EFFECT OF MANGANESE DOPING ON PIN-PMN-PT SINGLE CRYSTALS FOR HIGH POWER APPLICATIONS

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ABSTRACT

Single crystals based on relaxor-lead titanate (relaxor-PT) solid solutions have advanced the world of piezoelectric materials for the past two decades with their giant piezoelectric properties achieved by domain engineered configurations. When single crystals of lead magnesium niobate-lead titanate (PMN-PT) solid solution in the rhombohedral phase were poled along [001]_c direction with “4R” domain configuration, they exhibited high piezoelectric charge coefficient (d_{33} >2000 pC/N) and high electromechanical coupling (k_{33} >0.9) which led to their widespread use in advanced medical imaging systems and underwater acoustic devices. However, PMN-PT crystals suffer from low phase transition temperature (T_{rt} ~85-95 °C) and lower coercive field (depolarizing electric field, E_c ~2-3 kV/cm). Lead indium niobate - lead magnesium niobate - lead titanate (PIN-PMN-PT) ternary single crystals formed by adding indium as another constituent exhibit higher coercive field (E_c ~5kV/cm) and higher Curie temperature (T_c >210 °C) than the binary PMN-PT crystals (E_c ~2.5 kV/cm and T_c <140 °C). When these ternary PIN-PMN-PT crystals are doped with manganese (Mn:PIN-PMN-PT), they behave like hard piezoelectric materials demonstrating an internal bias field (E_i ~0.8-1.6 kV/cm), leading to low elastic losses and high mechanical Q-factor (Q_m >600) compared to the undoped binary crystals (Q_m of PMN-PT <150).

Although the spontaneous polarization directions for these rhombohedral crystals are in the <111>_c directions, the giant piezoelectric effect (d_{33} >2000 pC/N for PMN-PT) occurs in the [001]_c poled crystals, which is attributed to the polarization rotation mechanisms. Hence, domain engineering configurations induced by poling these crystals in orientations other than their polarization axis are critical for achieving large piezoelectric effects. Based on the phase diagram of these solid solutions, with the increase in PT content beyond the rhombohedral phase region, orthorhombic/monoclinic and tetragonal phases are formed. In the orthorhombic and tetragonal phases, the spontaneous polarization directions are in the [011]_c and [001]_c directions respectively. Similar to the “4R” domain configuration achieved in [001]_c poled rhombohedral
crystals, other domain configurations can be achieved by poling the single crystals in different orientations, leading to multitude of properties that are useful for various specified applications. The unique properties and configurations arise from the large anisotropy of the single crystalline materials and various polarization rotation mechanisms that are associated with these multi-domain configurations.

This dissertation is focused on the properties of manganese doped PIN-PMN-PT ternary single crystals in the rhombohedral phase. By poling them in either [001]c, [011]c, or [111]c, 4R, 2R or 1R domain configuration can be achieved respectively. Longitudinal vibration mode, d_{33}, or k_{33} is the most useful mode from 4R configuration. The “2R” domain state is obtained by poling the rhombohedral phase crystal along [011]_c crystallographic direction. Investigation of “2R” Mn:PIN-PMN-PT single crystals and their properties lead to unique resonance modes (d_{32}, “2R d_{15}”, and d_{36}') that are very useful and relevant to practical applications.

Considering the large anisotropy and various symmetries exhibited by these crystals, full set of dielectric, piezoelectric, and elastic properties are extremely critical to understand different modes and their overall behavior in devices. Inconsistencies in full set of properties may be caused by complex methods involved in performing characterization measurements and also inhomogeneity among samples used for the measurements. Due to the large number of coefficients that need to be determined for full property material data, a methodology combining resonance and ultrasound methods is the most widely used technique for consistent measurement of full set properties for these materials. Full property measurements (elastic, dielectric, and piezoelectric) for the “2R” Mn:PIN-PMN-PT single crystal poled into orthorhombic mm2 macroscopic symmetry ([011]_c poled crystals) and for “4R” configuration ([001]_c poled crystals) were conducted and the data was analyzed based on their macroscopic crystallographic symmetry. Full property data was measured for the 1R configuration of the Mn:PIN-PMN-PT single crystal to understand the monodomain properties and the orientation dependence of dielectric, elastic, and piezoelectric properties. Domain averaging and matrix
transformation was performed with the monodomain data to calculate 4R data and compare with that of experimental 4R data. Orientation dependence of the properties is also presented to understand the crystallographic directions that are best suited for the various applications.

The high sensitivity of PMN-PT and the high $Q_m$ of Mn:PIN-PMN-PT provide designers with soft and hard piezoelectric material choices in the relaxor-PT single crystals family. While much work has been done on PMN-PT crystals, research efforts on the Mn:PIN-PMN-PT crystals are limited. Investigation of the $Q_m$ for Mn-doped crystals under high power drive conditions is essential for the practical application of these crystals for devices. High power characteristics of the Mn:PIN-PMN-PT single crystals were measured with emphasis on specific modes (transverse mode, $d_{32}$, and face shear mode, $d_{36}'$) based on a constant vibration velocity method using a high power characterization system (HiPoCs), and the degradation of $Q_m$ as a function of vibration velocity was studied in order to understand the self-heating behavior and device limitations. Practical devices that are useful for various applications were designed and performance of these prototype devices was quantitatively evaluated.

This thesis work provides a concrete advancement in the understanding of doped ternary relaxor-PT ferroelectric single crystals and the influence of their domain engineered configurations on their properties. The emphasis is on vibration modes related to piezoelectric vibrators with the multi-domain single crystals having macroscopic mm2 symmetry. In the last chapter, limitations and future perspectives are also discussed.
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Chapter 1

Introduction

1.1 Motivation

Ferroelectrics based on mixed-oxide perovskites (ABO$_3$ type materials) have found their use in wide variety of dielectric and piezoelectric applications. Discovery of the morphotropic phase boundary (MPB) in lead zirconium titanate, Pb(Zr$_x$Ti$_{1-x}$)O$_3$, (PZT) system \cite{1-4} for $x = 0.52$ with very high electromechanical properties led to the investigation of other similar binary ferroelectric material systems that can exhibit good functional properties. After decades of dominance by lead zirconium titanate (PZT) ceramics in the piezoelectrics industry, single crystal lead magnesium niobate-lead titanate (PMN-PT) has been adopted into new commercial ultrasound transducers and arrays due to the much improved performance compared to PZTs. As a solid solution of PMN relaxor and PT ferroelectric, giant piezoelectric effect was observed in domain engineered PMN-PT single crystals of rhombohedral phase with composition near the morphotropic phase boundary. The five-fold increase in piezoelectricity and 30-40% increase in electromechanical coupling factor result in higher sensitivity and wider bandwidth \cite{5, 6}. Though, the spontaneous polarization axis for these rhombohedral crystals is in the [111]$_c$ direction, the giant piezoelectric effect ($d_{33} > 2000$ pC/N for PMN-PT) is obtained in [001]$_c$ poled crystals, which is attributed to the polarization rotation mechanisms, hence domain engineering by poling the crystals in orientations other than their spontaneous polarization directions is critical to identifying the appropriate resonance modes for the various applications.
To overcome the low coercive field and low T<sub>c</sub> of PMN-PT, ternary single crystals of the same family were obtained by doping with indium (0.27PIN-35PMN-28PT) and they exhibit higher coercive field (E<sub>c</sub> ~5.5 kV/cm) and higher Curie temperature (T<sub>c</sub> ~210 °C) than the binary PMN-PT crystals (E<sub>c</sub> ~2.5 kV/cm and T<sub>c</sub> ~145 C). However, the elastic loss in these materials can lead to self-heating and energy losses during higher power operation. There was a need for developing new single crystal materials that can withstand high drive and can be used for high power applications. To achieve this goal, various dopants were added to generate internal bias in the ternary PIN-PMN-PT single crystals based on their site occupancy and valence. When these ternary PIN-PMN-PT crystals are doped with manganese, they exhibit internal bias (E<sub>i</sub>) (~0.8-1.6 kV/cm) resulting in very high mechanical Q (Q<sub>m</sub> ~600) compared to the undoped crystals (Q<sub>m</sub> of PMN-PT <150). Mn-doped PIN-PMN-PT (Mn:PIN-PMN-PT) presents the
opportunity for a high power applications of relaxor-PT single crystal materials. Full property characterization of the Mn:PIN-PMN-PT single crystals was performed to understand the dielectric, piezoelectric, and elastic parameters for different poling directions.

When rhombohedral single crystals are poled along [011]c crystallographic direction, it results in “2R” domain configuration with “mm2” macroscopic symmetry. For these rhombohedral crystals in “2R” domain configuration, much higher transverse piezoelectric coefficient “d32” (for example d32 is about -1500 pC/N for [011]c poled PMN-31PT single crystal) is achieved in [100]c direction compared to the “d31” achieved in “4R” configuration (for example, d31 ~600 pC/N for [001]c poled PMN-31PT single crystal). For the [011]c poled crystals, along with the high negative d32, there is also a positive d31 in the third direction [0-11]c. When properties of [011]c poled crystals are rotated along the Z-axis by 45°, the combination of d32’ (rotated d32) and d31’ (rotated d31) gives rise to a very large d36, leading to a face shear effect. The piezoelectric charge coefficient for the face shear mode d36 defined as d36 = 2(sinθcosθd31-sinθcosθd32), is accompanied by a very high compliance s66 that is comparable to s55. For crystals poled along [011]c direction, very high compliance values are found for s22 and s66 compared to the crystals poled along [001]c and [111]c directions. Combined with the high Qm obtained by Mn-doping, the high compliances of d32 and d36 modes, it is possible to design high power and low frequency transducers.

In general, [011]c poled crystals exhibit high Qm compared to those poled along [001]c and [111]c directions. Combination of Mn doping and [011]c poling results in very high Qm values that are useful for high power devices. Low field behavior of the Mn-doped crystals was measured. Investigation of the Qm behavior for Mn-doped crystals under high power drive conditions is essential for the practical application of these devices. The high power characteristics of the Mn-doped crystals were measured using HiPoCs system and the degradation of Qm as a function of vibration velocity was discussed. Impact of self-heating and degradation of Qm as function of vibration velocity
near resonance were characterized for these materials in the $d_{32}$, and $d_{36}'$ resonance modes. Device designs that incorporate the $d_{32}$, $d_{15}$, and $d_{36}'$ modes were proposed and prototype performance was discussed.

1.2 Organization of Dissertation

The dissertation is organized into seven chapters. Chapter 1 is the background for this dissertation and also describes the motivation for the research and organization of this dissertation. Chapter 2 provides a brief background for piezoelectricity and explains the status of relaxor-PT single crystals. The crystal growth method is illustrated along with doping studies in connection with the development of the manganese doped ternary single crystals. The three generations of relaxor-PT single crystals (PMN-PT, PIN-PMN-PT, and Mn:PIN-PMN-PT) are compared based on their properties, such as coercive field and Curie temperature, etc. Chapter 3 briefly describes the domain engineering method and the property dependence on crystal composition and orientation, and gives an overview of domain states that are achievable in relaxor-PT single crystals. Additionally, the critical modes correspond to these domain oriented configurations are also discussed with emphasis on the rhombohedral phase crystal poled along $[011]_c$ direction. Chapter 4 presents the full set material constants (dielectric, piezoelectric, and elastic constants) for Mn:PIN-PMN-PT single crystals with description and comparison to other crystals and modes.

Chapter 5 is a summary of high power characterization of the Mn-doped crystals, which exhibit hard piezoelectric behavior so that it is more suitable for high power applications compared to the binary and undoped ternary single crystals. High power characteristics of two critical resonant modes for practical applications, i.e., the $d_{32}$ and $d_{36}'$ modes, were evaluated for various crystal compositions. Degradation of performance through self-heating with increasing vibration velocity is also discussed for these modes. Chapter 6 provides a practical guide to the design of devices using various modes with
particular emphasis on resonance modes involving the mm2 macroscopic symmetry (rhombohedral phase poled along \([011]\)) and also presents discussion of various prototype devices and their performance for different applications. Chapter 7 is focused on future work that outlines possible research directions as well as potential advancement in related science and technology.

1.3 References


Chapter 2

Background

2.1 Piezoelectricity

Piezoelectricity is defined as the generation of electric charges in response to applied stress. Piezoelectric materials can also produce strain when electric field is applied, resulting in converse piezoelectric effect. Out of the 32 crystallographic point groups, 20 of them exhibit piezoelectric effect and 10 out of these 20 exhibit spontaneous polarization or pyroelectricity. Ferroelectricity is defined as the property of materials with spontaneous polarization that can be reversed using an external electric field. Hence, all ferroelectric crystals by virtue of their spontaneous polarization are pyroelectric. The characteristic behavior of ferroelectric crystals is the polarization hysteresis loop as shown in Figure 2.1. \( E_c \) denotes the coercive field or depolarization field and is an important parameter for understanding poling conditions and limits of operation voltage. In ferroelectric materials, the piezoelectricity is imparted after the material undergoes the poling process.

![Ferroelectric hysteresis loop](image)

Figure 2.1 Ferroelectric hysteresis loop
Figure 2.2 shows the Heckmann diagram that relates stress, temperature, and electric field and the associated material properties that arise from this thermodynamic relationship. Both direct and indirect effects are present in piezoelectric materials, which allow them to be used as sensors or resonators. Based on the thermodynamic relationships between electric field (E), stress (X), strain(x) and dielectric displacement (D), the four possible conditions are depicted in Figure 2.3 and related equations are shown in Table 2.1. The dielectric, piezoelectric, and elastic properties are thermodynamically related using these equations.

Figure 2.2. Heckmann diagram relating electric field, mechanical stress, and temperature [1].
Figure 2.3 Representation of various ferroelectric hysteresis loops based on stress-free and short-circuit conditions.

Table 2.1 Thermodynamic relationship of various constants for piezoelectric materials

<table>
<thead>
<tr>
<th>Stress-Charge Form</th>
<th>Strain-Charge Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D = e^x \cdot E + e \cdot x$</td>
<td>$D = d \cdot X + \varepsilon^x \cdot E$</td>
</tr>
<tr>
<td>$X = c^E \cdot x - e^x \cdot E$</td>
<td>$x = s^E \cdot X + d^x \cdot E$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stress-Voltage Form</th>
<th>Strain-Voltage Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E = - h \cdot x + \left( e^x \right)^{-1} \cdot D$</td>
<td>$E = - g \cdot X + \left( \varepsilon^x \right)^{-1} \cdot D$</td>
</tr>
<tr>
<td>$X = c^D \cdot x - h^x \cdot D$</td>
<td>$x = s^D \cdot X + g^x \cdot D$</td>
</tr>
</tbody>
</table>
2.2 Relaxor-PT Single Crystals

Relaxor ferroelectrics, in particular, complex perovskites with the general formula Pb\(B^{1/3},B^{′′2/3}\)O\(_3\) and Pb\(B^{′1/2},B^{′′1/2}\)O\(_3\) such as Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) (PMN) and Pb(Sc\(_{1/2}\)Ta\(_{1/2}\))O\(_3\) (PST), are of high interest due to their excellent dielectric, electrostrictive, and pyroelectric properties [1]. Their solid solutions with PbTiO\(_3\) exhibit exceptionally high electromechanical coupling (k >85%) and are excellent materials for high performance sensors and actuators [2].

Domain engineered Pb(Zn\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PZN-PT) and Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PMN-PT) rhombohedral crystals with composition near the morphotropic phase boundary (MPB) and poled along the pseudo-cubic <001> direction exhibit high electromechanical coupling factors and piezoelectric coefficients for the longitudinal mode. Electromechanical coupling factors > 0.90 and piezoelectric coefficients higher than 1200 pC/N are common for most relaxor-PT single crystals [2-5]. The direction of spontaneous polarization for rhombohedral PMN-PT (x <31%) is [111]; however, high longitudinal piezoelectric charge coefficient d\(_{33}\) (2000 pC/N) and k\(_{33}\) (90%) are achieved when poled along the [001]\(_c\) direction. It was found that the domain configuration in the “4R” domain state is relatively stable after poling along the [001]\(_c\) direction. Macroscopically, the crystal achieves a tetragonal symmetry (4mm) when poled along [001]\(_c\). The maximum d\(_{33}\) achieved in the [001]\(_c\) direction was associated with the easy rotation of the polarization in the “4R” domain state with the application of an electric field (Figure 2.4). There is a field-induced R-T phase transition at a sufficiently high electric field (E\(_{rt}\) ~18-20 kV/cm for x ~ 0.29).
Figure 2.4 Polarization rotation in relaxor PT single crystals – poling a rhombohedral composition in [001]c direction [2]

2.3 Development of Relaxor-PT Single Crystals

For the past 50 years, perovskite Pb(Zr$_x$Ti$_{1-x}$)O$_3$ (PZT) piezoelectric ceramics have dominated the commercial market of electromechanical devices, including piezoelectric sensors, actuators and medical ultrasonic transducers, due to their high piezoelectric and electromechanical coupling factors. For example, the shear piezoelectric coefficient $d_{15}$ and electromechanical coupling factor $k_{15}$ for PZT5A type (DoD Type II) materials are found to be on the order of ~500-550 pC/N and ~70%, respectively. Although PZT continues to be a commercially important piezoelectric material, the incongruent melting of Zr and Ti and the refractory nature of Zr has limited growth of PZT single crystals from melt. In an effort to find material systems that can be possibly grown in the single crystal form, other perovskite type material systems with the presence of MPB were investigated [Ref 7-9]. Lead magnesium niobate - lead titanate (1-$x$)PMN-$x$PT (PMN-PT) is one such material system that exhibits an MPB (Figure 2.5) at $x \sim 0.33$ with very high functional properties and is currently one of the most important materials due to its giant piezoelectric effect in its single crystal form.
Innovations in electronic devices have been the driving force for new developments in piezoelectric materials, including relaxor-PT single crystals. The excellent piezoelectric properties of relaxor-PT single crystals have attracted considerable interest over the last decade, particularly for applications in high performance medical transducers. However, their commercial use has been primarily limited to high-end medical imaging devices due to the low coercive field ($E_c \sim 2.5$ kV/cm), low transition temperature ($T_{rt} \sim 85$ °C) and high elastic losses ($Q_m < 150$) and also high cost. With the giant piezoelectric properties also comes the low operating temperature and very high temperature dependence (change in dielectric and piezoelectric properties with respect to temperature).

To overcome the low $T_c$ and low $E_c$ of PMN-PT crystals, Pb(In$_{0.5}$Nb$_{0.5}$)O$_3$-$\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$-$\text{PbTiO}_3$ ("PIN-PMN-PT") was developed using indium as a major constituent resulting in a ternary single crystal system, also referred to as Generation 2 relaxor-PT single crystal (Figure 2.6). PIN-PMN-PT exhibits higher Curie temperature $T_c$ and rhombohedral to tetragonal transition temperature $T_{rt}$ ($\sim 180$–$220$ °C and $\sim 100$–$140$ °C, respectively, which are about 30 °C higher than the PMN-PT binary system) and
higher coercive field $E_c$ (about twice that for the PMN-PT crystals), showing much improved temperature stability and electric field stability, without sacrificing the high piezoelectric properties [12-13].

![Figure 2.6 PIN-PMN-PT Single Crystal boule with Increased Tn, Tc and Ec](image)

**2.4 Doped Single Crystals**

In polycrystalline piezoceramics, the “hard” piezoelectric behavior is explained due to pinning of domain walls by acceptor dopants where the domain wall motions (extrinsic) contribute predominantly to the high dielectric and piezoelectric properties compared to what is expected from phenomenological theories (intrinsic). Acceptor dopants generally have lower valence than the original site occupant ions. Typically, the acceptor dopant would result in higher coercive field, internal bias, lower dielectric constant, and higher $Q_m$ [14, 15].
General rule of thumb for site occupancy preference for doping based on the Goldschmidt tolerance factor is that the dopant ionic radius is within +/-15% of the original site occupant ion [15]. In PZT ceramics, acceptor doping has been most successful in achieving internal bias, and high Q_m, such as in PZT-4 and PZT-8 piezoceramics. Ternary PIN-PMN-PT single crystals were doped with various dopants (labeled as A-E) as shown in Table 2.2 and polarization measurements were performed to check for internal bias. Since the dopant information is related to proprietary information, they are identified as shown in Table 2.2. Doping level for all dopants varied from 0 to 6 mol%.

Table 2.2 Dopants for ternary PIN-PMN-PT single crystals and summary of behavior from polarization measurements

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Dopant ID</th>
<th>Remnant Polarization, P_R (C/m²)</th>
<th>Coercive Field, E_c (kV/cm)</th>
<th>Internal bias, E_i (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped PIN-PMN-PT</td>
<td>-</td>
<td>0.32</td>
<td>5.5</td>
<td>-</td>
</tr>
<tr>
<td>B-site Acceptor (+2, +3)</td>
<td>A</td>
<td>0.27</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>B-site Acceptor (+2, +3)</td>
<td>B</td>
<td>0.27</td>
<td>3.8</td>
<td>-</td>
</tr>
<tr>
<td>B-site Acceptor (+2, +3)</td>
<td>C</td>
<td>0.27</td>
<td>3.4</td>
<td>-</td>
</tr>
<tr>
<td>B-site Acceptor (+1, +2)</td>
<td>D</td>
<td>0.3</td>
<td>4.4</td>
<td>-</td>
</tr>
<tr>
<td>B-site Acceptor (+2, +3)</td>
<td>E</td>
<td>0.26</td>
<td>3.7</td>
<td>-</td>
</tr>
<tr>
<td>Mn B-site Acceptor (+2, +3, +4)</td>
<td>I</td>
<td>0.32</td>
<td>7.3</td>
<td>1.3 kV/cm</td>
</tr>
</tbody>
</table>

When doping the PIN-PMN-PT with dopants A-E, they did not result in any internal bias field. The internal bias field was observed only for reasonable levels of manganese doping. Manganese doped ternary PIN-PMN-PT single crystal is discussed in detail in section 2.5. Polarization and strain loop measurements for each dopant from A-E
and comparison for all these dopants are illustrated in Figures 2.7 to Figures 2.18. Remnant polarization and coercive field values are noted for the PE loops in Table 2.2.

**Figure 2.7** PE loop for PIN single crystal with Dopant A

**Figure 2.8** PE loop for PIN single crystal with Dopant B
Figure 2.9 PE loop for PIN single crystal with Dopant C

Figure 2.10 PE loop for PIN single crystal with Dopant D
Figure 2.11 PE loop for PIN single crystal with Dopant E

Figure 2.12 PE loop comparisons for PIN single crystal with Dopant A-E
Figures 2.13 Strain Loop (SE) for Dopant A

Figures 2.14 Strain Loop (SE) for Dopant B
Figures 2.15 Strain Loop (SE) for Dopant C

Figures 2.16 Strain Loop (SE) for Dopant D
Figure 2.17 Strain Loop (SE) for Dopant E

Figures 2.18 Strain Loop (SE) Comparison for Dopants A-E
2.5 Manganese Doped Single Crystals with Internal Bias

Manganese (Mn) doping is used as an acceptor doping in PZT materials [14] and has been previously investigated for PZN-PT and PMN-PT single crystals as well [16-17]. Manganese is a B-site acceptor dopant in its +2, +3, and +4 ionic states, as per its compatibility based on ionic radius and coordination number with that of B-site atoms (ionic radii, valence states, and site preference of various elements are shown in Appendix B). Based on the valence state, acceptor-oxygen defect dipoles form the mobile carriers that result in internal bias (shifted PE loop in Figure 2.18b) and hence the hard material behavior with high mechanical Q ($Q_m$).

A Mn-doped PIN-PMN-PT single crystal boule is shown in Figure 2.19 (Courtesy of TRS Technologies Inc). As shown in Table 2.2, for Mn:PIN-PMN-PT crystals when compared to the PMN-PT and PIN-PMN-PT single crystals, the dielectric constant is lowered, dielectric loss is reduced, coercive field ($E_c$) is increased, $d_{33}$ is lowered, internal bias field is induced, and $Q_m$ is increased. Figure 2.19 (b) shows the PE loop with the internal bias field of ~1.3 kV/cm. These are almost similar characteristic differences that are observed when hard PZTs are compared to that of soft ones. Figure 2.20 is a comparison of $k_{33}$ (electromechanical coupling) and $d_{33}$ as a function of temperature. Although the Curie temperature defines the absolute depolarization of the material, from the standpoint of practical application, the limiting temperature is the rhombohedral to tetragonal phase transition temperature ($T_{rt}$) that occurs in the rhombohedral phase single crystals. For binary PMN-PT single crystals, the $T_{rt}$ is ~95 °C, whereas for PIN-PMN-PT and the Mn:PIN-PMN-PT, the $T_{rt}$ is pushed up to ~130 °C.
Figure 2.19 (a) Mn:PIN-PMN-PT single crystal boule (Courtesy of TRS Technologies Inc) and (b) Ferroelectric hysteresis (P-E) loop of [011]<sub>c</sub> poled Mn:PIN-PMN-PT single crystal showing $E_c$ of 7.3 kV/cm and $E_i$ of ~1.3 kV/cm

Figure 2.20 Comparison of electromechanical coupling and $d_{33}$ as function of temperature for all three crystal types – increased operating temperature for ternary crystals compared to binary PMN-PT single crystal
Table 2.3: Property comparison of single crystals and polycrystalline ceramics

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c$</th>
<th>$T_{RT}$</th>
<th>$\varepsilon_{33}^{I}$</th>
<th>loss</th>
<th>$d_{33}$</th>
<th>$k_{33}$</th>
<th>$s_{33}^E$</th>
<th>$E_c$</th>
<th>$Q_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-PT [001]$_c$</td>
<td>135</td>
<td>95</td>
<td>5400</td>
<td>0.002</td>
<td>1540</td>
<td>0.91</td>
<td>60.0</td>
<td>2.3</td>
<td>150</td>
</tr>
<tr>
<td>PIN-PMN-PT [001]$_c$</td>
<td>191</td>
<td>125</td>
<td>4400</td>
<td>0.002</td>
<td>1510</td>
<td>0.92</td>
<td>69.0</td>
<td>5.0</td>
<td>180</td>
</tr>
<tr>
<td>Mn:PIN-PMN-PT [001]$_c$</td>
<td>193</td>
<td>128</td>
<td>3810</td>
<td>0.002</td>
<td>1340</td>
<td>0.92</td>
<td>62.4</td>
<td>5.0</td>
<td>700</td>
</tr>
<tr>
<td>PZT5H</td>
<td>193</td>
<td>/</td>
<td>3400</td>
<td>0.02</td>
<td>600</td>
<td>0.75</td>
<td>20.7</td>
<td>7.0</td>
<td>70</td>
</tr>
<tr>
<td>PZT5A</td>
<td>365</td>
<td>/</td>
<td>1700</td>
<td>0.02</td>
<td>370</td>
<td>0.71</td>
<td>18.8</td>
<td>15</td>
<td>70</td>
</tr>
<tr>
<td>PZT4</td>
<td>328</td>
<td>/</td>
<td>1300</td>
<td>0.004</td>
<td>290</td>
<td>0.70</td>
<td>14.9</td>
<td>12</td>
<td>500</td>
</tr>
<tr>
<td>PZT8</td>
<td>300</td>
<td>/</td>
<td>1000</td>
<td>0.004</td>
<td>230</td>
<td>0.64</td>
<td>14.6</td>
<td>16</td>
<td>1000</td>
</tr>
</tbody>
</table>

2.6 Single Crystal Growth Process

Relaxor-PT single crystals are grown using various growth methods including flux-assisted Bridgman, solid-state crystal growth, and modified Bridgman process. All relaxor-PT single crystals used in this research effort were grown using a modified Bridgman method at Materials Research Institute and at TRS Technologies Inc. The process of crystal growth and sample preparation is outlined in Figure 2.21 below. After the growth, the single crystal boules are oriented for crystallographic directions using Laue X-ray or X-ray diffraction methods as needed for different resonant modes of operation and they are machined and poled to prepare the various geometries.
At melt temperatures, the PMN, PIN, and PT components are completely soluble in each other forming a good solid solution phase. While cooling below the melting temperature, crystallization occurs on the seed, and since the segregation of Ti is < 1, the PT content starts to increase along the growth direction resulting in a continuous gradient in composition. This is one of the biggest disadvantages of currently used Bridgman growth methods. All crystals used in this work are based on regular Bridgman method which results in composition gradient along the crystal boule length. Other modified Bridgman crystal growth methods have been shown to reduce the composition gradient by feeding the depleting component during the process [18-19]. Successful reduction in composition gradient and lower variation in properties along significant length of the boule has been demonstrated with these growth methods. More comments on this growth method and how it can help with future work are suggested in Chapter 7.
2.7 Measurement Setup

The polarization hysteresis loops of ferroelectric materials were measured using a Sawyer-Tower circuit (Figure 2.22). Strain hysteresis is measured using an LVDT attached to the PE loop system. The PE and SE loops are measured at ~1-10Hz. Permittivity measurements as a function of temperature was performed on the various samples with different compositions for the different orientations using an LCR meter (HP 4284A). These measurements were performed as a function of frequency at 1 kHz. Impedance analysis was performed using a HP 4194A impedance analyzer (Figure 2.24) and frequency sweeps were performed to detect resonance and anti-resonance frequencies for various vibration modes and to calculate electromechanical coupling and other full property coefficients obtained from resonance modes.

Figure 2.22 Schematic of Sawyer-Tower circuit for polarization measurements

Figure 2.23 HP 4194A analyzer used for impedance analysis
2.8 Summary and Discussion

High electromechanical coupling and excellent piezoelectric properties of relaxor-PT single crystals combined with significant improvement in the crystal growth process using Bridgman growth techniques have attracted considerable interest over the past two decades. Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3} (PMN-PT) and Pb(In\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3}-Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3} (PIN-PMN-PT) are the two main compositions that are playing a significant role as next generation piezoelectric materials to replace conventional lead zirconium titanate (PZT) materials. Rhombohedral single crystal compositions of PMN-PT and PIN-PMN-PT near their respective morphotropic phase boundaries (MPBs) (MPB and other phases are shown in Figure 2.25) exhibit longitudinal piezoelectric coefficients ($d_{33}$) greater than 1400 pC/N with electromechanical coupling factors higher than 90% when poled along the pseudo-cubic <001>\textsubscript{c} direction [1]. These excellent properties make relaxor-PT single crystals promising candidates for broadband and high sensitivity ultrasonic transducers, sensors and other electromechanical devices.

Figure 2.24 Schematic phase diagram for relaxor-PT based crystals, where R, O and T represent rhombohedral, orthorhombic/monoclinic and tetragonal phase regions [20].
Even with their large piezoelectric properties, rhombohedral PMN-PT single crystal materials suffers from a low phase transition temperature at \( \sim 95 \, ^\circ\text{C} \) (\( T_n \), rhombohedral to tetragonal) and low coercive field (\( E_c \sim 2\text{kV/cm} \)), limiting their applications to premium medical ultrasound imaging applications and few sensing applications. Furthermore, the low coercive field would necessitate the use of DC bias against depolarization, which complicates the drive electronics and is a significant disadvantage compared to PZT materials. The PIN-PMN-PT ternary composition showed more promise compared to the binary PMN-PT system with almost a 30 \(^\circ\text{C} \) increase in the phase transition temperature (\( T_n \)) and twice the coercive field. A third generation single crystal system obtained by manganese (Mn) doping of PIN-PMN-PT ternary material (Mn:PIN-PMN-PT) is of considerable interest due to its high mechanical quality factor and low loss comparable to the traditional hard PZT ceramics such as PZT-4 (Type I) and PZT-8 (Type III).

In comparison to PMN-PT and PIN-PMN-PT single crystals that behave like soft piezoceramics, such as PZT-5A and PZT-5H, Mn:PIN-PMN-PT single crystals are considered more suitable for wide range of high power applications (similar to hard piezoceramics such as PZT-4 and PZT-8). Specifically, certain applications of high power transducers in medical and underwater acoustics can benefit from the high power capabilities of Mn-PIN-PMN-PT single crystal.

2.9 References


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Chapter 3

Engineered Domain Configurations for Relaxor-PT Single Crystals

3.1 Engineered Domain Configurations

Regions of similar polarization states in ferroelectric materials form domains and are separated by domain walls. Domain engineering in ferroelectrics is referred to as the method of inducing and controlling desired domain configurations for enhancement in specific properties. Domain engineering is performed by processes such as doping and poling that affect the polarization states and enhanced domain configurations are achieved by using the anisotropy of ferroelectric single crystal materials.

For relaxor-PT based single crystals, when poled along various directions, different domain configurations are achieved. Depending on the crystal composition, there are 3 types of unpoled states – rhombohedral, orthorhombic, and tetragonal and these are denoted by 8R, 6T, and 12O respectively representing the number of polarization states that are possible. For ABO₃ crystal structure, when “B” site atom displaces toward “A” site atoms lying in the 4 corners of (110)ₐ or (1-10)ₐ planes, it denotes the 8 possible directions and hence the 8R configuration or rhombohedral phase crystal in its unpoled state. When the “B” atom displacement is in the (100)ₐ or (010)ₐ planes towards any of the “O” atoms in the edge center of these planes (oxygen octahedron), the 6T configuration for unpoled tetragonal phase is formed. When the “B” site atoms move towards the any of the 4 corners of either (100)ₐ or (010)ₐ or (001)ₐ plane (edge center between the A site atoms), then it relates to the 12O configuration of
orthorhombic phase. The unpoled states are depicted in Figure 3.1. Above explanation based on “B” atom shifting is only for simplified understanding the domain states without considering oxygen octahedron tilting, unit cell distortion, etc.

Figure 3.1 Unpoled domain states based on “B” atom shift in ABO$_3$ structure
For rhombohedral phase crystals (unpoled state is denoted as 8R), after poling in [001]c or [011]c or [111]c, macroscopic domain patterns become 4R, 2R, and 1R configurations, respectively. There are eight possible polarization orientations along the pseudo-cubic [111]c directions for rhombohedral relaxor-PT single crystals (3m symmetry). Upon applying an electric field, the dipoles reorient as close as possible to the applied electric field direction. For [001]c poled crystals, there are four equivalent polar vectors along the [111]c directions, with an inclined angle of -54.7° from the poling field. The four <111>c domains are equivalent with a domain engineered configuration resulting in a macroscopic 4mm crystallographic symmetry from the tetragonal crystal class as shown in Figure 2.2.

For [011]c poled crystals, there are two equivalent polar vectors along the [111]c direction, which will rotate 35.5° toward the applied field direction of [011]c with a designated domain engineered configuration of 2R. For this case, the macroscopic symmetry is mm2 belonging to the orthorhombic symmetry class. In contrast, there is only one polar vector along the [111]c direction for [111]c poled ferroelectric crystals, thus it will form a monodomain state of 1R, exhibiting macroscopic crystallographic symmetry of 3m belongs to the rhombohedral symmetry class. Similarly, we can obtain 1T, 2T, and 3T configurations that can be obtained for the tetragonal phase and 1O, 3O, and 4O domains are possible for orthorhombic phase crystals. All 12 possible engineered domain configurations based on crystal composition and poling direction are illustrated in Figure 3.2.

Based on the macroscopic crystallographic symmetry and the engineered domain configurations achieved after poling, resonant modes that are possible based on the existence of piezoelectric charge coefficients (d) can be determined. The d-matrix tensors for 4mm, mm2 and 3m symmetry are outlined in Table 3.1. With the crystallographic structure determined by the composition and the availability of the material controlled by the growth process, orientation dependence of properties and polarization process become critical to determine the best possible modes and their applications to practical
devices. The various resonance modes and how they are useful in application are discussed here with prototype device designs and their performance discussed in Chapter 6.

Figure 3.2 Domain engineered configurations for relaxor-PT single crystals [1-3]

As shown in Table 3.1, certain piezoelectric modes exist the available resonance modes and aspect ratios for different modes detailed in Appendix C. From Table 3.1, it can be seen that [011]c poled crystals exhibiting mm2 macroscopic symmetry, unique values of thickness shear coefficients $d_{24}$ and transverse coefficient $d_{32}$ exist, which is quite different compared to 4mm and 3m symmetry classes, where $d_{24} = d_{15}$ and $d_{32} = d_{31}$. 
Additionally, there is no $d_{16}$ coefficient for $[011]_c$ poled crystals thus eliminating any cross-talk with the thickness shear mode $d_{15}$. Thus, macroscopic mm2 symmetry achieved by poling in $[011]_c$ configuration and the corresponding unique resonant modes are key to many applications.

Table 3.1 Macroscopic crystallographic symmetries and associated dielectric tensor and piezoelectric charge coefficient matrix

<table>
<thead>
<tr>
<th>Crystal Poling direction</th>
<th>Macroscopic Symmetry</th>
<th>Dielectric Matrix</th>
<th>Piezoelectric Charge Coefficient Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001]$_c$</td>
<td>4mm (Tetragonal)</td>
<td>$\begin{bmatrix} \varepsilon_{11} &amp; 0 &amp; 0 \ 0 &amp; \varepsilon_{11} &amp; 0 \ 0 &amp; 0 &amp; \varepsilon_{33} \end{bmatrix}$</td>
<td>$\begin{bmatrix} 0 &amp; 0 &amp; 0 &amp; 0 &amp; d_{15} &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; d_{15} &amp; 0 &amp; 0 \ d_{31} &amp; d_{31} &amp; d_{33} &amp; 0 &amp; 0 &amp; 0 \end{bmatrix}$</td>
</tr>
<tr>
<td>[011]$_c$</td>
<td>mm2 (Orthorhombic)</td>
<td>$\begin{bmatrix} \varepsilon_{11} &amp; 0 &amp; 0 \ 0 &amp; \varepsilon_{22} &amp; 0 \ 0 &amp; 0 &amp; \varepsilon_{33} \end{bmatrix}$</td>
<td>$\begin{bmatrix} 0 &amp; 0 &amp; 0 &amp; 0 &amp; d_{15} &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; d_{24} &amp; 0 &amp; 0 \ d_{31} &amp; d_{32} &amp; d_{33} &amp; 0 &amp; 0 &amp; 0 \end{bmatrix}$</td>
</tr>
<tr>
<td>[111]$_c$</td>
<td>3m (Rhombohedral)</td>
<td>$\begin{bmatrix} \varepsilon_{11} &amp; 0 &amp; 0 \ 0 &amp; \varepsilon_{11} &amp; 0 \ 0 &amp; 0 &amp; \varepsilon_{33} \end{bmatrix}$</td>
<td>$\begin{bmatrix} 0 &amp; 0 &amp; 0 &amp; 0 &amp; d_{15} &amp; -d_{22} \ -d_{22} &amp; d_{22} &amp; 0 &amp; d_{15} &amp; 0 &amp; 0 \ d_{31} &amp; d_{31} &amp; d_{33} &amp; 0 &amp; 0 &amp; 0 \end{bmatrix}$</td>
</tr>
</tbody>
</table>

3.2 Macroscopic Orthorhombic Symmetry

As piezoelectric materials with large anisotropy, single crystals can exhibit various resonance modes based on their compositions and polarization directions. Possible resonant modes based on crystallographic symmetry, polarization orientation, and maximum strain directions are presented in Appendix C.

3.2.1 Orientation dependence of properties for engineered domain configurations

With the large anisotropy of the single crystal materials, there is also orientation dependence of their polarization behavior which is critical for the understanding of their
operational modes and strain behavior. Figure 3.3 shows the measured electric field induced polarization hysteresis loops for $<001>_c$, $<110>_c$ and $<111>_c$ oriented PMN-31PT crystals. The remnant polarization $P_r$ and coercive field $E_c$ were found to be dependent on the orientation. From the symmetric loops, the $P_r$ was found to be on the order of 0.24C/m², 0.34C/m² and 0.41C/m² for $<001>_c$, $<110>_c$ and $<111>_c$ orientations, while the coercive field $E_c$ was on the order of 2.5kV/cm, 2.9kV/cm and 3.2kV/cm, respectively. According to the domain engineered configurations, the polarization level derived from the hysteresis loops should correspond, in theory, to the intrinsic value along the polar axis of the monodomain crystal $P_s$, following $P_{r<001>}/\sqrt{2} = P_{r<110>}/\sqrt{4} = P_{r<111>}/\sqrt{8}^{8-10}$. As expected, the $P_r$ values for the different orientations obtained from Figure 3.3 corresponded well to the predicted values.

For PMN-PT crystals, the temperature dependence and phase transitions are shown in Figure 3.4 for two different compositions when poled along the three different orientations. From the permittivity measurements, the rhombohedral to orthorhombic phase transition is more pronounced for the PMN-PT binary crystal system when poled along [011]. It can be seen from Figure 3.5, where the PE loop and coercive field are compared for all three crystal types in rhombohedral phase, while [011] poling only
increases the $E_c$ for PMN-PT and PIN-PMN-PT crystals slightly ($E_c$ from 2 to 2.5 kV/cm for PMN-PT and 5 to 5.3 kV/cm for PIN-PMN-PT), the stabilization when poled along [011]$_c$ is much higher in Mn-doped PIN-PMN-PT crystals ($E_c$ is increased from 5.5 to $\sim$8.8 kV/cm). In line with the dissertation’s focus on macroscopic orthorhombic symmetry achieved by poling in [011]$_c$ direction, the higher $E_c$ in Mn:PIN-PMN-PT is of very high interest along with the high $E_i$ and $Q_m$ due to significant potential for use in high power applications. Table 3.2 summarizes the comparison of properties between piezoceramics, and crystals poled along [001]$_c$ and [011]$_c$ direction. All crystals were oriented by the Laue X-ray orientation system with an accuracy of 0.5º. Vacuum sputtered chrome/gold with thickness of 500/2000 Å was applied to the desired surfaces as electrodes for polarization and measurements. All PMN-PT samples were poled at a dc electric field of 3.5 kV/cm at room temperature for [001]$_c$ and [011]$_c$. PIN-PMN-PT crystals for both [001]$_c$ and [011]$_c$ orientation were poled at 10 kV/cm. For Mn:PIN-PMN-PT single crystals, [001]$_c$ poled crystals were poled at 10 kV/cm and [011]$_c$ poled samples were poled at 15 kV/cm. The temperature dependence of the dielectric permittivity was determined on $k_t$ type samples using HP4284A precision LCR meter at 1 kHz and 10 kHz, which were connected to a computer controlled high temperature furnace. Polarization and strain under high electric field were determined using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT) driven by a lock-in amplifier (Stanford Research system, Mode SR830).
Figure 3.4 Permittivity vs. temperature as function of orientation for PMN-PT crystals (for frequencies 1, 10 and 100 kHz)

Figure 3.5 Coercive field ($E_c$) comparison for [001]c poled and [011]c poled crystals for all three types of relaxor-PT crystals in rhombohedral phase
### Table 3.2 Summary of the [001] and [110] c-poled longitudinal mode piezoelectric and dielectric properties of relaxor-PT crystals

<table>
<thead>
<tr>
<th>Materials</th>
<th>Poling</th>
<th>$\varepsilon_{33}$</th>
<th>Loss (%)</th>
<th>$k_{33}$</th>
<th>$d_{33}$ (pC/N)</th>
<th>$T_C$ (°C)</th>
<th>$T_{rt}$ (°C)</th>
<th>$E_c$ (kV/cm)</th>
<th>$Q_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT5H (soft)</td>
<td>/</td>
<td>3500</td>
<td>1.8%</td>
<td>0.75</td>
<td>590</td>
<td>193</td>
<td>/</td>
<td>7.8</td>
<td>65</td>
</tr>
<tr>
<td>PZT8 (hard)</td>
<td>/</td>
<td>1000</td>
<td>0.4%</td>
<td>0.70</td>
<td>220</td>
<td>300</td>
<td>/</td>
<td>15</td>
<td>1000</td>
</tr>
<tr>
<td>PMN-PT crystals</td>
<td></td>
<td>≥5000</td>
<td>≤0.6</td>
<td>≥0.90</td>
<td>1500-2200</td>
<td>≥120</td>
<td>≥85</td>
<td>≥1.8</td>
<td>≥80</td>
</tr>
<tr>
<td>PIN-PMN-PT crystals</td>
<td>&lt;001&gt;</td>
<td>≥4000</td>
<td>≤0.6</td>
<td>≥0.90</td>
<td>1300-2000</td>
<td>≥120</td>
<td>≥120</td>
<td>≥4.5</td>
<td>≥100</td>
</tr>
<tr>
<td>Mn: PIN-PMN-PT crystals</td>
<td></td>
<td>≥2900</td>
<td>≤0.2</td>
<td>≥0.90</td>
<td>1080-1700</td>
<td>≥120</td>
<td>≥120</td>
<td>≥4.5</td>
<td>≥700</td>
</tr>
<tr>
<td>PMN-PT crystals</td>
<td></td>
<td>≥3500</td>
<td>≤0.6</td>
<td>≥0.87</td>
<td>1000-1500</td>
<td>≥120</td>
<td>≥75</td>
<td>≥1.8</td>
<td>≥400</td>
</tr>
<tr>
<td>PIN-PMN-PT crystals</td>
<td>&lt;110&gt;</td>
<td>≥3100</td>
<td>≤0.6</td>
<td>≥0.87</td>
<td>900-1300</td>
<td>≥120</td>
<td>≥110</td>
<td>≥4.5</td>
<td>≥500</td>
</tr>
<tr>
<td>Mn: PIN-PMN-PT crystals</td>
<td></td>
<td>≥2600</td>
<td>≤0.2</td>
<td>≥0.87</td>
<td>800-1100</td>
<td>≥120</td>
<td>≥110</td>
<td>≥8.0</td>
<td>≥1030</td>
</tr>
</tbody>
</table>

### 3.3 Resonant Modes from Macroscopic Orthorhombic Symmetry

As can be seen on the Table 3.1, the piezoelectrically coupled resonance modes correspond to their piezoelectric charge coefficients. With the $d_{33}$ being the mostly common mode used in medical devices ($k_t$ or thickness mode is still a variant of “33” mode with different boundary conditions), the other modes of interest are transverse ($d_{32}$, $d_{31}$) and shear modes ($d_{15}$, $d_{24}$, etc). For mm2 symmetry and rhombohedral phase (“2R” domain configuration), the $d_{32}$ mode is a very unique transverse mode with significant advantages for transducer design owing to piezoelectric charge coefficients comparable to that of the $d_{33}$ mode while still providing high capacitance (low impedance) which is attractive for drive circuitry. Thickness shear mode, $d_{15}$, with “2R” domain configuration (rhombohedral phase) is also very unique compared to other thickness shear modes due to the absence of cross-coupling coefficient “$d_{16}$”. Additionally, $d_{24}$ thickness shear coefficient exists for mm2 symmetry, and $d_{24}$ mode from monodomain orthorhombic configuration (“1 O”) offers very useful properties but, it is not a practical mode to use
due to very low material availability of orthorhombic phase material in the crystal boule based on current crystal growth methods. Along with $d_{32}$ and $d_{15}$ modes, the face shear “$d_{36}$” mode is also very notable for 2R engineered domain configuration. These modes, their advantages and disadvantages are described in the following sections.

3.3.1. Transverse Extensional Mode ($d_{32}$)

Transverse piezoelectric charge coefficients for most piezoceramics are typically much lower than their longitudinal coefficients (for example, PZT-5A, $d_{31} = \sim -200$ pC/N and $d_{33} = \sim 450$ pC/N). Rhombohedral PMN-PT single crystals poled along [001]$_c$ direction (4mm symmetry, 4R domain) exhibit high $d_{31} = d_{32} (\sim -600$ pC/N) compared to the highest $d_{31}$ in PZT ceramics (PZT-5H, $d_{31} = \sim 280$ pC/N). Due to such high piezoelectric charge coefficient, $d_{32}$ resonance mode is a very valuable design option compared to $d_{33}$ mode and Figure 3.6 illustrates the crystal orientation, poling direction and the maximum strain direction for both modes. Along with the high strain from $d_{32}$ mode, the impedance is lower compared to $d_{33}$ mode and also the voltage required to achieve the same strain level is lower compared to using $d_{33}$ mode. This unique transverse mode is notable with the macroscopic orthorhombic symmetry when rhombohedral crystals are poled in the “2R” domain configuration and this is attributed to the arrangement of dipoles in one plane as compared to the “4R” domain configuration as shown in Figure 3.7. Impedance sweep of a Mn-PIN-PMN-PT single crystal $d_{32}$ mode plate is shown in Figure 3.8 and the $d_{32}$ mode properties are compared to those of PMN-PT and PIN-PMN-PT materials in Table 3.3.
Figure 3.6 Comparison of \(d_{32}\) (or \(k_{32}\)) and \(d_{33}\) (or \(k_{33}\)) mode

Figure 3.7 Dipolar arrangements in “4R” \(d_{33}\) mode and “2R” \(d_{32}\) mode
Figure 3.8 Impedance sweep for Mn-PIN-PMN-PT $d_{32}$ mode plate

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon_{33}^{T}$</th>
<th>$d_{32}$ (pC/N)</th>
<th>$s_{22}^E$ (pm$^2$/N)</th>
<th>$N_{32}$ (Hz.m)</th>
<th>$k_{32}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>4000</td>
<td>-1400</td>
<td>61</td>
<td>750</td>
<td>0.88</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>3000</td>
<td>-1100</td>
<td>56</td>
<td>735</td>
<td>0.87</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>2800</td>
<td>-950</td>
<td>53</td>
<td>780</td>
<td>0.84</td>
</tr>
</tbody>
</table>

3.3.2. Face Shear Mode in “2R” Domain Configuration

Although, there is no $d_{36}$ coefficient in the piezoelectric tensor for mm2 orthorhombic symmetry, due to the existence of large negative $d_{32}$ and positive $d_{31}$ in “2R” domain configuration, when rotated along the Z-axis or [011]$_c$ poling axis, a reasonable face shear strain can be experienced [4-5]. The tensor rotation and the $d_{36}$ coefficient are shown below:
When rotated by an angle $\theta$ in the Z-plane, the combination of $d_{32}'$ (rotated $d_{32}$) and $d_{31}'$ (rotated $d_{31}$) gives rise to $d_{36}'$ – a face shear effect in PMN-PT based single crystals poled along [011] direction into mm2 symmetry. The piezoelectric charge coefficient for the face shear mode $d_{36}$ is defined as $d_{36}' = 2(\sin \theta d_{31} - \sin \theta d_{32}) = \sin 2\theta(d_{15} - d_{24})/2$. Plot of the rotated $d_{31}'$ ($d_{311}'$ in tensor notation) and $d_{32}'$ ($d_{322}'$ in tensor notation) is shown in Figure 3.9 for PMN-PT single crystal. The piezoelectric surface for $d_{31}'$ (rotated $d_{31}$) and $d_{32}'$ (rotated $d_{32}$) and the resulting face shear coefficient surface in X-Y plane are shown in 3.10, 3.11, and 3.12.

Figure 3.9 Piezoelectric coefficients $d_{31}'$, $d_{32}'$ and $d_{36}'$ as a function of rotation angle
Figure 3.10 Rotated $d_{31}'$ surface for PMN-PT

Figure 3.11 Rotated $d_{32}'$ surface for PMN-PT
Figure 3.12 Rotated $d_{36}'$ for PMN-PT in X-Y plane

**Rotated Face Shear Mode**

As mentioned above, for [011]$_c$ poled material, the transverse extension in one axis is strong and negative ($d_{32}$), while the extension in the other is weaker and positive ($d_{31}$). By rotating the crystallographic axes relative to the plate edges, an effective shear mode can be produced. This mode is a face shear and has multiple advantages. In this mode, both the poling direction and direction of applied electric field in operation are the same, rather than orthogonal as in typical thickness shear modes. This reduces the chance of depoling and provides higher field stability. The resonance is also dependent on the lateral dimensions of the plate, rather than the thickness, and since these are often much larger than thickness a low resonance frequency is obtained while maximizing capacitance.
Because this mode is a combination of the $d_{32}$ and $d_{31}$ modes and results in effective extensional coefficients $d_{31}'$ and $d_{32}'$, by crystallographically rotating the in-plane $<110>$ and $<001>$-family axes, one of these modes can be eliminated, producing a more “pure” shear. This engineered $d_{36}'$ face shear is illustrated in Figure 3.13 and Figure 3.14.

The face shear component piezoelectric coefficient $d_{36}'$ is dependent on the transverse piezoelectric coefficients $d_{31}$ and $d_{32}$ of the crystal before rotation. The crystal further exhibits an elimination or reduction of the rotated transverse piezoelectric coefficients $d_{31}'$ or $d_{32}'$ (i.e., the absolute value of the minimized rotated transverse width extensional piezoelectric coefficient is less than or equal to about 50 pC/N, preferably less than about 25 pC/N as shown in Figure 3.15). To eliminate or reduce $d_{31}'$, the crystal is rotated around the Z-axis by an angle:

$$\theta_{31} = \arctan\left(\frac{-d_{31}}{d_{32}}\right)$$

To eliminate or reduce $d_{32}'$ is, the crystal is rotated around the Z-axis by an angle:

$$\theta_{32} = \arctan\left(\frac{-d_{32}}{d_{31}}\right)$$

Impedance sweep characteristics for a Mn:PIN-PMN-PT rotated face shear ($d_{36}'$) plate is shown in Figure 3.16. The $d_{36}'$ mode properties are compared to those of PMN-PT and PIN-PMN-PT materials in Table 3.3.
Figure 3.13 Illustration of the face shear mode with elimination of cross-coupling [6]
Figure 3.14 $d_{36}'$ mode (rhombohedral phase) – stable face shear mode for high drive – unique advantage of having the poling electrode and operational electrode across the same faces [6]

Figure 3.15 Measured $d_{31}'$ and $d_{32}'$ strain field curves for a $d_{36}$ face shear [110]/(110) PMN-PT single crystal with ‘2R’ engineered domain configuration, showing near elimination of the $d_{32}'$
Table 3.4 Comparison of Mn:PIN-PMN-PT $d_{36}^{'}$ mode properties to those of PIN-PMN-PT and PMN-PT single crystals

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon_{33}$</th>
<th>$d_{36}$ (pC/N)</th>
<th>$s_{66}$ (pm²/N)</th>
<th>$N_{36}$ (Hz·m)</th>
<th>$k_{36}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>3900</td>
<td>1600</td>
<td>92.8</td>
<td>650</td>
<td>0.78</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>2800</td>
<td>1300</td>
<td>115</td>
<td>680</td>
<td>0.78</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>2450</td>
<td>1080</td>
<td>100</td>
<td>720</td>
<td>0.78</td>
</tr>
</tbody>
</table>

3.3.3. Thickness Shear Mode ($d_{15}$)

Traditional shear mode in piezoceramics with “6mm” or hexagonal macroscopic symmetry is based on thickness shear mode or $d_{15}$ mode. The elastic compliance $s_{55}^E$ is $\sim 30-40 \times 10^{-12} \text{m}^2/\text{N}$ for PZT-4 and PZT-8 materials. With the anisotropy in relaxor PT single crystals, various shear modes are possible. The traditional “1R $d_{15}$” shear mode properties obtained by poling the rhombohedral crystals in [111]c direction is compared with other shear modes in Table 3.5. The “1R $d_{15}$” shear mode is usually suffers from
inferior reliability due to microcracking from mono-domain configuration, cross-talk from “d_{16}”, and/or large temperature dependence of properties.

In applications of the shear mode, whether as sensors or transmitters, it is desirable to maximize the response in one axis while minimizing the response in the lateral axis. This is represented in Figure 3.17. The ideal shear deflection is shown in Figure 3.17a, where the top face shows translation only in the Z axis, and the non-ideal deflection is shown in Figure 3.17b, where the top face shows translation in both the Z and Y axes (the Y axis being the lateral axis). In applications such as sensors, this non-ideal shear deflection results in noise in signal due to cross-coupling. The response in the lateral axis can be reduced to zero or minimized through rotation of the crystal after poling.

![Diagram](a) Uniaxial shear (b) Shear with lateral component

Figure 3.17 (a) Desirable shear mode for many applications of sensors and transmitters in which the translation of the top face is purely in a single coordinate axis Z (b) Undesirable shear in which a lateral component perpendicular to the main axis Z also occurs with the main shear and the top face of the crystal moves in both the Z and Y axes.

It has been shown that a zero or minimum response for d_{16} could be obtained by rotating [111]_c direction poled, shear PMN-PT single crystal around the X axis as shown in the orientation dependence plot of d_{15} in Figure 3.18 [4]. Figure 3.19 illustrates the
rotation axis of the crystal relative to the spontaneous [111]c polarization. Figure 3.20 shows the measured $d_{15}$ and $d_{16}$ and trend curves for PIN-PMN-PT crystal with [111]c polarization and subsequent rotations of the sample geometries at different angles. From Figure 3.21 it can be seen that a zero $d_{16}$ value occurs near 25°. The general angle by which to rotate around the X axis is:

$$\gamma = \arctan\left(\frac{d_{16}}{d_{15}}\right),$$

where the $d_{16}$ and $d_{15}$ are the values at $\gamma = 0^\circ$.

Figure 3.18 Orientation dependence plot of $d_{15}$ for 1R domain configuration showing that the $d_{16}$ component would approach zero near angle of 22.5° [4]
Figure 3.19 Rotation about X axis to reduce or eliminate the $d_{16}$ coefficient while maintaining polarization in the [111]$_c$ axis for PIN-PMN-PT crystals with ‘1R’ domain configuration.

Figure 3.20 $d_{15}$ and $d_{16}$ values measured from strain hysteresis loops for [111]$_c$ poled crystals with ‘1R’ domain configuration [6].
3.3.4. Thickness shear mode ($d_{15}$) from “2R” domain configuration

Even with rotation to eliminate the $d_{16}$ cross-coupling, the 1R $d_{15}$ is very difficult to fabricate due to the monodomain rhombohedral configuration. When rhombohedral single crystals are poled along [011]$_c$, ‘2R’ engineered domain configuration is obtained with macroscopic mm2 symmetry and it does not exhibit a $d_{16}$ thickness shear mode. Figure 3.21, Figure 3.22 and Figure 3.23 show measured $d_{15}$ and $d_{16}$ strain hysteresis curves for PMN-PT, PIN-PMN-PT and Mn-doped PIN-PMN-PT poled along the [011]$_c$ direction. Both the PMN-PT and PIN-PMN-PT measurements were performed on single plates, and the Mn-doped PIN-PMN-PT measurements were obtained from an assembled stack of three plates bonded on the faces. Very small values of $d_{16}$ were measured, which might be due to a combination of measurement limitations and noise, and limitations in achieving exact alignments. All measured $d_{16}$ values are less than 3.5% of the $d_{15}$ values, showing a very small cross-coupling. The non-rotated spontaneous $<111>_c$ polarization exhibits values of $d_{16}$ approximately 40% of the $d_{15}$ values. When considering thickness shear mode applications, it is recommended to use the “2R” $d_{15}$ configuration as much as possible to achieve practically producible thickness shear mode parts.
Figure 3.21 Measured $d_{15}$ and $d_{16}$ shear strain field curves for [110]/(-110) PMN-PT crystal with ‘2R’ engineered domain configuration [6]

Figure 3.22 Measured $d_{15}$ and $d_{16}$ shear strain field curves for $d_{15}$ [110]/(-110) PIN-PMN-PT crystal with ‘2R’ engineered domain configuration [6]
3.3.5. Polarization Stability under Applied AC Field

Based on 2R domain configuration, the modes of interest for relaxor-PT single crystals are $d_{32}$, $d_{36}'$, and $d_{15}$. Compared to $d_{32}$ and $d_{36}'$ modes, the $d_{15}$ thickness shear mode has applied electric field perpendicular to the polarization direction which results in lower stability. Field stability of shear modes under drive conditions is important since the applied field would destabilize the polarization and causes a polarization rotation effect along the field direction. This depolarization effect is shown in Figure 3.24 and Figure 3.25 for 2R $d_{15}$ thickness shear mode sample made using PIN-PMN-PT single crystals and in figure 3.26 and 3.27 for Mn:PIN-PMN-PT single crystals.

Table 3.5 summarizes the properties of “1R” and “2R” $d_{15}$ thickness shear modes in pure and manganese doped PIN-PMN-PT single crystals. The piezoelectric shear coefficient, $d_{15}$, and electromechanical coupling factor, $k_{15}$, were found to be
approximately 3000 pC/N and >90%, respectively for undoped crystals, with allowable ac drive fields at about 2 kV/cm, less than half of their respective coercive field. Mn:PIN-PMN-PT were found to possess comparable shear piezoelectric properties to their undoped ternary counterparts, but with much higher allowable ac drive field levels, being on the order of 4-5kV/cm, due to their enhanced coercive fields and developed internal biases.

Figure 3.24. Polarization loops for the first and 5000th cycles at different electric field drive levels for pure d15 [110]/(-110) PIN-PMN-PT crystals with ‘2R’ engineered domain configuration [6-7]
Figure 3.25. Impedance characteristics for shear thickness vibration mode after 5000 cycles at different levels for $d_{15}$ [110]/(-110) PIN-PMN-PT crystals with ‘2R’ engineered domain configuration [6-7].

Figure 3.26. Polarization loops for the first and 5000th cycles at different electric field drive levels for Mn:PIN-PMN-PT crystals with 2R $d_{15}$ [110]/(-110) mode [6-7].
Figure 3.27. Impedance characteristics for shear thickness vibration mode after 5000 cycles at different levels for $d_{15} [110]/(-110)$ Mn: PIN-PMN-PT crystals with ‘2R’ engineered domain configuration [6-7]

From Table 3.5, it is interesting to note that the field stability levels (max allowable ac drive fields divided by their respective coercive fields) are on the order of approximately 40% for undoped crystals, while the values increased to about 60-70% for the manganese doped crystals. This is due to the developed internal bias and it is noted that field stability increases with increasing internal bias levels. Thus, both coercive field and internal bias play an important role in the polarization stability under applied field.
Table 3.5 Thickness shear mode (d15) properties compared for PIN-PMN-PT and Mn:PIN-PMN-PT single crystals

<table>
<thead>
<tr>
<th>Poling/electrode</th>
<th>Engineered domain</th>
<th>Crystal Poling axis</th>
<th>E_r (kV/cm)</th>
<th>E_i (kV/cm)</th>
<th>E_{11}^T (pC/N)</th>
<th>d_{33} (Hz.m)</th>
<th>k_{11}</th>
<th>N_{15} (Hz.m)</th>
<th>AC field stability (kV/cm)</th>
<th>Field Stability Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>111/1-10</td>
<td>1R (d_{15})</td>
<td>Pure PIN</td>
<td>4.5</td>
<td>/</td>
<td>6000</td>
<td>3500</td>
<td>0.93</td>
<td>470</td>
<td>2</td>
<td>44%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PIN-Mn</td>
<td>6.2</td>
<td>1.0</td>
<td>8000</td>
<td>4100</td>
<td>0.94</td>
<td>410</td>
<td>4</td>
<td>65%</td>
</tr>
<tr>
<td>110/-110</td>
<td>2R (d_{15})</td>
<td>Pure PIN</td>
<td>5.0</td>
<td>/</td>
<td>6500</td>
<td>2800</td>
<td>0.92</td>
<td>570</td>
<td>2</td>
<td>40%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PIN-Mn</td>
<td>7.3</td>
<td>1.2</td>
<td>4600</td>
<td>2200</td>
<td>0.91</td>
<td>520</td>
<td>5</td>
<td>68%</td>
</tr>
</tbody>
</table>

3.4 Summary and Discussion

Manganese doped ternary crystal exhibits internal bias and hence high Q_m similar to hard piezoceramic materials. Similar to PMN-PT single crystals, very high electromechanical coupling (k_{33} ~0.9) is obtained for 4R domain configuration with lowering of dielectric constant and d_{33} as expected from the acceptor doping. Additionally, due to the single crystal anisotropy, there are various modes that are possible due to engineered domain configurations. When rhombohedral Mn-PIN-PMN-PT is poled along [011]_c with the 2R domain configuration, there is a substantial increase in coercive field, (E_c ~8.5 kV/cm) compared to when poled along [001]_c configuration. Due to this high coercive field, resonance modes based on 2R domain configuration as of substantial interest for high power applications. Traditional thickness shear mode (1R d_{15}) design for rhombohedral relaxor PT crystals based on poling along [111]_c results in mono-domain configuration, which has inferior reliability due to low polarization.
stability. Moreover, the 1R $d_{15}$ shear mode exhibits a $d_{16}$ cross talk that reduces the sensitivity of the device. Alternate shear modes (patent pending by TRS Technologies Inc and Penn State University) classified as “2R $d_{15}$”, and $d_{36'}$ have been identified with reduced or zero cross talk. Each of them has their own additional advantages: 1) 2R $d_{15}$ shear mode has better electric field stability and has no cross-coupling term $d_{16}$, and 2) $d_{36'}$ is a rotated face shear mode with reduced crosstalk and high polarization stability as summarized in Table 3.6. The modes and their geometries are shown in Figure 3.28.

Table 3.6 Drive field stability of different vibration modes of Mn:PIN-PMN-PT single crystals [7]

<table>
<thead>
<tr>
<th>Material</th>
<th>Mode</th>
<th>$E_c$ (kV/cm)</th>
<th>Allowable drive field (kV/cm)</th>
<th>Field Stability ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>$d_{15}$ (2R)</td>
<td>2.5</td>
<td>1.0</td>
<td>40%</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>$d_{15}$ (2R)</td>
<td>5</td>
<td>2.0</td>
<td>40%</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>$d_{15}$ (2R)</td>
<td>7.3</td>
<td>5.0</td>
<td>68%</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>$d_{36'}$ (2R)</td>
<td>7.3</td>
<td>7.0</td>
<td>95%</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>$d_{32}$ (2R)</td>
<td>7.3</td>
<td>7.0</td>
<td>95%</td>
</tr>
</tbody>
</table>

For macroscopic orthorhombic symmetry and engineered “2R” domain configuration, the modes of primary importance from the standpoint of device design are $d_{32}$, $d_{15}$, and $d_{36'}$.

- $d_{32}$ mode - unique transverse mode with high capacitance and strain comparable to $d_{33}$ mode
- $d_{36'}$ mode (rhombohedral phase) – face shear – unique advantage of having the poling electrode and operational electrode as the same pair of faces making this a very stable shear for high drive conditions.
- “2R $d_{15}$” shear (rhombohedral phase) – high field stability compared to “1R $d_{15}$” mode
Summary of these resonance modes and their tradeoffs are shown in Table 3.7.

Figure 3.28 Crystallographic orientation for 2R $d_{15}$ shear – plate C in above and $d_{36}'$ – shown in the right [7]

Table 3.7. Summary of various modes and tradeoffs in using them for design

<table>
<thead>
<tr>
<th>Mode</th>
<th>$d_{i\alpha}$ (pC/N)</th>
<th>$N$ (Hz.m)</th>
<th>$E_c^*$ (kV/cm)</th>
<th>Max. Field*</th>
<th>Tradeoffs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1R $[111]<em>c$ $d</em>{15}$</td>
<td>3000</td>
<td>470</td>
<td>~2.5</td>
<td>~1.3</td>
<td>✓ High piezoelectric coefficient</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>× Low stability with temperature and field</td>
</tr>
<tr>
<td>2R $[011]<em>c$ $d</em>{15}$</td>
<td>2800</td>
<td>570</td>
<td>5.0</td>
<td>2.0</td>
<td>✓ Good combination of properties.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>× Field/poling not parallel</td>
</tr>
<tr>
<td>2R $[011]<em>c$ $d</em>{36}'$</td>
<td>~2000</td>
<td>570</td>
<td>4.5</td>
<td>~2.3</td>
<td>✓ Poling/electric. field parallel</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>× Isolation of mode is challenging</td>
</tr>
<tr>
<td>2R $[011]<em>c$ $d</em>{32}$</td>
<td>~2000</td>
<td>570</td>
<td>4.5</td>
<td>~2.3</td>
<td>✓ Poling/electric field parallel</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>× Positive $d_{31}$ may interfere</td>
</tr>
</tbody>
</table>
3.5 References


Chapter 4

Full Material Property Characterization of Manganese doped PIN-PMN-PT Single Crystals

4.1 Full Property Measurement for 2R engineered domain configuration

For device design using any finite element software like ATILA, PZFlex, ANSYS, COMSOL, etc, it is important to enter the full property tensor of the material which includes the dielectric, piezoelectric, and elastic tensors. The tensor matrices for different physical properties of any crystal symmetry class are obtained by applying the Neumann’s law based on their point group symmetries. For the macroscopic orthorhombic symmetry that is of interest in this research, the crystallographic mm2 symmetry refers to the symmetry elements $m_{\perp Z_1}$ and $m_{\perp Z_2}$ as shown in Figure 4.1.

![Stereographic projection for mm2 symmetry](image)

Figure 4.1 Stereographic projection for mm2 symmetry, two mirror planes ($m_{\perp Z_1}$ and $m_{\perp Z_2}$) which lead to a 2-fold rotation axis along $Z_3$. 
Table 4.1 Full Property Testing – elastic coefficients based on macroscopic symmetry

<table>
<thead>
<tr>
<th>Crystal Poling direction</th>
<th>Macroscopic Symmetry</th>
<th>Elastic Coefficient Matrix – Stiffness</th>
</tr>
</thead>
</table>
| [001]_c                  | 4mm (Tetragonal)     | \[
\begin{pmatrix}
    c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\
    c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\
    c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\
    0 & 0 & 0 & c_{44} & 0 & 0 \\
    0 & 0 & 0 & 0 & c_{44} & 0 \\
    0 & 0 & 0 & 0 & 0 & c_{66}
\end{pmatrix}
\] |
| [110]_c                  | mm2 (Orthorhombic)  | \[
\begin{pmatrix}
    c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\
    c_{12} & c_{22} & c_{23} & 0 & 0 & 0 \\
    c_{13} & c_{23} & c_{33} & 0 & 0 & 0 \\
    0 & 0 & 0 & c_{44} & 0 & 0 \\
    0 & 0 & 0 & 0 & c_{55} & 0 \\
    0 & 0 & 0 & 0 & 0 & c_{66}
\end{pmatrix}
\] |
| [111]_c                  | 3m (Rhombohedral)   | \[
\begin{pmatrix}
    c_{11} & c_{12} & c_{13} & c_{14} & 0 & 0 \\
    c_{12} & c_{11} & c_{13} & -c_{14} & 0 & 0 \\
    c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\
    c_{14} & -c_{14} & 0 & c_{44} & 0 & 0 \\
    0 & 0 & 0 & 0 & c_{44} & c_{14} \\
    0 & 0 & 0 & 0 & c_{14} & \frac{1}{2}(c_{11} - c_{12})
\end{pmatrix}
\] |

The physical properties can be obtained by using the transformation matrices given by:

\[
m_{\perp Z_1} = \begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\text{ and } m_{\perp Z_2} = \begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

For the three classes of crystal symmetry, the dielectric and piezoelectric tensors are shown in Table 3.1 and elastic tensor is shown in Table 4.1. The mm2 symmetry would be applicable for 2R, 2T, and 1O domain states as shown on Figure 4.1.
For rhombohedral crystals poled along [001]$_c$ direction, macroscopic symmetry is 4mm and the domains exhibit “4R” symmetry and for crystals poled along [011]$_c$ direction, macroscopic symmetry is mm2 and the domains exhibit “2R” symmetry. Table 4.1 shows the comparison of how the poling affects the presence/absence of certain elastic coefficients in the full property matrix between the various domain configurations.

Apart from the longitudinal elongation mode for 4R domain which exhibits the highest $d_{33}$ and $k_{33}$ for all 3 crystals, the three resonance modes of interest ($d_{32}$, $d_{15}$ and $d_{36}'$) that are under investigation in this dissertation research are based on [011]$_c$ poling direction with 2R domain configuration. Samples require for full set property measurement for mm2 symmetry are shown in Figure 4.2. For the [011]$_c$ poled rhombohedral crystals with “2R” engineered domain state, the macroscopic symmetry is mm2, so that there are 17 independent material constants: 9 elastic constants, 5 piezoelectric constants and 3 dielectric permittivities. Combination of resonance and ultrasonic methods is used to get the full property data [1-3].

![Figure 4.2 Various samples for full property measurement for crystal with mm2 symmetry](image)
4.1.1 Combined Resonance and Ultrasound Method for mm2 symmetry

For determination of full property matrices of the mm2 symmetry, typically 1 ultrasonic sample and 6 resonance mode samples are used as shown in Table 4.2. According to the IEEE standards on piezoelectricity [5], the pseudo-cubic crystallographic [011]c direction is defined as the X axis, and [100]c, [011]c are defined as the Y and Z axes, respectively. The complete set of material constants was determined by combined resonance and ultrasonic methods. The resonance and anti-resonance frequencies were measured using an HP4194A impedance-phase gain analyzer [16]. Longitudinal and shear wave transducers were used to measure the phase velocities on cube samples with the dimensions of 5.0×5.0×5.0 mm³, from which, corresponding elastic stiffness constants: $c_{11}^E$, $c_{22}^E$, $c_{33}^D$, $c_{44}^E$, $c_{44}^D$, $c_{55}^E$, and $c_{66}^E$ could be calculated.

The full property matrix for Mn:PIN-PMN-29PT and Mn:PIN-PMN-31PT in 2R configuration was determined as shown. A full sample set was processed from a single 2” diameter Mn:PIN-PMN-PT crystal grown in the <011> direction for two different PT content levels. The Curie temperature was measured on all samples from capacitance vs. temperature measurements. This was used as a verification that the composition variation is $\pm 3\%$ for all samples. For the resonance mode samples, they were poled along the [011]c configuration as per the geometry, crystal orientation, and aspect ratio and the piezoelectric and dielectric properties were measured by using an impedance analyzer (HP 4194A) and a LCR Meter (HP 4294A). The free and clamped capacitance values were measured to obtain the permittivity matrix.

$$\varepsilon_{ii}^T = \frac{C_{ii}^T}{lW} \quad \text{Eq 4.1}$$

$$\varepsilon_{ii}^S = \frac{C_{ii}^S}{lW} \quad \text{Eq 4.2}$$

$$\beta_{ii}^T = \frac{1}{\varepsilon_{ii}^T} \quad \text{Eq 4.3}$$
\[ \beta_i^S = \frac{1}{\varepsilon_{ii}^S} \quad \text{Eq 4.4} \]

**Values Calculated From Resonance Samples:**

**Using \( k_{31} \) bar**

\[ s_{11}^E = \frac{1}{4l^2 \rho f_r^2} \quad \text{Eq 4.5} \]

\[ \frac{k_{31}^2}{1 - k_{31}^2} = \frac{\pi f_a}{2 f_r} \tan \left( \frac{\pi \Delta f}{2 f_r} \right) \quad \text{Eq 4.6} \]

\[ d_{31} = k_{31} \sqrt{\varepsilon_{31}^T s_{11}^E} \quad \text{Eq 4.7} \]

**Using \( k_{32} \) bar**

\[ s_{22}^E = \frac{1}{4l^2 \rho f_r^2} \quad \text{Eq 4.8} \]

\[ \frac{k_{32}^2}{1 - k_{32}^2} = \frac{\pi f_a}{2 f_r} \tan \left( \frac{\pi \Delta f}{2 f_r} \right) \quad \text{Eq 4.9} \]

\[ d_{32} = k_{32} \sqrt{\varepsilon_{32}^T s_{22}^E} \quad \text{Eq 4.10} \]

**Using \( k_{33} \) bar**

\[ s_{33}^S = \frac{1}{4t^2 \rho f_a^2} \quad \text{Eq 4.11} \]

\[ k_{33}^2 = \frac{\pi f_r}{2 f_a} \tan \left( \frac{\pi \Delta f}{2 f_a} \right) \quad \text{Eq 4.12} \]

\[ d_{33} = k_{33} \sqrt{\varepsilon_{33}^T s_{33}^E} \quad \text{Eq 4.13} \]
Using $k_2$ mode plate

\[ c_{33}^D = 4t^2 \rho f_a^2 \]  
Eq 4.14

\[ k_2^2 = \frac{\pi f_r}{2 f_a} \tan \left( \frac{\pi \Delta f}{2 f_a} \right) \]  
Eq 4.15

\[ e_{33} = k_r \sqrt{E_{13}^S c_{33}^D} \]  
Eq 4.16

From $k_{24}$ mode plate

\[ k_{24} = \frac{d_{24}}{\sqrt{E_{22}^T s_{44}^E}} \]  
Eq 4.17

\[ d_{24} = \sqrt{E_{22}^T \left( \frac{1}{c_{44}^E} - \frac{1}{c_{44}^D} \right)} \]  
Eq 4.18

From $k_{15}$ mode plate

\[ k_{15} = \frac{d_{15}}{\sqrt{E_{11}^T s_{55}^E}} \]  
Eq 4.19

\[ d_{15} = \sqrt{E_{11}^T \left( \frac{1}{c_{55}^E} - \frac{1}{c_{55}^D} \right)} \]  
Eq 4.20

Other Equations:

\[ s_{11}^E = \frac{c_{22}^E c_{33}^E - (c_{23}^E)^2}{C} \]  
Eq 4.21

\[ s_{22}^E = \frac{c_{11}^E c_{33}^E - (c_{13}^E)^2}{C} \]  
Eq 4.22
Solving equations 4.21 to 4.24, we can obtain \( c_{12}^E, c_{13}^E, c_{23}^E \). Summary of the samples and the relevant coefficients obtained from each samples is shown in Table 4.3. The full matrix properties for the 2R configuration of Mn: PIN-PMN-PT single crystals are shown in Table 4.4 and discussed in section 4.1.2.

**Ultrasound Velocity Measurements**

Table 4.2 Coefficients obtained using contact ultrasound measurement (longitudinal and shear transducers are used) for mm\(^2\) symmetry

<table>
<thead>
<tr>
<th>Wave direction</th>
<th>[011] (_c)</th>
<th>[011] (_c)</th>
<th>[011] (_c)</th>
<th>[0-11] (_c)</th>
<th>[0-11] (_c)</th>
<th>[100] (_c)</th>
<th>[100] (_c)</th>
<th>[100] (_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v ) ( \rho )(^2 )</td>
<td>( c_{33}^D )</td>
<td>( c_{55}^E )</td>
<td>( c_{44}^E )</td>
<td>( c_{11}^E )</td>
<td>( c_{55}^D )</td>
<td>( c_{66}^E )</td>
<td>( c_{22}^E )</td>
<td>( c_{44}^D )</td>
</tr>
</tbody>
</table>

Figure 4.3 Sample pulse from ultrasonic pulse-echo method that uses time of flight to obtain sound velocity through the material and elastic constants.
Table 4.3 Sample Dimensions, Crystal Orientation and Measured Properties for mm2

<table>
<thead>
<tr>
<th>Resonance Mode</th>
<th>Schematic</th>
<th>Dimensions</th>
<th>Properties and Equations for elastic and piezo coefficients</th>
</tr>
</thead>
</table>
| \( k_{31} \)  | ![Schematic](image1) | \( t = 0.7 \text{ mm}, \{011\} \)  
\( w = 1.4 \text{ mm}, \{100\} \)  
\( l = 7 \text{ mm}, \{0-11\} \)  | \( s_{11}^E = \frac{1}{4l^2 \rho_f^2} \)  
\( d_{31} = k_{31} \sqrt{\varepsilon_{31}^T s_{11}^E} \) |
| \( k_{32} \)  | ![Schematic](image2) | \( t = 0.7 \text{ mm}, \{011\} \)  
\( w = 1.4 \text{ mm}, \{0-11\} \)  
\( l = 7 \text{ mm}, \{100\} \)  | \( s_{22}^E = \frac{1}{4l^2 \rho_f^2} \)  
\( d_{32} = k_{32} \sqrt{\varepsilon_{33}^T s_{22}^E} \) |
| \( k_{33} \)  | ![Schematic](image3) | \( t = 1 \text{ mm}, \{0-11\} \)  
\( w = 1 \text{ mm}, \{100\} \)  
\( l = 7 \text{ mm}, \{011\} \)  | \( s_{33}^D = \frac{1}{4l^2 \rho_f^2} \)  
\( d_{33} = k_{33} \sqrt{\varepsilon_{33}^T s_{33}^D} \) |
| \( k_t \)  | ![Schematic](image4) | \( t = 0.5 \text{ mm}, \{011\} \)  
\( w = 5 \text{ mm}, \{0-11\} \)  
\( l = 5 \text{ mm}, \{100\} \)  | \( c_{33}^D = 4l^2 \rho_f^2 \)  
\( e_{33}^T = k_t \sqrt{\varepsilon_{33}^T e_{33}^T} \) |
| \( k_{15} \)  | ![Schematic](image5) | \( t = 0.5 \text{ mm}, \{0-11\} \) (apply electrodes after poling)  
\( w = 3.5 \text{ mm}, \{100\} \)  
\( l = 7 \text{ mm}, \{011\} \) (remove electrodes after poling)  | \( k_{15} = \frac{d_{15}}{\sqrt{\varepsilon_{11}^T s_{55}^E}} \)  
\( d_{15} = \sqrt{\varepsilon_{11}^T \left( \frac{1}{c_{55}^E} - \frac{1}{c_{55}^D} \right)} \) |
| \( k_{24} \)  | ![Schematic](image6) | \( t = 0.5 \text{ mm}, \{001\} \) (apply electrodes after poling)  
\( w = 3.5 \text{ mm}, \{0-11\} \)  
\( l = 7 \text{ mm}, \{011\} \) (remove electrodes after poling)  | \( k_{24} = \frac{d_{24}}{\sqrt{\varepsilon_{22}^T s_{44}^E}} \)  
\( d_{24} = \sqrt{\varepsilon_{22}^T \left( \frac{1}{c_{44}^E} - \frac{1}{c_{44}^D} \right)} \) |
| **Cube**  | ![Schematic](image7) | \( t = 5 \text{ mm}, \{011\} \)  
\( w = 5 \text{ mm}, \{0-11\} \)  
\( l = 5 \text{ mm}, \{100\} \)  | \( c = \rho v^2 \) |
4.1.2 Full Property Data for Rhombohedral Mn-doped Single Crystals Poled in 2R Domain Configuration

The complete set of material constants were determined for Mn modified rhombohedral Pb(In$_{0.5}$Nb$_{0.5}$)O$_3$-Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (Mn:PIN-PMN-PT) single crystals poled along [011]$_c$ of the pseudo-cubic coordinates using combined resonance and ultrasonic methods. Mn modified PIN-PMN-PT single crystals with a nominal starting composition of 0.26PIN-0.42PMN-0.32PT were grown using the modified Bridgman technique. For determination of the full property matrix, two sets of resonance mode and ultrasound velocity samples were prepared from two ends of the single crystal boule with varying PT content in the rhombohedral phase. Similar to PMN-PT and PIN-PMN-PT, Mn:PIN-PMN-PT crystals exhibit composition gradient along the growth direction due to the segregation of Ti. For the Mn:PIN-PMN-PT crystals, the lower PT (~28%PT) is denoted as Part A and the higher PT (~31%PT) is denoted as Part B.

The full property coefficients for the two compositions are shown in Table 4.4. The longitudinal piezoelectric coefficient $d_{33}$ and coupling factor $k_{33}$ were ~ 1050 pC/N and 0.90 respectively. The internal bias field exhibited by Mn:PIN-PMN-PT single crystals is responsible for the high mechanical quality factor $Q_{33} >$900, which is very comparable to “hard” piezoelectrics such as PZT4 and PZT-8.
Table 4.4. Measurement data for full property measurement for Mn:PIN-PMN-PT rhombohedral phase poled along [011]c (2R domain)

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic stiffness constants: $c^E$, $c^D$ ($10^{10}$ N/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$c^E_{11}$ $c^E_{12}$ $c^E_{13}$ $c^E_{22}$ $c^E_{23}$ $c^E_{33}$ $c^E_{44}$ $c^E_{55}$ $c^E_{66}$</td>
</tr>
<tr>
<td>A</td>
<td>19.1 12.2 7.43 13.3 11.9 15.2 6.44 0.86 5.00</td>
</tr>
<tr>
<td>B</td>
<td>19.5 13.6 8.32 15.1 13.0 15.1 6.16 0.53 4.67</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic compliance constants: $s^E$, $s^D$ ($10^{-12}$ m$^2$/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$s^E_{11}$ $s^E_{12}$ $s^E_{13}$ $s^E_{22}$ $s^E_{23}$ $s^E_{33}$ $s^E_{44}$ $s^E_{55}$ $s^E_{66}$</td>
</tr>
<tr>
<td>A</td>
<td>18.0 -28.0 13.1 68.1 -39.4 30.9 15.5 116.3 20.0</td>
</tr>
<tr>
<td>B</td>
<td>23.5 -39.0 20.6 90.4 -56.4 43.8 16.2 189 21.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Piezoelectric constants: $d$ ($10^{-12}$ C/N), $e$ (C/m$^2$), $g$ ($10^{-3}$ V/m), $h$ ($10^8$ V/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d_{15}$ $d_{24}$ $d_{31}$ $d_{32}$ $d_{33}$ $e_{15}$ $e_{24}$ $e_{31}$ $e_{32}$ $e_{33}$</td>
</tr>
<tr>
<td>A</td>
<td>2030 125 455 -1200 810 17.5 8.05 1.23 -8.52 14.8</td>
</tr>
<tr>
<td>B</td>
<td>2986 160 608 -1508 1053 15.8 9.86 1.08 -7.83 13.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric constants: $\varepsilon$ ($\varepsilon_0$), $\beta$ ($10^4$/$\varepsilon_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon^S_{11}$ $\varepsilon^S_{22}$ $\varepsilon^S_{33}$ $\varepsilon^T_{11}$ $\varepsilon^T_{22}$ $\varepsilon^T_{33}$ $\beta^S_{11}$ $\beta^S_{22}$ $\beta^S_{33}$ $\beta^T_{11}$ $\beta^T_{22}$ $\beta^T_{33}$</td>
</tr>
<tr>
<td>A</td>
<td>912 970 635 4916 1084 3213 11.0 10.3 15.7 2.03 9.23 3.11</td>
</tr>
<tr>
<td>B</td>
<td>935 1320 515 6274 1499 3523 10.7 7.57 19.4 1.59 6.67 2.84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Electromechanical coupling constants: $k_{ij}$ and density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{15}$ $k_{24}$ $k_{31}$ $k_{32}$ $k_{33}$ $k_t$ $\rho$ (kg/m$^3$) $Q_{33}$ $Q_{15}$</td>
</tr>
<tr>
<td>A</td>
<td>0.90 0.32 0.64 0.86 0.86 0.45 8160 980 95</td>
</tr>
<tr>
<td>B</td>
<td>0.92 0.34 0.71 0.90 0.90 0.46 8160 1000 130</td>
</tr>
</tbody>
</table>

Figure 4.4(a) shows the temperature dependence of dielectric permittivity and dielectric loss for the two compositions of rhombohedral Mn:PIN-PMN-PT single crystals (A is ~28%PT and B is 31%PT). The dielectric permittivity at room temperature was found to increase with increasing PT, due to the composition approaching to MPB. The Curie temperature of composition B was found to be ~197 °C, while the Curie
temperature of composition A was found to be \( \sim 188 \) °C. For composition A, a rhombohedral-tetragonal phase transition \((T_n)\) was found to be \( \sim 128 \) °C, while for composition B, two ferroelectric phase transitions were observed below the Curie temperature, corresponding to rhombohedral-monoclinic \((T_{rm} \sim 106 \) °C) and monoclinic-tetragonal \((T_{mt} \sim 121\) °C) phase transitions. The dielectric loss for Mn:PIN-PMN-PT single crystals exhibited peak values at the associated phase transitions, as given in Figure 4.4(b).

Table 4.4 gives the complete set of elastic, piezoelectric and dielectric constants of [011]c poled and [001]c poled Mn:PIN-PMN-PT rhombohedral single crystals. All of the piezoelectric properties for composition B with “2R” engineered domain configuration were found to be higher than the values of composition A, where the piezoelectric coefficient \(d_{33}\) and electromechanical coupling factor \(k_{33}\) were found to be \( \sim 1050 \) pC/N and 0.90 for composition B crystals, respectively. Compared to “4R” domain engineered crystals, higher thickness shear piezoelectric \(d_{15}\) and electromechanical coupling factor \(k_{15}\) were observed, being on the order of \( \sim 3000 \) pC/N and 92%, respectively. The mechanical quality factors \(Q_m\) were evaluated for various vibration modes, where the mechanical \(Q_{31}\) (\(Q_{32}\)) for “4R” domain engineered crystals was found to be higher than those of “2R” crystals. In addition, the \(Q_{32}\) was lower than \(Q_{31}\) for “2R” crystals, exhibiting strong anisotropic mechanical properties in [011]c poled crystals. The longitudinal mechanical \(Q_{33}\) for “2R” domain engineered crystals was found to be \( \sim 1000\), comparable to “hard” PZT8 ceramics, and much higher than that of undoped PIN-PMN-PT single crystals. All the shear mechanical quality factors were found to be low, due to the facilitated “polarization rotation” and large rotation angle (90°) in the thickness shear vibration mode. In addition, the mechanical quality factors for composition B were found to be higher than the values of composition A. This may be due to the fact that the Mn dopant has large segregation along the growth direction, thus producing higher Mn
doped level in composition B, leading to a larger internal bias and hence enhancing the mechanical $Q_m$.

Figure 4.4. Dielectric permittivity and (a) and dielectric loss (b) as a function of temperature for [011]$_c$ poled rhombohedral Mn:PIN-PMN-PT single crystals.
Table 4.5. Comparison of electromechanical coupling factor $k_{ij}$ and piezoelectric coefficient $d_{ij}$ (pC/N) for “2R” domain engineered Mn:PIN-PMN-PT, PIN-PMN-PMN and PMN-PT crystals.

<table>
<thead>
<tr>
<th></th>
<th>$d_{15}$ (pC/N)</th>
<th>$d_{24}$ (pC/N)</th>
<th>$d_{31}$ (pC/N)</th>
<th>$d_{32}$ (pC/N)</th>
<th>$d_{33}$ (pC/N)</th>
<th>$k_{15}$</th>
<th>$k_{24}$</th>
<th>$k_{31}$</th>
<th>$k_{32}$</th>
<th>$k_{33}$</th>
<th>$k_{t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2R Mn-PIN-PMN-PT (A, $\sim$28%PT)</td>
<td>2030</td>
<td>125</td>
<td>455</td>
<td>-1200</td>
<td>810</td>
<td>0.90</td>
<td>0.32</td>
<td>0.64</td>
<td>0.86</td>
<td>0.86</td>
<td>0.45</td>
</tr>
<tr>
<td>2R Mn-PIN-PMN-PT (B, $\sim$31%PT)</td>
<td>2986</td>
<td>160</td>
<td>608</td>
<td>-1508</td>
<td>1053</td>
<td>0.92</td>
<td>0.34</td>
<td>0.71</td>
<td>0.90</td>
<td>0.90</td>
<td>0.46</td>
</tr>
<tr>
<td>PIN-PMN-28%PT</td>
<td>2203</td>
<td>114</td>
<td>460</td>
<td>-1156</td>
<td>782</td>
<td>0.90</td>
<td>0.30</td>
<td>0.67</td>
<td>0.86</td>
<td>0.87</td>
<td>0.49</td>
</tr>
<tr>
<td>PIN-PMN-31%PT</td>
<td>3354</td>
<td>162</td>
<td>744</td>
<td>-1781</td>
<td>1363</td>
<td>0.95</td>
<td>0.36</td>
<td>0.75</td>
<td>0.90</td>
<td>0.92</td>
<td>0.50</td>
</tr>
<tr>
<td>PMN-28%PT</td>
<td>2816</td>
<td>234</td>
<td>723</td>
<td>-1761</td>
<td>1766</td>
<td>0.90</td>
<td>0.30</td>
<td>0.65</td>
<td>0.89</td>
<td>0.91</td>
<td>0.50</td>
</tr>
<tr>
<td>PMN-31%PT</td>
<td>3262</td>
<td>289</td>
<td>813</td>
<td>-2116</td>
<td>1916</td>
<td>0.95</td>
<td>0.36</td>
<td>0.71</td>
<td>0.94</td>
<td>0.92</td>
<td>0.52</td>
</tr>
</tbody>
</table>

4.2 Full Property Matrix of Rhombohedral Mn-doped PIN-PMN-PT Single Crystals Poled in 4R Configuration

The 4R domain configuration is considered as a very stable engineered domain configuration for the rhombohedral phase single crystal and $d_{33}$ resonance mode is the most useful operating mode for devices. For the macroscopic 4mm symmetry there are 6 independent elastic constants, 2 dielectric constants, and 3 piezoelectric constants (total
of 11 constants compared to 19 for mm2 symmetry). Samples required for full property measurement for 4mm symmetry are shown in Figure 4.7.

Figure 4.5. Various samples for full property measurement for crystal with 4mm symmetry [4]
Table 4.6 Sample Dimensions, Crystal Orientation and Measured Properties for 4mm Resonance Mode

<table>
<thead>
<tr>
<th>Resonance Mode</th>
<th>Schematic</th>
<th>Dimensions</th>
<th>Properties and Equations for elastic and piezo coefficients</th>
</tr>
</thead>
</table>
| $k_{31}$       | ![Schematic](image) | $t=0.7$ mm, [011]$^p$  
$w=1.4$ mm, [100]  
$l=7$ mm, [0-11] | $s_{11}^E = \frac{1}{4\ell^2 \rho f_r^2}$  
$d_{31} = k_{31} \sqrt{\varepsilon_{33}^T s_{11}^E}$ |
| $k_{33}$       | ![Schematic](image) | $t=1$ mm, [0-11]  
$w=1$ mm, [100]  
$l=7$ mm, [011]$^p$ | $s_{33}^D = \frac{1}{4\ell^2 \rho f_a^2}$  
$d_{33} = k_{33} \sqrt{\varepsilon_{33}^T s_{33}^D}$ |
| $k_{15}$       | ![Schematic](image) | $t=0.5$ mm [0-11]  
(w=5 mm, [0-11]  
(l=5 mm, [100])  
(apply electrodes after poling)  
(w=3.5 mm [100]  
(l=7 mm [011]$^p$  
(remove electrodes after poling)) | $k_{15} = \frac{d_{15}}{\sqrt{\varepsilon_{11}^T s_{44}^E}}$  
$d_{15} = \sqrt{\varepsilon_{11}^T \left( \frac{1}{c_{44}^E} - \frac{1}{c_{33}^D} \right)}$ |
| Cube           | ![Schematic](image) | $t=5$ mm [011]$^p$  
$w=5$ mm [0-11]  
$l=5$ mm [100] | $c = \rho v^2$ |

Table 4.7 Coefficients obtained using Ultrasound velocity measurements

<table>
<thead>
<tr>
<th></th>
<th>[001]</th>
<th>[001]</th>
<th>[100]</th>
<th>[100]</th>
<th>[100]</th>
<th>[110]</th>
<th>[110]</th>
<th>[110]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho v^2$ =</td>
<td>$v_1$</td>
<td>$v_s$</td>
<td>$v_1$</td>
<td>$v_{s1}$</td>
<td>$v_{s2}$</td>
<td>$v_1$</td>
<td>$v_{s1}$</td>
<td>$v_{s2}$</td>
</tr>
<tr>
<td></td>
<td>$c_{33}^D$</td>
<td>$c_{44}^E$</td>
<td>$c_{11}^E$</td>
<td>$c_{66}^E$</td>
<td>$c_{44}^D$</td>
<td>$\frac{1}{2}(c_{11}^E + c_{12}^E + 2c_{66}^E)$</td>
<td>$\frac{1}{2}(c_{11}^E - c_{12}^E)$</td>
<td>$c_{44}^D$</td>
</tr>
</tbody>
</table>

Full property matrix for 4R domain of Mn-PIN-PMN-PT single crystal is shown below in Tables 4.8, 4.9 and 4.10 in comparison to that of PIN-PMN-PT and PMN-PT single crystals.
Table 4.8 Measured and Derived Elastic Compliance Constants, $s_{ij}$ ($10^{-12}$ m$^2$/N), and Elastic Stiffness Constants, $c_{ij}$ ($10^{10}$ N/m$^2$) – 4R domain configuration – Comparison for all 3 crystals

<table>
<thead>
<tr>
<th>Material</th>
<th>$s_{11}^E$</th>
<th>$s_{12}^E$</th>
<th>$s_{13}^E$</th>
<th>$s_{33}^E$</th>
<th>$s_{33}^D$</th>
<th>$s_{66}^E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>52.1</td>
<td>-24.6</td>
<td>-26.4</td>
<td>59.9</td>
<td>16.0</td>
<td>28.3</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>49.0</td>
<td>-20.0</td>
<td>-26.5</td>
<td>57.3</td>
<td>15.2</td>
<td>39.4</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>45.4</td>
<td>-15.9</td>
<td>-28.1</td>
<td>62.4</td>
<td>15.4</td>
<td>27.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>$s_{11}^D$</th>
<th>$s_{12}^D$</th>
<th>$s_{13}^D$</th>
<th>$s_{33}^D$</th>
<th>$s_{33}^D$</th>
<th>$s_{66}^D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>41.8</td>
<td>-34.8</td>
<td>-3.9</td>
<td>10.3</td>
<td>14.0</td>
<td>28.3</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>38.2</td>
<td>-30.8</td>
<td>-4.0</td>
<td>10.3</td>
<td>14.3</td>
<td>39.4</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>34.4</td>
<td>-26.9</td>
<td>-3.9</td>
<td>9.2</td>
<td>13.9</td>
<td>27.8</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>$c_{11}^E$</th>
<th>$c_{12}^E$</th>
<th>$c_{13}^E$</th>
<th>$c_{33}^E$</th>
<th>$c_{33}^E$</th>
<th>$c_{66}^E$</th>
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</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>12.4</td>
<td>11.1</td>
<td>10.4</td>
<td>10.8</td>
<td>6.3</td>
<td>3.5</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>11.9</td>
<td>10.5</td>
<td>10.4</td>
<td>11.4</td>
<td>6.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>12.8</td>
<td>11.1</td>
<td>10.8</td>
<td>11.3</td>
<td>6.5</td>
<td>3.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>$c_{11}^D$</th>
<th>$c_{12}^D$</th>
<th>$c_{13}^D$</th>
<th>$c_{33}^D$</th>
<th>$c_{33}^D$</th>
<th>$c_{66}^D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>12.6</td>
<td>11.3</td>
<td>9.3</td>
<td>16.8</td>
<td>7.1</td>
<td>3.5</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>12.3</td>
<td>10.9</td>
<td>9.0</td>
<td>16.7</td>
<td>7.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>13.3</td>
<td>11.7</td>
<td>9.0</td>
<td>17.0</td>
<td>7.2</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 4.8 continued

Table 4.9. Piezoelectric Coefficients, $d_{ij}$ (pC/N), $e_{ij}$ (C/m²), $g_{ij}$ ($10^{-3}$V/m), $h_{ij}$ ($10^8$V/m), and Electromechanical Coupling Factors, $k_{ij}$, 4R domain configuration – Comparison for all 3 crystals

<table>
<thead>
<tr>
<th>Material</th>
<th>$d_{33}$</th>
<th>$d_{31}$</th>
<th>$d_{15}$</th>
<th>$e_{33}$</th>
<th>$e_{31}$</th>
<th>$e_{15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
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<td>-699</td>
<td>164</td>
<td>22.3</td>
<td>-3.9</td>
<td>10.3</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>1320</td>
<td>-634</td>
<td>105</td>
<td>18.6</td>
<td>-4.8</td>
<td>6.9</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>1340</td>
<td>-609</td>
<td>133</td>
<td>16.8</td>
<td>-5.2</td>
<td>8.6</td>
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</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>$g_{33}$</th>
<th>$g_{31}$</th>
<th>$g_{15}$</th>
<th>$h_{33}$</th>
<th>$h_{31}$</th>
<th>$h_{15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>32.2</td>
<td>-14.6</td>
<td>11.9</td>
<td>27.7</td>
<td>-4.8</td>
<td>8.7</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>35.6</td>
<td>-17.0</td>
<td>8.8</td>
<td>28.9</td>
<td>-7.4</td>
<td>6.5</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>39.7</td>
<td>-18.1</td>
<td>11.3</td>
<td>34.2</td>
<td>-10.7</td>
<td>8.3</td>
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</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>$k_{33}$</th>
<th>$k_{31}$</th>
<th>$k_{15}$</th>
<th>$k_{1}$</th>
<th>$k_{31}(45^\circ)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>0.91</td>
<td>0.44</td>
<td>0.35</td>
<td>0.60</td>
<td>0.81</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>0.91</td>
<td>0.47</td>
<td>0.25</td>
<td>0.57</td>
<td>0.80</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>0.92</td>
<td>0.49</td>
<td>0.31</td>
<td>0.58</td>
<td>0.80</td>
</tr>
</tbody>
</table>
Table 4.10. Dielectric Constants, $\varepsilon_{ij} (\varepsilon_0)$, and Dielectric Impedance Constants, $\beta (10^4/\varepsilon_0)$, 4R domain configuration – Comparison for all 3 crystals

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon_{33}^T$</th>
<th>$\varepsilon_{11}^T$</th>
<th>$\varepsilon_{33}^S$</th>
<th>$\varepsilon_{11}^S$</th>
<th>$\beta_{33}^T$</th>
<th>$\beta_{11}^T$</th>
<th>$\beta_{33}^S$</th>
<th>$\beta_{11}^S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>5400</td>
<td>1560</td>
<td>910</td>
<td>1340</td>
<td>1.85</td>
<td>6.41</td>
<td>10.99</td>
<td>7.46</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>4200</td>
<td>1335</td>
<td>729</td>
<td>1200</td>
<td>2.38</td>
<td>7.49</td>
<td>13.71</td>
<td>8.33</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>3811</td>
<td>1326</td>
<td>553</td>
<td>1169</td>
<td>2.62</td>
<td>7.54</td>
<td>18.08</td>
<td>8.55</td>
</tr>
</tbody>
</table>

4.3 Full Matrix Properties for Rhombohedral Mn-doped PIN-PMN-PT Single Crystals with Monodomain Configuration

Analogous to “hard” PZT ceramics, acceptor doping is an effective method to improve the mechanical quality factor, which can be confirmed by the Mn modified Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (Mn:PZN-PT), and Mn:PMN-PT single crystals. However, the effect of Mn on mechanical quality factors for different domain structures and different vibration modes have not been investigated up to date. With full properties of single-domain rhombohedral Mn:PIN-PMN-PT single crystals, orientation dependence of functional properties can be analyzed and also intrinsic and extrinsic contributions can be compared. In addition, the complete set of self-consistent material properties are needed for practical device design of using finite element simulations. The full set material constants for single domain Mn:PIN-PMN-PT single crystal poled along [111]$_c$ were measured to obtain properties for mono-domain configurations (1R). Samples required for full property measurement of 3m samples are shown in Figure 4.8
Figure 4.6. Various samples for full property measurement for crystal with 3m symmetry [4]

Table 4.1 Coefficients obtained using ultrasound velocity measurements

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_l$</td>
<td>$v_4$</td>
<td>$v_4$</td>
<td>$v_4$</td>
<td>$v_4$</td>
<td>$v_4$</td>
<td>$v_4$</td>
<td>$v_4$</td>
<td>$v_4$</td>
</tr>
<tr>
<td>$\rho v^2$</td>
<td>$c^D_{33}$</td>
<td>$c^E_{44}$</td>
<td>$c^E_{11}$</td>
<td>$c^E_{11}$</td>
<td>$c^E_{11}$</td>
<td>$c^E_{11}$</td>
<td>$c^E_{11}$</td>
<td>$c^E_{11}$</td>
</tr>
</tbody>
</table>

*For 3m symmetry, $c^D_{44} = \frac{c_1 c_2 - c_3 c_4}{c_1 + c_2 - c_3 - c_4}$; $c^D_{66} = c_1 + c_2 - c_4$; $c^E_{14} = \sqrt{c^D_{44} c^D_{66} - c_1 c_2}$

| Elastic stiffness constants: \(c^{E}_{ijc}\) and \(D^{D}_{ijc}\) (10\(^10\) N/m\(^2\)) |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \(c_{11}^{E}\)   | \(c_{12}^{E}\)   | \(c_{13}^{E}\)   | \(c_{14}^{E}\)   | \(c_{33}^{E}\)   | \(c_{44}^{E}\)   | \(c_{66}^{E}\)   | \(c_{11}^{D}\)   | \(c_{12}^{D}\)   | \(c_{13}^{D}\)   | \(c_{14}^{D}\)   |
| 19.2            | 8.10            | 6.35            | 1.10            | 18.2           | 1.14           | 5.57           | 20.8           | 7.24           | 5.67           | -              |
| \(D_{c11}\)     | \(D_{c12}\)     | \(D_{c13}\)     | \(D_{c14}\)     | \(D_{c33}\)     | \(D_{c44}\)     | \(D_{c66}\)     | 19.6           | 5.16           | 6.76           | 1.08           |

| Elastic compliance constants: \(s^{E}_{ijc}\) and \(s^{D}_{ijc}\) (10\(^{-12}\) m\(^2\)/N) |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \(s_{11}^{E}\)   | \(s_{12}^{E}\)   | \(s_{13}^{E}\)   | \(s_{14}^{E}\)   | \(s_{33}^{E}\)   | \(s_{44}^{E}\)   | \(s_{66}^{E}\)   | \(s_{11}^{D}\)   | \(s_{12}^{D}\)   | \(s_{13}^{D}\)   | \(s_{14}^{D}\)   |
| 7.74            | -               | -               | 6.58           | 109.           | 22.2           | 5.85           | -               | -               | 1.61           | 5.79           |
| \(s_{33}^{D}\)   | \(s_{44}^{D}\)   | \(s_{66}^{D}\)   | \(s_{11}^{D}\)   | \(s_{12}^{D}\)   | \(s_{13}^{D}\)   | \(s_{14}^{D}\)   | \(s_{33}^{D}\)   | \(s_{34}^{D}\)   | \(s_{36}^{D}\)   | \(s_{36}^{D}\)   |
| 1.80            | 1.53            | 10.8            | 0              | 1.61           | 5.79           | 20.0           | 15.3           | 5              | 5              | 5              |

| Piezoelectric coefficients: \(d_{ijc}\) (C/m\(^2\)), \(g_{ijc}\) (10\(^{-12}\) C/N), \(h_{ijc}\) (10\(^3\) V/m), and \(\lambda_{ijc}\) (10\(^8\) V/m) |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \(e_{15}\)     | \(e_{31}\)     | \(e_{22}\)     | \(e_{33}\)     | \(d_{15}\)     | \(d_{31}\)     | \(d_{22}\)     | \(d_{33}\)     | \(g_{15}\)     | \(g_{31}\)     | \(g_{22}\)     |
| 17.             | -               | 9.5            | 11.            | 21             | -43            | 29             | 95             | -              | 5.8            | 8.2            |
| \(g_{33}\)     | \(h_{15}\)     | \(h_{31}\)     | \(h_{22}\)     | \(h_{33}\)     | 1              | 3.7            | 8              | 0              | 5.8            | 5.8            |
| 5               | 5.7            | 22             | 11             | 8              | 1              | 3.7            | 8              | 0              | 5.8            | 5.8            |
| 8               | 6              | 4              | 6              | 4              | 6              | 4              | 6              | 4              | 6              | 4              |

| Dielectric constants: \(\varepsilon_{ijc}\) (\(\varepsilon_0\)) and \(\beta_{ijc}\) (10\(^{-4}\)\(/\varepsilon_0\)) |
|-----------------|----------------|----------------|----------------|----------------|----------------|
| \(\varepsilon_{11}^{T}\) | \(\varepsilon_{33}^{T}\) | \(\varepsilon_{11}^{S}\) | \(\varepsilon_{33}^{S}\) | \(\beta_{11}^{T}\) | \(\beta_{33}^{T}\) | \(\beta_{11}^{S}\) | \(\beta_{33}^{S}\) | \(k_{15}\) | \(k_{31}\) | \(k_{33}\) | \(k_t\) |
| 5659            | 1299           | 858            | 1117           | 1.77           | 7.70           | 11.7           | 8.96           | 0.88           | 0.14           | 0.34           | 0.26           |

4.3.1. Orientation Dependence of Properties

Figure 4.9 shows the polarization hysteresis loops for [001]c and [111]c oriented samples measured at 1 Hz. The remnant polarization \(P_r\) for the [001]c and [111]c oriented samples are 27.4 and 43.8 \(\mu\)C/cm\(^2\), respectively. In order to determine the orientation dependence of the piezoelectric coefficient \(d_{33}^*\), dielectric constant \(\varepsilon_{33}^*\) and electromechanical coupling factor \(k_{33}^*\), matrix transformation has been performed in space coordinates using the “1R” single domain data and the results are given in Figures 4.10-4.12 in the (1-10)c crystallographic plane. All material parameters show strong
orientation dependence. It can be seen from Figure 4.10 that the highest $d^{*}_{33}$ value is 982 pC/N, being $57^\circ$C from [111]$_{c}$. The dielectric constant $\varepsilon^{*}_{33}$ increases as the orientation deviated from the [111]$_{c}$, due to the larger $\varepsilon_{11}$ in the single domain state. The highest electromechanical coupling factor $k^{*}_{33}$ was found to be 0.865 at $61^\circ$ inclined from [111]$_{c}$, as shown in Figure 4.11, but the $k^{*}_{33}$ value changes much slowly with orientation compared to $d^{*}_{33}$. Based on the above results, the best piezoelectric and electromechanical properties can be obtained near the [001]$_{c}$, which is $54.7^\circ$ from [111]$_{c}$.

![Polarization hysteresis loops](image)

**Figure 4.7.** Polarization hysteresis loops for Mn:PIN-PMN-PT single crystals measured at 30kV/cm and frequency of 1 Hz [2].
Figure 4.8. Orientation dependence of $d_{33}^*$ for single domain rhombohedral Mn:PIN-PMN-PT crystals in the (1-10)$_c$ crystallographic plane [2].

Figure 4.9. Orientation dependence of $\varepsilon_{33}^*$ for single domain rhombohedral Mn:PIN-PMN-PT crystals in the (1-10)$_c$ crystallographic plane [2].
Figure 4.10. Orientation dependence of $k_{33}^*$ for single domain rhombohedral Mn:PIN-PMN-PT crystals in the (1-10)$_c$ crystallographic plane [2].

Table 4.13. Property comparison among rhombohedral single domain Mn:PIN-PMN-28PT, PIN-PMN-28PT and PMN-28PT single crystals [2].

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c$ (°C)</th>
<th>$T_{RT}$ (°C)</th>
<th>$d_{15}$ (pC/N)</th>
<th>$d_{33}$ (pC/N)</th>
<th>$\varepsilon_{11}^r$</th>
<th>$\varepsilon_{33}^r$</th>
<th>$k_{15}$</th>
<th>$k_{33}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>194</td>
<td>135</td>
<td>2111</td>
<td>95</td>
<td>5659</td>
<td>1299</td>
<td>0.883</td>
<td>0.346</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>~190</td>
<td>130</td>
<td>2190</td>
<td>74</td>
<td>6286</td>
<td>702</td>
<td>0.92</td>
<td>0.36</td>
</tr>
<tr>
<td>PMN-28PT</td>
<td>~145</td>
<td>~90</td>
<td>2382</td>
<td>97</td>
<td>4983</td>
<td>593</td>
<td>0.94</td>
<td>0.53</td>
</tr>
</tbody>
</table>

4.3.2. Calculated Properties of 4R Domain Configuration from Monodomain Data

Using the single domain data, we can calculate the piezoelectric coefficients, elastic constants and electromechanical coupling factors of [001]$_c$ poled crystals using coordinate transformation. Neglecting domain wall contributions, the effective properties in the “4R” domain state can be obtained from the data of single domain rhombohedral state:
The electromechanical coupling factors can be calculated according to the formula:

\[ k_{ij}^{AR} = \frac{d_{ij}}{\sqrt{\varepsilon_{ii}^{TAR} + S_{ij}^{EAR}}} \]  

Eq 4.30

where the material constants on the right hand side are the single domain data and the parameters on the left hand side, such as \( d_{33}^{AR} \), \( d_{31}^{AR} \), etc. are predicted data for the “4R” domain engineered crystals.

The corresponding material constants of [001], poled single crystals with the same composition are measured for comparison, as listed in Table III. It can be seen that the calculated values of the longitudinal and lateral mode are very close to the measured results, indicating that the extrinsic contributions from the domain wall motions are minimal, the high piezoelectric and electromechanical properties of “4R” domain engineered crystals are dominated by the intrinsic contributions of orientation effect. From the difference of the measured and calculated \( d_{33} \), it can be estimated that the extrinsic contributions to the longitudinal piezoelectric property is about 3.3%, consistent with the value determined by the Rayleigh analysis for compositions away from the MPB [26].
Table 4.14. Calculated and measured materials constants for “4R” domain engineered Mn:PIN-PMN-28PT single crystals.

<table>
<thead>
<tr>
<th>Mn-PIN-PMN-28PT</th>
<th>$d_{33}$</th>
<th>$d_{31}$</th>
<th>$\varepsilon_{33}^{r}$</th>
<th>$s_{11}^{E}$</th>
<th>$s_{33}^{E}$</th>
<th>$k_{33}$</th>
<th>$k_{31}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>975</td>
<td>-485</td>
<td>4205</td>
<td>34.5</td>
<td>34.5</td>
<td>0.860</td>
<td>0.428</td>
</tr>
<tr>
<td>Measured</td>
<td>1009</td>
<td>-481</td>
<td>3315</td>
<td>38.5</td>
<td>45.1</td>
<td>0.877</td>
<td>0.453</td>
</tr>
</tbody>
</table>

4.4 Summary and Discussion

Full matrix properties of Mn:PIN-PMN-PT single crystals were measured and analyzed for 1R, 2R and 4R engineered domain configurations. 4R full property is useful for designing medical ultrasound and other piezoelectric devices utilizing the very high piezoelectric coefficient ($d_{33}$) and electromechanical coupling ($k_{33}$). Full property for 2R domain configuration is useful for the high transverse properties achieved with $d_{32}$ resonance mode, the stable thickness shear mode (2R $d_{15}$) and the face shear mode ($d_{36}$). Full property from 1R domain configuration is useful for designing devices based on thickness shear mode (1R $d_{15}$) and also to understand orientation dependence of the properties based on the monodomain configuration. Multi-domain properties can be predicted using the monodomain data and to understand orientation dependence of elastic, dielectric, and piezoelectric properties.
4.5 References


Chapter 5

High Power Characterization of Relaxor-PT Single Crystals

5.1 Mechanical Quality Factor ($Q_m$)

High power devices typically operate at resonance where the impedance is a minimum. Mechanical quality factor is the inverse of mechanical loss factor and signifies the number of cycles taken by the resonator to reduce its intensity to half the value. High mechanical quality factor ($Q_m$) is considered a key characteristic for better performance since dynamic strain is proportional to the product of piezoelectric charge coefficient $d_{ij}$, $Q_m$ and applied field $E$. $Q_m$ values are typically reported for materials based on small signal measurements performed using impedance analyzer.

It has been shown by Uchino et al [1] that in PZT ceramics vibrational velocity of resonators is the key figure of merit for high power applications and is related to the high motional current. At resonance, $Q_m$ decreases with vibrational velocity due to amplification of losses at resonance and heating associated with these losses. High power characterization of the Mn:PIN-PMN-PT single crystal based on vibrational velocity and $Q_m$ is important to understand their usefulness for high power applications compared to traditional PZTs and other relaxor PT single crystals.
5.2 Mechanical Quality Factor ($Q_m$) and Internal Bias

In the Mn modified PIN-PMN-PT single crystals, the acceptor cations Mn$^{2+}$ and Mn$^{3+}$ substitute Ti$^{4+}$ owing to their similar ionic radius and coordination number. To maintain charge balance, oxygen vacancies are formed resulting in acceptor-oxygen defect dipoles, which occupy energetically preferred sites in the crystal lattice and form anisotropic centers in the domain. These defect dipoles realign themselves along a preferential direction of the spontaneous polarization, giving rise to the internal bias. The internal biases of the [111]$c$ and [001]$c$ oriented samples were found to be the same values, being on the order of 0.4-1.5 kV/cm. Thus, the internal bias is independent of crystallographic orientation, but associated with the composition and Mn dopant levels.

As mentioned above, the introduction of Mn leads to internal bias, which clamps the domain wall motions, stabilizes the domains and restricts the polarization rotation, therefore high mechanical quality factors can be expected. Table 5.1 summarizes the mechanical quality factors of different vibration modes for Mn:PIN-PMN-PT single crystals with “1R” and “4R” domain configurations. From Table 5.1, it can be seen that in the single domain state, $Q_{15}$ is much lower than $Q_{33}$, indicating that the rotation of spontaneous polarization induced by the vertical electrical field is the dominant factor for the low quality factor of the thickness shear mode.
Table 5.1. Comparison of mechanical quality factors with different domain structures [2].

<table>
<thead>
<tr>
<th>Material</th>
<th>Domain configuration</th>
<th>$Q_{33}$</th>
<th>$Q_{31}$</th>
<th>$Q_{32}$</th>
<th>$Q_{36}$</th>
<th>$Q_{15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>4R</td>
<td>650</td>
<td>200</td>
<td>-</td>
<td>-</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>1R</td>
<td>1200</td>
<td>350</td>
<td>-</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>2R</td>
<td>1000</td>
<td>260</td>
<td>600</td>
<td>850</td>
<td>130</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>4R</td>
<td>160</td>
<td>150</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2R</td>
<td>500</td>
<td>210</td>
<td>700</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>PMN-30PT</td>
<td>4R</td>
<td>120</td>
<td>-</td>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1R</td>
<td>1130</td>
<td>-</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2R</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>435</td>
</tr>
</tbody>
</table>

The corresponding $Q_m$ values for all three generation of single crystals with different domain configurations are also listed in table IV for comparison. For the single domain state crystals, rhombohedral PMN-PT and Mn:PIN-PMN-PT with domain state of “1R”, the $Q_{33}$ values are all on the order of $>1000$, independent of composition, phase structure and orientation. For the domain engineered crystals, the longitudinal mechanical quality factor was increased significantly by the introduction of acceptor dopants. The $Q_{33}$ of “4R” domain structure without Mn doping are on the order of 100–200, and increased to 650 after Mn doping. Same phenomenon is observed in the “2R” domain structure, being 500 for the material without Mn and 1000 for that with Mn doping. For the domain-engineered crystals, the accepter dopants can help to improve the longitudinal mechanical quality factor $Q_{33}$, due to the fact that the internal bias restrict the polarization rotation and clamp the domain wall motion. For the thickness shear mode $Q_{15}$, both single domain crystals and domain-engineered crystals with “4R” and “2R” structure significantly increased by the introduction of the Mn ions.
5.3 $Q_m$ Measurements Based on Constant Vibration Velocity Method Using HiPoCS (High Power Characterization) System

$Q_m$ can be determined by using the 3dB method (Figure 5.1) where the impedance values at either side of resonance frequency ($f_r$) are at values of 3dB or $\sqrt{2}$ times $Z_{\text{min}}$ (lowest impedance measured at $f_r$) and the corresponding frequencies are $f_1$ and $f_2$. $Q_m$ is given by:

$$Q_m = f_r/(f_1-f_2) \quad \text{Eq 5.1}$$

With the impedance analyzer, it is a small signal measurement with a voltage of 0.5 V RMS and has no consideration for vibration velocity of the resonator. So, $Q_m$ has to be measured and understood as a function of vibration velocity. The drop in $Q_m$ leads to heating and limits high power operations. The high power measurement is significant for device designs, for understanding non-linear behavior, and for finding out device limitations based on heat generation for high power devices.

![Figure 5.1. 3dB method for determining $Q_m$ from impedance [3]](image)

$Q_m$ typically drops for all PZT materials and other lead-based piezoelectrics with increase in vibration velocity. Figure 5.2 below shows the $Q_A$ and $Q_B$ measurement for a hard PZT in $d_{31}$ mode (length extensional or transverse mode). With the increase in vibration velocity, both $Q_A$ and $Q_B$ tend to decrease and the impedance at $f_r$ tend to
increase while at \( f_a \) tend to decrease. As an observation, if the temperature gets \(~15^\circ\text{C}\) above the ambient temperature while measuring \( Q_m \), then the material has reached its limits of vibration velocity at which point, there is no efficient electromechanical energy conversion. From the design perspective, this temperature rise indicates the practical limitation in high power devices.

Figure 5.2. High power measurements for PZT materials [3]

The high power characterization was performed using a HiPoCS (high power characterization) system at Materials Research Laboratory, which is part of the ICAT centre (International Centre for Actuators and Transducers). The block diagram showing the operation of this system is illustrated in Figure 5.3. The HiPoCS system is capable of measuring the impedance/admittance curves at 1) constant voltage, 2) constant current, 3) constant vibration velocity, and 4) constant input power. In addition, an Infrared camera is part of the system to monitor the heat generation on the sample. The HiPoCs system is limited to frequencies below 500 kHz.
5.4. High Power Analysis using HiPoCS

As discussed earlier, the important resonant modes from the 2R domain configuration are the 2R $d_{15}$, $d_{36}$ and $d_{32}$. Thickness shear mode is usually very challenging and they exhibit lots of spurious modes and interference from other modes when the sample aspect ratio is less than 10:1 [4]. Hence, the vibration velocity measurements were performed on $d_{32}$ and $d_{36}$' modes for Mn:PIN-PMN-PT crystals and compared to that of PMN-PT and PIN-PMN-PT.
5.4.1. Small Signal Characterization of Samples for HiPoCs Measurement

Primary focus of the high power measurement is to understand the behavior of the manganese-doped PIN-PMN-PT single crystals. Their behavior is compared with those of PMN-PT, and PIN-PMN-PT single crystals. The internal bias of the Mn:PIN-PMN-PT single crystal is compared with PZT-4 and PZT-8 hard piezoceramics. The coercive field and internal bias values are compared in Table 5.1 to understand the “hard piezoelectric” behavior.

Table 5.2. Comparison of internal bias in hard materials

<table>
<thead>
<tr>
<th>Material</th>
<th>(E_c) (kV/cm)</th>
<th>(E_i) (kV/cm)</th>
<th>(P_r) ((\mu)C/cm(^2))</th>
<th>(P_s) ((\mu)C/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRS 101 (PZT-4)</td>
<td>15.5</td>
<td>6.6</td>
<td>32</td>
<td>37</td>
</tr>
<tr>
<td>TRS 301 (PZT-8)</td>
<td>15.8</td>
<td>11.6</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>PMN-28PT</td>
<td>2.5</td>
<td>-</td>
<td>32</td>
<td>37</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>5</td>
<td>-</td>
<td>31</td>
<td>36</td>
</tr>
<tr>
<td>Mn:PIN-PMN-28PT</td>
<td>8.8</td>
<td>1.5</td>
<td>29</td>
<td>33</td>
</tr>
</tbody>
</table>

\(Q_m\) measurement – small signal using impedance analyzer

Transverse (\(d_{32}\)) resonance mode and rotated face shear (\(d_{36'}\)) mode samples were prepared for PMN-PT, PIN-PMN-PT, and Mn:PIN-PMN-PT single crystals. For the \(d_{32}\) mode samples, the dimensions were 4 x 4 x 12 mm and for the \(d_{36'}\) samples, they were 7 x 7 x 1 mm. Before performing the HiPoCs measurement, small signal measurement was performed at 0.5 V using impedance analyzer and \(Q_m\) at resonance was measured using the 3dB method. Table 5.3 is the summary of small signal \(Q_m\) measurements for all \(d_{32}\) mode samples. Figure 5.4- 5.9 shows the impedance sweeps for the samples. As seen in Table 5.3, Mn-PIN-PMN-PT single crystal has the highest \(Q_m\) from small signal measurement.
Table 5.3. Summary of $Q_m$ measured with 3dB method using impedance analyzer for $d_{32}$ mode samples

<table>
<thead>
<tr>
<th></th>
<th>$Z_{\text{min}}$ (ohms)</th>
<th>$Z_{\text{min}} + 3\text{dB}$ (ohms)</th>
<th>$f_r$ (kHz)</th>
<th>$f_1$ (kHz)</th>
<th>$f_2$ (Hz)</th>
<th>$Q_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>2.90</td>
<td>4.10</td>
<td>59.2</td>
<td>59.1</td>
<td>59.3</td>
<td>390</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>7.64</td>
<td>10.80</td>
<td>61.6</td>
<td>61.5</td>
<td>61.7</td>
<td>415</td>
</tr>
<tr>
<td>Mn :PIN-PMN-28PT</td>
<td>14.64</td>
<td>20.7</td>
<td>76.6</td>
<td>76.5</td>
<td>76.6</td>
<td>590</td>
</tr>
</tbody>
</table>

Figure 5.4 Impedance sweep – PMN-PT ($d_{32}$ mode)
Figure 5.5. Impedance at $f_r$ – PMN-PT ($d_{32}$ mode)
Figure 5.6. Impedance sweep – PIN-PMN-PT ($d_{32}$ mode)
Figure 5.7. Impedance at $f_r$ – PIN-PMN-PT ($d_{32}$ mode)
Figure 5.8. Impedance sweep – Mn:PIN-PMN-PT (d_{32} mode)
Table 5.4 summarizes the small signal $Q_m$ measurement at resonance for the face shear mode samples calculated using the 3dB method. Figures 5.10-5.15 shows the impedance sweeps of the various face shear mode samples used for the HiPoCs measurement. As can be seen in Table 5.4, Mn-PIN-PMN-PT face shear mode samples have the highest $Q_m$ $\sim$1000 comparable to that of values measured for PZT-4 and PZT-8.

Table 5.4. Summary of $Q_m$ measured with 3dB method using impedance analyzer for $d_{36}$ mode samples

<table>
<thead>
<tr>
<th></th>
<th>$Z_{\text{min}}$ (ohms)</th>
<th>$Z_{\text{min}} + 3\text{dB}$ (ohms)</th>
<th>$f_r$ (kHz)</th>
<th>$f_1$ (kHz)</th>
<th>$f_2$ (kHz)</th>
<th>$Q_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN-28PT</td>
<td>4.98</td>
<td>7.04</td>
<td>129.7</td>
<td>129.5</td>
<td>129.8</td>
<td>435</td>
</tr>
<tr>
<td>PIN-PMN-28PT</td>
<td>5.28</td>
<td>7.47</td>
<td>136.5</td>
<td>136.4</td>
<td>136.5</td>
<td>900</td>
</tr>
<tr>
<td>Mn :PIN-PMN-28PT</td>
<td>4.25</td>
<td>6.01</td>
<td>102.5</td>
<td>102.4</td>
<td>102.5</td>
<td>1085</td>
</tr>
</tbody>
</table>
Figure 5.10. Impedance sweep – PMN-PT (d_{36}) – rotated face shear mode
Figure 5.11. Impedance sweep at $f_r$ – PMN-PT ($d_{36}$) – rotated face shear mode
Figure 5.12. Impedance sweep – PIN-PMN-PT ($d_{36}^\prime$) – rotated face shear mode
Figure 5.13. Impedance sweep at $f_r$ – PIN-PMN-PT ($d_{36}$) – rotated face shear mode
Figure 5.14. Impedance sweep – Mn-PIN-PMN-PT ($d_{36}$) – rotated face shear mode
5.4.2. High power analysis

Once the $Q_m$ was analyzed for the $d_{32}$ and $d_{36}'$ mode samples using the small signal method, the samples were characterized using the HiPoCS system as illustrated in Figure 5.3. Due to the large displacement of the single crystals, HiPoCS beyond vibration velocity of 150 mm/s is very challenging. Figure 5.17 and 5.18 shows the $Q_m$ behavior as a function of vibration velocity for $d_{32}$ mode plates of PIN-PMN-PT and Mn:PIN-PMN-PT single crystals respectively. Figure 5.19 is the $Q_m$ behavior for Mn:PIN-PMN-PT rotated face shear ($d_{36}'$) plate. As expected, in all cases the $Q_m$ drops with increase in vibration velocity due to the increase in elastic loss.
Figure 5.16. Mechanical quality factor ($Q_m$), impedance at resonance, and $f_r$ shift as a function of vibration velocity for PIN-PMN-PT single crystal in $d_{32}$ mode

Figure 5.17. Mechanical quality factor ($Q_m$), impedance at resonance, and resonance frequency shift as a function of vibration velocity for Mn: PIN-PMN-PT single crystal in $d_{32}$ mode
Figure 5.18. Mechanical quality factor ($Q_m$), impedance at resonance, and resonance frequency shift as a function of vibration velocity for Mn:PIN-PMN-PT single crystal in $d_{36}$ mode.

Figure 5.20 is the $Q_m$ and temperature variation as a function of vibration velocity for Mn-PIN-PMN-PT $d_{36}$ mode plate. The measured $Q_m$ and temperature of the sample is summarized in Table 5.5 and the temperature increases to a value of 41 °C for a vibration velocity of 300 mm/s. Temperature at ~250 mm/s was about 36 °C. Figure 5.20 is an important result, which shows that the behavior of Mn:PIN-PMN-PT single crystal is similar to that of a hard piezoceramic, like PZT-4.

Mn:PIN-PMN-PT single crystals have great potential as high power material - high mechanical quality factor and high coupling makes this a unique material and a “hard piezoelectric” single crystal with broadband capability. Along with $Q_m$ and ‘k’, large compliance of modes such as $d_{32}$ and $d_{36}$ face shear, can lead to compact, low frequency, high power devices. The high power results based on vibration velocity are
significant for understanding the practical limitation of high power devices and limitation from heat generation – decrease in $Q_m$ results in self-heating of the resonator.

Figure 5.19. $Q_m$ and Temperature variation for Mn-PIN-PMN-PT $d_{36}$ resonance mode plate
Table 5.5. Measured $Q_m$ and temperature for Mn:PIN-PMN-PT $d_{36}$ face shear plate at different vibration velocities

<table>
<thead>
<tr>
<th>Vibration velocity (mm/s)</th>
<th>$Q_m$ at resonance from HiPoCS</th>
<th>Temperature of sample (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>820</td>
<td>23</td>
</tr>
<tr>
<td>150</td>
<td>410</td>
<td>27</td>
</tr>
<tr>
<td>200</td>
<td>275</td>
<td>31</td>
</tr>
<tr>
<td>300</td>
<td>NA</td>
<td>41</td>
</tr>
</tbody>
</table>

5.5 Summary and Discussion

High power piezoelectric devices are used in variety of applications using ultrasonic cleaning, ultrasonic welding, ultrasonic bonding, industrial cleaning, lithotripsy, therapeutic ultrasound, ultrasonic surgery, high intensity focused ultrasound for various medical applications, fish finders, sonar, sonochemistry, non-destructive testing, ultrasonic motors, piezo-transformers, food drying, homogenization and emulsification, waste sludge/effluent treatment, microbial deactivation, de-foaming, degassing, viscosity reduction, enzyme reactions, etc. Apart from medical imaging applications, frequencies for most applications are lower (few kHz to few hundred kHz) and the high compliance of face shear mode enables designing compact devices for high power applications.

High power piezoelectric devices typically operated at resonance to take advantage of the large strain. However, the high electromechanical quality factor (low mechanical loss) can be misleading when it comes to driving the device at high power. The vibrational velocity is the most important parameter for a device operated at high power. $Q_m$ drops with the increase of vibrational velocity, leading to increased heating at resonance and increased losses at higher vibrational velocities.
One of the objectives of this doctoral dissertation is to develop the scientific and technical understanding of Mn-doped PIN-PMN-PT single crystals in their promise as candidate materials for high power applications. In particular, rotated face shear and transverse resonance modes exhibit high mechanical quality factor ($Q_m$) making it better for low frequency high power applications. Along with the high $Q_m$, high electromechanical coupling, high ‘$d_{ij}$’ and large elastic compliance, compared to hard piezoceramics allows for design of compact, broadband, high power devices. In Chapter 6, some prototype devices using Mn:PIN-PMN-PT single crystals are discussed along with their performance.

5.5 References


Chapter 6

Applications Using Mn-Doped PIN-PMN-PT Single Crystals

6.1 Applications for Mn-doped PIN-PMN-PT Single Crystals

For more than a decade, PMN-PT single crystals have dominated the premium ultrasound imaging market, over the PZT-5H ceramics, due to their very high electromechanical coupling. With the Mn:PIN-PMN-PT single crystal added as a promising candidate material for designers with improved temperature capability and mechanical Q ($Q_m$), the following applications can potentially exhibit significant benefits by using them in transducer design:

- High power (High $Q_m$):
  - Therapeutic ultrasound with high intensity focused ultrasound
  - Industrial cleaning, drying
  - Food Processing
  - Piezo transformers
  - Non-destructive testing (NDT)
  - Piezomotors
  - Ultrasound transducers for surgical tools
  - Sonar transducers
- Medical ultrasound (High coupling)
  - Transducers with inherent broad-band operation and high sensitivity
  - High resolution ultrasound imaging
  - Combined imaging and therapeutic transducers
Table 6.1. Comparison of single crystal and PZT ceramic showing advantages of crystal

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>SINGLE CRYSTAL</th>
<th>PZT CERAMICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electromechanical coupling</td>
<td>• 90-93% for multiple orientations</td>
<td>• 50-70% for most applications</td>
</tr>
<tr>
<td></td>
<td>• 2-3 octave bandwidth</td>
<td>• 1 octave bandwidth</td>
</tr>
<tr>
<td>Elastic compliance and piezoelectric</td>
<td>• Less input power needed</td>
<td>• Hard material makes long transducers</td>
</tr>
<tr>
<td>response</td>
<td>• Compact device for same frequency as ceramic</td>
<td>• Low piezoelectricity so need to drive hard</td>
</tr>
<tr>
<td>Material stability</td>
<td>• Ternary crystal range to &gt;110ºC</td>
<td>• High duty cycle operation</td>
</tr>
<tr>
<td></td>
<td>• High duty cycle capable</td>
<td>• Temperature range to &gt;130ºC</td>
</tr>
<tr>
<td>Transducer cost</td>
<td>• Less material used hence cost is reduced</td>
<td>• Standard cost</td>
</tr>
<tr>
<td></td>
<td>• Overall system cost may be reduced</td>
<td></td>
</tr>
</tbody>
</table>

Determination of the full set properties of the Mn-PIN-PMN-PT single crystals is very useful for the applications. Transducers can be designed using FEM software such as ATILA, ANSYS, PZFlex, COMSOL, etc using the full property matrices to obtain
modeled performance. Some application examples utilizing the Mn-PIN-PMN-PT single crystals are discussed below and the transducer performance is discussed.

6.2. Application Example 1: Wideband Transducer for Bone Characterization using Mn:PIN-PMN-PT Single Crystals using combination of 2R $d_{32}$ and 4R $d_{33}$ resonance modes

6.2.1. Application Background

The micro-gravity conditions of space travel result in unique physiological demands on the human body. In particular, the absence of the continual mechanical stresses on the skeletal system, which are present on Earth causes the bones to decalcify. Trabecular structure (see Figure 6.2) decreases in thickness and increases in spacing, resulting in decreased bone strength and increased risk of injury. Thus monitoring of bone health is a high priority for long-term space travel such as the International Space Station program.

Figure 6.2. Bone cross section showing trabecular structure. Metrics such as trabecular size and spacing are important for characterizing bone health and are subject to characterization by ultrasound techniques (Image Courtesy: Jean-Hervé Prévost, Daniel Dabbs, Ilhan Aksay and Erin Long - Princeton University)
Due to the payload constraints of space travel, any characterization device for monitoring bone health must have reduced size, weight, and power consumption. Among the existing methods of bone characterization, ultrasound monitoring device for bond health seems to be the most promising approach to meet these constraints. Figure 6.3., for example, shows a compact, self-contained ultrasound diagnostic system. The wideband single crystal transducer is based on the goal of contributing to bone health monitoring in space travel by combining a unique design with the superior performance characteristics of single-crystal piezoelectric material to create a single ultrasound transducer with the ability to characterize a wide range of bone health parameters.

A series of non-invasive diagnostic tools for bone analysis have been utilized over the years, including dual-energy x-ray absorptiometry (DXA), biomechanical computer tomography (BCT), magnetic resonance imaging (MRI) and ultrasound [1, 5, 6]. DXA is the most widely used method of bone mineral density (BMD), and is a fairly accurate and low cost technique; however, it is an ionizing radiation source. Though it provides a low dose, this dose would be compounding to the amount of radiation inundating astronauts outside the protective stratosphere of earth. BCT, which is a fusing of biomechanics, computer simulations and CT-imaging, has the same ionizing radiation issue, and could be too complex to implement in a constrained area such as a space capsule. MRI can provide a very high resolution capability, though power, cooling and size issues are also expected to be significant hurdles to implementation. Additionally, issues do exist with calibration related to differences in bone marrow and other specific tissues.

Ultrasound has been used extensively for visualization of soft tissues for medical diagnoses, and has become an integral part of internal medicine. Imaging of the skeleton is much less studied due to the large signal reflections at the bone surface and irregular surfaces that make formation of 2D images difficult. With advances in processing and devices, 2D imaging has been performed, but of more relevance is research related to acquiring data from individual scan lines. A series of ultrasound parameters have been identified as relating to bone composition, density and micro-structure. Apparent
integrated backscatter (AIB), net time delay (NTD), speed of sound (SOS), frequency modulated attenuation (FMA), and frequency-dependent broadband ultrasound attenuation (BUA), are all methods evaluated for BMD and strength determination. As mentioned above, these parameters have varying relevance depending on the frequency band. Table 6.2 summarizes a few of the methods and the frequency regimes where they have the best correlation with histology/strength.

Figure 6.3. Compact ultrasound system

Table 6.2. Summary of different ultrasound methods and their relevance to bone structure; characterization methods are apparent integrated backscatter (AIB), net time delay (NTD), speed of sound (SOS), frequency modulated attenuation (FMA), and broadband ultrasound attenuation (BUA)

<table>
<thead>
<tr>
<th>Frequency (MHz)</th>
<th>Method</th>
<th>Structural Relevance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 - 0.7</td>
<td>FMA</td>
<td>Trabecular thickness</td>
</tr>
<tr>
<td>1.0</td>
<td>AIB, BUA &amp; SOS</td>
<td>Bone volume per total volume</td>
</tr>
<tr>
<td>2.25</td>
<td>NTD</td>
<td>Bone mineral density</td>
</tr>
<tr>
<td>3.5</td>
<td>AIB, BUA</td>
<td>Trabecular separation</td>
</tr>
<tr>
<td>5.0</td>
<td>AIB</td>
<td>Collagen content per bone volume</td>
</tr>
</tbody>
</table>
6.2.2. Technical Approach

Each of the ultrasound methods described above could be useful individually to fabricate small ultrasound monitoring systems, however, the significant challenge is developing a single probe to cover the very large range of frequencies. Multiple probes could cover the same range, but ideally measurements performed at the same spot at the same time would allow for greater analysis and interpretation of the data. A single probe covering all frequency bands of interest would be ideal for such a measurement and this would also minimize storage space and eliminate the complexity of integrating multiple probes.

Commercial ultrasound transducers are based on piezoceramic materials, i.e. piezoelectric materials with a polycrystalline microstructure. These materials are robust and dependable, but their performance is limited by an effective “averaging” of their intrinsic properties due to the random crystal orientations at the microscale. The introduction of single-crystal piezoelectric material in recent years has allowed for optimization of performance by extending the intrinsic properties of the material to macroscopic scale. Transducers can be built with significantly improved source level, sensitivity, and bandwidth, while minimizing size and power requirements. Of particular interest for the current application is the extended bandwidth of this material, which begins to address the wide frequency range of the diagnostic frequencies and techniques listed in Table 6.2. The ideal goal of utilizing a single ultrasonic probe that covers all the frequencies with superior performance and reduces complexity of electronics integration is only possible with the wideband ultrasound transducer such as the one discussed here based on Mn-doped PIN-PMN-PT single crystals. Compared to the undoped PIN-PMN-PT single crystals, the Mn:PIN-PMN-PT based transducers enables higher source level (higher $E_c$, 8.8 kV/cm for Mn:PIN-PMN-PT compared to 5 kV/cm for PIN-PMN-PT) with reduced self-heating due to the high $Q_m$. 
The ultrasound transducer built for this goal combines this unique material with a unique design that extends the bandwidth of the transducer to cover the entire range of bone characterization frequencies. The design uses laser micromachining to create resonators of different sizes (and therefore resonant frequencies). As shown in Figure 6., the resonators have overlapping spectra, and a broad, smooth response results from using them together. The transducer design takes advantage of the strong lateral vibration characteristic ($d_{32}$ resonance mode) of 2R domain to achieve the wide frequency bandwidth. The resonator pattern is then wrapped around a central mandrel to create a flat, circular face.

Wide band characteristics of the transducer from 0.3 to 5 MHz is achieved by using multiple transverse mode resonators of different resonance frequencies from 0.3 to 4 MHz and a 1-3 composite element for the 5 MHz frequency band. Modeled impedance sweep and displacement response are shown in Figures 6.4 (a) and (b) respectively for the different $d_{32}$ mode resonators. Broad band response is achieved using averaging of response over the frequencies and the average acoustic power over the wide frequency range is shown in Figure 6.5. Specifications of the transducer design including the elemental dimensions and resonance frequencies used for the wide band configuration are shown in Table 6.3.

<table>
<thead>
<tr>
<th>Piezoelectric Material</th>
<th>Mn-PIN-PMN-PT – $d_{32}$ mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite Parameters</td>
<td>100 micron thick – 20 micron kerf</td>
</tr>
<tr>
<td>Element Frequencies</td>
<td>0.36, 0.97, 1.67, 2.5, 3.75 MHz</td>
</tr>
<tr>
<td>Substrate thickness</td>
<td>~200 microns</td>
</tr>
<tr>
<td>Transducer diameter</td>
<td>~9.5 mm</td>
</tr>
<tr>
<td>Filling material</td>
<td>Hysol epoxy</td>
</tr>
</tbody>
</table>
Figure 6.4 (a) Multi-resonant frequency response – impedance sweep (b) Displacement vs. Frequency

Figure 6.5. Acoustic power vs. frequency: multiple resonators with overlapping frequency spectra are used to create a broadband characteristic.
Figure 6.6. General design aspects of Nautilus transducer showing etching pattern of single crystal bars, rolled flex circuit with bars and “cross-sectional” view of finishing transducer in housing with cabling.

### 6.2.4. Finite Element Modeling of Transducer

Figure 6.7 shows the FEM model of the transducer array pattern. The piezoelectric single crystal material is shown in red, the passive material in the transducer (urethane, in this case), is shown in blue, and the green is the medium into which ultrasound is radiated. The transducer design is simplified in this model in order to accommodate the constraints of the FEM software. While the resonator pattern is repeated many times in the actual transducer and it is wrapped on a mandrel, a single linear array configuration is modeled as the first step in Figure 6.7. In-air impedance response of the transducer is shown in Figure 6.8. FEM of individual resonator group forming the transducer was analyzed for individual response as shown in Figure 6.9.
Figure 6.7. FEM model of the array pattern

Figure 6.8. In-air electrical impedance - modeled
Figure 6.9. FEM model showing displacement profile for each resonator group in array pattern.

Along with the $d_{12}$ mode resonators that are wrapped on the circumference of the central mandrel, a 1-3 composite using Mn-PIN-PMN-PT was fabricated and bonded to
the face of the mandrel for the 5MHz frequency as shown in Figure 6.10. The 1-3 composite augments the higher frequency band and compensates for the attenuation at higher frequencies. The 1-3 composite was fabricated using the following parameters: post width – 120 microns, kerf – 50 microns, thickness 0.25 mm, diameter, 9.5 mm. The sharpness of the impedance peak for Mn-PIN composite compared to the PIN composite is due to the higher mechanical Q (Q_m) for Mn-PIN-PMN-PT single crystal. The measured resonance parameters are shown in Table 6.4 in comparison to composite made with PIN-PMN-PT single crystals.

![Figure 6.10. Final transducer configuration with the d_{32} mode resonators wrapped on the circumference on the mandrel and the 1-3 composite forming the face of the mandrel](image)
Figure 6.11. Impedance sweep of 1-3 composite fabricated using Mn-PIN-PMN-PT and compared with that of PIN-PMN-PT composite

Table 6.4. Measured data for the Mn:PIN-PMN-PT single crystal 1-3 composite – compared with that of PIN-PMN-PT

<table>
<thead>
<tr>
<th></th>
<th>$f_s$ (MHz)</th>
<th>$f_p$ (MHz)</th>
<th>$C_p$ (nF)</th>
<th>tan $\delta$</th>
<th>$k_{eff}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIN-PMN-PT</td>
<td>4.63</td>
<td>6.9</td>
<td>3.31</td>
<td>0.009</td>
<td>0.87</td>
</tr>
<tr>
<td>Mn:PIN-PMN-PT</td>
<td>4.6</td>
<td>6.77</td>
<td>3.30</td>
<td>0.004</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Another important goal of the transducer of the transducer is to achieve uniform spatial intensity over 100 mm to accommodate characterization of lumbar and hip spine over patients with different body mass index (BMI). A Labview program was used to achieve the acoustic field profile for the transducer and the resulting spatial acoustic intensity profile is shown in Figure 6.12.
6.2.5. Transducer Fabrication

After designing the wide band transducer, prototypes were built using various microfabrication techniques including reactive ion etching, laser micromachining, etc. Laser micromachining produced the best quality of the array pattern and the least labor-intensive process. Prototype \( d_{32} \) mode composite arrays fabricated using laser micromachining are shown in Figure 6.13. 1-3 composites were diced using dicing saw with blade kerf of 40-50 microns. Packaged transducer was assembled using central mandrel, epoxy, shell housing, and electrical connectors as shown in Figure 6.15 and the finished transducer is shown in Figure 6.16. Frequency response of the assembled prototype transducer is shown in Figure 6.17 demonstrating the wide band performance.
Figure 6.13. Linear array pattern for transducer

Figure 6.14. Diced 1-3 Composite
Figure 6.15. Parts for assembling the wide band NAUTILUS transducer

Figure 6.16. Packaged wide band for bone characterization
6.3. Application Example 2: Tonpilz Transducers using Thickness Shear Mode (2R d_{15} mode)

Single crystal technology has shown the most promise for commercial use in medical ultrasound transducers. As seen on application example 1, wideband characteristics can be achieved with single crystal technology easily. Since the cost of single crystal is higher than that of PZT ceramics ($0.80/mm^3$ for single crystals compared to $0.15/mm^3$ for PZT), when used in medical ultrasound application where the frequency for the application is >1 MHz, volume of material used is very small. In low frequency applications, current PZT transducers use big ceramic component to achieve the lower frequency. One example is a Tonpilz transducer that is commonly used for projector designs used in surgical tools or underwater acoustics, where big d_{33} mode rings are used under compressive pre-stress using a central bolt to achieve good response. Due to the large piezoelectric coefficient, larger displacements can be achieved using single crystals, but the coercive field limits the drive levels. Also, low Q_m limits them from being used in high power applications. In Chapter 5, it was shown that Mn-PIN-PMN-PT poled along [011]_c has 3 times higher coercive field (~8.8 kV/cm) compared to PMN-PT.
and exhibits very good high power characteristics. If transducers were designed based on the properties of Mn-PIN-PMN-PT, they can be successfully used in commercial applications.

The relaxor crystal “15” shear mode with polarization along the <111> crystallographic direction exhibits the highest combination of piezoelectric coefficient, coupling constant, and elastic compliance ever reported. The high elastic compliance in particular allows the development of as compact a low frequency transducer as possible because compliance is inversely proportional to the square of the resonance frequency. The shear compliance in the resonating direction for <111> polarized material is over 5 times greater than <001> polarized crystal (“33” mode) which will result in a 55% lower resonance frequency for resonators of the same size.

To date, the “15” shear mode has not been used in projector designs because the current commercial relaxor crystal, PMN-PT, has very poor polarization stability for <111> polarized shear components. Although, PMN-PT polarized along <111> has been successfully used in sensors, the application of an electric field large enough to generate appreciable acoustic power will depolarize PMN-PT shear mode crystals. Mn-PIN-PMN-PT has higher polarization stability compared to the PMN-PT single crystals. As a result the development of cost effective, low frequency crystal projectors utilizing the “15” shear mode can be considered more practical. The significance of such a development would be to provide a broadband, high acoustic power, compact projector technology. Summary of electrical parameters related to resonance design are shown in Table 6.5.
Table 6.5. Piezoelectric parameters for 2R $d_{15}$ thickness shear resonance modes in comparison with other modes.

<table>
<thead>
<tr>
<th>Resonance Mode</th>
<th>$s_{33}^{E}$ (x10^{-12} m^2/N)</th>
<th>$T_{RT}/T_{c}$ (ºC)</th>
<th>$d_{33}$ (pC/N)</th>
<th>$k_{33}$</th>
<th>$e_{33}^{T}$</th>
<th>$E_{c}$ (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001] – 4R $d_{33}$ (standard)</td>
<td>57</td>
<td>125</td>
<td>1500</td>
<td>0.92</td>
<td>4800</td>
<td>5.0</td>
</tr>
<tr>
<td>[011] – 2R $d_{36}$ (face shear)</td>
<td>180</td>
<td>~130</td>
<td>~2200</td>
<td>0.81</td>
<td>5000</td>
<td>5.0</td>
</tr>
<tr>
<td>[111] – 1R $d_{15}$ (thickness shear)</td>
<td>190</td>
<td>125</td>
<td>3300</td>
<td>0.92</td>
<td>6000</td>
<td>2.0</td>
</tr>
<tr>
<td>[011] – 2R $d_{15}$ (thickness shear)</td>
<td>160</td>
<td>~125</td>
<td>2800</td>
<td>0.92</td>
<td>6500</td>
<td>5.0</td>
</tr>
<tr>
<td>PZT-8 (thickness shear)</td>
<td>32</td>
<td>300</td>
<td>330</td>
<td>0.55</td>
<td>1300</td>
<td>~15.0</td>
</tr>
</tbody>
</table>

As seen in Chapter 3 (section 3.3.3), the thickness shear mode resonance using 2R domain configuration (2R $d_{15}$) of Mn:PIN-PMN-PT is very useful for designing low frequency shear mode transducers. The high compliance of the shear mode resonance exhibited by Mn-PIN-PMN-PT single crystal can result in compact low frequency transducers.

Traditional tonpilz type transducers use a piston type head mass based on $d_{33}$ resonance mode. A wide variety of flextensional transducer designs (Figure 6.18) can be used to amplify the effective piezoelectric coefficient (strain vs. electric field) and to reduce the resonance frequency by lowering of the effective elastic stiffness. Though the bulk of PZT cymbals are round in shape due to the symmetry of the $d_{31}$ coefficient, rectangular cymbals have been used as higher power transmitters operating at resonance for therapeutic transdermal insulin delivery. The rectangular shape is also a key factor in maintaining the high strain amplification when using single crystal, since the anisotropy can produce less output in an axi-symmetric or circular cymbal design.
Two types of shear mode Tonpilz transducer configurations are possible based on the head design: a) a piston type transducer for high acoustic source level and b) a flextensional design for very broad bandwidth. These two configurations are compared to traditional $d_{33}$ Tonpilz configuration in Figure 6.19.

For the flextensional transducer the $d_{15}$ plates or stacks are placed end-to-end with their polarization oriented in opposite directions. Either plates or stacks are connected to a common flextensional frame. If the plates are driven electrically in parallel they will oscillate mechanically out phase, pushing and pulling on the flextensional frame with each oscillation. This will cause the diaphragm centered over the stacks to oscillate in the vertical direction. Similar arrangements could be made using face shear ($d_{36}$), transverse mode ($d_{32}$), or bending mode resonators.
Figure 6.20. Prototype flextensional shear transducer with two stacks of Mn-PIN-PMN-PT resonating in 2R \(d_{15}\) mode.

Figure 6.21. Measured impedance performance of flextensional shear transducer

Figure 6.22 is an illustration of a device configuration with common tail mass that can be used for omnidirectional performance.

As shown in Figure 6.18, there are various configurations for flextensional transducers using shear, transverse and thickness modes. The application example in this section is for a flextensional transducer using transverse 2R $d_{32}$ resonance mode. While the thickness shear mode can be used to design compact low frequency transducers due to the high compliance ($s_{55}^E > 180 \text{ m}^2/\text{N}$), the polarization stability may be something that needs to considered for some device designs. The $d_{32}$ resonance mode is very useful due to the high piezoelectric coefficient ($d_{32} > -1000 \text{ pC/N}$) and also higher capacitance can be achieved compared to $d_{33}$ mode. The compliance $s_{22}^E$ for 2R $d_{32}$ mode is $\sim 70 \times 10^{-12} \text{ m}^2/\text{N}$ still allowing for compact low frequency transducers compared to $d_{33}$ mode.
Table 6.6. Piezoelectric parameters for 2R $d_{32}$ more in comparison to other modes

<table>
<thead>
<tr>
<th>Resonance Mode</th>
<th>$s_{ij}^E$ (x10^{-12} m^2/N)</th>
<th>$d_{ij}$ (pC/N)</th>
<th>$k_{ij}$</th>
<th>$K^T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001] – 4R $d_{33}$ (standard)</td>
<td>57</td>
<td>1500</td>
<td>0.92</td>
<td>4800</td>
</tr>
<tr>
<td>[110] – 2R $d_{32}$</td>
<td>63</td>
<td>1400</td>
<td>0.90</td>
<td>4000</td>
</tr>
<tr>
<td>[110] – 2R $d_{36}$ (face shear)</td>
<td>180</td>
<td>~2200</td>
<td>0.81</td>
<td>5000</td>
</tr>
<tr>
<td>[111] – 1R $d_{15}$</td>
<td>190</td>
<td>3300</td>
<td>0.92</td>
<td>6000</td>
</tr>
<tr>
<td>[110] – 2R $d_{15}$</td>
<td>96</td>
<td>2800</td>
<td>0.92</td>
<td>6500</td>
</tr>
<tr>
<td>PZT-8 ceramic $d_{15}$</td>
<td>32</td>
<td>330</td>
<td>0.55</td>
<td>1300</td>
</tr>
</tbody>
</table>

The transducer prototype was constructed using four stacks of Mn: PIN-PMN-PT $d_{32}$ plates. Each stack was fabricated using 4 layers of $d_{32}$ mode plates. The prototype transducer build is shown in Figure 6.24.

![Figure 6.23. Flextensional tonpilz transducer design using transverse piezo stack ($d_{32}$ mode)](image-url)
Figure 6.24. (A) Transducer CAD model isometric view assembled. (B) Transducer CAD model isometric view exploded. (C) Transducer CAD model isometric view with transparent head mass. (D) Fabricated transducer prototype isometric view. (E) Fabricated transducer prototype top view.

The overall dimensions of the assembled transducer prototype are ~3” in diameter and ~2” tall. The total mass of the prototype is ~1 kg with a resonance frequency ~1.6 kHz as shown in Figure 6.25.
Prototype transducer has resonance frequency of ~1.6 kHz, which is a significant step in achieving compact low frequency transducers using single crystals. Resonance frequency can be further lowered using this design and also omnidirectionality can be improved using design as shown in Figure 6.22.

6.5 Summary and Discussion

Application examples that highlight the use of various resonance modes using 2R( d_{15}, d_{32}) and 4R (d_{33}) domain configuration have been demonstrated. Mn:PIN-PMN-PT single crystal provides various operational advantages over PMN-PT. The temperature limit based on the rhombohedral-tetragonal phase transition temperature is 30°C higher than PMN-PT, and the coercive field 3 times higher. The increase in these
parameters related to operational limits is particularly important for the non-standard orientations such as $d_{15}$, $d_{36}^*$ and $d_{32}$ for consideration in practical device design. The shear orientations of single crystal provide a very large increase in elastic compliance, meaning the resonance of transducers can be decreased by as much as 50%. The development of Mn:PIN-PMN-PT in particular, enable this shear mode to be practically evaluated for devices because the coercive field (corresponds to polarization stability) is increased to practical usage levels than that of the first generation PMN-PT crystals.

Full property measurements for the various macroscopic domain configurations were very useful for design of the various transducers based on different resonance modes. Small signal measurement of the properties and the high power characteristics have been successfully integrated for practical device design that would demonstrate the full potential of the Mn-PIN-PMN-PT single crystals. It is imperative that the scientific advancement achieved in this dissertation towards understanding the material properties of Mn:PIN-PMN-PT single crystals is continued towards additional device designs that are practical and pave way for commercial development of piezoelectric transducers using this material. Chapter 7 provides suggestions for research areas that can further contribute to the advancement of science for Mn-PIN-PMN-PT piezoelectric single crystals.

6.6 References


Chapter 7

Suggested Future Work

7.1. Domains in Mn:PIN-PMN-PT crystals

Understanding the domain structures in Mn:PIN-PMN-PT crystals is also a challenge due to poor resolution of optical techniques like polarized light microscopy due to low transmission of light compared to PMN-PT and PIN-PMN-PT single crystals. Optical second harmonic generation [1-2] that works on the principle of photon inversion by crystal structures that lack inversion symmetry is ideal for understanding the domains of Mn:PIN-PMN-PT single crystals.

Figure 7.1. Secondary Harmonic Generation (SHG) technique for analysis of non-180 degree domains [1]

Other optical methods such as polarized light microscopy are used to see through the domains in the direction of the light direction. SHG allows domain observation and
symmetry analysis on the surface perpendicular to the laser direction, thereby providing a method of analysis for non-180 domains.

7.2. Self-Consistent Full Property for Crystals Using Just One Sample

Finite element modeling has become the primary tool in device designs. One could now accurately simulate device performance, hence to optimize the design of devices, before doing any prototyping. It can greatly reduce the cost of R&D both in terms of time and money. There are numerous well established finite software packages for modeling piezoelectric devices, such as transducers, sensors and actuators. Among them, PZFlex, ANSYS and ATILA are the three most frequently used packages. The key to producing reliable simulation results lies in the input data, a common saying of “garbage in, garbage out” describes the importance of input data. For piezoelectric materials, the input data include: elastic constants, piezoelectric coefficients and dielectric constant. These data are in matrix form, hence, it is critical to be self-consistent. Although there is IEEE standard for the measurement of piezoelectric materials, it is very difficult to achieve self-consistency due to two reasons: 1) There are too many independent constants to be determined so that several samples are needed. 2) One could not make all samples identical because the poling degree depends on the geometry of the ferroelectric sample. Robust determination methods to achieve such self-consistent data set for room temperature measurements still need several samples. The best way to achieve self-consistency is to get all data from one sample, which totally eliminates the sample to sample variation problem. Resonance Ultrasound Spectroscopy (RUS) is one possible technique to achieve this and a preliminary demonstration of this technique was shown for [001]c poled Mn–doped PIN-PMN-PT single crystals [3].

7.2.1. Resonance Ultrasonic Spectroscopy (RUS)

In the RUS measurement, an excitation signal is sent from one corner of a cubic sample and the signal is detected from the opposite corner. Since we can accurately
obtain the resonance peaks at room temperature, we can obtain all material constants from only one sample. Both piezoelectrically coupled and non-piezoelectrically coupled modes can be excited. The principle of RUS is shown in Figure 7.2. Typical measurement results from RUS are shown in Figure 7.3.

![Figure 7.2. Illustration of the RUS technique.](image)

On the other hand, one could solve the coupled differential equation to get all modes, which in finite element language is to perform “modal analysis”, if all the input material constants are accurate. By solving the backward problem against the measured resonance frequencies, one could get the set of material constants. There are more than enough modes to determine these constants. For example, the aluminum sample used to
obtain Figure 7.2 has only 3 independent elastic constants but there are so many peaks obtained, which provide more than sufficient checks to get these 3 constants.

7.2.2. Temperature Dependence of Material Constants

In many cases, the device temperature will increase during operation, for example, in high power ultrasound applications, the transducer temperature could change up to 100 °C. On the other hand, material properties do change a lot with temperature, particularly near the phase transitions. This limits the validity of the finite element modeling results because all input data are treated as temperature independent. Even if the temperature dependence can be coded into the finite element package, there is very limited data available in the literature to allow such simulation. By performing the RUS technique, we can follow the change of the resonance pattern to derive the temperature dependence of the full matrix properties.
7.3. References


## Appendix A

### Interplanar Angles for Cubic Crystal Lattice

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<th>Starting Orientation</th>
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### Appendix B

**Ionic Radius for Various Dopants and Preferred Site Occupancy**

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<th>Site preference</th>
<th>Ionic radii (Å)</th>
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<td>Li</td>
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<td>K</td>
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Pb (+2): 1.33 Å, Ti (+4): 0.745 Å
Appendix C

Possible Resonance Modes for Various Engineered Domain States

<table>
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<tr>
<th>Composition</th>
<th>Domain State</th>
<th>Poling Direction and Macroscopic Crystal Symmetry</th>
<th>Resonance Mode</th>
<th>Ideal Aspect Ratio (L:W:T)</th>
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</table>

For thickness mode (kₜ) which is an elastically clamped mode for d₃₃ or d₂₂, aspect ratio is 10:10:1
VITA

Raffi Sahul is an Indian American Material Scientist who has worked extensively in nanomaterials technology and other smart materials such as piezoelectric materials, magnetic fluids, shape memory alloys, etc. After completing his Bachelor's degree in Mechanical Engineering in 1999 from Anna University, Chennai, India, he completed his Master's degree in Mechanical Engineering from Clemson University, South Carolina in 2001 and went onto work in small business research programs. While working in Pennsylvania as a business director for single crystal piezoelectric technology, he completed his PhD as a part-time student with Penn State University on single crystals for high power applications. He has extensive background on single crystal piezoelectric materials, piezoelectric ceramics and their applications and has worked on smart materials processing technology and applications for more than 15 years. He has guided and managed cross-functional teams on several research and commercial efforts on single crystal applications involving medical transducers, industrial sensors, and actuators. As a Principal Investigator, he had led several (> 15) SBIR and other research programs with NSF, NASA, EPA, ONR, MDA, ONR, and other DoD agencies, and he has managed more than 30 SBIR programs as team leader and R&D manager. He has worked extensively towards commercialization of single crystal materials for sonar applications and other medical devices. He is very knowledgeable in the field of ferroelectrics and dielectrics for capacitor and other FEG applications. He is a lifetime MENSA member and also member of other professional societies like, IEEE, ASA, ASME, ASM International, etc. He is the author and co-author of several publications, patents, conference proceedings, and journal papers. Some examples are shown below:


M.E. Manley, J.W. Lynn, D.L. Abernathy, E.D. Specht, O. Delaire, A.R. Bishop, R. Sahul, and J.D. Budai, Phonon Localization as a Driver for Polar Nanoregions in Relaxor Ferroelectrics, ISAF/IWATMD, May 2014, State College, PA, USA