation is valid only for plane wave behavior, however, these principles are successfully used for quarter wave matching layers and therefore should be adequate here (O’Donnell 1981).

If the reflected wave is out of the near field, then the pressure reflected back upon the transducer at the transducer-substrate interface from a reflector much larger than the transducer, \( P_r \), is given as (Krautkrämer 1983)
\[ P_r = P_o \frac{S}{2D\lambda} \]  \hfill (3.7)

Where \( P_o \) is the initial sound pressure, \( S \) is the area of the transducer, \( D \) is the distance traveled, and \( \lambda \) the wavelength. The initial pressure, \( P_o \), is the pressure that is transmitted into the substrate, \( P_{St} \). If attenuation is accounted for, then the pressure incident upon the transducer after a round trip through the substrate is

\[ P_{Si} = P_{St} \frac{S}{2D\lambda} e^{-\alpha D} \]  \hfill (3.8)

The transmission coefficient, \( T_2 \), for a wave leaving the substrate and incident upon the transducer is given as,

\[ T_2 = \frac{P_{Tt}}{P_{Si}} = \frac{2Z_t}{Z_t + Z_s} \]  \hfill (3.9)

Substituting into Eqn (3.4) from Eqn (3.3) for \( P_{Si} \) gives

\[ T_2 = \frac{P_{Tt}}{P_{St}} \frac{2D\lambda}{Se^{-\alpha D}} \]  \hfill (3.10)

Now if the assumption is made that the generated pressure wave is linearly proportional to the input voltage by some factor, \( m \), then,

\[ P_{Ti} = mV_{in} \]  \hfill (3.11)

And if it is assumed that the voltage generated upon reception of the echo on the on is also linear by some factor \( g \), then this can be described as,

\[ V_{out} = gP_{Tt} \]  \hfill (3.12)

Then \( V_{out}/V_{in} \) is

\[ \frac{V_{out}}{V_{in}} = \frac{mgP_{Tt}}{P_{Ti}} \]  \hfill (3.13)

Or,

\[ mg = \frac{V_{out}P_{Ti}}{V_{in}P_{Tt}} \]  \hfill (3.14)
With these definitions, $m$ can be thought of as the constant relating to transducer actuation and $g$ is the constant representing the transducers strength in sensing a signal. This is analogous to the piezoelectric voltage constant, $g_{33}$ (used to describe a piezoelectric materials strength as a receiver), and the piezoelectric strain constant $d_{33}$. A typical figure of merit for transducers is the hydrostatic figure of merit (HFOM) which is the product of $g$ and $d$. So, in a fashion analogous to the HFOM, $mg$ is then chosen as the figure of merit here.

$P_{T1}$ and $P_{T2}$ can be solved from the equations above as,

$$\frac{P_{T1}}{P_{T2}} = \frac{2D\lambda}{T_1T_2Se^{-aD}} \quad 3.15$$

Thus the figure of merit, $mg$, becomes,

$$mg = \frac{V_{out}2D\lambda}{V_{in}T_1T_2Se^{-aD}} \quad 3.16$$

If the assumption of reciprocity is made then $m=g$ and the figure of merit becomes $m^2$. A figure of merit with parameters that are familiar to most in the field and can be calculated or measured with ease has now been established. It should be noted that although $\alpha$ is frequency dependent it can easily be measured if at least two round trip echoes are detected on a case by case basis. Since this figure of merit will most likely be primarily used for materials with lower piezoelectric strength, it can be assumed that a gain of a value $x$ will be used to increase the signal, this is given as

$$x = 20\log \frac{V_{out}}{V_o} \quad 3.17$$

Then,

$$V_o = \frac{V_{out}}{10^{x/20}} \quad 3.18$$

Thus, $mg$ now becomes

$$mg = \frac{V_{out}2D\lambda}{V_{in}T_1T_2Se^{-aD}10^{x/20}} \quad 3.19$$
With $x$ being the gain (in dB) used during the measurement.

Some care should be taken in order to obtain a proper measurement of $V_{out}$. One will need to adjust the gain/attenuation of the signal to ensure that saturation of the signal from an excessive gain is occurring in order to ensure a proper measurement is taken. This should be done such that the exponential decrease in the amplitudes of subsequent backwalls are observed.

Another item of importance is that measuring the excitation voltage, $V_{in}$, must be performed accurately. If the impedance of the pulser, $R_o$, during excitation is known, then the voltage across the piezoelectric (so long as it has a relatively weak coupling coefficient) can be calculated from (Auld 1973) (see Figure 3.14)

$$V_{in} = V_o \frac{1}{\frac{1}{R_o} + \frac{1}{i\omega C_o}}$$  \hspace{1cm} 3.20

where $\omega$ is the angular frequency and $C_o$ is the effective capacitance, which is given by

$$C_o = \frac{\varepsilon S}{t}$$  \hspace{1cm} 3.21

$S$ is once again the transducer area, $t$ is the transducer thickness, and $\varepsilon$ is the material permittivity. $R_o$ can be calculated by measuring the voltage, $V_L$, across a known load, $R_L$ (50 $\Omega$), and by measuring the opening the open circuit voltage, $V_o$, and utilizing the following relation (Schmerr 2007) (see Figure 3.15)

$$R_o = R_L \left(\frac{V_o}{V_L} - 1\right)$$  \hspace{1cm} 3.22

Measurement for $R_o$ has been performed on a Panametrics 5052 PR pulser-receiver and the results are shown in Figure 3.16. The numbers seem reasonable. Thus for a transducer operating with a frequency of say 6 MHz a value for $R_o$ of about 200 $\Omega$ would be used to calculate the voltage across the transducer.
FIGURE 3.14 Model of ultrasonic excitation system. $V_m$ is the voltage delivered to the piezoelectric. 

FIGURE 3.15 Setup for measuring pulser impedance, $R_o$. 

FIGURE 3.16 Measurement of $R_o$ for a Panametrics 5052 PR pulser-receiver.
Of course, there are some fall backs for this figure merit. The first is that the impedance of the transducer can be matched to the pulser/receiver and thus change the signal output strength as well as the bandwidth. There is no real “correct” way to determine what the impedance should be set to, since increase in signal strength usually means sacrificing the bandwidth. Accordingly, what setting to use will have to be left up to those reporting their measurements. However this brings up another important point, and that is if this figure of merit is to be used to quantify a transducers’ signal strength, the bandwidth (\(Q_{6dB}\)) must also be presented alongside it in order to fully characterize the transducer. Since the figure of merit is dependent upon pulser impedance and any electrical matching impedances used, this suggests that this figure of merit could be used to compare transducer performance for various pulser-receivers as well as with any electrical matching circuits developed to enhance transducer performance.

This technique has been applied to compare FOM’s of a commercial transducer and a spray-on bismuth titanate film. The results are shown in Table 3.1. For the commercial transducer, values of PZT-5H were used. The results correspond well with intuition (numbers reported here are \(x10^{-3}\)) . The commercial transducer showed a FOM of 62 while the bismuth titanate film had one of 4.6. These numbers make sense since PZT has a piezoelectric strength an order of magnitude higher than what is predicted of the bismuth titanate films. These results would appear to validate the use of the FOM derived herein.

<table>
<thead>
<tr>
<th>Transducer</th>
<th>Figure of Merit (x10^{-3})</th>
<th>Q_{6dB}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>62</td>
<td>3.8</td>
</tr>
<tr>
<td>Bi_{4}Ti_{3}O_{12} Film</td>
<td>4.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>
4 OPTIMIZED FABRICATION PROCESS AND TRANSDUCER PERFORMANCE

4.1 OPTIMIZED FABRICATION PROCESS AND FILM PROPERTIES AND LONGITUDINAL TRANSUDER RESPONSE

In this section transducer performance at room temperature is discussed. All films were deposited on 1 inch thick, 1 inch diameter stainless steel 316 substrates with 10 mm diameter electrode area. As per Section 2.1.2, two ratios of powder to solution were tested and these were 2 g: 1.2 mL and 3.2 g : 1 mL. Two different conditions of microwave sintering produced functional transducers. One was at 850 °C for 10 minutes. The second was 1. heating to 850 °C for 10 minutes, 2. Allowing transducers to cool to room temperature, 3. Followed by reheating to 850 °C again and holding for 10 minutes. Blow torch treatments were also performed and are considered here (Section 2.2.2). Treatment of films using conventional furnaces could not reliably produce well adhered films and was subsequently abandoned and this processing condition is not considered here.

Films fabricated using a solution to powder ratio of 2 g : 1 mL quickly proved to be far superior than those with ratios of 3.2 g: 1 mL. Films fabricated with the latter ratio always had figures of merit low by an order of magnitude or more. Additionally, films fabricated with larger powder to solution ratio also showed erratic properties. Film thicknesses exhibited larger variations and other measured properties, such as conductivity and density, were also quite erratic. Adhesion of films with the higher powder to solution ratio was also typically much poorer. While they often survived the sintering process, delamination from routine handling would often occur. This is attributed to inhomogeneous microstructure within the material between deposited layers. Poling field strengths that could be achieved with these films were also lower.
Table 4.1 shows a comparison measured density, conductivity, relative permittivity, $d_{33}$ measured approximately with a $d_{33}$ meter, elastic modulus and poling field strength for samples processed under different parameters. Table 4.2 shows comparisons of transducers fabricated with different processing conditions and their measured Figures of Merit. Again, as per Section 3.6, the measurements made with the $d_{33}$ meter are only approximate. However, the poling field strengths seem to indicate that these numbers could be somewhat accurate. Typically, maximum poling field strengths for bulk bismuth titanate do not exceed 20 kV/cm which give rise to values of $d_{33}$ not exceeding 3.5 pC/N. Given that in the lower powder to solution ratios a range of 50-70 kV/cm was achieved with measured values of $d_{33}$ being in the range of 12-16 pC/N. Thus, with samples poled with field strengths 3.5 times greater than 20 kV/cm, one would expect a value for $d_{33}$ also 3.5 times greater. This corresponds to a $d_{33}$ of about 13, which is in the range of what is measured. Although there is no way to prove with any certainty, it seems that these high values (respectively for bismuth titanate) of $d_{33}$ are possibly being achieved.

The question which immediately arises then is why are these films capable of withstanding higher field strengths? In fact, due to the high porosity of these films one would be inclined to hypothesize a priori that field strength would be lower. It has been

<table>
<thead>
<tr>
<th>Powder to Solution Ratio</th>
<th>Sintering Condition</th>
<th>$\rho$ (kg/cm$^3$)</th>
<th>$\varepsilon$</th>
<th>$d_{33}^*$</th>
<th>$\sigma$ at 200 °C (10$^{-7}$/Ω·m)</th>
<th>$c$ (GPa)</th>
<th>Thickness (µm)</th>
<th>$E_c$ at 150 °C (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 g : 1.2 mL</td>
<td>MW: 850 C, 10 minutes</td>
<td>2.6-3.2</td>
<td>90-95</td>
<td>12-16</td>
<td>1-4</td>
<td>9-20</td>
<td>80-140</td>
<td>50-70</td>
</tr>
<tr>
<td>2 g : 1.2 mL</td>
<td>Blow Torch (~800 °C)</td>
<td>2.6-3.2</td>
<td>40-60</td>
<td>12-16</td>
<td>2-6</td>
<td>4-10</td>
<td>80-140</td>
<td>60-70</td>
</tr>
<tr>
<td>3.2 g : 1 mL</td>
<td>MW: 850 C, 10 minutes</td>
<td>4</td>
<td>30-45</td>
<td>2-7</td>
<td>Erratic (0.1-100)</td>
<td>10-20</td>
<td>300-400</td>
<td>20-40</td>
</tr>
</tbody>
</table>
**TABLE 4.2** Comparison of transducers fabricated with different processing conditions.

<table>
<thead>
<tr>
<th>Solution to powder ratio</th>
<th>Sintering Condition</th>
<th>Figure of Merit (10^3)</th>
<th>$Q_{4dB}$</th>
<th>$\varepsilon$</th>
<th>$E_c$ at 150 °C (kV/cm)</th>
<th>$\rho$ (kg/cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 g : 1.2 mL</td>
<td>MW, 10 min at 850 C</td>
<td>4.6</td>
<td>1.7</td>
<td>90-95</td>
<td>50-70</td>
<td>2.6-3.2</td>
</tr>
<tr>
<td>2 g : 1.2 mL</td>
<td>Blow Torch</td>
<td>3</td>
<td>1.4</td>
<td>40-60</td>
<td>60-70</td>
<td>2.6-3.2</td>
</tr>
<tr>
<td>3.2 g : 1 mL</td>
<td>MW, 10 min at 850 C</td>
<td>&gt;0.1</td>
<td>2.8</td>
<td>30-45</td>
<td>20-40</td>
<td>4</td>
</tr>
</tbody>
</table>

well documented that bismuth titanate fabricated through standard solid state reaction techniques that plate like grains will form, and for higher temperatures and extended hold times, these grains will grow anisotropically--preferentially in the $ab$ plane (Jardiel 2008). This becomes a problem because although the spontaneous polarization of bismuth titanate is strongest in this direction, its conductivity is also highest in this direction, making poling difficult due to breakdown. A way to overcome these problems is to employ alternative fabrication processes such as synthesis via citrate or coprecipitation methods (Dhage, 2004; Villegas, 1996). As was reported by Dhage, this method can be used to produce nanocrystalline ferroelectric bismuth titanate and effectively eliminate formation of platelets (Dhage 2004). In the work reported by Dhage, field strengths as high as 40 kV/cm were reported. Given this information and the fact the microstructures of the spray on films also do not exhibit plate like morphology one would potentially conclude this is the reason higher fields can be applied to the films. However, the measured conductivities of the films are equivalent to textured bismuth titanate ceramics. The fact that the conductivities are on the same order of magnitude implies that the microstructure is not the reason for these field strengths.

However, a potential explanation for the obtainable field strengths can be discovered if one considers what form of breakdown may be occurring. As was mentioned in Section 1.3.1 there are several types of breakdown mechanisms, including
thermal breakdown. With thermal breakdown it has been documented that the breakdown strength varies inversely with decreasing thickness, \( t \); with the variation being proportional to the range of \( t^{-1/3} - t^{-1/2} \) (Hench & West, 1990; Smith, 1997; Lanagan, 2012). The explanation behind an increase in breakdown strength as sample thickness decreases is due to the fact that the localized heating responsible for thermal breakdown can be eliminated since thinner samples are kept in thermal equilibrium with greater ease—in essence it’s a matter of more rapid heat dissipation. An exact equation for the breakdown strength as a function of temperature is given by (Smith, 1997)

\[
E_c' = \left( \frac{3\alpha c_v R_o \Delta \theta}{t} \right)^{1/3}
\]

Where \( \alpha \) is the voltage ramp rate, \( c_v \) is the material heat capacity, \( R_o \) is the resistivity, \( t \) is sample thickness, and the product \( \Delta \theta \Delta \) are terms derived from the temperature dependence of the material resistivity. Assuming the numerator on the right side of this equation is constant for bulk and thin film bismuth titanate, the product of \( E_c t^{1/3} \) can be used to verify this trend. Using data from Shulman (\( E_c=20 \) kV/cm, \( t=0.8\)mm) one obtains a value for \( E_c t^{1/3} \) of 8.61 kV/cm\(^{2/3} \). Using values from films made with a powder ratio of 2 g : 1 mL, one obtains an approximate range of values between 6.4-7.8 kV/cm\(^{2/3} \). These values are of fairly good agreement, considering that \( c_v \) may differ between the bulk material and films due to the porosity (one would assume a lower value as is observed here). Supporting this notion is that samples made with the higher powder to solution ratio were typically thicker and could withstand field strengths as large as those films fabricated from a lower solution to powder ratio. Accordingly, their approximate \( d_{33} \) values were lower. However, it should be noted that about 15% of samples fabricated with the high powder to solution ratio could withstand larger field strengths and thus have higher \( d_{33} \) values. For instance, in a typical batch of 10 samples, 2 would outright breakdown, 2 would be able to withstand similar field strengths, while the rest would fall somewhere in the middle. This suggests that perhaps another mechanism may be
involved; however the erratic electrical properties, as well as mechanical properties, suggest that a large amount of inhomogeneity present in samples thus making it more difficult to draw a solid conclusion about their behavior.

Another interesting result was discovered for samples made with ratios of powder to solution ratio of 2 g : 1.2 mL. Samples sintered using microwave heating typically had a higher permittivity, whereas those samples which were blow torched typically had smaller permittivities. The lower permittivity of the blow torched samples may be a result of the oxygen diffusing out of the samples due to the reducing environment created by the blow torch. Similar results were obtained for thin films annealed in air and in $O_2$ environments (Simoes 2007). Additionally, blow torched samples typically had lower elastic modulii, indicating that the reducing environment may be softening the material. Furthermore, blow torched samples had equal approximate $d_{33}$ values, yet, as is discussed below, typically had lower figures of merit. This can be attributed to the differences in permittivity. Since the samples with higher permittivity had larger figures of merit this would indicate that the impedances are matched better to the pulser-receiver.

Figure 4.1 shows a typical waveform and the associated frequency spectrum of the first backwall for a transducer microwave sintered at 850 $^\circ$C for 10 minutes with a powder to solution ratio of 2g : 1.2 mL. The excitation source was a Panametrics 5052 PR pulser-receiver. The excitation pulse was set on energy level 1 (open circuit voltage of approximately 200 V). The gain was 28 dB and damping set to 4. Figure 4.2 shows waveforms and the associated frequency spectrum for a sample fabricated with blow torching and powder to solution ratio of 2 g : 1.2 mL. The excitation was the same with the exception that a gain of 40 dB was used. Figure 4.3 shows a comparison of the first backwall for a transducer microwave sintered and one which was blow torched with figures of merit of 0.002 and 0.004, respectively, under the same gain conditions (28 dB,
FIGURE 4.1 (a) Entire wave train, (b) close up for first backwall, and (c) frequency spectrum of first backwall of the pulse eco response for a transducer fabricated with microwave sintering with a powder to solution ratio of 2 g : 1.2 mL.
FIGURE 4.2 (a) Entire wave train, (b) close up first back wall, and (c) frequency response of first backwall for the pulse echo response of a transducer via blow torch sintering with a powder to solution ratio of 2 g : 1.2 mL.
energy setting 1). This figure serves to illustrate amplitudes received for different figures of merit.

In summary, the best powder to solution ratio has been determined to be 2 g : 1.2 mL. The sintering conditions which reliably produced films with good adhesion and good transducer signal strength are either microwave sintering at 850 °C or via blow torch using the method described in Section 2.2.2.

4.2 High Temperature Performance Of Longitudinal Transducers

To test the short term operating temperature range of spray-deposited bismuth titanate films, transducers were exposed to elevated temperatures until they were no longer functional while operating in pulse-echo mode. Electrical connections were made to the transducer using a high temperature coaxial cable purchased from Omega®. Nickel mesh was adhered to the transducer electrode using silver paint and the positive lead of the coaxial was wound through the mesh. Figure 2.3 shows an image of sample ready for high temperature testing. Samples were heated at a rate of 1 °C/min and
measurements were made every 25 °C. A Panametrics 5052 PR was used as the pulser receiver.

Figure 4.4 (a) shows a typical plot of measured peak to peak voltages of the first backwall measured up to 675 °C. To better illustrate the relative strength of the signals, the measured signals have been normalized to the value of the peak to peak voltage measured at room temperature. Figure 4.4 (b) shows a 3D plot of the first backwall measured as a function of temperature to illustrate changes in the waveform as temperature is increased. All samples tested were capable of operation to 675 °C. As Figure 4.5 (a) illustrates, at 650 °C samples were capable of generating signals of equivalent strength relative to the room temperature performance. In fact, in the temperature range between 200-500 °C signals are typically stronger than waveforms measured below 200 °C. This increase in signal strength is likely from better electrical matching between the pulser-receiver as the films’ permittivity increases as the material approaches the ferroelectric to paraelectric phase transitions. Above 650 °C, depoling of the sample begins to occur and signal strength rapidly deteriorates as temperature increases.

Figure 4.5 (a)-(c) show plots pertaining to the frequency characteristics of the transducer throughout the temperature range. Generally, as Figure 4.5 (a) shows, the $Q_{6dB}$ of the transducer do not tend to vary too much below 575 °C. Above this temperature the $Q_{6dB}$ typically increases. However, as, is shown in Figure 4.5 (b), the center frequency can vary somewhat substantially. Strictly speaking in terms of mechanics, through a temperature range where no phase changes are occurring one would expect the center frequency of a body to go down as thermal expansion occurs and as the modulus decrease. Here this is not the case, however, due to the nature of the coupled field interactions (see Eqn. 1.24). The permittivity, modulus, and thermal expansion of the material are all competing parameters dictating the frequency behavior. Similarly, changes in the impedance of the cabling will have effects on the
center frequency. However, if a very precise center frequency is desired in a transducer, a variable tuning circuit could simply be employed to adjust center frequency.

**FIGURE 4.4** (a) Peak to peak voltages of first backwall echo normalized to room temperature signal measured between 25-685 °C and (b) plot of measured waveforms as function of temperature.
FIGURE 4.5 (a) Measured $Q_{6db}$ and (b) center frequency as a function of frequency. (c) shows plots of the transducer frequency spectrum at a few selected temperatures.
5 APPLICATIONS OF THICK FILM SPRAY-DEPOSITED TRANSDUCERS

5.1 LAMB WAVE TRANSDUCER

5.1.1 FABRICATION PROCESS OF LAMB WAVE TRANSDUCER

A common method of ultrasonic structural health monitoring employs the use of guided waves. Guided wave inspection is a well researched field and a powerful technique (Rose, 1999; Lissenden, 2010). To test the capabilities of the spray-on deposition method for guided wave applications, a Lamb wave transducer was fabricated. The deposition procedure was the same as outlined in Section 2.1. The sample was microwave sintered at 850 °C for 10 minutes and a powder to solution ratio of 2 g : 1.2 mL. The substrate was a 2 mm thick, 55 mm long stainless steel plate.

A common method of generating Lamb waves is by utilizing inter-digitized electrodes (IDE). This method was employed here. A gold IDE pattern with a finger width and spacing of 0.5 mm was sputtered onto a bismuth titanate film. To fully utilize the pattern, a different poling technique was used. In this technique, one side of the IDE pattern was put to high voltage and the other side put to ground during poling (150 °C, 10 minutes, substrate not grounded). This method proved to generate a much stronger signal than was observed with samples poled perpendicular to the plane of the transducer. The thinking behind this method of poling was that this would help the transducer to generate the shear component of the Lamb wave. Figure 5.1 shows an illustration of the envisioned electric field pattern during poling (and thus the poling direction). Figure 5.2 shows an image of the fabricated transducer and contains an illustration indicating the dimensions in the image. The transducer was capable of generating Lamb waves with good signal strength between 1-10 MHz in frequency. To ensure that both in plane and out of plane elastic waves were being generated, putty
FIGURE 5.1 Illustration of electric field pattern during poling.

FIGURE 5.2 Image of the fabricated sample and an illustration relating the dimensions.
was placed on the surface of the steel to see if any components of the wave would be dampened. Indeed this was the case and it was confirmed that both in plane and out of plane wave forms were being generated. To further confirm out of plane displacements, measurements of the surface displacements from the Lamb wave were taken with a Polytech OFVV-500 laser Doppler vibrometer (LDV), as is shown in Figure 5.3 (c) along with the dampened and undampened detected waveforms (excitation was a 300 V, 2.2 MHz toneburst with 50 dB signal gain).

5.1.2 LAMB WAVE TRANSDUCER HIGH TEMPERATURE PERFORMANCE

The fabricated Lamb wave transducer discussed was tested to see what temperatures a thick film Lamb wave transducer could potentially operate up to. The phase velocity dispersion curve for stainless steel was calculated and is shown in Figure 5.4 (a) (Reinhardt 2010). The activation line for mode generation for this case is also shown (slope of 1). Figure 5.4 (b) shows a comparison of two signals with 2.7 and 4.5 MHz, 300 V, tone burst excitation (50 dB gain).

For the high temperature testing the temperature ramp rate is the same as that which was used for the longitudinal transducer high temperature experiments. Results indicate that changes in the wavelets are quite sensitive to changes in temperature. Figure 5.4 (a) compares two signals with a frequency of 4.5 MHz at 25 °C and 50 °C. Figure 5.4 (b) compares signals at 25 °C and 150 °C. Changes in the structure of the wavelets are clearly visible. If one assumes a coefficient of thermal expansion of 17x10^{-6}/ °C, the fd product only changes by about 0.05%. However, mechanical properties of stainless steel, such as elastic modulus, are very dependent upon temperature and this is likely the cause.
FIGURE 5.3 (A) 2.2 MHz toneburst signal and (b) comparison of normal signal compared to signal dampened with putty. (c) Surface displacement measurements made with an LDV.
A 3D comparison of all the waveforms measured at 50 °C intervals is shown in Figure 5.6. Figure 5.6 shows that waveforms were detected right up until the Curie temperature of 685 °C. Signal amplitudes had good strength until 650 °C. After this, as the temperature increased amplitude of the signals died off rapidly. This effect is demonstrated in Figure 5.7 (a), where waveforms recorded at 25 °C, 600 °C, 650 °C, and 675 °C are compared. Figure 5.7 (b) shows the signal measured at 675 °C. Therefore, here it has been shown that at least for short time periods it is possible to generate Lamb waves of reasonable strength up to 650 °C. Above this temperature amplitude decays at a significant rate. Also, generation of Lamb waves suggests that generation of Rayleigh waves may be also be possible, however, this was not attempted here.
FIGURE 5.4 (a) Phase velocity dispersion curve for a stainless steel plate and (b) comparison of wavelets with frequencies at 2.7 and 4.5 MHz.
Figure 5.5 Comparison of a 4.5 MHz signal measured at 25 °C and 50 °C (b) at 25 °C and 150 °C.
FIGURE 5.6 Comparison of all waveforms measured at 50 °C intervals for a 4.5 MHz signal.
There is a need in the nuclear power industry to be able to accurately measure fluid level in a pipe. Cooling water pumps in reactors are extremely powerful and are capable of moving large volumes of water in short amounts of time. If the fluid level drops too low, there is a risk of damage to these pumps which are extremely expensive. Accordingly, some bench top tests were done to see if it may be possible to spray
deposit films onto a curved piped specimen and see if fluid levels within the pipe could be monitored.

In this study, bismuth titanate films were deposited onto a stainless steel pipe segment. Powder to solution ratio was 2 g : 1.2 mL and the film was microwave sintered at 850 °C for 10 minutes (see Figure 5.8 (b)). The pipe segment had an out diameter of 64 mm and an inner diameter of 40 mm (Figure 5.8 (a)). Two different electrode geometries were tested and compared. One electrode wrapped extensively around the pipe segments exterior (33 mm around the diameter), but was thinner in the direction of the pipe length (width of 4 mm). The other electrode did not wrap around the exterior as extensively (18 mm around the diameter) but was wider in the direction of the pipe length (8 mm width). See Figure 5.8 (c) for clarification of the dimensions. With both electrodes, large signal strengths were obtained from the pipe backwalls.

To test to see if fluid depth could be measured, slabs of Plexiglas were clamped onto the sides of the pipe segment so water could be added into the pipe segment (Figure 5.9). Water was then added to the pipe segment and received signals were measured (excitation: Panametrics 5052 PR, energy level 3, gain of 60). Of the two electrode geometries tested, the less curved and wider electrode, detected signals from the water-air interface with the greatest strength at higher fluid depths. At lower fluid depths, reflected signal amplitudes from the air-water interface were of equal strength between the two electrodes. This suggests that the thinner, more curved electrode, had higher beam spread due to its smaller width despite that it may be “focusing” more energy on the water-air interface. Figure 5.10 (a)-(c) shows comparisons of received signal for a no fluid condition compared to signals received when fluid was added for the thicker, less curved electrode. Figure 5.11 (a) and (b) show similar comparison for the thinner, more curved electrode. Calculations of the arrival time are in good agreement with measured arrival times. Assuming a wave velocity in steel of 5.75 mm/µm and a wave velocity of 1.5 mm/µs for water, the predicted arrival time of the
ultrasonic wave for a water depth of 5 mm is approximately 11 µs. This value corresponds well to what is observed in Figure 5.10(a) and Figure 5.11(a).
FIGURE 5.8 Dimensions of pipe segment used.

FIGURE 5.9 Pipe specimen with Plexiglas clamped onto sides for fluid level testing.
FIGURE 5.10 Comparison of waveforms for pipe empty and pipe filled with water to a depth of (a) 5 mm, (b) 12 mm, and (c) 20 mm (wider, less curved electrode geometry).
FIGURE 5.11 Comparison of signals received when pipe was empty to signals received when water was added to a depth (a) 5 mm and (b) 17 mm for the electrode which was thinner and wrapped more around the pipe diameter,

5.3 SUMMARY

In this chapter the versatility of spray-deposited bismuth titanate films has been explored. It has been shown that IDE based Lamb wave devices can be fabricated and are able to operate up until temperatures of 675 °C for short periods of time. Furthermore, generation of Lamb waves suggests that these transducers could be used to fabricate Rayleigh Wave transducers. It was also shown that spray-deposition of
bismuth titanate onto curved pipe specimens is possible and that transducer strength is strong enough for fluid level detection. As it was shown in Section 4.1, blow torching of samples can be used to fabricate films of equivalent strength. This implies that in-field deposition of bismuth titanate films on pipes for fluid level detection can be readily achieved.
6  CONCLUDING REMARKS

6.1  SUMMARY AND CONTRIBUTIONS TO THE FIELD

The overall objective to develop high temperature ultrasonic transducers using the spray-on deposition technique has been achieved and it has been shown that transducers are capable of, for at least short periods of time, operation up to 680 °C is possible—a previously unknown result. For the first time, this work has explored the effects of microwave sintering on fabricating these sensors and it was shown that microwave sintering is capable of producing quality high temperature transducers more effectively than conventional processes. Additionally, it has been shown that transducers of equal strength to those fabricated using microwave sintering can be fabricated if sintering is performed with a blow torch; inferring that on-site spray-deposition of transducers should be possible. Different ratios of solution to powder were explored, as well as different sintering times and temperatures and fabrication conditions have been proposed. The proposed powder to solution ratio is 2 g : 1.2 mL, and optimum sintering conditions have been determined to be: 1. With microwave sintering: 850 °C for ten minutes 2. With a blow torch as is outlined in Section 2.2.2 Extensive effort was given in this work to characterize the material properties of spray-deposited bismuth titanate. For the first time the conductivity of bismuth titanate fabricated in this fashion has been measured and was determined to not differ in a substantial amount to its bulk counterparts. Furthermore, the modulus of elasticity of these films has been calculated for the first time. In an effort to elucidate the electromechanical properties of these films, two different methods of curve fitting to analytical solutions was attempted but could not be performed successfully. The first was to a Mason model, as is common in the field for substrate supported materials. The Mason model was employed in this work to explain the lack of an observable resonance in the impedance. The model showed that due to the low coupling of bismuth titanate
and the high damping imposed upon the material from the substrate as well as from the films’ intrinsic porosity, resonances in the impedance spectrum of the material could not be measured. To overcome the inability to characterize the films electromechanical properties, a figure of merit was derived and demonstrated in this work to be able to quantify films fabricated in this manner. Approximate values of the $d_{33}$ of the films were obtained by using a commercial $d_{33}$ meter. For samples fabricated under conditions determined to be optimum, obtained values for $d_{33}$ were in the range between 13-16 pC/N, a number significantly larger than what has been demonstrated in previously reported work for bulk bismuth titanate. Although the measured $d_{33}$ values are approximate, it has been shown that films are capable of enduring fields approximately 3.5 times greater in strength during poling than what bulk ceramics can, therefore giving some validity to the measured $d_{33}$ values. However, it still remains to be proven that this is the material $d_{33}$. The larger breakdown strength of these films has been attributed to the breakdown mechanism in bismuth titanate being thermal breakdown and rough calculations indicate that the bismuth titanate field strength increases inversely proportional to the cube root of its thickness. The versatility of these films has also been demonstrated. It has been demonstrated that films fabricated with this processing technique can be used to fabricate IDE based Lamb wave devices which are capable of operation to 675 °C. Spray-deposition of these films onto curved pipe segments has also been demonstrated and fluid level detection within a pipe segment was successfully performed.

The above narrative on contributions of this work can be summarized in bullet point form as follows:

[1]The overall hypothesis was to prove that the sol gel technique could be used to create no-couplant piezoelectric ultrasonic transducers capable of operating at ~700 °C and has been confirmed herein.
[2] Operation up to 680 °C was shown with bismuth titanate transducers deposited using the spray-on technique-- a result which has previously not been demonstrated.

[3] For the first time microwave sintering has been used in the fabrication process. This processing technique has produced high quality piezoelectrics transducers.

[4] “On-site” fabrication via sintering by blow-torch has been shown to be feasible. Transducers of equal strength to those fabricated using microwave sintering have been produced.

[5] Different ratios of solution to powder were explored, as well as different sintering times and temperatures and optimum fabrication conditions have been proposed.

[6] For the first time the conductivity of bismuth titanate films fabricated with the spray-on technique has been measured and was determined not to differ in a substantial amount from its bulk counterparts.

[7] The modulus of elasticity of these spray-on transducers has been calculated for the first time.

[8] A figure of merit was derived and demonstrated to quantify films fabricated by the sol-gel process.

[9] Values for the $d_{33}$ of these films have been approximated to be within the range of 13-16 pC/N, a number significantly larger than what has been demonstrated in previously reported work for bulk bismuth titanate. The approximation is validated since it has been shown the films are capable of enduring fields approximately 3.5 times greater in strength during poling than what bulk ceramics can.

[10] The larger breakdown strength of these films has been attributed to the breakdown mechanism in bismuth titanate being thermal breakdown and rough calculations
indicate that the bismuth titanate field strength increases inversely proportional to the cube root of its thickness.

[11] Fabrication of IDE based Lamb wave sensors is possible with this deposition technique.

[12] Application of these films for fluid level detection within pipes is possible.

6.2 SUGGESTED FUTURE WORK

A potential major application for this fabrication is on-site deposition of these materials. The most serious factor currently preventing this is that an electrode material has not been found that will not destroy the conductivity of the films unless a diffusion boundary layer of gold is first deposited via sputter coating. A solution to this problem needs to be discovered. It is suggested that platinum paint, such as the one commercially available from SPI-Chem™, be tested. Another potential candidate is a silica-carbon based paint sold by Ted Pella.

It’s been demonstrated by Kobayashi that with this deposition technique it may be possible to make multi phase composites which benefit from the properties of each phase involved (Kobayashi 2007). In other words, it may be possible to tailor new composite materials for specific applications. But, as is explained above in this text, proper characterization of these materials remains to be performed. One potential material is bismuth titanate-lithium niobate based composites which have already been shown capable of generating ultrasound up to 1000 °C (Searfass, 2010). This material has yet to be properly characterized and it is recommended that it is done so in the same spirit as this thesis. Another material worth considering is Bi₃TiNbO₉ because of its impressive Curie temperature of 930 °C (Sagalowicz 2000). It is also worth pursuing the
effects of pulse poling on the efficiency of these films. Seth and Schulze reported that with pulse poling a $d_{33}$ of 26 pC/N can be obtained for bulk ceramics and it is likely that the same is true for thick film samples (Seth & Schulz, 1989/).
APPENDIX A

A.1 MASON MODEL

The approach of using an equivalent circuit for describing piezoelectric transducers was primarily originally developed by W.P. Mason. By realizing the analogy between force and velocity in differential equations in mechanical systems and voltage and current differential equations for electrical networks, respectively, the equivalent circuit was devised by developing an electrical network which has equations equivalent to those derived from the piezoelectric equations and the wave equation. The network is a 3 port network, with two ports representing mechanical loadings on the two faces of the transducer and one port for electrical loading. Thus, one side of the circuit represents the electrical behavior of the transducer and the other side representing the mechanical behavior. The sides are connected via an ideal transformer which represents electromechanical transduction. Physical interpretation and equations for the components of the Mason model is shown in Figure A.1. Using equivalent circuits has the advantage that network theory can be used to analyzed the system and that the model is an exact model so long as the assumptions underlying the system are true. The use of equivalent circuits for piezoelectric transducers has been thoroughly research and there are several excellent texts which provide good interpretation of them for various vibration modes of piezoelectric (Berlincourt, Curran, & Jaffe, 1964). The front and back mechanical loadings from the substrate and electrode cannot be considered as an infinite half-space and can be modeled as a two port network (infinite half-spaces are treated as purely resistive)—see Figure A.2 (O'Donnell 1981). These are then attached to the two mechanical ports in the model. Figure A.3 shows the circuit for the entire model. The equation for the impedance is quite large and is omitted here but can be ascertained from the computer code given in A.2.
**FIGURE A.1** Mason model for a piezoelectric transducer in thickness mode ($A$ is area, $t$ is thickness).

\[ C_0 = \frac{\varepsilon_{33} A}{t} \]
\[ v^0 = \sqrt{\left(\frac{c_{33}^0}{\rho}\right)} \]
\[ Z_0 = \rho A v^0 \]
\[ N = \frac{A k_t}{t} \sqrt{\varepsilon_{33} c_{33}^0} \]
\[ Z_a = \frac{-j Z_0}{\sin \frac{\omega t}{v^0}} \]
\[ Z_b = j Z_0 \tan \frac{\omega t}{2 v^0} \]

**FIGURE A.2** Two port model for a mechanical load.

\[ Z_a = j Z_0 \tan \frac{\omega t}{2} \]
\[ Z_\chi = \frac{-j Z_0}{\sin \frac{\omega t}{2}} \]
\[ Z_0 = \rho v A \]
**A.2  Computer Code (Written in Mathematica 7.0)**

\begin{verbatim}
(*Clear local kernel*)
Clear["Global"*""]
(*Load in experimental data*)
fspace=Import["fspace.dat","Table"];
mag=Import["mag.dat","Table"];
f=Transpose[fspace];
(*Create frequency and impedance magnitude linear spaces*)
freq1=Table[f[[i,1]],{i,1,Length[f]}];
mag2=Table[mag[[i,1]],{i,1,Length[f]}];
(*Plot experimental data*)
b=Show[ListPlot[Table[{freq1[[i]],mag2[[i,1]]},{i,1,201}]],TicksStyle->Directive[18],AxesLabel->Style["Frequency",Large],Style["Impedance",Large]]
\end{verbatim}
(*Define material parameters
eps is real part of relative permittivity
tande is imaginary part of permittivity
ko is electromechanical coupling coefficients
yo is real part of elastic modulus * Defined below in plots to make comparisons easier
tandum is imaginary part
p is density
t is film thickness
r is radius of electroded area
zback is air loading on the substrate and electrode
rhs and lhs in variables mean right hand side and left hand side, respectively, to acoustic branches of the loads in the mason model
trhs is thickness is thickness of electrode
prhs is density of electrode
rhs vel is ultrasonic wave velocity in electrode material
tlhs1 is thickness of substrate
plhs is density of substrate
lhsvel is velocity of substrate*)

tande=0.0078;
r=0.005;
eps=96*(1-(l*tande));
ko=0.09*(1+(l*0));
p=3200;
t=142.5*10^6;
yo=y*10^10;
epsilon=eps*8.85*10^-12;
zback=494*dim;
trhs1 = 50 * 10^-6;
prhs = 19200;
rhsvel = 3000;
zorhs = prhs * rhsvel * dim;
(*zorhs = 494 * dim;*)
krhs[freq_] := (2*p)*freq/rhsvel;
zaf[freq_] := (I*zorhs) * Tan[krhs[freq] * trhs1/2];
zbf[freq_] := (-I*zorhs) / Sin[krhs[freq] * trhs1];
thsl = 2.54/100;
plhs = 7900;
lhsvel = 5750;
zolhs = plhs * lhsvel * dim;
klhs[freq_] := (2*p)*freq/lhsvel;
zae[freq_] := (l*zolhs) * Tan[(tlhs1/2)*klhs[freq]]; 
zbe[freq_] := (-1*zae[freq]) / Sin[tlhs1*klhs[freq]]; 
zair = 494 * dim;
Co = epsilon * dim/t;
vel = 
phi = ko * vel;
(*Begin constructing electrical impedance function*)
beta[freq_] := 2*p*freq*sqrt[P y0];
za[freq_] := (I*zo) * Tan[beta[freq] * t/2];
zb[freq_] := (l*-1*zo) / Sin[beta[freq] * t];
zc[freq_] := (l*(-1)) / (2*p*Co*freq);
ze1[freq_] := zaf[freq] + zback;
ze2[freq_] := (ze1[freq] * zbf[freq]) / (zbf[freq] + ze1[freq]);
zr[freq_] := za[freq] + zaf[freq] + ze2[freq];
zh1[freq_] := zair + zae[freq];
zh2[freq_] := (zh1[freq] * zbe[freq]) / (zbe[freq] + zh1[freq]);
zL[freq_] := zh2[freq] + zae[freq] + za[freq];
zR[freq_] := (zL[freq] * zr[freq]) / (zL[freq] + zr[freq]);
zbeta[freq_] := zb[freq] + zm[freq];
zalp[freq_] := zbeta[freq] / (phi*phi);
zgamma[freq_] := zc[freq] + zalp[freq];
(*Complex function of electrical impedance*)
zin[freq_] := (zc[freq] * zgamma[freq]) / (zc[freq] + zgamma[freq]);
(*Magnitude of impedance*)
val[freq_] := (Re[zin[freq]]^2 + Im[zin[freq]]^2)^(1/2);
(* Plot of impedance. w is NOT angular frequency, standard frequency units. Be sure to specify proper elastic modulus of transducer yo defined above defines order of modulus aka GPa etc*)

a=Plot[val[ω]/.y->2.7*(1+(I*0.8)),{ω,1*10^6,10*10^6},PlotStyle->Red,TicksStyle->Directive[18],AxesLabel->{Style["Frequency",Large],Style["Impedance",Large]}]

d=Plot[val[ω]/.y->2.7*(1+(I*0.0)),{ω,1.5*10^6,8*10^6},PlotRange->{-1,400},PlotStyle->Green,TicksStyle->Directive[18],AxesLabel->{Style["Frequency",Large],Style["Impedance ",Large]},AxesLabel->{Frequency,Impedance}]
Show[d,a]

c = Plot[val[ω], {ω, 1*10^6, 5.5*10^6}, PlotRange -> {-1, 400}, PlotStyle -> Green, TicksStyle -> Directive[18], AxesLabel -> {Style["Frequency", Large], Style["Impedance", Large]}, AxesLabel -> {Frequency, Impedance}]
Appendix B

B.1 Background on Attempts At Extracting Material Properties Using the Method of Schmerr and Song

In their book “Ultrasonic Nodestructive Evaluation System: Models and Measurements”, Schmerr and Song were able to characterize ultrasonic transducers using a somewhat novel approach (Schmerr & Song, 2007). The models they developed agreed excellently with experimental results. It was thought that perhaps this modeling approach could be adapted here to extract material properties from fabricated by implementing curve fitting, similar to what is done with the Mason model for substrate supported films. Although this method was unsuccessful in determining properties of the spray-deposited films, it was successful in determining properties of a LiNbO₃ single crystal operating in pulse-echo mode. Thus, perhaps with more efficient programming or refinement/simplification of the model, it may be possible to use this method to obtain film properties and this is why details of this attempt have been included in this thesis.

The premise of the approach is to treat every component of an ultrasonic test system as a transfer function. The end result of this approach is that the output voltage of transducer(s) operating in either pulse-echo mode or through-transmission can then be accurately modeled for a variety of situations. The measured voltage of transducer operating in pulse-echo mode is given as

\[ V_R(\omega) = t_g(\omega)t_R(\omega)t_A(\omega)V_i(\omega) \]  

B.1

Where \( t_g \), \( t_R \), and \( t_A \) are transfer functions in the frequency domain representing the ultrasonic wave generation process, the reception process, and acoustic elastic transfer function (e.g. the traveling of the wave through a medium). \( V_i \) is the input voltage to the transducer. \( t_g \) is given by
\[ t_g(\omega) = \frac{Z_r^{A:a} S_{vl}^A}{Z_i^{A:e} T_{11} + T_{12} + Z_i^{A:e}(T_{21} + T_{22})} \]

Where \( Z_r^{A:a} \) is the transducer acoustic radiation impedance, \( T_{ij} \) represent cabling effects, and \( Z_i^{A:e} \) is the measured pulser impedance. \( S_{vl}^A \) and \( Z_i^{A:e} \) are the transducer sensitivity and input impedance, respectively, and are given as

\[ S_{vl}^A = \frac{1}{Z_r^{A:a} X_{21} + T_{22}} \]

\[ Z_i^{A:e} = \frac{Z_r^{A:a} X_{11} + X_{12}}{Z_r^{A:a} X_{21} + X_{22}} \]

The terms \( X_{ij}^A \) are a matrix representing the acoustic, electric, and electromechanical behavior of the transducer, and is given as (based on the Sittig model (Sittig 1967))

\[ X^A = \frac{1}{Z_b^a - iZ_b^a \tan \left( \frac{kd}{2} \right)} \left\{ \frac{1}{n} \sum_{i=0}^{n} \frac{1}{i \omega C} \right\} \left\{ \begin{array}{c} \frac{1}{Z_b^a + iZ_b^a \cot (kd) + (Z_b^a)^2 + iZ_b^a Z_b^a \cot (kd)} \\ Z_b^a - 2iZ_b^a \tan \left( \frac{kd}{2} \right) \end{array} \right\} \]

Where \( Z_b^a, Z_o^a, C_o, d, \) and \( k \) are the acoustic impedance of the backing, the plane wave impedance of the transducer, the capacitance of the transducer, the transducer thickness, and wave number of the piezoelectric, respectively. The parameter \( n \) is expressed as \( n = h_{33} C_o \), where \( h_{33} \) is the piezoelectric stiffness constant. This is the primary term to which the model was fit in order to try and extract material properties.

The acoustic-elastic transfer function, \( t_o \), is given as

\[ t_o(\omega) = D_p \left( \frac{k_p a^2}{D} \right) R_{12} e^{2ik_p D} \]

Where \( R_{12} \) is the plane wave reflection between the piezoelectric and the medium it is radiating into, \( k_p \) is the wavenumber and \( D \) is the distance the wave travels in the medium. The function \( D_p \) represents scattering of the wave and is given as

\[ D_p(u) = 2 \left\{ 1 - e^{iu} \right\} \left\{ J_0(u) - iJ_1(u) \right\} \]

Where \( J_0 \) and \( J_1 \) are Bessel functions of order 0 and 1, respectively. The transfer function for the reception process, \( t_r \), is given as
FIGURE B.1 (a) Measured pulser output impedance, (b) input impedance, and (c) pulser gain as functions of frequency.
\[ t_r(\omega) = \frac{KZ_o^e S_{vl}^B}{(Z_{in}^{B, e} T_{11} + T_{12}) + Z_o^e} \]

Where \( K \) is the gain of the pulser, \( S_{vl}^B \) and \( Z_{in}^{B, e} \) are sensitivities and electrical impedance of the receiving transducer (identical to \( S_{vl}^A \) and \( Z_{in}^{A, e} \) in the case of pulse-echo), and \( T_{ij} \) represent cable losses.

The parameters \( K, Z_i^e, Z_{in}^{A, e}, Z_o^e, \) and \( V_i \) must all be measured experimentally. In the case of impedances, both current and voltage must be measured. For instance, to measure the pulser impedance \( Z_o^e \), the voltage is measured across a large impedance and part of the shielding is removed from the coaxial and a current probe is used to measure the impedance. The impedance is then simply given as

\[ Z_o^e = \frac{V_o(\omega)}{I_o(\omega)} \]

Where \( V_o \) and \( I_o \) are the measured currents and voltages across the input of the pulser. Typically, a Wiener filter is need in these measurements in order to eliminate high frequency noise. Figure B.1 shows some measured data from a Panametrics 5052 PR pulser-receiver.

During the curve fitting process, these measured parameters of the ultrasonic testing setup need to be used as analytical functions, which the data does not provide. However, in Mathematica one can create an interpolating function which creates a smooth function that is fitted to the data on a point by point basis. This essentially gives an analytical function of the measured data for curve fitting. Figure B.2 shows an analytical function fitted to the pulser output impedance as an example. Once all the data of the impedances and gain behavior of the pulser were imported to Mathematica, followed by fitting of interpolating functions to the data, the FFT of the first backwall of the transducer was imported into Mathematica. The FFT of the first backwall was what was to be curve fitted to \( V_g \), which is now comprised of both analytical functions and
interpolating functions. The curve fitting worked reasonably well for a single crystal lithium niobate transducer. This is shown below Figure B.3.

FIGURE B.2 Interpolating function fitted to measured output impedance of Panametrics Pulser 5052 PR.

FIGURE B.3 Fitted data and experimental data for single crystal lithium niobate transducer
For the single crystal lithium niobate, the model predicted a $d_{33}$ of 5.6 pC/N and a permittivity of 31. Commonly reported values for lithium niobate are a $d_{33}$ of 6 pC/N and a permittivity of 31. Thus it seemed the model worked well in predicting the values for this material. However, when this model was fitted to the response of the bismuth titanate films, no reliable results could be obtained. While somewhat close fits could be obtained, the numbers which gave the close fits were not unique. That is, the model could give very similarly looking fits to the measured data, but parameters could vary substantially and give almost identical looking fits. Thus the numbers this model produced could not be trusted. The reason for the modeling not working on the bismuth titanate transducers is believed to be due to the fact that the material porosity is as high as 40 %, while the underlying model assumes a continuum. Therefore it can expected that films have high mechanical and electromechanical loss factors. These can be introduced into the model by making the modulus, permittivity, and electromechanical coupling factor complex quantities. However, this now doubles the number of parameters which need to be fitted. Between this and the use of interpolating functions the model becomes substantially complicated. Again, no unique set a variables could be obtained to give a “best fit”. It soon became clear that this approach would not be successful in characterizing these films and work began on developing the figure of merit described in this text in Section 3.7.
B.2 Computer Code for Curve Fitting

Clear["Global"=""]

(*Importing pulse frequency spectrum*)
k=Import["k2.dat","Table"];  
kimag=Import["kimag2.dat"];  
kcomplex=Table[k[[i,1]]+I*kimag[[i,1]],{i,1,Length[k]}];  
L=Import["f.dat","Table"];  
f=Transpose[L];  
freq=Table[f[[i,1]],{i,1,Length[f]}];  
test=Table[freq[[i]]*zreal[[i]],{i,1,Length[zreal]}];  
absk=Table[2*Abs[kcomplex[[i]]],{i,1,Length[k]}];  
KintStep1=Table[{freq[[i]],absk[[i]]},{i,1,Length[k]}];  
Kifun=Interpolation[KintStep1]
InterpolatingFunction[{{0.,1.96862×10^7}},<>]

(*Loading pulser input impedance and constructing interpolating function*)
VinputImag=Import["VinputImag.dat","Table"];  
VinputReal=Import["VinputReal.dat"];  
Vincomplex=Table[VinputReal[[i,1]]+I*VinputImag[[i,1]],{i,1,Length[k]}];  
absvin=Table[2*Abs[Vincomplex[[i]]],{i,1,Length[k]}];  
VintStep1=Table[{freq[[i]],absvin[[i]]},{i,1,Length[k]}];  
Vinfun=Interpolation[VintStep1]
InterpolatingFunction[{{0.,1.96862×10^7}},<>]

(*Loading pulser gain and constructing interpolating function*)
gainreal=Import["gainreal.dat","Table"];  
f2=Transpose[L2];  
freq2=Table[f[[i,1]],{i,1,Length[f]}];  
test=Table[freq2[[i]]*zreal[[i]],{i,1,Length[zreal]}];  
abszie=Table[2*Abs[ziecomplex[[i]]],{i,1,Length[ziereal]}];  
zieintStep1=Table[{freq2[[i]],abszie[[i]]},{i,1,Length[ziereal]}];  
Ziefun=Interpolation[zieintStep1]
InterpolatingFunction[{{0.,1.49554×10^7}},<>]

(*Loading pulser gain and constructing interpolating function*)
gainreal=Import["gainreal.dat","Table"];
gainimag=Import["gainimag.dat"]; gaincomplex=Table[gainreal[[i,1]]+I*gainimag[[i,1]],{i,1,Length[k]}]; absgain=Table[2*Abs[gaincomplex[[i]]],{i,1,Length[k]}]; gaininstep1=Table[{f[[i,1]],absgain[[i]]},{i,1,Length[k]}]; gaininfun=Interpolation[gaininstep1] InterpolatingFunction[{{0.,1.96862×10^7}},<>]

(*Enter material parameters for transducer
pBT is transducer density
r is transducer radius
t is thickness
values with "o" on end are order of magnitude of material properties*)
pBT=4650;
e0=8.85*10^-12;
r=0.005;
d33o=10^-12;
c33o=10^11;
t=1*10^-3;
d=pi*r^2;
Co=(eps+I*ep)*eps0*d/t;
h33=d33*d33o*(c33+I*cp)*c33o/(eps0*(eps+I*ep));
v=((c33+I*cp)*c33o/pBT)^(1/2);

(*Input material properties of substrate
pSS is density
vSS is wave velocity
Zab is impedance of backing*)
pSS=7900;
vSS=5750;
kBT[ω _]:=2*pi*ω/(v);
kSS[ω _]:=2*ω*pi/(vSS);
Zab=d*10490*((100*10^9)/10490)^(1/2);
n=h33*Co;
ZAar=pSS*vSS*d;
Zoa=pBT*v*d;

(*constructing model*)
Tge[ω _]:={
{1/n, n/(I*2*p*w*Co)},
\{-I*2*p*w*Co/n, 0\}
);

cable={
  {1, 0},
  {0, 1}
};

div[\omega _\_]:=(1/(Zab-l*Zoa*Tan[kBT[\omega ]*t/2]));

Tgamatrix[\omega _\_]:=
{(Zab+I*Zoa*Cot[kBT[\omega ]*t]), ((Zoa)^2+(I*Zoa*Zab*Cot[kBT[\omega ]*t]))},
{1, (Zab-(2*I*Zoa*Tan[kBT[\omega ]*t/2]))}
}

Da=0.0254;
Tga[\omega _\_]:=div[w]*Tgamatrix[\omega ];

ta[\omega _\_]:=
{Cos[\omega *Da/(vSS)], -I*pSS*vSS*d*Sin[\omega *Da/(vSS)]},
{-I*Sin[\omega *Da/(vSS)]/(pSS*vSS*d), Cos[\omega *Da/(vSS)]}
}

T[\omega _\_]:=Tge[\omega ].Tga[\omega ];

T2[\omega _\_]:=
{\{T[\omega ][[2,2]], T[\omega ][[1,2]]\},
\{T[\omega ][[2,1]], T[\omega ][[1,1]]\}
}

SBvl[\omega _\_]:=1/(ZAar*(T2[\omega ][[2,1]]+(T2[\omega ][[2,2]])));
ZBein[\omega _\_]:=((ZAar*T2[\omega ][[1,1]]+(T2[\omega ][[1,2]]))/((ZAar*T2[\omega ][[2,1]]+(T2[\omega ][[2,2]])));
ZAein[\omega _\_]:=((ZAar*T[\omega ][[1,1]]+(T[\omega ][[1,2]]))/((ZAar*T[\omega ][[2,1]]+(T[\omega ][[2,2]])));
SAvl[\omega _\_]:=1/(ZAar*(T[\omega ][[2,1]]+(T[\omega ][[2,2]])));

tg[\omega _\_]:=ZAar*SAvl[\omega ]/((ZAein[\omega ]*cable[[1,1]]+cable[[1,2]])+Ziefun[\omega ]*(ZAein[\omega ]*cable[[2,1]]+cable[[2,2]]));

da=0.0254;
R12=(pSS*vSS-494)/(pSS*vSS+494);

Dp[\omega _\_]:=2*(1-Exp[I*kSS[\omega ]*r^2/2Da]*(BesselI[0,kSS[\omega ]*r^2/(2*Da)]-I*BesselI[1,kSS[\omega ]*r^2/(2*Da)]));
\[
\text{taa1}[\omega_] := \text{Dp}[\omega] * R12 * \text{Exp}[kSS[\omega]2 * I * Da] * \text{Exp}[-2 * 27.13 * 0.0254];
\]

\[
\text{ZBar} = \text{ZAar};
\]

\[
\text{R} = \{(1, 0),
(0, 1)
\};
\]

\[
\text{Zoe} = k * \text{Zeo} * \text{SBvl} / ((\text{ZBein} * \text{R}[1,1] + \text{R}[1,2]) + \text{Zeo} * (\text{ZBein} * \text{R}[2,1] + \text{R}[2,2]));
\]

\[
\text{tr}[\omega_] := \text{gaininfun}[\omega] * \text{Kifun}[\omega] * \text{SBvl}[\omega] / (\text{ZBein}[\omega] * \text{R}[1,1] + \text{R}[1,2] + (\text{Kifun}[\omega] * (\text{ZBein}[\omega] * \text{R}[2,1] + \text{R}[2,2])));
\]

\[
\text{Vr}[\omega_] := \text{tr}[\omega] * \text{tg}[\omega] * \text{taa1}[\omega] * \text{Vinfun}[\omega];
\]

(*AbsV is FFT of modeled transducer*)

\[
\text{absV}[\omega_] := 2 * \text{Abs}[	ext{Vr}[\nu]];
\]

(*Import measured transducer data for fit*)

\[
\text{samplereal} = \text{Import}["realsamplefft.dat","Table"];
\]

\[
\text{sampleimag} = \text{Import}["imagsamplefft.dat"];
\]

\[
\text{samplecomplex} = \text{Table}[\text{samplereal}[i,1] + I * \text{sampleimag}[i,1],\{i,1,\text{Length}[\text{samplereal}]\}];
\]

\[
\text{abssample} = \text{Table}[\text{Abs}[\text{samplecomplex}[i]],\{i,1,\text{Length}[\text{samplecomplex}]\}];
\]

\[
\text{abssam} = \text{Table}[\{i/(4.088*10^{-6}),\text{abssample}[i]\},\{i,1,22\}];
\]

\[
\text{b} = \text{Show}[\text{ListPlot}[\text{Table}[\{i/(4.088*10^{-6}),\text{abssample}[i]\},\{i,1,50\}],\text{PlotRange}->\{0,0.08\}];
\]

(*Finding fit to data*)

\[
\text{FindFit}[\text{abssam},\{\text{absV}[\omega],d33<10,d33>1,c33<3.5,c33>1,\epsilon_p>-10,\epsilon_p<0,\epsilon_p>20,\epsilon_p<40,d33>0,\epsilon_p<0,\epsilon_p<10,\{d33,6\},\{c33,2.42\},\{\epsilon_p,27\},\{\epsilon_p,0.1\},\{\epsilon_p,0.1\}\},\omega,\text{Method}->\text{NMinimize},\text{Gradient}->\"FiniteElement\",\text{NormFunction}->\{\text{Norm}[#,2]\&\}]
\]

\[
\{d33->5.42458,c33->3.43794,\epsilon_p->31.648,\epsilon_p->-6.32133,\epsilon_p->2.55713\}
\]

\[
\text{a} = \text{Plot}[\text{absV}[\omega]/.\%,\{\omega,10^6,8*10^6\},\text{PlotRange}->\{0,0.05\}];
\]

(*Plot fit and experimental data*)

\[
\text{Show}[\text{a},\text{b}]
\]
Appendix C Non-Technical Abstract

Non-destructive evaluation is a scientific field which concerns itself with non-destructive determination of material properties as well as the characterization of a systems’ mechanical integrity. When mechanical integrity is in question, surface and sub-surface defects are typically of primary concern. Such defects include, but are not limited to, cracks and corrosion. Monitoring of crack growth and corrosion are essential in preventing structural failure of several key components of society’s infrastructure, including bridges, gas and water lines, transportation (aerospace, automotive, and rail industries), power generation, as well as various military applications. An example of where non-destructive evaluation could have been useful was the recent problem with the Fukushima Daiichi nuclear power plant leaking radioactive water into the sea after the plant was damaged by a 46 ft. tsunami. The leak was caused by an 8 inch crack that formed in a maintenance pit at the plant. Earlier detection of the crack via non-destructive evaluation may have led to a quicker response to fix the crack and thus prevent less radioactive waste from leaking into the ocean.

One of the most common ways of performing non-destructive evaluation is using ultrasonic non-destructive evaluation (UNDE). For example with a sonogram, such as what women receive during pregnancies to obtain images of the fetus, ultrasonic waves are sent into the body and the reflected ultrasonic waves are detected and are used to construct an image. In industrial UNDE, such as the evaluation of turbine blade integrity, similar approaches are used to determine if an excess amount of flaws are present and could lead to failure of the turbine blade. The most common method for the generation and reception of ultrasonic waves which is required for UNDE is by the use of piezoelectric materials. These materials are capable of generating and detecting ultrasonic waves. Devices used for ultrasonic inspection are known as transducers and they typically consist of piezoelectric elements for the use of generation and detection.
of ultrasonic waves which enable the user to inspect an object for both surface and subsurface defects. Piezoelectric materials have the advantages over other methods of UNDE in that they are small and light weight, can be produced with relative ease and reproducibility, and are fairly cheap.

Systems which operate at high temperatures (temperatures exceeding 750 °F) are particularly challenging from an engineering design standpoint. Such areas of application which operate at high temperatures include the power generation industry, for instance fuel rods in a nuclear power plant, and the aerospace industry, where integrity of engine components is of major concern. With the current state of the art, non-destructive evaluation of parts whose service environment is at high temperature requires that the system be shut down such that the component can be removed and inspected. This costs both time and money, and is disadvantageous since evaluation of parts in real time during service is not performed. In fact, it was reported in 2003 that United States Air Force spent over 1 billion dollars on fleet maintenance. If a method for evaluation of engine components during service can be established both financial expenses and fleet down town time would be minimized significantly. As far as UNDE of high temperature systems is concerned, major obstacles include fabricating a material capable of generating and receiving ultrasound with significant strength and sensitivity, respectively, at the specified operating temperature, as well as establishing a way to enable ultrasound to enter and leave the structure requiring evaluation (such as how a gel is used during a sonogram).

In this dissertation, a method for spray coating objects for UNDE with an air gun, similar to what one would use to paint a wall, with a material capable generating ultrasound at temperatures greater than 1000 °F for extended periods of time has been developed. The spray coating technique is advantageous for several reasons. The first is that a developing a means of coupling ultrasound from the transducer to the structure requiring UNDE is eliminated. The second major advantage of this technique, as it has been demonstrated in this work, is that it is a fairly portable deposition technique. This
means that systems already in service can have a transducer coated onto them without being removed from service (such as a cooling pipe in an already operating nuclear power plant). These discoveries have shown UNDE of high temperature systems is close to realization and may even be employed in next generation nuclear power plants whose construction in the United States is already being planned in several states. Several applications have also been demonstrated in this dissertation, such as fluid level detection in pipes, as well as generation of waves confined near the surface of an object which could be used to determine surface defects, such as corrosion to structures.
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Cliff Searfass was born in Allentown, Pennsylvania in 1983. He graduated from Emmaus High School in 2001, after which he attended the Pennsylvania State University for his undergraduate degree. In 2003, he began work under Dr. Bernhard R. Tittmann and his work with piezoelectric materials began with developing piezoelectric transformers and piezoelectric-magnetostrictive current sensors. He graduated with honors in 2005 with a B.S. in Engineering Science and Mechanics, the Pennsylvania State University’s honors college of Engineering, along with minors in physics and Engineering Mechanics. His major interest is physics of the solid state, with particular emphasis on ferroelectrics, as well as microwave processing of materials.