RESEARCH ON LOW FREQUENCY COMPOSITE TRANSDUCERS
FABRICATED USING A SOL-GEL SPRAY-ON METHOD

A Thesis in
Engineering Science
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

December 2012
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Abstract

Ultrasonic nondestructive evaluation is currently used in countless applications to maintain a system’s operational integrity. Piezoelectric transducers are the devices commonly used in this field to search for defects. A sol-gel fabrication method utilizing a spray-on deposition method has proven to produce ultrasonic transducers useful in harsh environments. This procedure produces thin film transducers, which adhere directly to a substrate making it favorable in use with irregular surface geometries. These transducers operate at relatively high frequencies due to their minute thickness. The objective of this research is to investigate the ability for low frequency operation into the low kilohertz range.

Depositing thicker layers of piezoelectric composites, including bismuth titanate and lead zirconate titanate, led to adhesion problems between the metal substrates and ceramic material. Delamination of the piezoelectric elements was determined to be caused by a large mismatch in thermal expansion coefficients. Adaptations were made to the stainless steel substrates being used in order to overcome this problem. Additionally, invar substrates were used to greatly decrease the mismatch in thermal expansion coefficients between the substrate and ceramic composite.

Fabricated samples were found to operate efficiently as longitudinal transducers at frequencies well into the low kilohertz range. Transducers were tested in modes of pulse-echo and through-transmission, acting as both the transmitter and receiver. The results presented in this thesis show that sol-gel spray-on fabricated transducers have the ability to operate effectively at frequencies as low as 250 kHz.
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Acknowledgments

I would like to thank my father Bob, and my mother Pam, for all of their support, in all forms, throughout my academic career, especially the past year and a half. The love and support of all of my family members has helped fuel my desire and drive for success. They were always there when everything seemed overwhelming and frustrating. I also want to thank my girlfriend Sam, her unbelievable patience and support kept me determined and pushed me to work harder than ever before.

I would like to thank Dr. Bernhard R. Tittmann for allowing me to join his lab as a graduate student. He supplied me with several great opportunities and kept faith in me through all of the trials and tribulations faced during this research. I would also like to thank all of my lab mates and friends, especially Brian Reinhardt, Dr. Cliff Searfass, Kyle Sinding, Christiane Pheil, and Jeong Nyeon Kim. Other faculty in the Engineering Science and Mechanics Department I would like to thank are Dr. Cliff Lissenden and Dr. Mark Horn for their support and helpful insights. Thank you also to Ardell Hosterman for always being available to help when needed. I would also like to thank Jeff Long, Maria DiCola and the rest of the staff in the Electrical Characterization Lab in the Millennium Science Complex for all their help.

This material is based upon work supported by the Nuclear Energy Universities Program under Award number 00120237.
Chapter 1

Introduction

1.1 Introduction to Piezoelectricity

The American Society of Nondestructive Testing defines nondestructive evaluation (NDE) as the examination of an object with technology that does not affect the object's future usefulness [13]. There are several methods of nondestructive evaluation including optical, x-ray, thermography, magnetism, and perhaps the most popular, ultrasound. The use of sound waves has been employed for centuries by listening to the natural frequency of an object, which would be distorted by sizeable damage. In order to detect smaller defects that still may be detrimental to overall integrity, higher frequencies of ultrasound must be used. For this method of nondestructive evaluation to be efficiently utilized the development of a readily available source of ultrasound was necessary as well as detection techniques.

This source was discovered in 1880 when Pierre and Jacques Curie found an interesting property during their study of Rochelle salt and quartz. Both of these materials are known ferroelectric crystals. A ferroelectric material exhibits a spontaneous polarization, the direction of which can be reversed with the application of an external electric field [11]. The Curie brothers observed that the compression of asymmetric crystals created an electric polarization, and their decompression resulted in an electric response with the opposite sign [14]. This newly discovered phenomenon resembled the already known theory of pyroelectricity. The pyroelectric effect describes how the direction of spontaneous polarization in a ferroelectric material is dependent on temperature. When a pyroelectric crystal is heated an electric charge flow is generated on its surface. Similarly, these crystals exhibited a relationship between applied pressure and voltage that was aptly named the piezoelectric effect. The word piezoelectricity means electricity from pressure and is derived from the Greek word piezein, meaning to squeeze or press.

One year after the Curies discovery, Gabriel Lippmann theoretically formulated the converse of the piezoelectric effect. Lippmann claimed that an applied electric field would cause the crystal to strain linearly. The Curie brothers later confirmed this as they went on to further develop the
theory of piezoelectricity.

Throughout the 20th century the study and advancement of piezoelectric materials continued. One key usage was sonar for ships at sea, especially submarine detection during the First and Second World Wars. Following the war, research of ultrasound using piezoelectrics continued to grow at a rapid pace and devices used for flaw-detection became mainstream. The first pulse-echo transducer was in place by the mid-1940s, and by 1960 ultrasound had taken the place of previous nondestructive evaluation methods such as x-rays [13]. Today the majority of ultrasonic transducers comprise of a piezoelectric element, along with several, more everyday devices such as speakers, lighters, wristwatches, and many electronic components.

The piezoelectric effect stems from an asymmetry on the atomic level in the crystalline structure of a material. It is this lack of symmetry between positively and negatively charged ions that results in a net polarization. When a strain is applied the separation between the oppositely charges ions grows and a greater net polarization is created, and therefore a voltage. Conversely, if an electric field is applied there are forces that “mechanically” push on the cations and anions resulting in a strain. Figure 1.1 is an illustration of a single domain of bismuth titanate, $Bi_4Ti_3O_{12}$, in two dimensions with red representing bismuth atoms, white representing oxygen atoms, and the black is a titanium atom. Notice how the positively charged titanium atom is off-center creating the net polarization in the unstrained state [4]. In (b) the titanium atom is displaced by an applied stress creating a charge on the surface of the material.

![Figure 1.1](image)

**Figure 1.1.** Two-dimensional representation of bismuth titanate ($Bi_4Ti_3O_{12}$) single domain; (a) unstrained and (b) under a tensile load. Figure adapted from [1].

Piezoelectric transducers function as both transmitters and receivers in applications of ultrasonic nondestructive evaluation. In general, a voltage pulse is sent through the transducer and is transformed into an ultrasonic wave via the indirect piezoelectric effect. The applied electric field of the pulse causes the piezoelectric element to mechanically contract transmitting a sound wave into the sample being investigated. When this ultrasonic wave is reflected back to the transducer the piezoelectric element contracts from the pressure converting the energy back into an electric signal by the direct piezoelectric effect. This signal can then be analyzed using additional equipment for many applications, such as measuring material properties of the sample and
searching for defects. This example represented a transducer operating in the pulse-echo mode, but the same type of investigation can be done in through-transmission mode with the addition of a second transducer. Measurements of these types are the basis of scanned image microscopy.

Figure 1.2. Illustration of a transducer operating in pulse-echo mode. Point 1 represents the launching of the ultrasonic wave and point 2 is its reflection.

Figure 1.2 illustrates how a piezoelectric transducer is used for flaw detection in pulse-echo form. The “main bang” signal spike at point 1 signifies the ultrasonic wave entering the sample. The signal at point 2 is the reflected wave from the back wall of the sample that has traveled back to the transducer. Its amplitude is smaller due to attenuation, or the energy loss, of the wave as it travels through the sample. Notice the small signal spike in between points 1 and 2; this is caused by the reflection of a portion of the ultrasonic waves energy by some defect in the middle of the sample. This illustrated practice is a key principle in ultrasonic nondestructive evaluation.

1.2 Temperature Dependence and Electric Domains

There is a critical temperature, specific to each piezoelectric material, at which their spontaneous net polarization is lost. This loss of the piezoelectric effect occurs at a transition temperature known as the Curie-Weiss temperature, \( T_c \) [15]. At this temperature the crystal structure relaxes and the asymmetry that existed in the atomic structure ceases along with the net polarization. Table 1.1 shows the Curie-Weiss temperature for several piezoelectric materials. In most cases a material’s piezoelectric efficiency begins to decrease as it approaches its Curie-Weiss temperature, due to the relationship that the phase of spontaneous polarization is a decreasing function of temperature [15].

The net polarization in an anisotropic single crystal is naturally uniform in that it points completely in one direction. This is not generally the case with a polycrystalline material, such as a ceramic, as its individual grains have their own randomly oriented electric domain. In this
Table 1.1. Curie-Weiss Temperatures for Several Materials [2]

<table>
<thead>
<tr>
<th>Material</th>
<th>Curie-Weiss Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT-5H</td>
<td>210</td>
</tr>
<tr>
<td>Keramos Lead Metaniobate</td>
<td>400</td>
</tr>
<tr>
<td>Bismuth Titanate</td>
<td>685</td>
</tr>
<tr>
<td>Aluminum Nitride</td>
<td>1600-1800</td>
</tr>
<tr>
<td>Lithium Niobate</td>
<td>1000</td>
</tr>
</tbody>
</table>

state a material will not exhibit the piezoelectric effect, as it is essentially isotropic in nature. The electric domains of the grains must be aligned to produce a net polarization in the bulk material. This net polarization is created in a process known as poling [15].

The practice of poling involves raising the temperature of the polycrystalline material, in the range 100-200 °C, and applying a large electric field. The added thermal energy to the material allows for the displacement of the atoms in each grain when the electric field is applied. These displacements force the electric domains of individual grains to point in one common direction and generate a net polarization. The large electric field is held across the material until it cools to room temperature. Without the added thermal energy the atoms cannot displace back to their original state, and the spontaneous polarization is locked-in. The piezoelectric efficiency of the poled material is directly related to the percentage of alignment of the electric domains. The maximum value that can be reached is approximately 80-90% of the optimal single crystal value [15]. Figure 1.3 illustrates how the poling process aligns the electric domains inside the material.

Figure 1.3. (a) Polycrystalline material before poling, the arrows show the random orientation of electric domains within the material. (b) A large electric field is applied to the material at an elevated temperature and held as it cools. (c) Cooled material with resulting net polarization. Illustration from [2].
Oil bath poling is a technique that has proven effective for use with piezoelectric ceramics. A high voltage lead is placed in contact with an electrode that has been deposited onto the surface of the piezoelectric sample and the system is submerged into an oil bath with temperature between 150-200 °C. The oil surrounding the sample acts dual fold in uniformly heating the ceramic and preventing any electrical arching once the large electric field is applied. In general, the electric field is placed across the sample for a short period of time at elevated temperature, and then the sample and oil are cooled back to room temperature with the electric field still applied.

1.3 Linear Theory of Piezoelectricity

The mathematical theory of piezoelectricity is by no means trivial to employ due to the anisotropic nature of the ceramics. This means that when equal forces are applied in different directions, they do not result in the same displacements. Piezoelectric ceramics are elastic materials that can experience both normal and shear stresses and strains. This theory utilizes matrices and tensors to account for these complications.

The linear theory of piezoelectricity stems from reducing the nonlinear electroelastic equations by only considering infinitesimal deformations and fields [16]. Essentially only the effects caused by small mechanical and electrical loads are considered. Under this assumption the gradients of the displacement (\(u_i\)) and electrical potential (\(\phi\)) are infinitesimal, such that

\[
\left\| \frac{\partial u_i}{\partial x_k} \right\| \ll 1 \quad \text{and} \quad \left\| \frac{\partial u_i}{\partial \phi_k} \right\| \ll 1. \quad (1.1)
\]

With this assumption in place there are then four pairs of matrix equations that can sufficiently describe the behavior of a piezoelectric material based on mechanical and electrical responses. The choice of which to use depends on which characteristics are known and which would like to be investigated. A common choice is to express the strain, \(S_{ij}\) and the electric displacement (electric flux density), \(D_i\), as

\[
S_{ij} = s^{E}_{ijkl}T_{kl} + d_{kij}E_k \quad (1.2)
\]

\[
D_i = d_{ikl}T_{kl} + \varepsilon^{T}_{ik}E_k \quad (1.3)
\]

Where \(s^{E}_{ijkl}\) is the elastic compliance tensor, \(T_{kl}\) is the stress tensor, \(d_{kij}\) is the piezoelectric coefficient tensor, \(\varepsilon^{T}_{ik}\) is the permittivity tensor, and \(E_k\) is the electric field tensor. The superscript \(E\) on the compliance tensor denotes that the compliance was measured while exposed to a constant electric field. The superscript \(T\) on the permittivity matrix indicates a free state of zero stress in which the material was allowed to deform during the permittivity measurement [16]. This pair of piezoelectric equations is often chosen to work with because the effects of an applied stress or electric field are easily observed. The stress, \(T_{kl}\), is applied in equation 1.2, and is a result of the indirect piezoelectric effect in 1.3. Similarly, the electric field is applied in equation
1.3, and is induced by the direct piezoelectric effect in 1.2.

The fact that the piezoelectric coefficient tensor is symmetric in the \( i \) and \( j \) directions allows it to be reduced (i.e. \( d_{kl} \)) enabling the use of matrices in working with the above equations [4]. With the matrix \( d_{ki} \), the subscript \( i \) represents the direction of poling, which is always the 3-direction, and the \( k \) subscript signifies the direction of applied stress or induced strain. This physical constant represents the amount of charge generated by a force and the converse. The units of the piezoelectric coefficient are charge per unit force (\( \frac{C}{N} \)). A quick evaluation of a material’s piezoelectric ability is done by performing a \( d_{33} \) measurement, which measures how much electric charge is generated per applied force in the direction parallel to polarization.

### 1.4 Lead Zirconate Titanate

Lead zirconate titanate (PZT) is a perovskite-like piezoelectric ceramic. A perovskite crystal form is one that mimics the structure of the \( CaTiO_3 \) (perovskite) mineral. Perovskites are oxide ceramics with the general chemical formula of \( ABO_3 \), where \( O \) is oxygen, \( A \) is a cation of larger ionic radius, and \( B \) is a cation of smaller ionic radius. The crystal structure of a perovskite can be described as a cubic close-packed arrangement of the oxygen and \( A \) ions with the \( B \) ions filling in the octahedral interstitial positions [11]. The \( A \) cations make up the corners of the cubic structure and the oxygen anions are situated in the center of the six faces of the cube. Figure 1.4 is an illustration of the perovskite structure of PZT below its Curie-Weiss temperature. These crystalline structures can orient so that they join at the corners, held in place by the \( A \) ions. This arrangement can effectively increase the coupling of the net polarization of each unit cell, and thus improve the overall piezoelectric effect in the material [17].

![Figure 1.4. Perovskite crystal structure of PZT below its Curie-Weiss temperature. Adapted from [3].](image)
Jaffe first reported the ferroelectric properties of PZT in 1954. Its high piezoelectric efficiency quickly made it a favorite among the ferroelectric industries and it is now the most widely used piezo-ceramic [3]. The solid-state reaction process to form PZT powder involves mixing the proper amounts of raw \( \text{PbO} \), \( \text{ZrO}_2 \), and \( \text{TiO}_2 \) powders. The mixture is then calcinated for approximately 1-2 hours at 800-900 °C and then processed into fine powder. Two disadvantages of this method are that the grain size of the powder is often larger than desired and that contamination is practically unavoidable during ball milling. It can also be difficult to obtain the necessary components in solid, powder form so other approaches are explored. One promising procedure uses a two-stage method consisting of a sol gel solution combined with commercially available powder. This method is both effective and cost efficient and will be discussed in more depth in the coming chapters [4].

The crystalline structure’s symmetry of solid-state PZT is dependent upon the molar percentage of zirconium atoms from the compound \( \text{PbZrO}_3 \). Figure 1.5 shows the phase diagram for the PZT system. The near vertical line the separates the tetragonal and rhombohedral phases is known as the morphotropic phase boundary (MPB). This line coincides with a molar percentage of 52 percent zirconium. It is believed that the boundary is not actually a distinct line of phase change, but a point where both phases coexist. The piezoelectric coefficient has its highest values at the MPB and therefore a distinct heightening of piezoelectric efficiency. This improvement is due to the increased ease of reorienting the electric dipoles in the material with an applied electric field [4]. In other words at the MPB a higher percentage of ferroelectric domains will be aligned creating a stronger net polarization.

Figure 1.5. Phase diagram of PZT [4].
Figure 1.6. Dependence of several d constants on Zr composition near the MPB [4].

PZT is a superior ferroelectric material because of its high piezoelectric constants. Some of these properties of PZT are summarized in Table 1.2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Curie-Weiss Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>7.5 - 7.6</td>
</tr>
<tr>
<td>Curie-Weiss Temperature $T_C$ (°C)</td>
<td>180-350</td>
</tr>
<tr>
<td>Piezoelectric Coefficient $d_{31}$ ($\times 10^{-12}$ C/N)</td>
<td>-27 - -274</td>
</tr>
<tr>
<td>Piezoelectric Coefficient $d_{33}$ ($\times 10^{-12}$ C/N)</td>
<td>71 - 590</td>
</tr>
<tr>
<td>Elastic Compliance Coefficient $s_{11}^E$ ($\times 10^{-12}$ m²/N)</td>
<td>9 - 16.5</td>
</tr>
<tr>
<td>Elastic Compliance Coefficient $s_{33}^E$ ($\times 10^{-12}$ m²/N)</td>
<td>9 - 20</td>
</tr>
<tr>
<td>Mechanical Quality Factor $Q_m$</td>
<td>65 - 1200</td>
</tr>
<tr>
<td>Planar Coupling $k_P$ (%)</td>
<td>25 - 65</td>
</tr>
</tbody>
</table>

Table 1.2. Electrical and Mechanical Properties of PZT Ceramic [11].

PZT is actually rarely used in its pure form, and is instead often doped with other compounds to further enhance its piezoelectric capabilities. There are two types of dopants: donor and acceptors. Donor dopants are of a higher charge than the ions they replace and leave cation vacancies. Acceptor dopants have a lower charge than that of the replaced ions and leave oxygen vacancies. In PZT, donor doping decreases the amount of oxygen vacancies which reduces the number of domain-stabilizing defect pairs. This makes switching the direction of electric dipoles easier and therefore increases characteristics such as permittivity, dielectric losses, elastic compliance, and coupling coefficients. The addition of acceptor dopants tends to have similar affects, but to a lesser extent. For this reason donor doped PZT ceramics more efficiently convert mechanical energy into electric potential [3]. One common donor dopant is bismuth ($Bi^{3+}$), which can be effectively added via the compound bismuth titanate, $Bi_4Ti_3O_{12}$.

1.5 Bismuth Titanate

Bismuth titante ($Bi_4Ti_3O_{12}$) is a ferroelectric material of the bismuth layer perovskite family. Its structure consists of alternating oxygen octahedron and ($Bi_2O_2$)$^{2+}$ layers. This structure
is shown in Figure 1.7. The general chemical formula is \((Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}\) for this family of crystal structure, where \(m=1,2,\ldots,5\) and A and B are ions with appropriate ionic radii and number of valence electrons [11]. In the case of bismuth titanate, the A ion is bismuth (Bi), the B ion is titanium (Ti), and the value of \(m\) is 3.

There is a general consensus of worry with the use of PZT due to its content of lead. Bismuth titanate is a prime candidate for quelling these concerns due to its high piezoelectric coefficient of approximately \(200 \times 10^{-12} \frac{C}{N}\). It also is more suited for high temperature applications as its Curie-Weiss temperature is 675 °C. Below this temperature bismuth titanate exists in a ferroelectric monoclinic phase [11]. The piezoelectric coefficients of bismuth titanate are high compared to many other ceramics, but still are only about half that of PZT. This means that the amplitude of a received signal will be smaller when working with a bismuth titanate transducer for ultrasonic nondestructive evaluation applications. This concession is made when capability is needed with higher temperatures and when the volatile nature of PZT is a concern.

A composite ceramic of PZT and bismuth titanate has been developed in the recent past and currently is in use. This is one of the main materials of focus during this research. PZT doped with bismuth titanate combines the benefits of the individual materials, namely large piezoelectric coefficients and high temperature capabilities. These composites were prepared using a sol gel procedure that will be described in depth in the next chapter. A theoretical model was also developed describing the trade-off of high-temperature capability and signal amplitude through the volume fraction of PZT and bismuth titanate in the composite.

Figure 1.7. Crystal Structure of bismuth titante \((Bi_4Ti_3O_{12})\) [5].
1.6 Sintering

A piezoceramic transducer can be fabricated in a few different ways. In the solid-state reaction process the powders are formed into the desired shape through the application of thermal energy and mechanical pressure. Several methods of deposition have been explored with the sol gel process; the technique employed with this research uses a pressurized spray gun and the addition of thermal energy. Regardless of the manner used, the formed ceramic transducer must be further densified through a process known as sintering. This is done at a high temperature, which is less than the melting point of the material. The primary purpose of sintering is increasing the density of the ceramic by eliminating pores between grains in the crystal structure [4].

Prior to sintering, atoms on the surface of a grain only feel forces on one side due to neighboring atoms inside the grain. This is because the distance between grain surfaces is sufficiently large that the forces from atoms on the opposite side of the grain can be neglected. In this state the surface energy is relatively high. As the temperature rises during sintering, the grains expand with the added energy. The atoms become more energetic and their motion increases along with the contact area in between grains. After a sufficient time at high temperature there is only one interface left between two grains [11]. The large amount of atomic motion stimulates crystal bonding at the interface between neighboring particles [4]. In this state of lower surface energy, a single atom on the grain surface is heavily affected by the force-fields imposed by all the near by atoms. At this point the sintering process is complete and the ceramic is sufficiently densified [11]. Figure 1.8 illustrates the effects of sintering.

There are other noteworthy details of sintering that describe how the crystal structure is affected throughout the process. Before sintering the grains are held together by physical forces between atoms, but after sintering they are bound by the newly formed grain boundaries. Lattice distortions and internal strains that exist in the crystalline structure decrease in number as the grain size increases during sintering. These defects are eliminated through atomic diffusion in what is known as the recovery process. This occurs early in the heating of the material, and is followed by second process called recrystallization at higher temperatures. This is the stage in
which the grains grow via atomic diffusion. The growth is facilitated by the movement of grain boundaries, during which several grains can combine into one [11].

Grains grow during sintering causing their shape to change considerably [4]. It is believed that grain size is dependent on sintering temperature and time since their growth is caused by atomic diffusion. Sintering at a higher temperature for a longer amount of time will result in larger grains in the structure. Caution must be used while sintering because doing so at too high of a temperature or for too long of a time will result in adverse affects in the final product. Doing so will actually cause the density of the ceramic to decrease, which is the opposite of the desired outcome of this process. An oxidizing atmosphere (air) must be present while sintering oxide ceramics such as PZT and bismuth titanate. It is important to keep organic substances away from the ceramic as they can cause a reducing atmosphere instead and ruin the sample [11].

The grain size of the raw powder used in producing a transducer has an effect on the time it must be sintered to achieve the necessary density. Recall that the driving force behind sintering is the surface energy of the grains. For finer powders the necessary diffusion length of the atoms is smaller so that less energy is needed to promote diffusion. This shows the relationship that the sintering rate increases as the grain size of the raw powder decreases. The use of fine powder for transducer fabrication results in ceramics with a high density. A commonly used equation relating grain size, $D$, and sintering period, $t$, is given as Equation 1.4. In the case of normal grain growth $\beta = 2$ and for abnormal grain growth $\beta = 3$ [4].

$$D^{\beta} - D_0^{\beta} \propto t$$  \hspace{1cm} (1.4)

When working with PZT there are a few precautions to be aware of while sintering. When temperatures in excess of 800 °C are reached, lead(II) oxide, PbO, begins to evaporate out of the ceramic. This loss of PbO lowers the quality of the transducer, as there is a decrease in resistivity, dielectric constant, and electromechanical coupling factor. One advantage with PZT is that the chemical reaction will continue during the sintering process if it does not reach full completion in the previous steps [11]. In this research PZT is doped with bismuth titanate, which will affect the sintering process. Its main influence is lowering the necessary sintering temperature. Secondary effects can involve grain growth, both inhibiting and increasing the rate of growth. An excess of PbO or bismuth oxide ($Bi_2O_3$) can cause grain growth to decrease in PZT [4].

### 1.6.1 Sintering Techniques

There are several techniques that can be utilized in sintering piezoelectric ceramics. One of the main methods is using conventional heating with a furnace to elevate the sample temperature for an extended period of time. This technique, although effective, is very time consuming. Sintering times almost always exceed ten hours and can easily approach twenty. In some cases mechanical pressure is also applied to the ceramic to further increase the final density of the transducer, but this does not decrease the necessary sintering time. Due to the large amounts of time associated with sintering via conventional heating, more efficient methods have been developed.
The use of microwaves to sinter ceramics is one of these newer techniques. Microwaves occupy the range on the electromagnetic spectrum of wavelengths between one millimeter and one meter (frequency between 0.3 GHz and 300 GHz). An advantage of microwaves is that locations of high-energy concentration can be controlled. This arises from the fact that microwaves are both coherent and polarized. The mechanism behind conventional, conductive heating is the collisions of ions and electric charges inside of the material. With polarized microwaves, heat is mostly produced from the rotation of the electric dipoles within the material [18]. So while conventional heating methods rely on surface heating, microwaves utilize volumetric heating. During volumetric heating the sample itself actually radiates heat to the surroundings, instead of the surrounding being heated and the sample being heated from the outside into the interior. Conventional heating is achieved through the transfer of energy, whereas microwave heating is via energy conversion. This can greatly accelerate the heating rate of the sample significantly compared to conventional methods [19].

There are other added benefits of using microwaves to sinter dielectric materials. The spontaneous polarization of these materials helps to accelerate the heating process in that the rotation of the dipoles is the main source of generating heat. There are some dielectric materials that do not efficiently absorb microwave energy at low temperature, so a hybrid heating method has been developed. This process involves heating the sample sufficiently via alternative means until it reaches a temperature at which it can absorb the microwaves. This initial heating is done either by conventional means or with the use of susceptors. Susceptor materials such as silicon carbide (SiC) effectively absorb microwaves at low temperature. They are placed near the target sample and radiate heat, which raises the samples temperature until it can begin absorbing microwaves on its own. The material properties of samples sintered using microwaves have been shown to be equal to, and in some cases better, than those achieved with conventional sintering methods [6].

In previous research, namely that of Dr. Cliff Searfass, the piezo-ceramic films were sintered using microwaves. A hybrid heating process was used in which a sample was surrounded by susceptors made of silicon carbide. Samples were heated to 850 °C and held for ten minutes at this temperature. A forward power of approximately 1.8 kilowatts was necessary to achieve this temperature in about 30 minutes. The samples were then allowed to cool for about 90 minutes to ensure a safe removal. Sintering times greater than ten minutes led to an increase in delamination of the ceramic from the metal substrate. Although microwave sintering is efficient and requires less time, yet another method of sintering has been developed which further decreases sintering times.

It has been found that a propane blowtorch, although simple and crude, offers to be an effective sintering source. Previous research has shown efficient transducers have been made with using a blowtorch to sinter ceramic films. Scientifically speaking this is a less precise method in that controlling the temperature of the sample proves more difficult as it is not easily measured. The use of a blowtorch reduces sintering times to roughly seven minutes accompanied by a cooling period that takes about an hour. This again is a significant decrease in time from that with the use of microwaves. The main advantage for this technology is that it is ready for in-field use. For
example the spray-on technique can be used to deposit a transducer onto a petroleum pipeline and easily sintered with a blowtorch. The development of a blowtorch sintering method adds to the over-all field-readiness of this entire fabrication process. Throughout this research the primary sintering method used the blowtorch, and the details of this procedure will be given in Chapter 2.

1.7 Thesis Objectives and Outline

The primary objective of this research was the design and fabrication of a high temperature thick film composite piezoelectric transducer capable of low frequency operation, with a target of 250 kHz. Several benefits of sol-gel fabrication and spray-on deposition for ultrasonic transducers are already understood, but their frequency of operation is generally 5 megahertz and higher. Further development of this technology with the addition of low frequency operation increases its capabilities in the UNDE industry.

Two types of piezoelectric ceramics were involved in this research: pure phase bismuth titanate and a composite of lead zirconate titanate and bismuth titanate. The fabrication of transducers composed of both of these materials is presented in Chapter 2. During this research the large thickness of the ceramic films proved to be a formidable challenge especially regarding adhesion. Adaptations were made to the substrates which the ceramic composites were deposited along with exploring deposition onto new materials. Results showing low frequency operation are shown in Chapters 4 and 5.
Chapter 2

Sol-gel Fabrication

2.1 Introduction to the Sol-gel Procedure

The sol-gel method to create thin films of ceramics has been increasing in popularity over the past two decades. A sol is a colloidal suspension of solid ions in a solvent. It is the solution formed by mixing the proper chemical precursors for the desired ceramic. The gel is formed when this solution is hydrolyzed. As the solvent in the solution evaporates it becomes more dense and viscous forming a semi-rigid mass. Through pyrolysis the gel can form into an amorphous oxide and eventually crystallize with further heat treatment [5],[20]. The sol-gel procedure has many advantages such as short fabrication times and low temperature processing. Controlling the chemical composition of the ceramic is also enhanced. In fact, compositions can be created that traditional, solid-state procedures cannot. The cost of sol-gel fabrication is also comparatively low [21],[22].

A composite material is most often formed during sol-gel fabrication. Ceramic powders are dispersed in the sol-gel solution creating a thin-film matrix upon deposition. A helpful analogy describing this composite matrix symbolizes the sol-gel as the mortar and the ceramic particles as the bricks in a wall. When the ceramic particles are the same as the sol-gel solution, the material properties of thin-film ceramics have been found to be comparable to that of the bulk material [23]. This is important as it shows their viability for use as ultrasonic transducers.

There is growing interest in the sol-gel process from the field of ultrasonic nondestructive evaluation. Films of piezoelectric ceramics can be used as ultrasonic transducers for several applications. One area of demand is high temperature NDE, such as monitoring systems of power generation and of the petrochemical industry [22]. This thesis focuses on the use of bismuth titanate and PZT ceramic composites fabricated via a sol-gel procedure and spray-on deposition technique. There are several methods for the sol-gel fabrication of these piezo-ceramics, with some of the best-documented by Yi and Sayer, Kobayashi, and Searfass [21, 24, 6]. The procedures presented later in this chapter follows the work of Dr. Searfass [6], whose was originally based
Numerous means of depositions have been developed to go along with sol-gel fabricated piezo-ceramics. The method used in this research is one of the newest, using a spray gun powered simply with air pressure. Other techniques include spin- and dip-deposition along with simple painting [23]. Kobayashi first implemented the spray-on technique in search of increasing deposition efficiency. Other methods such as spin- and dip-coating are less capable in covering larger surface areas. The spray-on technique can easily coat large samples as well as irregular geometries and curved surfaces. This last aspect is critical in that it is extremely difficult to couple a traditional commercial transducer to any curved surface. A sol-gel fabricated transducer deposited via a spray-on technique eliminates the need for any additional coupling as the transducer is directly, mechanically coupled to the substrate. Traditional transducers must be coupled with a gel-like couplant and/or pressure to increase the transfer of energy. These ultrasonic couplants are generally water-based and cannot sustain high temperature environments. The elimination for additional coupling and the high temperature resistivity of these composites makes sol-gel transducers ideal for harsh environment applications [24].

Strong adhesion of sol-gel transducers is another component that has led to their success. During the spray-on procedure multiple layers are deposited until the desired thickness of the transducer is met. The individual layers strongly adhere to both metallic substrates, especially those with an oxide layer, and the oxide surface of the ceramic itself. On an oxide surface there are hydroxyl groups through which these bonds are formed. The macroclusters that form in the sol-gel during hydrolyzation react with these surface hydroxyl groups forming strong bonds. The same hydroxyl groups exist on the surface of deposited layers of ceramic, to which successive layers then adhere. The overall result is strong bonds between the substrate and ceramic as well as between individual layers [23]. Oddly enough the main difficulty experienced in this research was the ceramic layers delaminating from the stainless steel substrates. These challenges will be addressed in a later chapter as well as the steps taken to address them.

2.2 Fabrication Process

The following chapter outlines the sol-gel fabrication procedure used in creating the piezoelectric transducers. This research dealt with two different ceramic composites: bismuth titanate/bismuth titanate and PZT/bismuth titanate. The naming of the composites is ordered so that the first chemical compound is the sol-gel and the second is the added ceramic powder. These procedures, to be outlined in the following sections, are similar with only the chemical precursors and stoichiometric ratios differing. For this reason the mixing of the precursors will be detailed for each composite, but the rest of the fabrication process will be explained as one since it is nearly identical for both.
2.2.1 Sample Preparation

Before a sample is ready for deposition there are a few steps that must be taken to increase adhesion between the surface of the substrate and the ceramic. First the surface is roughened using sand paper or sand blasting to create dangling bonds for the ceramic to “grab onto.” The samples are then cleaned using an industrial cleaner and water. Cleanliness cannot be stressed enough throughout this entire procedure as any contamination can jeopardize the integrity of a transducer. After being cleaned, the surface can be treated with both acetone and isopropyl alcohol. Acetone creates an oxide layer, which improves bonding between the metal substrate and the ceramic. The isopropyl alcohol is used afterwards to remove any residual film that may be left on the substrate, which could have a negative effect on the transducers mechanical integrity. Following all of these cleaning techniques the substrate is placed on a hot plate at 400 °C for 20 to 30 minutes. This burn out ensures that any remaining organic compounds are evaporated off the substrates surface. Once the samples are cooled, they are ready for spray-on deposition.

2.2.2 Bismuth Titanate/Bismuth Titanate

The chemical precursors in this sol-gel procedure are bismuth nitrate pentahydrate $\text{(Bi(NO}_3\text{)}\text{_3 \cdot 5H}_2\text{O)}$ and titanium isopropoxide $\text{(Ti[OCH(CH}_3\text{)}\text{_2]}\text{_4)}$. Bismuth nitrate pentahydrate is dissolved in a solvent of glacial acetic acid $\text{(CH}_3\text{COOH)}$ at 80 °C with constant stirring. A thermocouple is used to mix during this step so that the temperature can be monitored. Once completely mixed the solution is allowed to cool to 30-34 °C. At this point titanium isopropoxide is added in the appropriate stoichiometric amount. The solution is rigorously mixed followed by the addition of distilled water in a ratio of solution to water of 2:1. Hydrolyzing the solution helps to stabilize it. The final reaction of the addition of titanium isopropoxide is noticeably exothermic. The mixed solution is then allowed to sit for one hour to allow the full reaction to occur.
When the solution is ready to be deposited, bismuth titanate ceramic powder is mixed with the solution. A mixture of 2 grams of powder with 1.2 milliliters of solution was found to be optimal in previous work. The solution and powder are combined with an ultrasonic horn to obtain a uniform mixture on the molecular level. Obtaining this level of mixture is absolutely critical because powder agglomerates can create sites of high stress levels in the deposited film. This can lead to the cracking or delamination of the ceramic composite during sintering. Once thoroughly mixed, the solution is then ready to be sprayed on to the target substrates. In general, cylindrical samples are laid on their side during spraying with no more than three samples at a time. This ensures that each sample receives a substantial and uniform layer during each round of deposition. The solution is poured into the gravity feed cup and moderate air pressure is used to spray the substrates. A photograph of the spray gun used in this research is shown in Figure 2.1. After being sprayed, the samples are placed on a hot plate at 400 °C for ten minutes, during which the solvent in the solution evaporates leaving behind the desired amorphous oxide. The samples are then allowed to cool and this procedure is repeated until the chosen thickness is reached. This entire procedure is summarized in Figure 2.2.
Figure 2.2. General fabrication procedure for sol-gel spray-on $\text{Bi}_4\text{Ti}_3\text{O}_{12} / \text{Bi}_4\text{Ti}_3\text{O}_{12}$ transducers.
2.2.3 PZT/Bismuth Titanate

The chemical precursors for creating a PZT sol-gel are lead acetate \((\text{Pb}(\text{CH}_3\text{CO}_2)\cdot 3\text{H}_2\text{O})\), zirconium propoxide \((\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4)\), and titanium isopropoxide \((\text{Ti}[\text{OCH}(\text{CH}_3)]_2)_4\). These chemicals are used to create two solutions that are combined to form the PZT solution. The first is formed from dissolving lead acetate in acetic acid \((\text{CH}_3\text{COOH})\) at 100 °C. The solution is then left on a hot plate at 100 °C for approximately 20 minutes, during which it should slightly boil. The second precursor solution is prepared by combining zirconium propoxide and titanium isopropoxide in the correct stoichiometric amounts. When the first solution is cooled to room temperature, the two are mixed into one. Thorough stirring is critical during this step to ensure the completion of the chemical reaction, which is also exothermic in this process. Distilled water is then added to stabilize the solution. The completed solution is then allowed to sit for about 45 minutes allowing for the completion of the overall reaction.

![Figure 2.3. Ultrasonic horn used to mix the sol-gel material in this procedure.](image)

When the solution is ready to be deposited, the PZT solution is doped with bismuth titanate powder. This formation of a composite ceramic combines the favorable characteristics of each material, namely the superlative signal strength of PZT and the high temperature capabilities of bismuth titanate. The solution and powder are mixed using an ultrasonic horn as discussed earlier with pure phase bismuth titanate. Figure 2.3 shows this ultrasonic horn. This horn is driven by numerous PZT-5H disks connected in the proper orientation and the generated energy
is focused using a titanium waveguide. The repeated spraying process is also the same as earlier. This general procedure for $PZT/Bi_4Ti_3O_{12}$ is summarized in Figure 2.4.

**Figure 2.4.** Generalized fabrication procedure for sol-gel spray-on $PZT/Bi_4Ti_3O_{12}$ transducers.
It should be noted that the mixing of the chemical precursors is not a trivial step in the fabrication process. In order to create high quality transducers the mixing must be done accurately with attention paid to the details of each step. A single mistake in the process can compromise the entire mixture and generally results in the need to start over. The end result for both of the materials above is a clear solution without any floating particulates. The main offender to lowering a solution’s quality is titanium isopropoxide as it is highly volatile in nature. Its sensitivity to moisture requires it be handled in a dry environment as it is even reactive with the water vapor in the air. The electronegativity of the titanium atom is what causes this sensitivity to moisture. Titanium isopropoxide can be stabilized using acetic acid. A mixture in a 4:1 ratio of acetic acid to titanium isopropoxide allows it to be kept in larger quantities and safely exposed to the air [22]. It is imperative that solutions remain stable with a constant viscosity during use. An altering viscosity could result in varying densities among deposited layers that could also decrease a transducers overall quality. Investigations continue to search for new ways of making sol-gel fabrication more efficient, especially pertaining to large-scale processing of transducers.

2.2.4 Sintering

The primary method of sintering during this research used the propane blowtorch. It was chosen based on efficiency and ease of accessibility. The sintering times are significantly shorter than the other available methods and samples could be quickly sintered after fabrication instead of needing to be transported to the appropriate facilities. Also this technique is very promising for in-field use and needs to be further explored and developed. The sintering process is essentially the same for both composites, $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ and $PZT/Bi_4Ti_3O_{12}$. The only difference is that the chemical composition of PZT requires that those samples be sintered twice.

Caution must be used while using the blowtorch to sinter, as incorrect technique can lead to poor transducer quality and even destroy them all together. The metal substrate must be sufficiently heated before the ceramic film can be exposed directly to the flame. It has been seen that if the transducer itself is heated too quickly the layers will delaminate. This is thought to be caused by the introduction of hydrocarbons during the burning of the blowtorch’s fuel. These hydrocarbons react with the bonds between the oxide layers and the substrate, effectively ruining them, and leading to delamination of the ceramic.

The samples to be sintered are first placed on a hot plate at 400 °C for about 20 minutes. This is done simply to raise the temperature of the metallic substrate making it easier to reach the desired temperature with the blowtorch. The substrates are laid on their side while being sintered. An effective way to monitor the temperature of the ceramic is to observe how quickly the blackened, charred appearance disappears after the flame is removed from the ceramic. At first the flame is introduced to the ceramic very quickly, less than second, causing the surface to become blackened. The flame is then applied only to the metal substrate. As the substrate heats the blackened appearance of the ceramic will disappear and the natural white color returns. The ceramic can then again be tested with the flame to see how long the black color remains.
It generally takes about seven minutes to sufficiently heat a stainless steel substrate one inch in length with one-inch diameter. The steel has a noticeable orange glow and is approximately 800 °C. At this temperature the blackened appearance will disappear as soon as the flame is removed from the sample. The flame can then be directly applied to the ceramic for 30-45 seconds to complete the sintering process. The ceramic turns a yellowish-brown color from being sintered.

2.2.5 Electrodes and Poling

Before a sample can be poled an electrode must be applied in order to make a contact for the application of the high voltage. The general choice for electrodes is high purity silver paint because of its strong conductivity and its cost efficiency. Silver is not the ideal choice because it is chemically aggressive and can actually eat-through the ceramic layers. In other words the atomic radii of silver ions are small enough that they can penetrate into the ceramic resulting in the ceramic becoming conductive, effectively ruining the transducer. Platinum paint solves this problem and can be applied directly to the ceramic, but it is extremely expensive. The issues accompanied with the use of silver paint are addressed with a thin base-layer of gold. A sputter coater is used to deposit 1500 angstroms of gold onto the ceramic. This layer of gold is thick enough to block the invasive silver ions from penetrating into the ceramic layers. The silver paint is then added on top of this layer of gold to complete the electrode.

In this research an oil bath poling unit was utilized. The samples are poled before the addition of the silver paint, using just the deposited gold electrode. A sample is placed into the poling cage in which the metal bottom is grounded and therefore so is the bottom of the metallic substrate. A high voltage lead is contacted to the gold electrode and the whole system is immersed into heated silicone oil at 150 °C. A high electric field is then placed across the sample, aligning the internal dipoles of the ceramic. In previous work with thinner films, dielectric breakdown due to large spikes in current was a concern. In this research the ceramic layers were substantially
thicker making this type of breakdown less of a concern. Samples were generally poled with approximately 3.0 kilovolts for 20 minutes. This is triple the voltage and double the time applied compared to that previously used with the thinner films. After twenty minutes the oil heater is turned off and the sample is allowed to cool for a period of time with the high voltage still applied.

![Figure 2.6. Oil Bath Poling Unit.](image)

Following the poling in the oil bath, the samples must be cleaned up to remove any residual oil. The samples are generally placed on a hot plate at 400 °C for 20-30 minutes to burn out the oil left in the ceramic. Precaution must be taken in this step because silicone oil evaporates formaldehyde, which is harmful if inhaled. For this reason the samples must be placed inside of a fume hood during the burn out. After this, the electrode is finished by the addition of silver paint as discussed above. The transducers are then ready to be tested experimentally.
Previous Work

Time needs to be taken to acknowledge all of the previous research that has gone into the development of this technology. The main predecessor in this field is Dr. Cliff Searfass, with contributions from Christiane Pheil B.S. and Kyle Sinding. Their research focused on optimizing the fabrication process to produce the highest quality transducers. The ratio of solution to powder used in this research was set by their earlier work. Other ratios were tested and found to result in lower quality transducers. The ceramic films appeared to be less uniform in thickness and therefore density, as well as frequently exhibiting poor adhesion. Some experimenting with the solution to powder ratio in this research confirmed that straying from the previously set numbers results in lesser transducers.

Several characteristics of the thick film piezo-ceramic transducers have also previously been examined. To avoid repetition not all of the same characteristics will be examined in this work, but they will be mentioned in this section. Along with those highlighted below, some of these include permittivity, conductivity, elastic modulus and impedance.

The density of the ceramics films is easily obtained through measurements of mass and thickness. Substrates are weighed with an electronic scale before and after deposition with the difference equal to the mass of the ceramic. The thickness can then be measured using an Olympus optical microscope. A small area of the film is removed to reveal the bare metal substrate and the microscope is focused on this spot to create the zero point. The microscope is then defocused to the top of the ceramic and the difference in height is recorded. The accuracy of these measurements is by no means perfect so this procedure is repeated several times and an average thickness found. Once the thickness and mass are known a simple calculation produces the density of the composite ceramic.

A scanning electron microscope (SEM) was used to image the microstructure of the ceramic films. These images were helpful in optimizing the solution to powder ratio based on what treatment resulted in the most uniform microstructure. The SEM images were also used to examine the viability of sintering with microwaves and the blowtorch. Some of the images are
shown in Figure 3.1 below. It was discovered that the differences were small in the microstructure of samples sintered with the two methods. Samples sintered with microwaves had a somewhat finer and more uniform microstructure than those sintered with the blowtorch. Despite this fact, these images qualified the somewhat crude sintering technique as it produced comparable results in microstructure.

![Figure 3.1. Comparison of samples sintered using microwaves, (a) and (b), and samples sintered with a blowtorch, (c) and (d) [6].](image)

The main investigation into the piezo-ceramic thick films was their functionality as an ultrasonic transducer. Samples were tested in pulse-echo mode acting as longitudinal transducers using a voltage tone burst of excitation. The signal amplitude of back wall reflections was measured to test the efficiency of the fabricated transducers. The first set of experiments was conducted at room temperature. Comparisons were made between different solution to powder ratios as well as the two sintering techniques. Results again reflected blowtorch sintering produced efficient transducers with signal amplitude similar to samples sintered using microwaves. An example of these measurements is shown below in Figure 3.2.
Perhaps the most interesting results from this previous work involved the operation of the fabricated transducers at high temperatures. This was the main investigation of this research once the viability of the transducers were proven. The operation of pure phase bismuth titanate transducers at high temperature was as expected. Bismuth titanate has a high Curie-Weiss temperature ($T_C = 685^\circ C$) allowing these transducer to maintain signal amplitude at high temperatures. Signal amplitude was observed to vary minimally up to the Curie point, where the signal disappeared. Figure 3.3 shows the collected data.

Figure 3.2. PZT/Bi$_4$Ti$_3$O$_{12}$ transducer operating in pulse-echo mode [7].

Figure 3.3. Bi$_4$Ti$_3$O$_{12}$/Bi$_4$Ti$_3$O$_{12}$ transducer’s first echo signal amplitude over a range of temperatures [7].

PZT has a relatively low Curie-Weiss temperature ($T_C = 210^\circ C$), which negates its use in high temperature applications. PZT transducers have signal strength orders of magnitude higher than
that of other materials, making them appealing for use in UNDE. $PZT/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ composite transducers are fabricated with the purpose of combining the strong signal strength of PZT with the high temperature tolerance of bismuth titanate. The results found with these transducers was both surprising and encouraging. The transducers maintained an efficient signal amplitude at temperatures in excess of 650 °C. In fact the signal strength did not show signs of significant decrease until approximately 550 °C. Figure 3.4 shows these collected data. These results are superior to any others previously reported, with the highest operational temperature being 450 °C [25]. The capabilities of these transducers is an immense advantage for use in UNDE.

![Figure 3.4](image-url)  

**Figure 3.4.** $PZT/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ transducer’s first echo signal amplitude over a range of temperatures [7].
Chapter 4

Low Frequency Ultrasonic Transducers

4.1 Thickness Dependence

An ultrasonic transducer’s center frequency is directly dependent on the thickness of its piezoelectric element. The element vibrates at a wavelength that is twice its thickness. For this reason general practice is to cut the piezoelectric elements to a thickness that is one-half of the desired wavelength. The relationship between wavelength and frequency is given in the equation below.

\[ \lambda = \frac{v}{f} \] (4.1)

In Equation 4.1, \( \lambda \) is the wavelength, \( f \) is the frequency, and \( v \) is the speed of sound in the given medium. It then follows that the relationship between center frequency and thickness is given by Equation 4.2.

\[ f = \frac{v}{2d} \] (4.2)

In Equation 4.2, \( f \) is the center frequency, \( v \) is the speed of sound through a given medium, and \( d \) is the thickness of the piezoelectric element. From this relation we see that thinner transducers operate at higher frequencies, and thicker transducers at lower frequencies. Choosing the appropriate thickness is one of the most integral parts of transducer fabrication.

Previous transducers fabricated via this sol-gel spray-on method were relatively thin, despite being called “thick-films.” It has been observed that each spray of material applied adds approximately 75 microns. Prior samples generally consisted of a maximum of five sprays yielding a total thickness of 375 microns or 0.375 millimeters. These transducers had a center frequency around 5 MHz. The goal of this research is to fabricate a transducer that operates at frequencies in the low kilohertz range, down to 250 kHz. The thickness of the fabricated transducers must
be increased significantly in order to reach these low frequencies. According to the formulae presented above in order for a transducer to have a center frequency of 250 kHz, the piezoelectric elements needs to be approximately 9 millimeters thick. This takes thick-films to an all-new level. The broadband nature of these transducers will hopefully reduce the necessary thickness needed to achieve operation at low frequencies. This means that the center frequency of the transducer does not need to be 250 kHz, it only needs to be able to generate and receive sufficiently strong signals at this frequency. Regardless, a thickness of a few millimeters will be needed for these transducers to operate at such low frequencies. This is a new challenge for this sol-gel spray-on fabrication technique.

### 4.2 Initial Testing

To begin the investigation into these truly thick-film transducers the number of sprays was simply doubled. Ten sprays of pure phase bismuth titanate were deposited onto two stainless steel cylinders one inch in length with half-inch diameter. The ceramic films were sintered using the blowtorch technique and then poled in an oil bath poling unit. The transducers showed decent piezoelectric properties with measured values of $d_{33} = 7.5 \frac{pC}{N}$ and $6.5 \frac{pC}{N}$ and capacitence of 33.6 $pF$ and 32.0 $pF$. The thickness of these transducers was measured to be approximately 0.90 millimeters. Thickness measurements were conducted using a scanning acoustic microscope (SAM). Note that this thickness is merely one-tenth of the calculated value given earlier.

These samples were then tested as longitudinal transducers excited with a voltage tone burst. Selections of the collected waveforms are shown below. A frequency sweep revealed that the center frequency was around 2 MHz, a considerable drop from those previous fabricated. The peak-to-peak voltage at 2.25 MHz was measured to be approximately 190 millivolts, and approximately 210 millivolts at 1.80 MHz. Waveforms captured at both of these frequencies are shown in Figures 4.1 and 4.2. These transducers also showed significant signal amplitude at frequencies around 1 MHz. This was an encouraging sign in that by just doubling the thickness of the ceramic film a significant drop in operational frequency was observed. It was decided to continue increasing the thickness in a similar manner, going to 15 and then 20 sprays. Unfortunately this plan was halted by adhesion difficulties between the ceramic film and steel substrate.
Figure 4.1. Ten spray $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ transducer pulsed at 2.25 MHz.
4.3 Adhesion Difficulties and Solutions

As the thickness of the ceramic films increased adhesion problems developed. The films would “pop-off” from the stainless steel substrates, most commonly after the sintering process. In most cases the ceramic would delaminate in one piece as a wafer. A crack would appear around the edge of the cylinder and grow around its circumference until reaching the critical point of failure by delamination. The ceramic layer would then slide off without being coerced. Usually, some material residue was left on the substrates surface showing signs that there was some remaining bonding. Figure 4.3 below shows two samples in which this delamination occurred.

Figure 4.3. Two examples of $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ which experienced total delamination post-sintering.
Other samples cracked during sintering with the blowtorch in an almost violent fashion in which there was an audible “cracking” and the ceramic split into several pieces. Figure 4.4 below shows a $PZT/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ sample in which this occurred. Notice the large amount of material remaining bonded to the surface of the stainless steel substrate. This evidence suggests that there are bonds forming between the substrate and the ceramic that are reasonably strong. There must be other forces that come into play when working with such thick layers of ceramic material.

![Figure 4.4. A $PZT/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ which experienced cracking delamination during sintering.](image)

### 4.4 Thermal Expansion

A careful review of the prescribed fabrication procedure was conducted, ensuring the same steps were being taken presently as in the past. This method has produced several highly operational transducers in the past with the only changing variable being the thickness of the ceramic film. Adhesion difficulties such as these seem to point toward a mismatch in thermal expansion coefficients causing the delamination of the ceramic from the steel substrate. In general metals with high melting points, such as stainless steel, and strongly bonded ceramics both have low thermal expansion coefficients. Despite this fact the difference may be significant enough, especially at the high temperatures reached during sintering, to result in delamination.

The dimensions of most substances become deformed when they are heated at a constant pressure. Most cases find the dimensions increasing along with temperature, but some materials contract upon heating. There are even some materials that will expand in one direction and contract in another. The term *thermal expansion* is used in reference to all changes of dimension with increasing temperature. For crystalline structures this concept is generalized further to *internal thermal expansion*. This is the description of thermal changes within the crystal structure that describes the arrangement of atoms within the cell [26].
It is difficult to completely understand thermal expansion at the atomic level so a simplified model of the thermodynamic description is offered. Recall that temperature is the measure of total internal kinetic energy of a system. That is a measurement of the energy of the atoms within a system. In a solid, temperature is a measure of the vibrational energy of the atoms in the crystal structure. As the temperature increases more energy enters the crystal structure causing the atoms to vibrate at greater amplitudes. As the vibrational amplitude increases the average distance between atoms becomes greater. Eventually with the addition of enough energy, atoms will vibrate at large enough amplitudes to overcome the restraining bonds holding the solid together. At this point the solid melts. The coefficient of thermal expansion is inversely proportional to the bond strength of a material, and therefore to the melting point of the material [27]. This description only deals with the general longitudinal vibrations of atoms within the crystal structure. There is also a transverse motion of the atoms that must be taken into consideration. This motion actually brings atoms toward each other decreasing the average distance between them, therefore having the opposite effect as the longitudinal vibrations. In most cases one of these mechanisms will dominate and dictate whether the material will expand or contract due to increasing temperature [26].

The theory which describes thermal expansion can be represented in many different forms, depending on the material of interest. Both of the theories briefly presented below are generalized approximations for macroscopically homogeneous materials to the first order in strain. These strain measurements are generally assumed to be taken under conditions of zero stress and constant (atmospheric) pressure. Linear strain is defined with respect to some reference length, most commonly that at room temperature. The linear strain can then be represented as in Equation 4.3, where \( l_0 \) is the reference length and \( \delta l = l - l_0 \).

\[
\varepsilon = \int_{l_0}^{l} \frac{dl}{l} = \ln \left( \frac{l}{l_0} \right) = \ln \left[ 1 + \frac{\delta l}{l_0} \right]
\] (4.3)

Taking the derivative with respect to temperature of this expression yields the linear thermal expansion coefficient \( \alpha \). The subscript \( P \) signifies the partial derivative is evaluated with pressure held constant.

\[
\alpha = \left( \frac{\partial \ln l}{\partial T} \right)_P = \left( \frac{1}{l} \right) \left( \frac{\partial l}{\partial T} \right)_P
\] (4.4)

This mathematical model can be adjusted to look at volume strains instead of linear strains. The volumetric strain is measured compared to some reference volume, \( V_0 \), again generally one at room temperature. This strain is most commonly defined as in Equation 4.5, where \( \delta V = V - V_0 \). Notice the second order term included in this expression for volumetric strain.

\[
\ln \left( \frac{V}{V_0} \right) = \ln \left[ 1 + \frac{\delta V}{V_0} \right] - \frac{1}{2} \left( \frac{\delta V}{V_0} \right)^2 + \ldots
\] (4.5)

The coefficient of thermal expansion is obtained in the same manner as the linear, by taking a temperature derivative while holding pressure fixed. Equation 4.6 is the familiar bulk thermal...
expansion coefficient, $\beta$ [26].

$$\beta = \left( \frac{\partial \ln V}{\partial T} \right)_p = \left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_p$$  \hspace{1cm} (4.6)

### 4.5 Attempts of Solving Adhesion Problem

The main concern with the mismatch of thermal expansion coefficients is the ceramic layer and steel substrate expanding/contracting at different rates as the sample is heated/cooled. The most prominent step for this to occur in our fabrication process is during sintering with temperatures of 850 °C being reached. The blowtorch technique that is employed has been shown to work previously, but is still admittedly crude. The exact temperature of the flame is not known during the process so neither is the temperature of the sample. Without having these measurements during sintering, it is more of a practiced skill that is employed. The individual sintering must monitor the time a sample is exposed to the flame along with knowing the signs that signify that the sintering process is nearing completion.

The two major worries of sintering with the blowtorch are unknowingly over-heating the samples and having too great of a heating rate. Cracking can occur due to volume changes when there is a sudden change in temperature. This \textit{thermal shock} is especially apparent in brittle materials such as ceramics. The formation of these cracks is contributed to by a combination of (a) expansion or contraction constraints, (b) temperature gradients due to the thermal conductivity, and (c) phase transformations [28]. With the intense heat of the blowtorch’s flame increasing the temperature of the sample at a rapid rate the ceramic deposition layer becomes susceptible to cracking. With such a large temperature gradient it is also easy to over-heat the sample past the target temperature. Figures 4.5 and 4.6 show how the thermal expansion of bismuth titanate and PZT as temperatures increase. Notice the large increase near 800 °C, showing that there is a significant change in material properties at the temperatures we are working at. Even though Figure 4.5 compares bismuth titanate to platinum, it still serves as a comparison between the ceramic and a metallic substrate.

To address these questions pertaining to the use of the blowtorch, samples were sintered using microwaves as in previous work. This method of sintering offers a controlled method in which the temperature of the sample is constantly monitored. The heating of the ceramic is also more gradual with microwaves compared to the intense heat of the blowtorch. The samples used for this test were prepared in the same manner as those previously involved in this research. The temperature of the samples was gradually increased to 850 °C and then held at this temperature for ten minutes. After the samples cooled it was found that they suffered the same sort of delamination of those prepared with the blowtorch. A crack grew around the circumference of the cylinder, near the rim, and the ceramic layer delaminated in one piece. With the results being the same from both sintering techniques, the validity of the blowtorch method is preserved and its use will be continued in this research.
4.5.1 Matching Layer

The next investigation to resolve the adhesion problems was to place a matching layer in between the steel substrate and ceramic. This matching layer would have a thermal expansion coefficient in between that of stainless steel and the chosen ceramic composite. It was decided that viable materials for a matching layer were tin, copper, or a combination of the two. Depositing a layer of tin onto the substrate was attempted using both solder and fine powder with the addition of heat. Neither source of tin could produce a sufficient and uniform matching layer. This method was then abandoned for another involving mixing the metal powder into our prepared solution with hopes of then using the spray gun to apply it to a substrate in a uniform layer. A bismuth titanate solution was prepared and then mixed with tin powder. This mixture resulted in an unknown chemical reaction that was extremely exothermic in nature. The mixture then
solidified somewhat into a thick paste, which could not be sprayed as hoped. It is also unknown if the products of this chemical reaction were still bismuth titanate and tin. This matching layer technique was then also abandoned. This is not to say that creating a matching layer is not a viable solution, it just requires more development.

4.5.2 Flat-Bottom Well Samples

When dealing with thicker films of ceramic, there is more material expanding during heating. It is possible that the shear forces acting within the microstructure of the ceramic then become strong enough to break the bonds at the interface between the surface of the substrate and the ceramic. With these considerations new designs were developed pertaining to the shaping of the stainless steel substrates. The main focus of these designs was to prevent the expansion and contraction of the substrate during sintering from compromising adhesion. The first of these involved drilling a flat-bottom well into cylinders with half-inch diameter that were one inch in length. The depth of the wells was 5 millimeters with a wall thickness of approximately 1 millimeter. $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ was deposited with the same technique as used before, filling up the well more with each successive spray. The samples were sintered after every round of spraying, with each round consisting of 8-10 individual sprays. The ceramic remained intact after sintering with no signs of delamination from the inside of the well. After about 65 sprays the wells were sufficiently full of material in order to test. The wells contained roughly 4 millimeters of the bismuth titanate composite. One noticeable issue with this design was that the wells did not fill up uniformly due to the well walls blocking the path of the sprayed material. This caused the middle to build up faster and the transducer took-on a sort of rounded dome-shape. Figure 4.7 shows one of the fabricated flat-bottom well samples.

![Figure 4.7. Flat-bottom well designed $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ transducer](image)

A gold electrode was sputter coated onto the $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ and the samples were
poled using an oil bath poling unit. Due to the added thickness of these samples poling voltage and duration had to be increased in order to align the internal electric domains. Initially the voltage was increased only slightly but the time it was applied across the sample was nearly tripled. The time was chosen to be increased more significantly due to concerns of dielectric breakdown occurring at higher voltage levels. After poling the piezoelectric efficiency of the samples was evaluated. Measurements yielded a $d_{33}$ of $1 - 2 \frac{pC}{N}$ and a capacitance of less than $1 pf$, showing effectively zero piezoelectric efficiency.

This lack of piezoelectric properties with these flat-bottom well samples was attributed to the $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ not being efficiently poled. It is believed that the metal walls of the well induced a secondary electric field across the sample in a direction perpendicular to the desired field. The summation of these electric fields is believed to be parabolic in shape following the well of the sample. An electric field with this direction will not result in aligning the ferroelectric domains within the $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ and it will not be an effective piezoelectric.

An attempt was then made to improve how efficiently these flat-bottom well samples were poled. The size of the electrode on the samples was minimized to put as much insulting ceramic between the conductive walls of the well and the remaining electrode. This was done with hopes of minimizing the strength and effect of the secondary electric field that is hindering the alignment of the ferroelectric domains within the material. The samples were re-poled with almost triple the voltage as the first trial to ensure that the problem was not too low of an applied electric field with such substantial thickness. Once again the samples showed practically zero piezoelectric characteristics, with no significant change in $d_{33}$ or capacitance measurements. The flat-bottom well design worked to solve the adhesion problem, but in turn introduced a new difficulty in the poling process.

It has been determined that having a well to fill-in with composite material eliminates the adhesion problems, but too deep of a well has adverse affects on the poling process. There were no signs of the ceramic delaminating from the bottom or the sides of the well after being sintered, a layer of $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ roughly four millimeters thick was successfully fabricated via this sol-gel spray-on method. The issue though was that this thick layer was surrounded by the metallic well wall, which interfered with the electric field for poling. The flat-bottom well design needed to be adjusted in order to keep its beneficial attributes while addressing the issues preventing the fabrication of an operational transducer.

### 4.6 Shallow Well Samples

The crucial modification that needed to be made to the flat-bottom well design was to eliminate the prominent sides of the well in order to alleviate the poling difficulties. It was decided to machine a more shallow well in the stainless steel substrates. A larger diameter steel cylinder of one-inch was also chosen in order to increase the amount of insulating ceramic between the electrode and metallic well wall. A two millimeter flat-bottom well was machined into a number of these cylinders. Another change made was tapering the sides of well to allow for a more
uniform fill during spray deposition. This design will eliminate the rounded dome-shape that developed with the previous flat-bottom well samples. Figure 4.8 illustrates this shallow well design.

![Diagram](image)

**Figure 4.8.** Illustration of the shallow well design substrate.

Several samples were prepared using both $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{PZT}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Two $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ samples were fabricated consisting of 45 sprays, with the ceramic being sintered after every 9 sprays. Two $\text{PZT}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ samples were also fabricated, one consisting of 8 sprays and the other 11 sprays. Just as with the other flat-bottom well samples no adhesion problems were observed. Both of these samples were sintered at the halfway point of spraying and again upon completion. Gold electrodes were sputter coated onto the samples and they were poled using the oil bath poling unit. Increased levels of voltage were applied over the samples for longer periods of time to again compensate for their thickness. All of the samples poled exhibited strong piezoelectric properties proving that the shallow well design can produce efficient transducers. Figures 4.9 and 4.10 show one of each of the composite shallow well samples.

![Images](image)

**Figure 4.9.** Images of the fabricated $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ shallow well sample.
Both of the figures above includes a close-up in order to show the thickness of the ceramic film on the sample. The $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ transducer consisting of 45 sprays had a measured thickness of around 1.0 millimeter. The $\text{PZT}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ transducer consisting of 8 sprays had a measured thickness of approximately 0.75 millimeters, and the $\text{PZT}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ consisting of 11 sprays was roughly 0.45 millimeters. This discrepancy in thickness and number of sprays had to do with the density of the spray-on material. The solution used to fabricate the 11-spray sample was allowed to “gel” for two days on the hotplate at 70 °C. This technique allows some of the solvent to evaporate out of the solution prior to its use. This increases the density of the solution, but to maintain the consistency of the mixture for spraying, a smaller powder to solution ratio was used. This reduction in the amount of powder to the same amount of solution, despite it being “gelled,” decreases the overall density of the composite material. This decrease in density causes the thickness of each applied layer to also decrease. Table 4.1 below summarizes the measured properties of the three best transducers.

<table>
<thead>
<tr>
<th>Material (# of sprays)</th>
<th>$d_{33}(\text{pC/N})$</th>
<th>Capacitance (pf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Bi}_4\text{Ti}<em>3\text{O}</em>{12}/\text{Bi}_4\text{Ti}<em>3\text{O}</em>{12}$ (45 sprays)</td>
<td>11</td>
<td>40</td>
</tr>
<tr>
<td>$\text{PZT}/\text{Bi}_4\text{Ti}<em>3\text{O}</em>{12}$ (8 sprays)</td>
<td>6</td>
<td>39</td>
</tr>
<tr>
<td>$\text{PZT}/\text{Bi}_4\text{Ti}<em>3\text{O}</em>{12}$ (11 sprays)</td>
<td>15</td>
<td>130</td>
</tr>
</tbody>
</table>

Table 4.1. Measured piezoelectric properties of fabricated shallow well transducers.

These samples were then tested as longitudinal transducers operating in pulse-echo mode. The transducers were excited with a voltage tone burst and the signal amplitude of the first back wall reflection was measured over a frequency sweep of 1-5 MHz. It was discovered that each of the transducers had a center frequency around 2.75 MHz. The signals produced with these transducers had very high signal-to-noise ratios as well as signal amplitudes. All of these characteristics showed that these shallow well transducers were far superior to any others created thus far in this research.

As expected the $\text{PZT}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ transducers had greater signal amplitude along with more
broadband operation. The $PZT/Bi_4Ti_3O_{12}$ transducer’s signal amplitude was in fact greater all throughout the frequency sweep than that of the $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ at its center frequency. This makes the $PZT/Bi_4Ti_3O_{12}$ composite the more promising choice to achieve operation at the desired low frequency. Figure 4.11 shows the captured waveform at center frequency for the best transducer of each composite along with a plot of signal amplitude of the first back wall reflection over a frequency sweep between 1-5 MHz.

Figure 4.11. The top two images are the waveform at center frequency and a plot of signal amplitude of the first back wall reflection as a function of frequency for the $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ transducer. The bottom two are the same for the $PZT/Bi_4Ti_3O_{12}$ transducer.
4.6.1 Low Frequency Testing of the Shallow Well Transducers

The most efficient PZT/Bi$_4$Ti$_3$O$_{12}$ transducer was chosen for low frequency testing. This transducer not only exhibited the highest signal amplitude, but also was the most broadband in operation. A definite response could be seen from the transducer while operating in pulse-echo mode at frequencies less than 1 MHz, but the signal-to-noise ratio decreased significantly. The reflections of the back wall became more difficult to distinguish. Figure 4.12 is of the captured waveform with the transducer operating at 550 kHz. In this image the first two echoes form the back wall seem to be evident, but none further. It is also apparent that the amount of noise has increased making the signal less discernable. Below this frequency the signal all together diminished significantly.

An issue that arises with testing these transducers at these lower frequencies is that the wavelength of the ultrasonic wave becomes comparable to the length of the cylinder substrate. For example, the wavelength at 250 kHz is approximately 1.8 centimeters. With the length of the substrate being one inch (2.54 cm), only one complete wavelength can pass through the steel before the wave is reflected by the back wall. This is not ideal for the formation of a waveform as too few cycles are allowed to pass through the medium. In an attempt to allow more cycles to pass before reflection an additional length of stainless steel was coupled to the bottom of the cylinder using ultrasonic gel. This set up is shown in Figure 4.13.
Figure 4.13. PZT/Bi$_4$Ti$_3$O$_{12}$ shallow well transducer coupled to an added length of stainless steel.

The waveform in Figure 4.14 was captured with the transducer operating in pulse-echo mode at 500 kHz with the added length of stainless steel. Comparing this waveform to the one in Figure 4.12, there was not a large improvement as hoped. The first two echoes were again distinguishable, but the signal-to-noise ratio did not improve. Unfortunately, UNDE applications not feasible with signals of this quality.
Figure 4.14. Waveform of the $\text{PZT/Bi}_4\text{Ti}_3\text{O}_{12}$ shallow well transducer coupled to an added length of stainless steel operating in pulse-echo mode at 500 kHz.

Pulsing these ceramic films at such low frequencies causes them to vibrate with large amplitudes. It may be possible that the still relatively thin films of these transducers cannot handle operating in pulse-echo mode at low frequencies. The vibrations caused by both transmitted and received ultrasonic signals could interfere with one another in a manner detrimental to the overall quality of the waveform. For this reasoning, this $\text{PZT/Bi}_4\text{Ti}_3\text{O}_{12}$ transducer was investigated when acting as the receiver in through-transmission operating mode. The fabricated transducer was again coupled to the top of the added length of steel and a commercial transducer, with center frequency of 0.5 MHz, was coupled to the bottom. The commercial transducer acted as the transmitter in this set-up being pulsed at 250 and 500 kHz. Figure 4.15 shows the received signal from the fabricated $\text{PZT/Bi}_4\text{Ti}_3\text{O}_{12}$ transducer when the commercial receiver was pulsed at 500 kHz, and Figure 4.16 shows it when the commercial transducer was pulsed at 250 kHz.
Figure 4.15. Waveform of the $PZT/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ shallow well transducer operating as the receiver in through-transmission at 500 kHz.

Figure 4.16. Waveform of the $PZT/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ shallow well transducer operating as the receiver in through-transmission at 250 kHz.
The response of the fabricated $PZT/Bi_4Ti_3O_{12}$ transducer was very clear when acting as the receiver in through transmission mode. The signal-to-noise ratio was greatly improved and the signal was much clearer operating in this fashion. In both waveforms the first two pulses are clearly visible. There appears to be a secondary pulse that is being received in between the two pulses from the transmitting commercial transducer. This may be the cause of another harmonic being generated in the ultrasonic wave or some other reverberation adding to the signal.

4.7 Conclusions

These results prove that sol-gel fabricated $PZT/Bi_4Ti_3O_{12}$ transducers can operate low frequencies, but the target frequency of 250 kHz was not reached in pulse-echo mode. It was shown that the transducer could effectively receive signals of frequencies in the low kilohertz range when operating in through-transmission mode. A discernable signal was observed as low as 500 kHz, but the quality of the waveform was poor and would not have proven useful in most applications. The thickness of this transducer was still relatively thin, especially for low frequency operation. The broadband nature of this transducer was very evident in its testing in that its center frequency was around 2.75 MHz, but could still operate below 1.0 MHz. The $Bi_4Ti_3O_{12}/Bi_4Ti_3O_{12}$ transducer was also tested for low frequency operation, but it was considerably less effective. The signal effectively disappeared at frequencies much below 1 MHz. This again shows the great advantage to the use of the $PZT/Bi_4Ti_3O_{12}$ composite. The $PZT/Bi_4Ti_3O_{12}$ had a much greater signal amplitude and was more broadband allowing it to operate at lower frequencies. Thicker $PZT/Bi_4Ti_3O_{12}$ transducers should therefore further enhance operation at low frequencies. A thicker piezoelectric element should improve operation in pulse-echo mode with increasing signal amplitude and signal-to-noise ratio.
5.1 The Invar Anomaly

Invar is a ferromagnetic iron-nickel alloy that exhibits little to no volumetric expansion upon heating. It was discovered in 1897 by the Swiss physicist Charles Guillaume. The alloy consists of approximately 65 percent iron and 35 percent nickel. Guillaume named his discovery invar because of its length being invariant with temperature [29]. At room temperature invar has a thermal expansion coefficient of effectively zero. As the temperature rises significantly above room temperature this value increases as well, but not nearly as much as for other metals and alloys. The reason for this thermal expansion anomaly has intrigued physicists and engineers for many years. Computer modeling has improved the theoretical understanding of this alloy in the past few decades, but it is still not completely understood.

The phenomenon of having such a low thermal expansion coefficient along with some other strange characteristics of invar is known as the “invar effect.” These alloys show large negative pressure effects on the magnetization and Curie temperature. Ferromagnetic materials, just as ferroelectric materials, have a specific Curie temperature at which they lose their permanent magnetic dipoles. Above the Curie temperature materials become paramagnetic and do not respond strongly to magnetic fields. The Curie temperature of invar has been estimated to be 280 °C. Invar exhibits large forced volume magnetostriction, which is the volume expansion induced by an applied magnetic field. Other characteristics include large high field susceptibility, large residual resistivity, and abnormal temperature dependence of elastic constants [10].

It is believed that the “invar effect” is closely related to the magnetism of metals, but it is still not fully understood [10]. The low thermal expansion coefficient of invar has been primarily attributed to a large value of spontaneous volume magnetostriction. This is caused by aharmonic vibrations in the lattice and sublattice. When this vibrational energy becomes large enough it cancels out the normal lattice vibrations that cause thermal expansion. This leads to a small or even negative thermal expansion coefficient as illustrated in Figure 5.2. Spontaneous volume
magnetostriction is caused by interactions inducing ferromagnetic or antiferromagnetic spin polarization of the electrons in the 3d band. This leads to an increase of kinetic energy of the 3d electrons. Generally, a reduction in the 3d bandwidth and therefore an increase in its density lead to volume expansion causing energy loss. This volume expansion can be considerable in most metals, including those iron-based. However, this volume change is not observed in invar alloys, not even above their respectable Curie temperatures. This is explained with the assumption that in invar the local magnetic moments still exist in the 3d band, even above the Curie temperature [10, 30].

![Figure 5.1. Illustration of the “invar effect.” The dashed line represents the thermal expansion of normal metal alloys, whereas the solid line represents that of invar. The difference between the two curves represents the spontaneous volume magnetostriction [10].](image)

It is easy to understand the reasons why invar has become so popular for use of several industrial applications. The fact that it has a thermal expansion coefficient of essentially zero alone makes it a very beneficial alloy. Additional elements can also be added to the classical invar alloy consisting of Fe-Ni. Common additions are manganese (Mn), chromium (Cr), and cobalt (Co). These elements can improve the physical, chemical, and mechanical properties of the invar alloy and maximize its efficiency depending on its desired application and environment of use. Examples of hybrid alloys are “Stainless Invar” (FeCoCr) and “Super Invar” (FeNiCo). Some common uses for invar are in precision instruments, structural components, and recently electronic devices. Instruments such as laser sources, lead frames, and seismographic devices often use invar alloys [31]. Examples of structural components containing invar are LNG (liquefied natural gas) containers and core wires of long-distance power cables [10].
5.2 Invar Substrates

Since mismatch of thermal expansion coefficients has been determined to be the cause of the adhesion problems in this research, it was a natural decision to turn to invar. An invar rod was obtained with a half-inch diameter. The rod was cut down into one inch long substrates with one end of each being sand-blasted to increase surface roughness. This again was to promote better adhesion by creating dangling bonds for the ceramic film to grab on to. The extremely low coefficient of thermal expansion should eliminate the delaminations occurring during and after the sintering process. Invar will not expand nearly as much as a stainless steel substrate so it should not pull away from the ceramic and cause delamination. The generated shear force from expansion and contraction will be considerably less and therefore not strong enough to break the interface bonds between the invar substrate and composite. Table 5.1 shows the large difference in thermal expansion coefficient between invar and two common alloys of stainless steel.

<table>
<thead>
<tr>
<th>Material</th>
<th>Linear Thermal Expansion Coefficient (μm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Invar (36 Ni)</td>
<td>0 to 2</td>
</tr>
<tr>
<td>Stainless Steel (316)</td>
<td>16.0</td>
</tr>
<tr>
<td>Stainless Steel (304)</td>
<td>17.3</td>
</tr>
</tbody>
</table>

Table 5.1. Linear Thermal Expansion Coefficients of Invar and Stainless Steel [12].

\( \text{PZT}/\text{Bi}_4\text{Ti}_3\text{O}_{12} \) samples were prepared via the same fabrication and deposition methods described earlier. At first 5 sprays were applied to the invar substrates. Due to the smaller surface area of these samples more material could be deposited with each spray. So the film deposited with 5 sprays was considerably thicker than with previous samples of larger surface areas. These substrates were sintered using the blowtorch just as previous samples were and no signs of delamination were observed afterwards. Then 5 more sprays of \( \text{PZT}/\text{Bi}_4\text{Ti}_3\text{O}_{12} \) were applied to these samples increasing their overall thickness. The samples were again sintered with the blowtorch and once again the films still adhered strongly. The use of invar for the substrates was a solution to the re-occurring adhesion problem. The next task was to continue work with invar substrates, depositing a thick transducer using this procedure to be tested at low frequency.

Deposition continued onto these invar samples until two samples were completed. The first, labeled \( I_1 \), consisted of 15 sprays of \( \text{PZT}/\text{Bi}_4\text{Ti}_3\text{O}_{12} \), and the second, labeled \( I_2 \), of 20 sprays. This in fact completed a goal of this research set in the beginning after initial testing, but could not be achieved with stainless steel substrates. These two samples were finished in the same manner as previous in this research. Larger electric fields were again used during poling due to the greater thickness of their composite layers. For each sample over 3.5 kilovolts was applied for 25 minutes at 150 °C, and remained applied as they cooled for another 15 minutes. Both samples exhibited strong piezoelectric coefficients, which are given in Table 5.2.

The efficiency of the thicker transducer was not as high as hoped, but its \( d_{33} \) was still substantial. The sample consisting of 15 sprays had a high measurement that was promising for not only strong signal amplitudes, but also great broadband operation. The piezoelectric elements were significantly thick for both of these transducers, which appeared promising for low frequency
Table 5.2. Measurements of $d_{33}$ and capacitance of the $PZT/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ on invar substrates.

<table>
<thead>
<tr>
<th>Sample (# of sprays)</th>
<th>$d_{33}(\text{pC/N})$</th>
<th>Capacitance (pf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_1$ (15 sprays)</td>
<td>10.5</td>
<td>23</td>
</tr>
<tr>
<td>$I_2$ (21 sprays)</td>
<td>6.5</td>
<td>31</td>
</tr>
</tbody>
</table>

At first the invar samples were tested as longitudinal transducers operating in pulse-echo mode. The operation of the $I_2$ transducer was an extreme disappointment. A response could be seen when excited with a voltage tone burst, but a clear-cut waveform could not be captured. The greatest response from the transducer was observed at or just below a frequency of 1.0 megahertz. A center frequency this low is promising, as the transducer should have operated effectively down into the low kilohertz range. Upon closer investigation the integrity of the transducer may have been compromised by cracking starting to form along the edge of the circumference of the cylinder. If this crack had grown enough to decrease the adhesion between the composite layer and the invar substrate, the efficiency of the transducer would be substantially decreased. The transfer of energy would be poor due to this lack of adhesion, as the air gap would cause significant attenuation. This was most likely the cause for the poor performance of this transducer as it measured a high enough $d_{33}$ value to be an effective transducer. This crack formation raises the question if there is a limit to the thickness of ceramic that can be deposited onto an invar substrate. Even though invar has a very small coefficient of thermal expansion, these composite ceramics have a value larger in magnitude. This value for the ceramics is lower than that of stainless steel for example, but its larger than that of invar, again creating a mismatch. As the deposited layers increase in thickness there is more material expanding/contracting upon heating/cooling and therefore the internal forces generated are greater. Eventually this will lead to the same problem observed earlier in this research and delamination will begin to occur. A
further investigation needs to be conducted as to whether or not adhesion problems continued at these thicknesses in order to determine if there is a limit to depositing onto invar substrates.

The second transducer, $I_2$, was a much more effective transducer upon testing. Operating as a longitudinal transducer in pulse-echo mode a center frequency of approximately 1.1 MHz was observed. The signal amplitude of the waveform along with its signal-to-noise ratio was significantly large. Figure 5.3 is of the waveform at this transducer’s center frequency. The signal amplitude at 1.1 MHz was measured to be about 2.20 volts peak-to-peak. A frequency sweep was then conducted to test how broadband this transducer was. The results are shown in the plot of frequency as a function of signal amplitude in Figure 5.4. Once again this $\text{PZT/Bi}_4\text{Ti}_3\text{O}_{12}$ transducer was very broadband in nature and could operate effectively in a large range of frequencies around its center frequency. Highly efficient operation was achieved at frequencies as low as 600 kHz, where a peak-to-peak signal amplitude of 1.28 volts was measured. The waveform captured at 600 kHz is shown in Figure 5.5. These results showed improvement upon those previously found with the shallow well samples operating at low frequency.

![Figure 5.3. Waveform of PZT/Bi$_4$Ti$_3$O$_{12}$ transducer on invar substrate operating in pulse-echo mode at its center frequency.](image)
There again appeared to be a threshold in the range of 500-600 kHz at which the signal amplitude would sharply decline. A measurable response could still be seen at lower frequencies such as 250 kHz in pulse-echo mode, with the signal being amplified by a significant amount of gain. Nonetheless the first echo from the back wall of the invar substrate was clearly observable and a peak-to-peak signal amplitude was measured as 350 mV. This signal is shown in Figure 5.6. This can be viewed as a success for this research as such a clear signal had not been before achieved with one of these fabricated transducers operating in pulse-echo mode at such low frequencies.

Similar strategies were then employed as previously in this research, namely extending the length of the substrate and using the fabricated transducer as the receiver/pulser in through-transmission mode with a commercial transducer acting as the converse.

To improve the number of cycles passing through the substrate before the ultrasonic wave was reflected, this transducer was coupled to an invar rod. The rod was approximately 30 cm in length with a diameter of 2.5 cm. An improvement in operation was not observed at any frequency in pulse-echo mode. The peak-to-peak signal amplitudes were essentially the same as when measured without the added length. The voltages were actually slightly less than before due to the increase of attenuation associated with the added length.

The $PZT/Bi_4Ti_3O_{12}$ transducer was then tested in through-transmission to test its ability to both generate and receive low frequency signals. The same commercial transducer that was used
to test the shallow well samples in through-transmission was also used in this application. The fabricated composite transducer was used as both the transmitter and receiver at 500 and 250 kHz. Once again a response was visible from the transducer operating in both functions at both frequencies. The signal was not as easily discernable compared to those observed in pulse-echo mode, but their operation was very evident. The captured waveforms associated with these four operating modes are shown in below in Figure 5.7. These results confirm that this fabricated $PZT/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ transducer can both transmit and receive signals at frequencies as low as 250 kHz.

Figure 5.5. Waveform of $PZT/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ transducer on invar substrate operating in pulse-echo at 600 kHz.
Figure 5.6. Waveform of $PZT/Bi_4Ti_3O_{12}$ transducer on invar substrate operating in pulse-echo at 250 kHz.
Figure 5.7. The top images are the waveforms captured of the $PZT/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ transducer on an invar substrate acting as the receiver/transmitter in through-transmission at 500 kHz. The bottom are the same, but operating at 250 kHz.
5.3 FFT Analysis

A Fast Fourier Transform (FFT) is an algorithm that when applied to an ultrasonic waveform yields its frequency spectrum. Examining this spectrum for the signals obtained from the fabricated transducers will yield the frequency at which they are mainly operating. This information is very useful to this research as it can confirm that the transducers are truly operating at the desired frequency and that the signal is not being generated by other means. All of the results presented in this section were found using a program in MATLAB. The first frequency spectrum shown in Figure 5.8 is an FFT of the waveform captured at the transducer’s center frequency, which was about 1.1 MHz. The main peak in this spectrum coincides with a frequency of about 1.3 MHz, which is close to the measured center frequency of the transducer. This illustrates how this analysis is conducted as the investigation turns to the more interesting low frequency results.

![FFT of PZT/Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} transducer on invar substrate operating at its center frequency of 1.1 MHz.]

An FFT analysis was next conducted on the waveforms captured with the transducer operating in pulse-echo mode at low frequencies. Recall that this transducer exhibited a strong signal as low as 600 kHz, with a measurable response down to 250 kHz. The frequency spectrums for both of these instances revealed interesting results. The largest peaks observed were not of low frequencies, but instead ones more toward the center frequency of 1.1 MHz. When pulsed at 600 kHz, the main frequency response in the spectrum was about 1.2 MHz. Similarly the main peak was roughly 1.1 MHz for the waveform captured when the transducer was pulsed at 250 kHz.
Both of these spectrums are shown in Figure 5.9.

![Frequency Spectra](image)

**Figure 5.9.** The image on the left shows the frequency spectrum for the PZT/Bi$_4$Ti$_3$O$_{12}$ transducer on an invar substrate pulsed at 600kHz. The image on the left shows the same pulsed at 250 kHz.

Judging from these results it would appear that despite being pulsed at a low frequency this PZT/Bi$_4$Ti$_3$O$_{12}$ transducer was generating signals at a higher level near its center frequency. This result was not overly surprising with the fact that the thickness of the piezoelectric element was still only about 1.0 mm. Recall that for a center frequency of 250 kHz, a thickness of 9.0 millimeters is necessary. Despite not seeing a strong low frequency response in this transducer’s operation, a substantial enough signal was observed even when excited at 250 kHz that could prove useful in UNDE applications.

The waveforms collected with the fabricated composite transducer operating as a transmitter and receiver in through-transmission were also analyzed. A spectrum was produced for each of the four waveforms shown in the previous section with this fabricated transducer operating at both 500 and 250 kHz. These frequency spectrums are shown in Figure 5.10.

Each of these frequency spectrums had more than one large peak unlike those obtained from the pulse-echo waveforms. In all four spectrums that majority of the spikes, including all of the major ones, were associated with frequencies less than one megahertz. This is a promising notion that this transducer is capable of producing signals at the desired low frequencies in the kilohertz range. Each spectrum had a large spike around 500 kHz along with some more minor peaks as low as 300 kHz. Each spectrum showed a minor response at 250 kHz, but nowhere near the magnitudes seen at slightly higher frequencies. These FFT analyses of the gathered waveforms have proven the operational capabilities of these sol-gel fabricated transducers at low frequencies.
Figure 5.10. The top two images are the frequency spectrums associated with the waveforms captured of the $PZT/ Bi_4Ti_3O_{12}$ transducer on an invar substrate acting as the receiver/transmitter in through-transmission at 500 kHz. The bottom two are the same, but operating at 250 kHz.
Chapter 6

Conclusions

6.1 Results

The sol-gel spray-on fabrication method used in this research has been proven to be able of producing thick composite piezoelectric transducers capable of operation at low frequencies. Parts of this procedure had to be modified in order to create these thick piezoelectric elements. The major modifications made during this research were a direct result of the adhesion difficulties brought about by depositing thicker layers of the composite ceramics. The geometry of the standard stainless steel cylinder substrates was changed to reduce the amount of shear force generated during the expansion and contraction of the samples. This shear force would break the bonds at the interface between the substrate and composite causing delamination. It was determined that the shallow well design solved the adhesion problems and produced highly efficient transducers. Another solution that was discovered was the use of invar for the substrates upon which the \( \text{Bi}_4\text{Ti}_3\text{O}_{12} / \text{Bi}_4\text{Ti}_3\text{O}_{12} \) and \( \text{PZT} / \text{Bi}_4\text{Ti}_3\text{O}_{12} \) are deposited. The extremely small thermal expansion coefficient of invar eliminated the large mismatch previously present with the use of stainless steel. Efficient \( \text{PZT} / \text{Bi}_4\text{Ti}_3\text{O}_{12} \) transducers were also fabricated on invar cylinder substrates.

It has been shown that transducers of both designs mentioned above can operate at low frequencies in the kilohertz range. The broadband nature of these composties allowed for low frequency operation at thicknesses reasonably obtainable with this fabrication process. The shallow well design was able to produce longitudinal transducers operating efficiently in pulse-echo mode down to about 800 kHz. These transducers were also found to generate strong signals acting as a receiver in through-transmission at both 500 and 250 kHz. \( \text{PZT} / \text{Bi}_4\text{Ti}_3\text{O}_{12} \) transducers deposited on invar cylinders were found to yield even better results operating at low frequencies in pulse-echo mode. These samples produced strong signals when excited at frequencies as low as 600 kHz, and a distinctly measureable signal was observed at 250 kHz. These transducers were also shown to be capable of operating as both a transmitter and receiver in through-transmission at frequencies of 500 and 250 kHz. It was proven that this fabrication
method is capable of producing thick composite transducers that can efficiently operate at low
frequencies. This is a newly added benefit to those already existing with composite transducers
fabricated with a sol-gel, spray-on deposition method.

6.2 Recommendations for Future Work

Several areas of this research require further investigation, as mentioned below.

1. Increasing the Thickness of the Shallow Well Samples
   The shallow well transducers produced in this research operated efficiently in pulse-echo mode
to frequencies as low as 800 kHz. It is believed that with a thicker piezoelectric element, this
operational frequency can be decreased further. The depth of the well on these samples was 2
mm, and further work is recommended to fill the well in completely before testing.

2. Conventional Methods of Sintering
   Adhesion difficulties were observed when fabricating thick layers onto traditional stainless
steel cylinder substrates. The delamination of the composite ceramics generally occurred after
sintering, and was observed with both blowtorch and microwave techniques. Samples should be
prepared and sintered with a tube furnace in which the heating and cooling rates can be better
controlled.

3. Investigate Deposition Limit onto Invar Substrates
   The thicker of the two transducers fabricated on invar cylinders showed signs of cracking,
which seems to have led to partial delamination between the substrate and $\text{PZT/}B\text{i}_4\text{T}_3\text{O}_{12}$. Several samples around the same thickness should be evaluated to see if this is a recurring
problem as there may be a limit to how thick the ceramic layers can be deposited, even onto
invar.

4. Flaw Detection at Low Frequency
   The ability of the transducers needs to be tested as if it were being used in some UNDE
application. A simple experiment involving the detection of an internal flaw would be a proper
place to begin this investigation. The ultrasonic wave at these low frequencies must contain
enough energy for a portion to be reflected back to the transducer and interpreted accurately
to locate the flaw. Other applications to be tested involve the use of guided waves to generate
second harmonics within a substrate.

5. Investigation of New Materials
   The continued research of fabricated two-phase, and possibly even three-phase, composites is
essential to optimizing the sol-gel fabrication and spray-on deposition method for any range of
UNDE applications. One particular material of interest is lead magnesium niobate-lead titanate
or PMN-PT. The efficiency of PMN-PT is reported to be greater than PZT with a 6-10 times
greater strain energy density. It has a higher piezoelectric coefficient that improves bandwidth, sensitivity, and source level. PMN-PT seems to be extremely promising for improvements of low frequency operation. The common trade off of piezoelectric efficiency and Curie temperature is again observed here, as PMN-PT’s is reported to be 90 °C. Forming a composite using a PZT sol-gel doped with a combination of $Bi_4Ti_3O_{12}$ and PMN-PT may have the ability to produce a transducer with high temperature capabilities and piezoelectric efficiency never before seen.
Bibliography


