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UNIVERSITY OF CALGARY

Synthesis and Characterization of Novel Piezoelectric Solid

Solutions

by

Thomas Michael Rowe

A THESIS SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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Abstract

This thesis presents three studies in the synthesis and characterization of three ferroelectric solid solutions that were hypothesized to be viable replacements for the lead-based industry standard material Pb(Zr,Ti)O₃ (PZT), due to both environmental concerns and physical property limitations. The first chapter is an introduction to ferro and piezoelectricity along with the perovskite structure. It also describes how element selection and structural deviation can be utilized to design novel materials with targeted properties. The first research chapter involves the (1-x) $Na_{0.5}Bi_{0.5}TiO_3 - (x)BaTiO_3$ (NBT-BT) system doping in group 13 elements onto the Bsite in order to improve the ferroelectric properties. The third chapter explores the idea of using a polarization extension to form a Morphotropic Phase Boundary (MPB) between paraelectric and ferroelectric phases through compositional changes. The solid solution (1-x) NaNbO₃ – $(x)BaZrO_3$ (NN-BZ) was synthesized, and the electromechanical properties were measured in order to see if there was in increase in the piezoelectric response. Chapter four describes the synthesis of a ferroelectric solid solution that improves on PZT's Curie temperature. Due to this research, a new solid solution (1-x)Bi(Fe_{2/8}Ti_{3/8}Mg_{3/8})O₃ - (x)PbTiO₃ (BFTM-PT) was synthesized, and the electromechanical properties were measured.

Preface

Portions of chapter 2 can be found in McQuade et al. of which I am an author. I performed significant synthesis/processing and physical properties measurements. Dr. McQuade performed some of the physical properties measurements and led the structural analysis. Dr. Manjón-Sanz advised on the project. Dr. Dolgos was the principal investigator. Ms. De la Puente was an undergraduate and helped out as needed. The manuscript was written collaboratively by McQuade, Rowe, and Dolgos.

• R. McQuade, <u>T. Rowe</u>, A. Manjón-Sanz, L. de la Puente, M. R. Dolgos, An Investigation into Group 13 (Al, Ga, In) Substituted (Na_{0.5}Bi_{0.5})TiO₃-BaTiO₃ (NBT-BT) Lead-Free Piezoelectrics. *J. Alloy Compd.* **2018**, 762, 378-388.

Chapter 3 is original, unpublished, independent work by the author, T. Rowe.

Portions of chapter 4 can be found in Rowe et al. of which I am an author. I led the project. Ms. Richtik performed the SEM analysis. Dr. Dolgos was the principal investigator. The manuscript was written collaboratively by Rowe, Richtik, and Dolgos.

 T. Rowe, B. N. Richtik, M. Dolgos, Synthesis and Characterization of a New Ferroelectric with Low Lead Content, a High Curie Temperature, and a High Piezoelectric Response. *Adv. Electron. Mater.* 2023, 2200910. https://doi.org/10.1002/aelm.202200910.

Appendix A consists of doped compositions of BFTM-PT which were included in the provisional patent but were not included in chapter 4.

• Dolgos et al. 2022. SOLID SOLUTION COMPOSITIONS AND USES THEREOF. U.S. Patent 63/350,993, filed June 10, 2022. Provisional Patent

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Thank you to my family, my parents and my brother and sister, who supported me throughout these many years of schooling.

Dedication

To my family for always supporting me.

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List of Symbols, Abbreviations, & Nomenclature

PZT	$Pb(Zr_{1-x}Ti_x)O_3$, Lead Zirconate Titanate		
MPB	Morphotropic Phase Boundary		
T _C	Curie Temperature		
NBT-BT	$(1\text{-}x)Na_{0.5}Bi_{0.5}TiO_3 - (x)BaTiO_3$		
NN-BZ	(1-x) NaNbO ₃ – (x) BaZrO ₃		
BFTM-PT	(1-x) Bi(Fe.25Mg.375Ti.375)O3 - (x) PbTiO3		
Di	Charge density		
d_{ijk}	Piezoelectric coefficient		
X_{jk}	Mechanical stress		
X_{ij}	Strain		
E_k	Electric field		
d_{int}	Intrinsic piezoelectric coefficient		
Q	Electrostriction coefficient		
Ps	Spontaneous polarization		
ε	Dielectric permittivity		
$P_{\rm m}$	Maximum polarization		
Pr	Remanent polarization		
Ec	Coercive field		
P _i	Polarization		
χ _{ij}	Dielectric susceptibility		
FE	Ferroelectric materials		
RFE	Relaxor ferroelectric		
T _m	Temperature of maximum permittivity		
P-E	Polarization vs electric field		
PNR	Polar Nano Region		
T _B	Burns temperature		

$T_{ m f}$	Freezing temperature		
PMN	Pb(Mg,Nb)O ₃ , Lead Magnesium Niobate		
AFE	Antiferroelectric		
NBT	Na _{0.5} Bi _{0.5} TiO ₃ , Sodium Bismuth Titanate		
NN	NaNbO ₃ , Sodium Niobate		
PZ	PbZrO ₃ , Lead Zirconate		
РТ	PbTiO ₃ , Lead Titanate		
РРТ	Polymorphic Phase Transition		
0.92NBT-0.06BT-0.02KNN	$(.92)Na_{0.5}Bi_{0.5}TiO_3 - (.06)BaTiO_3 - (.02)K_{0.5}Na_{0.5}NbO_3$		
KNN	K _{0.5} Na _{0.5} NbO ₃ , Potassium Sodium Niobate		
Ra	Ionic radii of the a-site cation		
Rb	Ionic radii of the b-site cation		
Ro	Ionic radii of oxygen		
t	Goldschmidt Tolerance factor		
SOJT	Second order Jahn-Teller distortion		
PMN-PT	$Pb(Mg,Nb)O_3 - PbTiO_3$		
BF-PT	$BiFeO_3 - PbTiO_3$		
BT	BaTiO ₃ , Barium Titanate		
°C	Degrees Celsius		
pC/N	Picocoulombs per Newton		
BS-PT	$(1-x)BiScO_3 - (x)PbTiO_3$		
T _{F-R}	Ferroelectric to relaxor transition temperature		
BA	BiAlO ₃ , Bismuth Aluminate		
BG	BiGaO ₃ , Bismuth Galliate		
BI	BiInO ₃ , Bismuth Indiate		
S-E	Strain vs. Electric field		
Hz	Hertz		
kV/cm	Kilovolts per centimeter		

XRD	X-ray diffraction
SXRD	Synchrotron X-ray diffraction
Å	Angstrom
λ	Wavelength
NPD	Neutron powder diffraction
FWHM	Full width half maximum
$\tan \delta$	Dielectric loss
ε _r	Relative permittivity
T _d	Depolarization temperature
TSDC	Thermally stimulated depolarization current
RT	Room temperature
ε'	Real permittivity
ln(freq)	Natural logarithm of frequency
<i>d</i> ₃₃	Low field dielectric constant
<i>d</i> ₃₃ *	High field dielectric constant
S _{max}	Maximum strain
E _{max}	Maximum electric field
pm/V	Picometers per volt
BNT-BKT	$(Bi_{0.5}Na_{0.5}TiO_3-Bi_{0.5}K_{0.5}TiO_3)$
$\mu C/cm^2$	Microcoulombs per centimeter squared
(111) _M	111 Reflection for monoclinic space group
(200) _T	200 Reflection for tetragonal space group
<i>c/a</i> ratio	Tetragonality
R _{wp} (%)	Weighted percentage remainder
(R) R3c	Rhombohedral R3c phase
SEM	Scanning electron microscopy
BFTM-LF-LMT	$Bi(Fe_{.25}Mg_{.375}Ti_{.375})O_3 - LaFeO_3 - La(Mg_{0.5}Ti_{0.5})O_3$
BFTM-CT	Bi(Fe.25Mg.375Ti.375)O3 -CaTiO3

Chapter 1 - Introduction

1.1 Motivation

Piezoelectric materials overall are one of the most useful classes of materials, influencing almost every aspect of our daily lives. Piezoelectrics convert between mechanical and electrical energy and vice versa, lending themselves to sensor, actuator, and transducer applications. Thus, they are currently used in a plethora of electronic devices including, but not limited to, cell phones, sonar equipment, engine knock sensors, pressure sensors, diesel fuel injectors, and medical devices. Business relating to piezoelectric materials has been growing year after year as more applications are developed, with the global piezoelectric materials market being valued at \$1.4 billion in 2021 and is projected to reach \$2.5 billion by 2031.[1] One such developing area involves utilizing the piezoelectric as an energy generation method, allowing natural repetitive motion and vibration to power devices. With the general increase in human population and the need for energy outside of fossil fuels, piezoelectric materials are poised to contribute to the energy supply from renewable resources.

Currently the industrial standard for piezoelectric materials is $Pb(Zr_{1-x}Ti_x)O_3$, (PZT) because of the morphotropic phase boundary (MPB), a region of phase instability, located at x=0.5, which drastically increases the electromechanical properties within the narrow composition range of the MPB.[2] While PZT is the industry standard, there are also drawbacks in its physical properties. The first and most concerning is that PZT is 60 percent by weight lead. Over the last 10-20 years multiple laws have been passed restricting the use of lead containing materials. Although due to their importance in electronic devices, PZT has been granted an exemption until a competitor is discovered that is able to substitute for lead containing materials in their myriad applications. This exemption is also on a rolling timer every 12-18 months, where if revoked all products containing greater than .1% by weight lead must be phased out.[3] The second main drawback is the low temperature operating range, since PZT undergoes a phase transition at its Curie temperature (T_C) of 350 °C. Above this, the material no longer acts as a piezoelectric, which causes PZT to be unusable for applications in harsh environments, such as high-pressure sensors and high temperature transducer applications.

Due to the hindrances in the current industry standard, it is important to design and characterize novel piezoelectric and ferroelectric materials. The use of structure and property relationships to influence these designs and develop high quality and performing materials allows for a more guided approach to producing these novel materials. In this first chapter, focus is placed on background information relating to these relationships. The properties of piezoelectricity, ferroelectricity, antiferroelectricity, and relaxor ferroelectricity are then introduced with a focus on the MPB. Finally, the perovskite structure is introduced as well as how it can be modified and tuned to look for the previously mentioned properties. Finally experimental techniques are introduces to test these novel materials. Chapter Two describes the effects of group-13 substitution on the structure and properties of (1-x) Na_{0.5}Bi_{0.5}TiO₃ – (x)BaTiO₃ (NBT-BT) which is a lead-free competitor to PZT. Chapter Three focuses on the attempt to utilize polarization extension to design the lead free (1-x) NaNbO₃ – (x) BaZrO₃ (NN-BZ) solid solution and characterize the structure-property relationship. Chapter Four presents an article on a novel reduced lead solid solution which operates at high temperatures, (1-x)Bi(Fe.25Mg.375Ti.375)O₃ – (x) PbTiO₃ (BFTM-PT). Chapter Five concludes with conclusions and final remarks.

1.2 Piezoelectricity

As previously mentioned, piezoelectrics convert between mechanical and electric energy and have a structural requirement of having a non-centrosymmetric space group. Piezoelectricity can be found in unit cells with 20 of the 21 non-centrosymmetric point groups as seen in Figure 1-1. Hermann-Mauguin notation will be used for all subsequent point and space groups due to the ability to adequately describe translational symmetry effects in crystalline solids. This effect is created from reversible distortions in the dipole moment and charged atoms in the unit cell caused by the applied stress. For these materials, upon the application of mechanical stress, an electric charge is generated, known as the direct piezoelectric effect. The opposite is also true, where upon an applied electric field will cause a volume change and strain in the material. This second effect is called the converse piezoelectric effect. Visually, these two effects are compared in Figure 1-2.

32 Point	Groups			
32 Point Groups		Piezoelectric Point Groups		
		*	1	3
21 Non-centrosymmetric	11 Centrosymmetric		2	32
· · · · · · · · · · · · · · · · · · ·			m	3m
20 Piezoelectric			222	6
	Polar Poi	nt Groups	mm2	-6
10 Pyroelectric	1	4mm	4	622
	2	3	-4	6mm
Ferroelectric	m	3m	422	-62m
(reversible polarization)	mm2	6	4mm	23
	4	6mm	-42m	-43m

Figure 1-1: Displays a flow chart relating how the crystallographic point groups influence the end properties. Additionally, the 20 piezoelectric point groups are noted to the right with the 10 polar point groups which lead to pyroelectric properties noted in the center.

Mathematically, the charge density of the direct piezoelectric effect is proportional to the applied stress as seen in Equation 1:[4]

$$D_i = d_{ijk} X_{jk}$$

With D_i representing the charge density, d_{ijk} is the tensor of the piezoelectric coefficient, and X_{jk} is the mechanical stress applied. The ijk notation is a method of denoting the corresponding vectors in the terms of its components, with i representing the x direction, j representing the y direction, and k corresponding to the z direction. Whereas for the converse piezoelectric effect, the equation is as follows:

$$\chi_{ij} = d_{kij} E_k \tag{2}$$

Where χ_{ij} represents the strain generated, d_{kij} is again the piezoelectric coefficient, and E_k is the electric field applied. While the piezoelectric coefficient, generally d_{ijk} , is a third rank tensor, the rank can be simplified to a two-dimensional tensor due to symmetry constraints. The coefficients most commonly measured are d_{33} , signifying that the applied field and measurement have the same orientation, in this case the z direction. If the coefficient is d_{31} however, the field is still applied in the z direction, but the measurement is oriented laterally to the field in the x direction. The d_{33} value is commonly the larger of the two although this does depend on the structure of the end material. [5]



Figure 1-2. Schematic depicting the mechanism for direct (top) and converse (bottom) piezoelectricity.[6]

This piezoelectric coefficient can be further divided into intrinsic and extrinsic contributions. The intrinsic contributions from ion and lattice displacements can be determined using the following formula:

$$d_{int} = 2QP_s\varepsilon \tag{3}$$

Where d_{int} represent the intrinsic piezoelectric coefficient, Q is the electrostriction coefficient, P_s is the spontaneous polarization, and ε is the dielectric permittivity. The Electrostriction effect is present in all materials and is defined as the mechanical displacement occurring under an external field. Besides these intrinsic effects, extrinsic mechanisms also contribute to the response. Some of these extrinsic mechanisms include domain wall motion, inter-phase boundaries, defect-dipole rotation, and phase changes. The main differences between the two are that intrinsic effects are always reversible while extrinsic effects can contribute to the piezoelectric hysteresis.

1.3 Ferroelectricity

Similar to piezoelectricity, ferroelectricity also has a dependence on point group symmetry. Out of the 20 piezoelectric point groups, there are 10 polar point groups which show pyroelectric properties. Then of those 10 point groups, if the polarization is reversible under electric field, the material can be said to be ferroelectric. The applied electric field reverses the polarization direction by changing between two different structures with similar free energies. While all ferroelectric materials are piezoelectric, the reverse is not true. Throughout this body of work, materials that are both piezoelectric and ferroelectric will be described.

To determine if a material displays ferroelectric character, one needs to measure the polarization vs electric field.[4, 7] Upon taking this measurement, traditional dielectric materials show a linear relationship with regards to polarization and electric field with no hysteresis, also colloquially known as linear dielectrics. On the other hand, for ferroelectric materials, a distinct hysteresis is found, as seen in Figure 1-3. The measurement, starting with a virgin pellet, first possesses no polarization because the domains are randomly aligned. Upon applying the field, the polarization increases with increasing field strength up to the maximum polarization (P_m). The field is then removed, but the polarization does not return to the original unpoled state but will have some amount of remanent polarization (P_r). The field is then reversed to switch the direction of the dipoles. The energy required for this dipole switching is called the coercive field (E_c).

Mathematically, the polarization is proportional to the applied electric field using the following formula:

$$P_i = \chi_{ij} E_j \tag{4}$$

Where P_i is the polarization, E_j is the applied electric field, and χ_{ij} is the dielectric susceptibility. This formula is only true when measuring dielectric materials, which have constant susceptibility under varying electric fields due to their low conductivity. These materials also have the ability to store charge due to the presence of dielectric polarization.





Ferroelectric materials (FE) at an elevated temperature, the Curie temperature ($T_{\rm C}$), undergo a phase change to a centrosymmetric structure, as seen in Figure 1-4. This structural transition causes the material to change to a paraelectric, meaning there is no longer any spontaneous polarization. The most conventional ferroelectric materials crystallize in either rhombohedral or tetragonal crystal systems, with the most common space groups being *R3c* and *P4mm* respectively. One such material is barium titanate (BaTiO₃) which was not only the first recognized ferroelectric, but also led the way for perovskites to be recognized as one of the most useful ferroelectric materials. Barium titanate and other perovskites will be described in more detail in later sections.



Figure 1-4: Shows that the perovskite structure changes from a) which is paraelectric and centrosymmetric above the Curie temperature to b) which is ferroelectric and non-centrosymmetric below the Curie temperature. Figure adapted from Shkuratov.[8]

1.4 Relaxor Ferroelectric

In attempts to make new ferroelectric/piezoelectric materials, the target compounds sometimes showed relaxor ferroelectric behavior rather than traditional ferroelectricity as described above. Relaxor ferroelectrics (RFE) are a subset of ferroelectrics and are very complex materials. They display unique properties caused by local disorder and inhomogeneities. Traditionally, they were first described by Smolenskii et al. as a type of ferroelectric with a diffuse phase transition.[9] The main difference between FE and RFE are that ferroelectrics show a sharp transition at the Curie temperature, which is related to the structural transition from the ferroelectric to paraelectric phase. RFEs on the other hand, have a diffuse transition at a temperature of maximum permittivity (T_m) which is unrelated to structural transitions, and is caused by the electric field's interaction with different sized polar nano regions, each with different time scales and Curie temperatures. RFEs also display *P*-*E* loops with a smaller hysteresis compared to traditional ferroelectric materials, although some relaxors can show enhanced strain response. The main differences between the two are noted in Figure 1-5. Compared to traditional ferroelectric materials, the underlying mechanisms are far less understood, although several models have been proposed.



Figure 1-5: Shows the differences between a ferroelectric and a relaxor.a) Shows the polarization vs electric field hysteresis loop with the main difference being the pinching present in the relaxor loop b) Shows the polarization vs temperature indicating that relaxor materials maintain polarization above $T_{\rm C}$. c) Shows the dielectric permittivity and the sharp vs broad transition present in ferroelectric and relaxor respectively. Figure taken from Samara et al.[10]

As previously mentioned, the easiest way to differentiate FE and RFE lies in the dielectric permittivity graph. (Figure 1-6) At very high temperatures, relaxors are no different than traditional ferroelectric materials in that both act as paraelectrics. However, as the temperature is lowered, the RFE reaches the Burns temperature (T_B) where upon the RFE enters

the ergodic relaxor phase. Within this phase, the formation of randomly distributed polar nanoregions (PNRs) occur. Although the driving force behind this formation is unclear, one theory believes it is caused by lowered entropy in the polarized state, causing small polar regions to form.[11] These PNRs are mobile within the ergodic phase and closely resemble the average state of the material. Materials in this regime have also been called superparaelectrics, particularly when used for energy storage applications.[12] Upon continuing to lower the temperature, the PNRs become larger and lose their movement, freezing into position at the eponymous freezing temperature (T_f). Below this temperature, the material can transition into either a traditional ferroelectric or enter into a non-ergodic region.



Figure 1-6: Shows the dielectric permittivity comparing ferroelectrics to relaxors. Also shows how the polarization vs electric field hysteresis changes depending on temperature/ ergodic or non-ergodic state. Figure adapted from Li et al.[13]

1.4.1 Ergodic Region

The ergodic region lies between the Burns (T_B) and freezing (T_f) temperatures. Here, the PNRs are weakly correlated, small, and able to rotate freely. (Figure 1-7) Thus, under an electric field, the material acts similarly to traditional ferroelectrics, but once the field is removed, the material returns to its previous state of randomly oriented dipoles, which disrupts the long-range ferroelectric ordering. Compositional disorder can also influence how the PNRs interact, which can change the polarization and permittivity of the solid solution. One example is that with increased cation disorder, less energy is needed to reorient the dipoles and break ferroelectric ordering, which will shift the T_f to lower temperatures. This shifting can cause a higher piezoelectric response near room temperature, but temperature stability is sacrificed.[14, 15]



Figure 1-7: Shows the difference in PNR size and electrical properties depending on whether the material is in a a) non-ergodic or b) ergodic phase. Figure adapted from Cho et al.[15]

1.4.2 Non-ergodic Region

Below $T_{\rm f}$ two possible states can occur, with the first being a non-ergodic phase and the second being a low temperature ferroelectric phase. For the non-ergodic phase, the structure remains pseudocubic at all temperatures and unless acted upon by an external electric field,

remains paraelectric. When a material in the non-ergodic regime becomes poled however, it will act similarly to a traditional ferroelectric losing the frequency dependence. Upon raising the temperature to the depolarization temperature, there is a transition back to an ergodic relaxor which is denoted as a second peak in the dielectric graph as seen in figure 1-6. To varying degrees, there can also be a transition to a ferroelectric phase at the T_f instead. This transition can be determined through the dielectric permittivity curve. If the permittivity remains frequency dependent and diffuse, the material has transitioned to a non-ergodic phase, whereas a sharp and frequency independent permittivity indicates the presence of long-range ferroelectricity. (Figure 1-8)



Figure 1-8: Shows two types of relaxor upon reaching the $T_{\rm f}$. In a) the material stays a relaxor with frequency dependence below $T_{\rm f}$ whereas in b) the material changes to a ferroelectric phase showing a sharp transition and less frequency dependence. Figure adapted from Bokov and Ye.[14]

1.4.3 Polar Nano Regions

Understanding polar nano regions (PNRs) is extremely important to understanding RFEs.[16, 17] The main structural attribute of RFEs is local compositional disorder creating heterogeneity which manifests as a disordered distribution of either isovalent or aliovalent ions on equivalent lattice positions. These substitutions cause this disorder due to the different cation sizes, charges, internal fields, and displacement positions of the relevant atoms. Early focus on lead-based relaxors only looked at the B-site disorder, like in Pb(Mg,Nb)O₃ (PMN)[18, 19], although A-site disorder can also induce relaxor properties. In addition, B-site disorder can disrupt A-site displacements, which also leads to relaxor properties.

Various models have been proposed to describe these polar nano regions and two main models have been developed.[20] The first model views PNRs as small areas of local displacements embedded within a cubic-like parent matrix (Figure 1-9a). This model also corresponds well to the random site model for statistical distribution of substituted ions, where regions of the sublattice remain ordered while the rest is randomly occupied. The second model describes PNRs as polar domains separated by pseudocubic domain walls (Figure 1-9b). It assumes PNRs form from interactions between internal fields caused by disorder, a random fields model. Other models have also been brought forward, although it is highly probable that the true model is a highly complex combination of all the varying models.



Figure 1-9: Shows the different models for describing PNRs. a) shows PNRs within a cubic matrix while b) shows the Polar domains separated by cubic domain walls. Figure taken from Macutkevic.[21]

1.5 Antiferroelectric

While this thesis does not aim to study antiferroelectric materials, in one case, the end member in a solid solution displays antiferroelectric behavior, as does PbZrO₃ in the Pb(Zr,Ti)O₃ (PZT) phase diagram. Antiferroelectricity, similarly to ferroelectric materials, occurs in materials with a net dipole moment. The difference is that for ferroelectric materials, the dipoles under zero field are found in random orientations, while for antiferroelectrics (AFE), the neighboring dipoles are poled antiparallel to each other meaning that there is a lack of macroscopic spontaneous polarization. Antiferroelectrics under zero-field will act as a dielectric showing no piezoelectricity. Upon applying a high enough field however, the antiparallel dipoles can be forced to flip, causing an AFE to FE phase transition to occur. This causes the signature double hysteresis loop to form in the polarization vs electric field measurement. (Figure 1-10) The concept of AFE was originally coined by Kittel in 1951 [22] with lead zirconate being the first recognized AFE material. Other lead-free antiferroelectric end members are also used in lead-free solid solutions such as sodium bismuth titanate (NBT) and sodium niobate (NN) which will be discussed in more detail in a later section.[23, 24]



Figure 1-10: Shows the differences in polarization vs electric field hysteresis loops between a) linear dielectrics, b) ferroelectrics, c) relaxors, and d) antiferroelectrics. Figure adapted from Chauhan et al.[25]

1.6 Morphotropic Phase Boundary

While materials like BaTiO₃ display both piezoelectricity and ferroelectricity, it is possible to greatly improve the properties by forming a solid solution with two or more end members. [26, 27]As previously mentioned, PZT is a solid solution between PbZrO₃ (PZ) and PbTiO₃ (PT). When the electronic properties for this solid solution were measured, they showed a distinct compositional dependence with the highest piezoelectric response occurring at 48 percent PZ. (Figure 1-11) This enhancement was also determined to be largely temperature independent, which differentiates this transition, henceforth called a morphotropic phase boundary (MPB), from a polymorphic phase transition (PPT).



Figure 1-11: Shows the phase diagram for the PZT solid solution. Also displays the flattening of the Gibbs free energy near the MPB. P1, P2, and P3 correspond to the polarization directions, x, y, and z respectively. For example, since the dipole for the rhombohedral structure is oriented in the [111] direction P1=P2=P3. Whereas for the cubic structure, polarization is zero, thus P1=P2=P3=0. Figure taken from Damjanovic et al.[4]

1.6.1 Polarization Rotation

Originally, it was thought that the electromechanical properties increased at the MPB due to an increased number of polarization directions. Looking at the Gibbs free energy, there is a flattening at the MPB between multiple ferroelectric structures, which allows for this increase in polarization and increase in the domain wall mobility. As previously mentioned, PZT displays an MPB at what was originally thought to be a two-phase mixture of the rhombohedral and tetragonal phases.[28] As technology advanced, higher resolution instruments were used to
determine the presence of a pseudocubic monoclinic phase in the middle of the rhombohedral and tetragonal phases. This monoclinic phase provides a low energy "polarization rotation" pathway from [111] to [001] through the (110) axis and vice versa. (Figure 1-12)



Figure 1-12: Displays the polarization rotation pathway through the (110) plane in the pseudo cubic unit cell. Figure adapted from Ogino et al.[29]

1.6.2 Polarization extension

While the polarization rotation mechanism is present in a large number of solid solutions with an MPB, needing both end members to be ferroelectric drastically narrows the number of possible compositions to start with. Thus, another mechanism for increasing the electromechanical properties was theorized which involved using a centrosymmetric structure in place of one of the ferroelectric end members. (Figure 1-13)[30] The goal is to take a similar mechanism causing the increase in properties seen at the Curie temperature, but make it compositionally dependent. It is aptly named because the polarization is extending, increasing in value going from the paraelectric to ferroelectric phase. Some examples of this mechanism include 0.92NBT-0.06BT-0.02KNN where a weakly polar *P4bm* undergoes a transition to the *R3c* structure and induces a large strain response.[31] Another PZT example involves the

transition from the AFE phase to FE R3c which occurs near x=0.1 PT.[32] Further utilization of this mechanism could open up a much larger phase space for new material design as there are significantly more non-ferroelectric end members to draw upon and use in the phase diagram.



Figure 1-13: Describes a theoretical phase diagram that could display polarization extension. Figure adapted from Damjanovic. [26]

1.7 Perovskites

As mentioned in the motivation, the use of ferroelectric materials in advanced technological devices has increased year after year. One of the primary crystal structures fueling this technological revolution is the perovskite structure. It displays the same structure as the mineral CaTiO₃ which was first discovered in 1839 by Gustav Rose and named after Lev Perovski, a Russian minerologist.[33] Perovskites are an extremely diverse set of materials and can display a large amount of variability in not only the composition and structure but also the vast variety of physical properties that can be manifested through materials design. (Figure 1-14) Perovskites are used in a variety of applications, such as multiferroics, ferroelectrics, ionic

conductors, solar power, and numerous others. This extensive variety is caused by the robust nature of the structure which will be discussed in a more complete nature in the next section.



Figure 1-14: General form of the perovskite structure and periodic table displaying elements commonly found in the A, B and X sites. Figure taken from Schlom et al.[34]

1.7.1 Structure

Considering that the parent mineral of the perovskite crystal structure is CaTiO₃, the ideal general structural formula for a perovskite is ABX₃, with A and B denoting the cations and the X representing the anion. If the material is an oxide, this general formula is more commonly denoted as ABO₃, and all following materials described in these chapters fall within this family. While the perovskite structure can be displayed in two different ways depending on whether the A or B site is the center of the cube, the structure is represented by anion cubic close packing with the oxygen atoms forming a network of corner-sharing octahedra. (Figure 1-15) The smaller B-site cation, usually a transition metal, sits in the center of the octahedra with a coordination number of six. The larger A-site cation then sits in a polyhedra between the octahedra and has a

coordination number of 12. The ideal perovskite crystallizes in the cubic crystal *Pm-3m*, space group 227.



Figure 1-15: Shows the two different ways to visualize the perovskite unit cell. a) Shows the unit cell with the a-site on (000) while b) has the b-site on (000).

While the ideal perovskite structure is cubic, depending on the sizes of the cations, the structure may reduce in symmetry and distort in order to accommodate other preferred bonding environments. This inherent ability of the structure allows for almost any element of the periodic table to be used, which leads to the wide variety of applications noted in previous chapters. To codify this change in structure and think about material design, Goldschmidt established some basic principles for perovskites introducing the concept of a tolerance factor. [35] This tolerance factor, t, was based on the geometry of the idealized cubic unit cell and can be defined as:

$$t = \frac{Ra + Ro}{\sqrt{2(Rb + Ro)}}$$
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where Ra, Rb, and Ro are the ionic radii of the A/B cations and oxygen respectively. The main use for the tolerance factor is as a guide for determining the stability and crystal system of a resulting composition. From this, three main regions can be described, the first being the tolerance factor is less than 1, meaning the A-site cation is too small or the B-site is too large. The second is essentially the opposite of the first region having a factor above one. For ideal perovskites, this factor will be 1, and for the majority of compounds, structural stability is achieved between 0.85 and 1.1. The end structure is also influenced with rhombohedral and orthorhombic structures usually being t < 1, while hexagonal and tetragonal structures typically have t > 1. For design of novel ferroelectrics in particular, the most common technique involves the use of elements which undergo the second order Jahn-Teller (SOJT) effect, meaning they displace in a polar fashion and occur because of the interaction of filled and empty orbitals with similar symmetry characteristics.[36] Due to this polar displacement, the resulting unit cell is non-centrosymmetric fulfilling the symmetry constraints for piezoelectricity as mentioned in section 1.2. This effect is primarily limited to d⁰ transition metals, such as Ti⁴⁺, Nb⁵⁺, and Ta⁵⁺, and cations with lone pair valence electrons, such as Pb²⁺, and Bi³⁺.

1.7.2 Octahedral Rotation

For materials that deviate from the ideal perovskite, multiple compensation methods such as atomic distortions and octahedral rotation can occur.[37] Octahedral rotations, also known as octahedral tilting, primarily occur when the A-site cation is smaller than the ideal size, allowing for smaller coordination environments compared to the 12-fold cubic ideal. To more accurately describe the tilt systems that could occur within perovskites, the crystallographer A.M. Glazer developed a simple notation hence forth called Glazer notation.[38] This consists of three letters (a, b, and c) denoting the magnitude of the tilt along the x, y, and z axis respectively, with the

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same magnitude using the same letter. After each letter, one of three superscripts are used, (+, -, 0) which indicate whether the tilt is in-phase, out of phase, or has no tilt, respectively. In more detail, in-phase indicates along the respective axis that all the tilts are in the same direction, whereas out of phase denotes that the tilts alternate along the axis. In summary, the most common space group for perovskites is the *Pnma* space group and is represented as a⁺b⁻b⁻ in Glazer notation. (Figure 1-16) Interestingly, octahedral rotations, due to the corner sharing nature inherent within the perovskite structure, cannot induce ferroelectricity within simple perovskites.[39] In fact, within proper ferroelectrics, the octahedral rotations and ferroelectric polar distortions occur independently.[40, 41] Very recently, improper and hybrid improper ferroelectrics in perovskite-like materials have been developed which can result in octahedral rotation induced ferroelectricity. These perovskite-like materials primarily involve layered structures, which create a ferrielectric mechanism from the A-site cations by breaking the B-site symmetry in the *Pnma* structure.



Figure 1-16: Shows the octahedral rotations present in the *Pnma* space group and compares to the undistorted cubic parent space group. Figure taken from Praveen et al. [42]

1.8 Traditional Ferroelectrics

The following section describes various important and established ferroelectric materials that will be used as end members in solid solutions or serve as important reference materials for comparison in the next research chapters.

1.8.1 Lead Based

1.8.1.1 PbTiO₃

Lead titanate (PT) crystallizes in the same structure at room temperature as the first synthesized modern ferroelectric material, barium titanate. That being the tetragonal noncentrosymmetric *P4mm* structure.[43] PT shows a larger lattice distortion and upon cooling, only has one phase transition from cubic to the previously mentioned tetragonal phase. It has high electromechanical properties with a $T_{\rm C}$ near 500 °C and a d_{33} around 433 pC/N.[44] The issues with these materials occur during synthesis, where the large spontaneous strain and thermal expansion induced upon the phase change between cubic and tetragonal structures causes the materials to often crack. The material also tend to show high conductivity values paired with a large coercive field, thus ruining any potential uses for applications. This is because the high coercive field combines deleteriously with the high conductivity, leading to large amounts of dielectric loss and shorting, which is where charges flow freely through the material. This means the material can no longer act as a dielectric and loses any ability to store charge. Thus, PT is often used as a dopant or end member with notable mentions being $Pb(Mg,Nb)O_3 - PbTiO_3$ (PMN-PT)[45], BiFeO₃ – PbTiO₃ (BF-PT)[46], as well as the current leader for perovskite functional materials PbZrO₃ – PbTiO₃ (PZT).

1.8.1.2 PbZrO₃ – PbTiO₃

PZT, along with all the possible dopants, is the current leading ferroelectric material for the industry, and essentially has been since its discovery in the mid 1950's.[27, 47] This is due to the ease of synthesis as well as overall ability to tune the relevant properties to whatever is required using various dopants. The primary composition used is 52 % PZ, which places the solid solution at the MPB leading to a temperature-independent piezoelectric response. The properties are highly tunable and, depending on the dopants used, show a high electrochemical response with a $T_{\rm C}$ between 300 and 400 °C and a d_{33} varying between 100 and 500 pC/N.[48] Thus, a thrust of ferroelectric research is to find new high temperature ferroelectric materials which will be expounded upon in a later section.

1.8.2 Lead Free Materials

While PZT is the most commonly used solid solution for industrial applications, many lead-free alternatives have been developed in order to address the shortcomings of PZT.[49-51] These shortcomings primarily revolve around the environmental concerns regarding the utilization of lead-containing products, as well as optimal temperature range, and a lack of fatigue resistance. Thus, ongoing research involving structure-property relationships, computational calculations, and modifying existing compounds have been utilized to synthesize potential lead-free candidates, several of which are to follow.

1.8.2.1 Na_{0.5}Bi_{0.5}TiO₃ - based

One commonly studied lead-free material involves a substitution on the A-site between sodium and bismuth with 50 % of each needed for charge balance.[52-54] Bismuth, in particular, is thought to be a potential substitute for lead due to both displaying the lone pair effect, while

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having a much lower toxicity. However, the ionic radii of bismuth is much smaller than lead causing difficulties for simple substitutions. NBT itself is technically a relaxor material and displays a Curie temperature of 320 °C with high remanent polarization, but with significant downsides such as a very high coercive field, 73 kV/cm, as well as high dielectric loss, meaning energy loss from heat, atomic reorientation, or conductivity, that makes poling difficult. Recently, the structure was determined to be monoclinic *Cc*. Upon using the MPB composition as an end member, multiple promising ferroelectric solid solutions have been discovered, such as $(1-x) Na_{0.5}Bi_{0.5}TiO_3 - (x) Bi_{0.5}K_{0.5}TiO_3 (NBT-BKT), (1-x) Na_{0.5}Bi_{0.5}TiO_3 - (x) NaNbO_3 (NBT NN), and the material focus for the upcoming chapter (1-x) Na_{0.5}Bi_{0.5}TiO_3 - (x) BaTiO_3 (NBT-$ BT).[55]

1.8.2.2 BaTiO₃ - based

Barium titanate (BT) is considered the classic ferroelectric and was one of the most important discoveries in the history of ferroelectric materials. From its first use as a capacitor, it was the first simple oxide system shown to display ferroelectricity. BT was also the first ferroelectric that has a tetragonal structure at room temperature with a low curie temperature of around 120 °C. The first relaxor was also discovered when BT was mixed with barium stannate.[17] When working with BT there are two main research drives, the first involves raising the low Curie temperature to expand the operating temperature, while the second is using BT to promote relaxor behavior.[56] BT is often used as an end member to synthesize new ferroelectric/piezoelectric solid solutions.

1.8.2.3 K_{0.5}Na_{0.5}NbO₃ - based

Finally, the last lead-free material highlighted is a solid solution between potassium and sodium niobate, called KNN. KNN displays multiple phase transitions throughout the solid

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solution, but the composition leading to the increase in properties occurs at 50 % of each end member.[57] At this particular composition, a polymorphic phase transition (PPT) exists between two different orthorhombic phases and displays strong properties with a d_{33} in the range of 160 pC/N and a Curie temperature of 420 °C. These values are close to non-doped PZT, and further modification with dopants on the A and B sites can increase the piezoelectricity further. [58, 59] Currently, this material is being applied for moderate temperature sensors, and due to the lack of lead and other toxic elements, it is also being explored as an in-vivo bio sensor that could eventually be placed inside a human body. It is also often used as an end member in ternary solid solutions.

1.9 High Temperature Materials

As previously mentioned, one of the main drawbacks for PZT is the low Curie temperature (350 °C), above which the material changes to a paraelectric, which makes it unusable for high temperature applications. Traditionally, piezoelectric crystals were used for high temperature applications, with quartz being the most common.[60] These crystals are only piezoelectric and not ferroelectric, meaning that they do not have a Curie temperature, and remain piezoelectric until they melt, thus, the crystals can operate at very high temperatures. One drawback is that their piezoelectric coefficients are traditionally very low, ~10 pC/N on average. To that end, current research focuses on attempting to raise the Curie temperature of existing ferroelectric materials or discovering new ferroelectric solid solutions.

$1.9.1 \text{ PbTiO}_3$ - based

One such material that has been used extensively as an end member for these novel solid solutions is lead titanate (PT). (Figure 1-17) The first reason being that it is one of the end

members for PZT, the current industry standard. PZ was the replaced end member, because between the two, PZ has a much lower Curie temperature (220 °C for PZ and 495 °C for PT), and PT is a ferroelectric at room temperature. Thus, many endmembers were paired with lead titanate and a trend formed where the further away the substituted endmember's tolerance factor is from unity, the higher the expected Curie temperature. That has lead to multiple high temperature ferroelectric solid solutions with the standouts being $(1-x)BiScO_3 - (x)PbTiO_3$ (BS-PT)[61], $(1-x)BiFeO_3 - (x)PbTiO_3$ (BF-PT)[62], and one of the chapters for this thesis (1-x)Bi(Fe_{.25}Mg_{.375}Ti_{.375})O₃ - (x) PbTiO₃ (BFTM-PT).



Figure 1-17: Shows the relationship between Curie temperature and end member tolerance factor. Figure adapted from Eitel et al.[63]

1.10 Diffraction

Structural determination is one of the backbones for true understanding and is the basis for learning the structure and property relationships inherent within materials. The main guiding principle for structure property relationships is called Neuman's principle which states that the symmetry elements of the crystal structure must be present in the symmetry elements of any individual property. As such, if the structure is known, the inherent properties can be understood. One such method to determine the crystal structure is through diffraction.[64]

Diffraction is defined as the constructive interference of waves which occur after hitting an obstacle, in this case a crystalline solid. Since the crystalline solids have a 3-dimensional arrangement of atoms, the waves will scatter in all directions upon impact. Thus, if the wavelength of the incident wave is similar to the distance between the scattering centers, both destructive and constructive interference will occur. This relationship was mathematically defined and is represented by Braggs law:

$$n\lambda = 2dsin\theta$$
 6

Where **n** represents the order of the reflection, λ is the wavelength of the incident wave, **d** is the distance between the scattering events, and θ is the incident angle. (Figure 1-18) Thankfully many techniques can be used, such as electrons, neutrons, and electromagnetic radiation, which all have appropriate wavelengths to determine the atomic spacing in these crystalline materials.



Figure 1-18: Displays a 2-dimensional representation of the Bragg diffraction conditions. Figure taken from Thomas.[65]

1.10.1 X-Ray Diffraction

For inorganic materials, the most common technique for probing the structure involves utilizing X-rays for diffraction.[64, 66] This is because X-rays can be easily generated by benchtop diffractometers while also only requiring a small amount of sample. In addition, this technique is also non-destructive, allowing the sample to be used in further research. Depending on the material probed and specific technique used, various metals can be used as the metal source, with copper and molybdenum being the most prevalent. X-rays are scattered in a solid through the interaction of the waves with the electrons of the target material, and X-rays scatter linearly with the size of the electron cloud. Meaning that the higher atomic number atoms will scatter the X-rays much more strongly than light atoms. As to some drawbacks, depending on technique and incident wavelength, most X-ray diffraction experiments are only able see the average surface structure, although this is enough for structure determination. Very light elements, as mentioned earlier, are poor scatterers and do not give high diffraction intensity. As such, if they are mixed with heavier elements, the light elements would essentially be overshadowed, unable to be seen. Also, if there are two elements with very similar atomic numbers, it can be difficult to differentiate same-site occupancy due to similarity of response. Finally, some elements will absorb and fluoresce certain wavelengths, so choosing the correct set up for each material studied is vital.

1.10.2 Neutron Diffraction

In addition to X-rays, neutrons can also be used for structural analysis.[67] Neutrons are neutrally charged particles and they only interact with the nucleus of the target. As such, neutrons penetrate much more deeply compared to X-rays, with neutrons probing ~1cm in depth whereas X-rays only penetrate several microns. This allows for data to be gathered from the total

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amount of a larger bulk sample, instead of only just a small amount past the surface. As for drawbacks, when utilizing neutrons for analysis, unlike X-rays, a normal research lab is unable to generate neutrons, needing either a nuclear reactor or a spallation source, limiting neutron diffraction to national labs. Also, depending on the source, much larger samples are needed for measurement and the final result can have low brilliance or resolution. For positives, compared to X-rays, however, the scattering cross section is not dependent on atomic number and as such can differentiate similar sized elements and can even differentiate different isotopes. (Figure 1-19) This, in particular, makes neutron diffraction valuable for the structural determination of oxide materials.



Figure 1-19: a) Total cross-sections for neutrons and X-rays with regards to different elements.[68]

1.10.3 Structure Analysis

Diffraction experiments are able to detect sample impurities, phase changes, crystallite size and strain, and can even determine the complete structure of a material.[69-71] In principle, the diffraction pattern should reveal the unique structural footprint for each measured sample, but in practice, the pattern, depending on sample, can be very complex and require computational

modeling and data fitting to completely elucidate the structural information. Diffraction can be performed on both single crystal and polycrystalline materials, although this thesis focuses only on polycrystalline samples. As for modeling, the process is usually completed in two steps with a Pawley or Le Bail fit first being performed, and then the resulting parameters are fed into a Rietveld refinement (Figure 1-20) for final analysis. There are multiple software solutions for modeling such as GSAS[72], Fullprof[73], and Topas Academic[74], with Topas Academic being the software of choice in this thesis.



Figure 1-20: Example Rietveld refinement with the tick marks denoting the *Pm-3m* cubic space group. Figure adapted from Jones et al.[75]

1.10.3.1 Pawley Fitting

Starting with the raw data, the initial structure parameters can be determined utilizing the Pawley fitting method, which does not need any a priori structural information, for example atomic positions, and is a whole powder pattern decomposition method (WPPD).[76, 77] With polycrystalline powder samples, diffraction peaks commonly overlap, and without good initial parameters these peaks are unable to be deconvoluted. Thus, in a Pawley fit the number and

positions of the peaks give information on both the lattice parameters and the space group of the unit cell, while also fitting the space group, background, and peak width. The end result can then be fed into the Rietveld analysis as accurate starting values.

1.10.3.2 Le bail Fitting

Instead of a Pawley fit, another useful method for determining the initial structure parameters for Rietveld refinements is the Le Bail method.[78] The Le Bail method similar to Pawley is also a WPPD, but arrives at the same answers in a different way. The main difference being, for a Le Bail fit each individual peak is assigned an intensity value instead of a leastsquares parameter. This allows for a faster and less computer memory intensive refinement, at the cost of some additional information received using a Pawley fit.

1.10.3.3 Rietveld Refinement

Considering the difficulty in synthesizing large enough crystals for single crystal analysis, techniques involving polycrystalline powder samples are invaluable. The Rietveld method is one such technique for full structural refinement of crystalline powder samples. This method is a least squares refinement, where a calculated pattern is matched to the collected pattern and is a structure dependent refinement method.[64, 70, 79]

Since the Rietveld refinement is structure dependent, the peak intensity is also refined by calculating the atomic scattering on the diffraction plane through:

$$F_{hkl} = \Sigma_j f_j e^{-2\pi i (hx_j + ky_j + lz_j)}$$

In this equation, F represents the structure factor, f is the atomic scattering factor, and x,y,z are the atomic coordinates of the hkl reflections. The total intensity of the calculated peak is then determined by:

$$y_i = s\Sigma_{hkl}L_{hkl}|F_{hkl}|^2 \Phi(2\theta_i - 2\theta_{hkl})T_{hkl}A_\theta + y_{bi}$$

where, y_i is the observed intensity, s is the scale factor, L is the Lorentz polarization, Φ is the reflection profile function, T is preferred orientation function, A_{θ} is the absorption factor, and y_{bi} is the background intensity for the reflection hkl, on the *i*th step. Considering this method is comparing the observed and calculated patterns, the S_y term of the calculated pattern is minimized by the least squares method until it converges to as close to the observed values as the constraints allow. Mathematically this is described as:

$$S_y = \Sigma_i w_i (y_i - y_{ci})^2$$

where, w_i is y_i^{-1} , and y_{ci} is calculated intensity at the *i*th step. Residuals are used to then show how close the agreement is between the two patterns. The most often residual is the weightedprofile residual as it contains the Sy term minimized by the least squared analysis.

$$R_{wp} = \left(\frac{S_y}{\Sigma_i (y_i)^2}\right)^{1/2}$$
 10

Depending on the fit, other terms might need to be refined as well, such as effects corresponding to peak broadening. This can come from a multitude of sources, such as experimental setup, optics, crystallite size and strain, and microstructure of the sample. Since the analysis only minimizes the differences, the Rietveld method is only as good as the initial inputs. If the initial values are poor, the researcher can be lead in an incorrect direction with false minima, unrealistic structures, and instability of the model can occur. Thus, while the Rietveld method is a useful technique for solving a variety of crystal structures, care needs to be taken in order to verify that the results are probable and realistic.

1.10.3.4 Distortion Mode Analysis

Distortion mode analysis is a type of Rietveld refinement, where instead of atomic xyz coordinates, specific symmetry-motivated amplitudes are refined.[39] The basis behind this type of analysis is when a crystal experiences a symmetry lowering distortion some of the symmetry elements of the parent, undistorted, space group are lost while others stay unchanged. These space group symmetry elements are represented by irreducible representations based on specific k points on the first Brillouin zone. In order to utilize this analysis, the ISODISTORT software must be used in conjunction with the Rietveld refinement software of choice. [80, 81]

1.11 Dielectric Permittivity

The dielectric response of a material is caused by five different polarization mechanisms, with each operating at different timescales and thus responding to different electric field frequencies. Starting with the fastest response, electronic polarization corresponds to the displacement of the electron cloud and is correlated to how many electrons each atom contains. This response is present in all materials. The next fastest is ionic polarization which involves the response of the positive and negative sublattices to the applied field. The above mechanisms are both considered intrinsic responses. Next is dipole polarization, also commonly known as orientation polarization, which corresponds to the alignment of dipoles to the electric field. Continuing, space charge polarization is next which involves charged particles moving in a confined space responding to the applied field. Finally, ferroelectric materials also display polarization through domain wall motion, which is when the wall grows to have more domains in the same direction as the applied field. (Figure 1-21) As such, when these five mechanisms are put together, they give the total polarization of a material and as such the total permittivity.[82, 83]

35



Figure 1-21: Shows the frequency dependence of the various polarization mechanisms. Figure taken from Dorey.[84]

As mentioned previously, in order to measure permittivity an external electric field is used. When this electrical field is applied, dielectric materials form internal dipole moments which generate a displacement field (\mathbf{D}_i), which is the sum of the induced polarization (\mathbf{P}_i) and the product of the applied electric field (\mathbf{E}_i) and the permittivity of free space ($\boldsymbol{\varepsilon}_0$).

$$D_i = \varepsilon_0 E_i + P_i \tag{11}$$

This induced polarization is a function of the density of these electronic dipoles which is proportional to the applied field:

$$P_i = \varepsilon_0 \chi E_i \tag{12}$$

The χ in the previous equation corresponds to the dielectric susceptibility which is a measure of how polarized a material can become when under field. This susceptibility is also

directly related to the relative permittivity (Equation 13), which is a ratio of the material's permittivity to the permittivity of free space. (Equation 14)

$$\varepsilon_r = \chi + 1$$
 13

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$
 14

In simpler terms, permittivity is a measurement of the ability of a material to store energy from an applied electric field. In practice, this phenomenon allows for greater charge generation in capacitors, and the capacitance is another way to measure the dielectric constant. (Figure 1-22) The equation is as follows:

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d}$$
 15

where **C** is capacitance, **A** is area of parallel plates, and **d** is the thickness between the plates. The dielectric permittivity has both real and imaginary components (Equation 16) and the dielectric loss is commonly expressed as a ratio between the imaginary and real permittivity. (Equation 17)

$$\varepsilon = \varepsilon' - i\varepsilon'' \tag{16}$$

$$tan\delta = \frac{\varepsilon''}{\varepsilon'}$$
 17

Generally, ferroelectric materials have high permittivity values.



Figure 1-22: Shows a diagram of a capacitor with a dielectric material between the parallel plates.[83]

1.12 Piezoelectric and Ferroelectric measurements

For piezoelectric materials, there are several figures of merit depending on application. One such important property includes the mechanical quality factor (Q_m), which measures the stability of a piezoelectric when working as an oscillator. The second is the electromechanical coupling factor (k^2), which describes the efficiency of the piezoelectric when relating to the input and stored energy. The d_{33} and d_{33} * piezoelectric coefficients are also considered to be figures of merit when the material is being used as an actuator.[4, 85]

Additionally, for actuators, the strain under field is determined by either unipolar or bipolar strain vs electric field measurements. For the ideal piezoelectric, the strain curve for bipolar loops will display what is colloquially known as a "butterfly" loop. (Figure A-6) With a virgin material the dipoles are in random orientations, thus the strain will start at 0. Then as the field is applied, the strain will increase in the direction of the electric field bias until the maximum strain is reached. The field is then reversed and the strain traces back through the origin. Since the dipoles will then be oriented in the opposite direction to the applied field, the strain reads as negative. Near the coercive field, the dipoles will then switch to the same direction as the field, causing the strain response to jump from negative to positive. The loop is then completed cycling between positive and negative electric fields. In unipolar measurements, the field is only applied in one direction, thus negative strain will not be seen. In real materials, the strain response will contain some nonlinearity caused by non 180-degree domain walls as well as other defects, which trap and pin the domain walls. Within this thesis instead of strain, all values are instead reported as strain percentage.

$$strain \% = \frac{\Delta t}{t} * 100\%$$
18

In this equation the t stands for thickness of sample, while Δt is the change in thickness.



Figure 1-23: a) Shows an ideal strain vs hysteresis loop for ferroelectric materials. Colloquially called a "butterfly loop" b) measurements taken on a PZT thin film. Figure taken from Damjanovic[4]

1.13 Thesis Research Goals

As previously mentioned, the search for and discovery of new materials is necessary to not only expand the field of ferroelectricity but to also provide future answers to economic and societal problems not yet encountered. Thus, the goals for this thesis start with taking as complete an approach in synthesis and characterization as time allows. This includes considering the background information when designing possible solid solutions and then utilizing the aforementioned experimental techniques to characterize the structure and property relationships. The areas of focus will include under-investigated and open issues present within the field, with a principal gaze on synthesis of novel materials to improve on lead zirconate titanate. Whether that be lead removal or improvement in areas where PZT is a poor choice, such as high temperature applications.

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Chapter 2 - An Investigation into Group 13 (Al, Ga, In) Substituted (Na_{0.5}Bi_{0.5})TiO₃-BaTiO₃ (NBT-BT) Lead-Free Piezoelectrics

2.1 Introduction

Piezoelectric materials are utilized in many commercial devices such as sensors, transducers, and actuators, and the market is continually expanding. [86] $Pb(Zr,Ti)O_3$ (PZT) is the most common material used in piezoelectric devices due to its high piezoelectric response and the ease with which the properties can be tuned through substitution.[47] Despite the outstanding properties of PZT, it has several disadvantages such as the toxicity of lead, a low operating temperature (below 200 °C), and a susceptibility to fatigue after many cycles.[51, 87-89] One promising material extensively studied for its potential to replace PZT is the solid solution between Na_{0.5}Bi_{0.5}TiO₃ and BaTiO₃, or NBT-xBT. NBT-BT was initially prepared to mimic the rhombohedral-tetragonal morphotropic phase boundary (MPB) where an enhanced piezoelectric effect occurs as demonstrated in PZT (Pb(Zr_{0.52}Ti_{0.48})O₃).[90] While NBT-BT has an established morphotropic phase boundary at approximately 5-7% BaTiO₃, the structural characteristics of the MPB are vastly different from that observed in PZT.[90-92] Under assynthesized conditions, NBT-BT behaves more like a relaxor ferroelectric, with a broad, frequency-dependent, maximum dielectric permittivity.[87] However, when the sample is poled above its coercive field, it undergoes a structural transition to a ferroelectric structure. At the MPB, this ferroelectric structure is observed up to ~100 °C. At this temperature ($T_{\text{F-R}}$), there is a

transition from the ferroelectric to relaxor phase which has a maximum permittivity temperature $(T_{\rm m})$ of 288 °C.[93]

The successful manipulation of PZT for use in many applications is in part due to the detailed understanding of its structure-property relationships.[94, 95] Unfortunately, the practical use of NBT-BT has not translated to the same success as PZT. The limitations stem from wildly complex short and long-range structures, which results in difficulty when trying to rationally tune its properties.[96]

This work systematically investigates the electromechanical properties of NBT-BT when substituted with group 13 based, bismuth compounds: $BiAlO_3$ (BA), $BiGaO_3$ (BG), $BiInO_3$ (BI). The rationale behind the investigation was to identify any changes in the structure-property relationships as a function of $Bi(M)O_3$ as M changes down group 13 on the periodic table. None of these three $Bi(M)O_3$ materials stabilize in the perovskite phase at ambient pressures due to the small size of the Bi^{3+} cation at the A-site. Therefore, $BiAlO_3$ and $BiInO_3$ must be synthesized at high pressures.[97] The perovskite phase of $BiGaO_3$ is only metastable at high pressures and changes to the pyroxene structure upon decompression.[98] Despite the high pressure requirements for each of these phases, they can stabilize under ambient conditions as a component of a solid solution.[63, 99-101]

Each of these Bi-based perovskites has a non-centrosymmetric space group under certain conditions. BiAlO₃ (Figure 2-1a) is found in the *R3c* space group and BiInO₃ (Figure 2-1c) in the *Pna2*₁ space group in ambient conditions (after high pressure synthesis).[97] BiGaO₃ (Figure 2-1b) is found in the space group *Cm* as a coexistent phase between approximately 3 and 6 GPa.[94] However, all three Bi(M)O₃ (M=Al, Ga, In) compounds show promising ferroelectric and piezoelectric properties (M=Al, In), or were predicted to have promising properties

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(*M*=Ga).[102, 103] In particular, the high Curie temperature (T_C) of BiAlO₃ (520 °C) and BiInO₃ (>550 °C) is attractive as their solid solutions may enhance properties of the ferroelectric regime in NBT-BT. [63, 103]

Our study focused on the ternary phase diagram of a Bi(*M*)O₃ end member (*M*=Al, Ga, In) with the 0.945Na_{0.5}Bi_{0.5}TiO₃ – 0.055 BaTiO₃ system. Although, BiAlO₃ was substituted into the B-site of NBT-6BT previously, the purpose of our work was to investigate the periodic trends of substituting BA, BG, and BI into NBT-5.5BT.[99, 104] We characterized the dielectric, ferroelectric, and piezoelectric properties of $(1-x)[0.945Na_{0.5}Bi_{0.5}TiO_3 - 0.055 BaTiO_3] -$ (x)Bi(*M*)O₃, with x = 0.02, 0.04 for *M*=Al³⁺, Ga³⁺ and x = 0.01, 0.02 when *M*=In³⁺. In addition, preliminary structural studies were performed using synchrotron X-ray and neutron diffraction to aid in understanding the structure-property relationships of these three systems.



Figure 2-1: Space groups of Group 13, bismuth-based perovskites: a) BiAlO₃, b) BiGaO₃, c) BiInO₃.

2.2 Experimental

2.2.1 Synthesis

Group 13 substituted samples of NBT-BT-BM were prepared with the following compositions: $(1-x)[0.945Na_{0.5}Bi_{0.5}TiO_3 - 0.055 BaTiO_3] - (x)Bi(M)O_3$, with x = 0.02, 0.04 for $M=Al^{3+}$, Ga^{3+} and x = 0.01, 0.02 when $M=In^{3+}$. For convenience, these compositions are described by the following shorthand notations: NBT-BT-BA2, NBT-BT-BA4, NBT-BT-BG2, NBT-BT-BG4, NBT-BT-BI1, and NBT-BT-BI2, with NBT-BT as the parent. Synthesis was performed using standard solid-state methods. The appropriate precursor oxides and carbonates were combined in stoichiometric amounts and ground in an agate mortar and pestle. The precursors used were Bi₂O₃ (Strem Chemicals Inc. 99.999%), Na₂CO₃ (Strem Chemicals Inc. 99.5%), TiO₂ (Cerac Inc. 99.9%), BaCO₃ (Strem Chemicals Inc. 99.9%), Al₂O₃ (Cerac Inc. 99.99%), Ga₂O₃ (Alfa Aesar 99.99%), and In₂O₃ (Alfa Aesar 99.9%). All carbonate reagents were dried in a 120 °C furnace for at least 48 hours. The mixed powders were ball milled for 6 hours at 350 rpm (10 minutes on, five minutes rest, and 10 minutes in the reverse direction) in a Fritsch Pulverisette 7 with 25 mL of ethanol and eight, 10 mm diameter, yttria-stabilized zirconia balls. The powders were then calcined at 850 °C for 2 hours and processed in a vibratory mill for six hours in ethanol with six yttria-stabilized zirconia rods (9.5 mm by 9.5 mm). To further prepare the samples for sintering, they were dried then mixed with a 3 wt % polyvinyl butyral (PVB, Butvar B-98, Sigma Aldrich) binder/ethanol solution. The powder was pressed in a Carver uniaxial press into pellets with a diameter of 13 mm and thickness of ~1.5 mm. Pellets were covered in sacrificial powder of the same composition, placed inside capped alumina crucibles and sintered between 1150 °C – 1200 °C for two hours (5 $^{\prime}$ minute ramp rate) depending on the composition. During the temperature ramp up, the temperature was held at 450 °C for four hours

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to remove the PVB binder. All physical properties were measured on pellets with densities greater than 95% of their crystallographic value as determined by a Mettler Toledo Archimedes kit.

2.2.2 Pellet Processing

Ceramic pellets for physical property measurements were carefully polished to an appropriate thickness of ~1 mm for dielectric measurements and < 0.5 mm for strain (*S*-*E*) and polarization (*P*-*E*) measurements. The polishing was completed using a LaboPol-5 (Struers) with #800, #1200, and #4000 SiC foils (Struers). For ferroelectric, room temperature ($25 \,^{\circ}C - 31 \,^{\circ}C$) measurements, pellets were painted with silver electrodes (SPI #05002-AB) and dried at 100 $\,^{\circ}C$ overnight. For temperature dependent dielectric measurements, electrodes of high-temperature silver paint (Heraeus C1000 HT) were applied to the parallel faces of each pellet before the pellet was heated to 750 $\,^{\circ}C$ for 30 minutes to cure the silver electrodes.

2.2.3 Physical Properties Measurements

Dielectric permittivity was measured using an HP 4192A LF Impedance Analyzer, a NorECsAS ProbostatTM, and a Carbolite tube furnace. The measurements were performed during cooling on unpoled samples as a function of temperature from 1 kHz to 1 MHz, from 550 °C at a 2 °C /min ramp rate to RT (room temperature, 25-31°C). For poled samples the measurements were performed as a function of temperature during heating from 1 kHz to 1 MHz, from RT (room temperature, 25-31°C) to 550 °C at a 2 °C /min ramp rate. Strain vs. electric field (*S*-*E*) and polarization vs. electric field (*P*-*E*) measurements were performed on a Radiant Precision Premier II, at a frequency of 0.1 Hz and 1 Hz respectively, with the sample pellet submerged in an insulating silicone oil. Poling was performed on the Radiant Precision Premier II at 50 kV/cm for 30 minutes at room temperature (25 °C). After 24 hours, the direct
piezoelectric effect was measured on a Berlincourt-type d_{33} meter (APC International, Ltd. YE2730A). Also, after the 24-hour resting period, the converse piezoelectric properties were measured using the Radiant Precision Premier II connected to an optical displacement MTI-2100 Photonic Sensor.

2.2.4 Diffraction Experiments

Phase purity of each sample was verified using X-ray diffraction (XRD) on a Rigaku Miniflex 600 (Cu K α , $\lambda = 1.541862$ Å, 2θ range from 10 to 65 °). XRD comparisons of poled and unpoled powder samples were also performed on the Rigaku Miniflex 600 (Cu K α , $\lambda = 1.541862$ Å, 2θ range from 20 ° to 60 °, 0.625 ° incident slit, 5 ° soller slit). Crushed powders were annealed at 450 °C for three hours. Synchrotron X-ray diffraction (SXRD) data was collected at the Advanced Photon Source at Argonne National Laboratory on the 11-BM beamline.[105] Samples were ground lightly with a mortar and pestle, annealed to relieve the stress from grinding, then loaded into quartz capillaries. Each sample was diluted with quartz wool to avoid absorption phenomena. Data was collected at room temperature for one hour in the 2θ range of 0.5 to 50 ° at a wavelength of 0.459980 Å.

Neutron powder diffraction (NPD) data was collected at Oak Ridge National Laboratory on the POWGEN diffractometer. Approximately 3 grams of each sample was loaded into vanadium containers and one-hour scans were performed at room temperature using a wavelength of 1.066 Å (*d*-spacing range of 0.276-4.606 Å).

Pawley fits were performed using Topas Academic software.[106] Neutron, two-phase refinements were performed with six Chebychev background terms, a Time of Flight (T.O.F.) sample peak shape function, and FWHM terms to adjust peak widths. For the APS, XRD data, six background terms were used as well as the Stephen's broadening model for monoclinic and

tetragonal phases. Four Pseudo-Voigt terms were used to fit background with the diffuse scattering and contributions from the quartz wool.

2.3 Results and Discussion

2.3.1 Dielectric Properties

2.3.1.1 NBT-BT

The dielectric permittivity and loss of the parent sample, NBT-BT, are shown in Figure 2-2a. Two dielectric features, typical of this composition were observed: a shoulder peak at ~115 °C which has caused much confusion in the literature, and a large, broad peak at 288 °C, which is referred to as the maximum permittivity temperature, $T_{\rm m}$. The large, frequency-dependent, diffuse peak is typical of relaxors and arises from the size and distribution of polar nano-regions (PNRs).[17] The shoulder peak is a debated phenomenon, but we agree with the study by Jo et al. attributing the anomaly to the thermal evolution of an increasing number of rhombohedral (*R3c*) to tetragonal (*P4bm*) PNRs.[107-109] We observed both of these dielectric features in varying degrees in both the parent and substituted samples.



Figure 2-2: Temperature dependence of the dielectric permittivity and tan δ of both a) unpoled and b) poled NBT-5.5BT.

As mentioned previously, NBT-BT undergoes a ferroelectric-relaxor transition under the application of an electric field. Therefore, the ferroelectric-relaxor transition temperature, denoted as $T_{\text{F-R}}$, was investigated by poling samples above their coercive field before measuring the dielectric permittivity as a function of temperature. At $T_{\text{F-R}}$, the thermal energy disrupts the correlated FE domains.[110, 111] Above $T_{\text{F-R}}$, broad, frequency dependent peaks, typical for relaxor ferroelectrics, are observed.[14] $T_{\text{F-R}}$ was determined from the complementary peak maximum in the loss at 1 kHz. Previously, this peak in tan δ was used to label the depolarization critical temperature, T_d , but recent studies define this temperature as the ferroelectric-relaxor temperature ($T_{\text{F-R}}$).[108] $T_{\text{F-R}}$ not only describes where this transition occurs, but it also provides insight into how strongly the FE domains are coupled together. It is generally 5-20 °C higher than the depolarization temperature, T_d , as measured by TSDC (thermally stimulated depolarization current).[108, 109] For the parent sample, NBT-BT, the $T_{\text{F-R}}$ was measured at 99 °C, a temperature consistent with reported values.[112] All the dielectric data for NBT-BT as summarized in Table 2-1 agree with previous work.[90, 113]

Composition	$arepsilon_{ m r}$ at $T_{ m m}$	$T_{\rm m}(^{\circ}{\rm C})$	Er †	tan δ †	$T_{\mathrm{F-R}}(^{\circ}\mathrm{C})$
NBT-BT	5333	288	1640	0.0523	99
NBT-BT-BA2	5456	258	1805	0.0547	75
NBT-BT-BA4	4224	243	1617	0.0533	46
NBT-BT-BG2	6626	259	1827	0.0559	94
NBT-BT-BG4	4616	252	1525	0.0515	80
NBT-BT-BI1	5537	284	1512	0.0475	70
NBT-BT-BI2	4520	289	1336	0.0495	71

Table 2-1: Summary of dielectric properties of unpoled samples.

† Dielectric data obtained at room temperature with a frequency of 1 kHz.

All data reported at a frequency of 1 kHz.

2.3.1.2 Unpoled NBT-BT-Bi(M)O₃

The frequency dependence of the room temperature dielectric permittivity (ε_r) is shown in Figure 2-3a. The frequency dependence is evident across all compositions in the dielectric permittivity, indicating their relaxor nature. NBT-BT-BG2 and NBT-BT-BA2 display a higher permittivity at room temperature compared to the parent compound, with permittivity values of 1827 and 1805 respectively (at 1 kHz). In addition, their frequency dispersion is larger than NBT-BT (Table 2-2). The remaining substituted compounds have a lower RT permittivity than NBT-BT and their frequency dispersion is slightly smaller than that of the parent compound.



Figure 2-3: Frequency dispersion data of (a) dielectric permittivity and (b) dielectric loss from unpoled samples at 31 °C.

	Table 2-2: Slope of ε ' vs ln((freq) from H	Figure 3a which indic	cates degree of freq	uency dependence.
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Composition	Slope of ε' vs. ln(freq)
NBT-BT	-59.23
NBT-BT-BA2	-64.79
NBT-BT-BA4	-59.67
NBT-BT-BG2	-69.22
NBT-BT-BG4	-52.75
NBT-BT-BI1	-51.84
NBT-BT-BI2	-42.31

The loss (tan δ) at RT also shows frequency dispersion across all samples with lower frequencies having lower loss than higher frequencies (Figure 2-3b). NBT-BT-BA2, NBT-BT-BA4, and NBT-BT-BG2 have dielectric losses of 0.0547, 0.0533, and 0.0559 respectively, at 1 kHz. These loss values are higher than NBT-BT at 0.0523, but fairly typical of lead-free piezoelectrics.[114, 115] NBT-BT-BI1 has the lowest loss at lower frequencies (0.05 at 10 kHz) and the highest at higher frequencies (0.0843 at 500 kHz) while NBT-BT-BI2 shows the lowest loss across all other frequencies (0.03 at 10 kHz).

The temperature dependent dielectric permittivity and loss of each unpoled composition is shown in Figure 2-4a with the data summarized in Table 2-1. The substituted compounds retain the relaxor features found in NBT-BT including the prominent shoulder feature observed in varying degrees for all new compositions. However, continued substitution results in a lowering of the permittivity and this shoulder becomes more convoluted into the diffuse dielectric peak.



Figure 2-4: Temperature dependence of the dielectric permittivity and tan δ of both a) unpoled and b) poled samples.

In general, when M = Al or Ga, the dielectric permittivity (ε_r), ε_r at T_m , and tan δ , initially increase upon addition of Bi(M)O₃, then decrease with further substitution. These trends indicate that there is some critical composition between 2% and 4% BA and BG that could possess the best ferroelectric and piezoelectric properties in those systems. Specifically, the NBT-BT-BA system demonstrates the best dielectric performance at ~2% BA, which corresponds to the reported critical MPB composition.[99, 104] The trends in the M = In compositions are more complicated. For the In family, ε_r at T_m , T_C , and tan δ increase with initial substitution, then decrease upon further addition, as in the Al and Ga systems. However, the trend with the In compounds varies in that ε_r decreases and T_m remains constant as more BiInO₃ is added.

2.3.1.3 Poled

All compositions were poled as described above to determine if an electric-field induced phase transition to a ferroelectric structure occurs as seen in the parent compound. It was observed that all samples, to varying degrees, undergo this transition where the electric field creates a ferroelectric state. Therefore, the dielectric permittivity of the poled samples deviates from the unpoled samples in the form of a frequency-independent vertical alignment of the permittivity data until the approximate temperature of the transition from a poled ferroelectric to a relaxor state. These poled materials remain ferroelectric up to the critical temperature, $T_{\text{F-R}}$, then display characteristics of ergodic relaxors, such as the inability to be poled and low remanent polarization. In each system, $T_{\text{F-R}}$ significantly decreases with increasing addition of the Bi(M)O₃ component.

The dielectric data indicates that all the compositions display non-ergodic relaxor behavior below the ferroelectric-relaxor temperature ($T_{\text{F-R}}$). The polar nano-regions in

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nonergodic phase regions are 'frozen' and can be poled so they display a strain response similar to other poled piezoelectric ceramics. The mechanism of the strain response is derived from an irreversible phase transition under an electric field from the nonpolar phase to a long-range ferroelectric structure. Above $T_{\text{F-R}}$ the materials transition to an ergodic state where the PNRs are mobile and the material loses the ability to retain long-range, concerted, polarized domains.[116-118] In a non-polar, or weakly polar, ergodic phase, the material may become ferroelectric as they undergo a phase transition to a long-range polar structure induced by the applied electric field. However, unlike in the non-ergodic state, this transition is reversible, as the difference between the free energy of the competing phases is small.[99, 116] Therefore, once the field is removed, the material returns to the unpoled, non-polar phase.

Substitution has the most profound impact on the dielectric properties in the BA series. The addition of BiAlO₃ resulted in increased disorder and the $T_{\text{F-R}}$ drastically lowered to near room temperature. The change in permittivity behavior is accompanied by a decrease in the sharpness of the $T_{\text{F-R}}$ loss peak (tan δ), making it difficult to determine the exact point the transition begins (reported at the peak of the 1 kHz tan δ). As the $T_{\text{F-R}}$ approaches RT with increasing substitution, the material will become more difficult to pole. This phenomenon is shown in the NBT-BT-BA4 sample where only the diffuse remnants of the transition remain in the loss peak data. Continued substitution would likely continue to decrease this transition temperature below room temperature. A $T_{\text{F-R}}$, at or near RT like that observed in the BA4 composition, could potentially display incipient piezoelectric properties that demonstrate giant strain which could be utilized in actuator devices.[119]

The trend shown in the NBT-BT-BG system is similar to that found in NBT-BT-BA. However, it is difficult to determine the transition with NBT-BT-BG4 as the peak in loss

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indicating $T_{\text{F-R}}$ appears more diffuse than in other samples. It does appear that the decrease in $T_{\text{F-R}}$ as a function of substitution is not nearly as dramatic in NBT-BT-BG compared to the BA system. A 4% BiGaO₃ substitution decreases the $T_{\text{F-R}}$ by ~20 °C compared to a ~50 °C degree decrease with the BiAlO₃ end member. This difference demonstrates that aluminum substitution more readily interrupts the correlation length of the PNRs compared to gallium. This could possibly result from the lower polarizability of aluminum.

It is more difficult to clearly determine the dielectric properties of the poled NBT-BT-BI system. NBT-BT-BI2 displays a $T_{\text{F-R}}$ peak in the loss data, but evidence of the transition in the real permittivity is lacking with only a slight anomaly left over from the poling state. The BiInO₃ system shifts $T_{\text{F-R}}$ down approximately 30 °C and, just like the BiAlO₃ and BiGaO₃ systems, the trend remains consistent with increased compositional substitution. Unfortunately, it is difficult to discuss any trends in these interesting compositions as BiInO₃ has such a low solubility in the parent system.

2.3.2 Piezoelectric Properties

The direct piezoelectric effect was measured on poled samples of all compositions, with the results shown in Figure 2-5a. The d_{33} of the parent compound NBT-BT was determined to be 135 pC/N, which falls within the reported values in the literature.[90, 104] Most of the substitutions of NBT-BT such as the BI compositions, NBT-BT-BG2 and NBT-BT-BA2 have little effect on d_{33} . Two of the samples show a significant decrease in d_{33} . The d_{33} of NBT-BT-BG4 decreases 20% to 106 pC/N and the d_{33} of NBT-BT-BA4 decreased 85% to 20 pC/N.



Figure 2-5: Piezoelectric coefficients, a) d_{33} , b) $d_{33}*(d_{33}* = S_{\text{max}}/E_{\text{max}})$, for all compositions. The gray bar represents parent system, blue bars represents the BI system, red represents the BG system, and green represents the BA system.

Unipolar (Figure 2-6), strain-electric field measurements (*S*-*E*) were performed on all compositions to determine their maximum strain and their high field piezoelectric response, d_{33}^* (Figure 2-5b), which indicate their potential for use in actuator applications. A sample of other reported d_{33} values for the NBT-BT system is shown in Table 2-3.



Figure 2-6: High-field, unipolar strain measurements (*S*-*E*) for each composition compared to the parent, NBT-BT.

The maximum strain for NBT-BT was measured at 60 kV/cm for the unipolar loops. In the BG and BI families, initial substitution increases the high-field strain, while further substitution causes the strain to decrease to values similar to or below that of the parent

composition NBT-BT. This trend is much more pronounced in the BG materials, while the addition of BI does not significantly affect the strain properties. In the BA series, the strain decreases dramatically (d_{33} *=212 pm/V) with the first substitution then increases significantly above the value of the parent with the second substitution (d_{33} *=695 pm/V). The d_{33} * of the NBT-BT parent is 383 pm/V. The effect of substitution on d_{33} * mirrors the trends in the strain results where NBT-BT-BA4 shows the largest increase in d_{33} * to 695 pm/V and NBT-BT-BG2 also shows a significant improvement to 570 pm/V. The piezoelectric property results are listed in Table 2-4.

The BI data show that BI substitution has little impact on the electromechanical properties of NBT-BT. A small amount of BG substitution, however, improves the maximum strain and d_{33} * significantly. Although, this substitution has little impact on d_{33} . A more detailed investigation of this system is underway to determine if the strain is related to the incipient piezoelectric mechanism. The BA system has the most interesting changes in the piezoelectric properties due to substitution. The piezoelectric data for the BA4 compound shows that this material can be classified as an incipient piezoelectric. An incipient piezoelectric displays an electric-field dependent, giant strain where the contributing mechanism is through a phase transition from a paraelectric to ferroelectric structure. Unlike the phase transition observed in the parent NBT-BT, this mechanism is reversible and the structure reverts to the paraelectric phase upon removal of the electric field.[118]

In 2007, Zhang et al. reported on one of the earliest known ergodic relaxors showing incipient piezoelectricity. They found a giant strain in NBT-BT-KNN ($K_{0.5}Na_{0.5}NbO_3$) of 0.45% (567 pm/V at 80 kV/cm) accompanied by a reduced direct d_{33} measurement of 30 pC/N.[55] This giant strain is only activated above a certain electric field with a very large

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hysteresis and also only occurs when the direct piezoelectric behavior is severely diminished.[120, 121] This same effect is seen in this BA4 sample where the high field d_{33} * is 695 pm/V and the macroscopic piezoelectric response d_{33} is only 20 pC/N. The literature shows this giant strain can often be encouraged with small substitutions in NBT-BT and BNT-BKT (Bi_{0.5}Na_{0.5}TiO₃-Bi_{0.5}K_{0.5}TiO₃) based systems.[115, 118, 122] Giant strain with d_{33} * values up to 1400 pm/V have been shown for some bismuth based systems, such as ((Bi_{0.5}(Na_{0.84}K_{0.16})-0.5)0.96Sr_{0.04})(Ti_{0.975}Nb_{0.025})O₃.[123] For pure NBT-BT based systems, reported values range from ~500-700 pm/V (values in Table 2-3). This NBT-BT-BA system displays a strain of 695 pm/V which is near the high-end of these reported values.

Sample	<i>d</i> ₃₃ * (pm/V)	Electric Field (kV/cm)	Reference
NBT-0.055BT-0.04BA	695	70	This work
NBT-0.06BT-0.02BA	533	70	Bai et al. [99]
NBT-0.06BT- 0.035BNiT	590	60	Bai et al. [124]
NBT-0.014BZ	573	40	Jin et al. [125]
NBT-0.065BT-0.03BZ	542	70	Rahman et al. [126]
NBT-0.065BT-0.02SZ	722	55	Maqbool et al. [127]
NBT-0.065BT-0.022ST	490	40	Wang et al.[128]
NBT-0.07BT-0.02AN	575	50	Jin et al.[129]
NBT-BKT-BT-La/Nb	680	60	Ge et al.[130]

Table 2-3: Example of high-strain, d_{33}^* values reported for the NBT-BT system.

In the parent compound and in all other samples, the bipolar strain-field data display a butterfly loop as shown in Figure 2-8. The loop has both a positive and negative component, which results from ferroelectric domain switching.[118] However, the strain-field of an incipient piezoelectric, is described as a "sprout-like" shape with no negative switching component due to the reversibility of the phase transformation back to a paraelectric phase after removal of the field. This sprout-like loop is observed in the BA4 sample only (Figure 2-8d), while the NBT-BT and all other compositions display a typical piezoelectric strain-field loop (Figure 2-7).



Figure 2-7: Bipolar S-E of parent NBT-BT (50kV/cm).

This behavior in BA4 can be explained by the low T_{F-R} transition temperature at ~45 °C, which is significantly lower than that of all the other compositions. This composition appears to show properties of an ergodic relaxor, despite a T_{F-R} above room temperature. One possible explanation for this is that the T_{F-R} reported might not be accurate. T_{F-R} is determined by the peak in dielectric loss (tan δ), which for this BA4 composition appears diffuse, making it difficult to pinpoint the exact maximum of the peak. An alternative explanation is the sample has a distribution of transitional ferroelectric to relaxor temperatures deriving from the coexistence of ergodic and nonergodic phases.[131] Combined ergodic and non-ergodic regions may also explain the weak, diffuse peak in the dielectric loss.



Figure 2-8: Bipolar, *S-E* (BSE) loops of a) NBT-BT-BG2, b) NBT-BT-BG4, c) NBT-BT-BA2, and d) NBT-BT-BA4 at 50 kV/cm.

2.3.3 Ferroelectric Properties

Composition	$P_{\rm m}$ (μ C/cm ²) †	$P_{\rm r}$ (μ C/cm ²) †	$E_{\rm c}$ (kV/cm) †	<i>d</i> ₃₃ * (pm/V) ††	<i>d</i> ₃₃ (pC/N) ††
NBT-BT	33.4	29.7	39.9	383	135
NBT-BT-BA2	36.1	31.2	38.1	212	143
NBT-BT-BA4	29.6	4.95	9.6	695	20
NBT-BT-BG2	37.1	31.7	33.2	570	131
NBT-BT-BG4	40.1	32.2	29.5	430	106
NBT-BT-BI1	38.4	31.3	35.2	436	124
NBT-BT-BI2	37.8	31.2	37.1	331	122

Table 2-4: Summary of ferroelectric and piezoelectric properties.

† Ferroelectric data obtained at room temperature with a frequency of 1 kHz.

†† Strain measurements obtained at room temperature with a frequency of 0.1 kHz.

 $d_{33}* = S_{\text{max}}/E_{\text{max}}$; where S_{max} is observed at maximum field.

Ferroelectric, polarization-electric field measurements (*P-E*) were performed at room temperature and are shown in Figure 2-9 for all samples at fields of 70 kV/cm. The ferroelectric property results are summarized in Table 2-4.



Figure 2-9: Polarization vs. electric field, ferroelectric, hysteresis loops for the parent composition plotted with each of the two substituted samples in each system for comparison (freq = 1 kHz, 70 kV/cm).

Based on the saturated *P-E* hysteresis data, the NBT-BT-BG and NBT-BT-BI systems perform as typical ferroelectric materials with only incremental increases in the ferroelectric properties of remanent polarization (P_r) and maximum polarization (P_m). In the NBT-BT-BG system, both substitutions perform similarly in *P-E* measurements. NBT-BT-BG2 shows an ~11 % increase in P_m , a ~7 % increase in P_r , and a decrease of ~17 % in the coercive field (E_c), compared to the NBT-BT parent. Further substitution of BG beyond 2 % marginally increases the polarization and lowers the coercive field a further 12 %. The inclusion of 1 % and 2 % BiInO₃ into the parent NBT-BT system only slightly improves the polarization response. NBT-BT-BI1 shows an increase in remanent polarization of ~5 % and an increase in maximum polarization of ~13 %. The coercive field decreases by ~11 % compared to the parent compound's 39.9 kV/cm. NBT-BT-BI2 has a ~5 % higher remanent polarization, while the maximum polarization increases by ~13 %, and the coercive field of decreases ~ 7 %, compared to the parent compound.

The NBT-BT-BA system behaves differently than the BG and BI systems. The NBT-BT-BA2 sample performs similarly to the parent, but NBT-BT-BA4 clearly deviates from all other compositions. The shape of the hysteresis loop of NBT-BT-BA4 more closely resembles a relaxor in the ergodic phase region. The remanent polarization drops to 4.95 μ C/cm² as the longrange ferroelectric ordering is destroyed upon the removal of the electric field. This evidence compliments the piezoelectric and dielectric properties observed above and supports the giant strain in this composition coming from an incipient piezoelectric effect.

2.3.4 Structure

2.3.4.1 X-ray and Neutron Diffraction Analysis

All synthesized ceramics exhibit a pseudo-cubic perovskite structure with no impurity phases present. While both synchrotron X-ray (Figure 2-11) and neutron diffraction (Figure 2-10) data were collected, the neutron data provides more useful information due to the subtle structural effects of the oxygen atoms and the pseudocubic nature of the X-ray diffraction. Therefore, the bulk of this discussion will focus on the neutron data.



Figure 2-10: Overlayed NBT-BT, NBT-BT-BA2, NBT-BT-BA4 neutron diffraction patterns showing increasing and decreasing superlattice reflections.



Figure 2-11: Comparison of synchrotron, X-ray diffraction data for NBT-BT, NBT-BT-BA2, NBT-BT-BA4. Inset displays close-ups of the $(111)_M$ and the $(200)_T$ reflections where peak-splitting takes place for the rhombohedral and tetragonal groups, respectively.

All three substitutions display the same trends in both their diffraction patterns. While the nature of the structure of NBT-BT is debated in the literature (Table 2-5), we found both NBT-BT and the substituted compounds crystallize into two polar phases: *P4bm* and *Cc*. The base-centered, monoclinic space group, *Cc*, has a Glazer tilt system of a a c , and a polarization plane between the tetragonal [001] and rhombohedral [111], with possible directions of [uuv].[132, 133] This space group is also the structure of the end member Na_{0.5}Bi_{0.5}TiO₃.[52, 134] The primitive, tetragonal *P4bm* has a tilt system of a⁰a⁰c⁺ and a polarization direction of [001].[38, 132] It has been suggested the complexity of the diffraction data could stem from more complex tilting arrangements than can be described by Glazer notation.[113] This twophase, monoclinic-tetragonal model is similar to previously reported models and no other dualphase refinement was as successful fitting the data.[134] Other common combinations that have been reported in the literature were considered during the analysis: *Cc*, *Cc* + *R3c*, *Cc* + *Pm*³*m*, *R3c* + *P4bm*, *R3c* + *P4mm* (Table 2-5), but they either missed some of the observed peaks or they did not fit the intensity profiles of the data and returned higher residual values than the selected *Cc* and *P4bm* space groups.[113, 114, 134-136] However, we do want to point out that conflicts between our assigned space groups and some reports in the literature are to be expected. These materials display a complex microstructure and are sensitive to synthesis and handling conditions.[14, 113, 137]

Composition	Reported Space Group	Reference
$0.945 \ Na_{0.5}Bi_{0.5}TiO_3 - 0.055 \ BaTiO_3$	R3c	Ranjan [135]
$0.94\ Na_{0.5}Bi_{0.5}TiO_3 - 0.06\ BaTiO_3$	R3c + P4bm	*Ma [114]
$0.95 \ Na_{0.5}Bi_{0.5}TiO_3 - 0.05 \ BaTiO_3$	Cc + P4bm	Ge [134]
$0.96\ Na_{0.5}Bi_{0.5}TiO_3 - 0.04\ BaTiO_3$	$Cc + Pm\bar{3}m$	Usher [136]
$0.95 \ Na_{0.5}Bi_{0.5}TiO_3 - 0.05 \ BaTiO_3$	Cc + R3c	Garg [113]

Table 2-5: Table of some reported space groups assigned to NBT-xBT.

* determined from TEM data

Substitution does not change the number of reflections from the parent compound in the diffraction patterns. However, the patterns of the substituted compositions clearly exhibit increases to the intensity of a series of peaks related to *P4bm* superlattice reflections. These superlattice reflections originate from the doubling of the unit cell due to octahedral tilting. Typically, the $\frac{1}{2}(000)$ (Miller indices of odd, odd, even), superlattice reflections are assigned to the *P4bm* space group and the $\frac{1}{2}(000)$ double cell reflections are assigned to the rhombohedral *R3c*.[113, 138] Our refinements assign the $\frac{1}{2}(000)$ reflection to the monoclinic *Cc*, which also displays these superlattice reflections.[132] The short, broad nature of the *P4bm* supercell reflections could be explained by the lamellar nature of the tetragonal phase observed in these

systems.[139, 140] While the relative fraction of *P4bm* increases with substitution, the degree of tetragonality remains essentially unchanged with a *c/a* ratio of 0.998 based on the Pawley fits from the neutron diffraction data (Table 2-6). The neutron diffraction pattern also reveals a decrease in the monoclinic phase, which is evident in the decrease in the series of peaks in Figure 10. While the tetragonality doesn't change significantly upon substitution, the a_m/b_m ratio, increases from 1.735 in NBT-BT to 1.751-1.772 in the indium and aluminum compositions (Table 2-6). The value of this ratio is $\sqrt{3}$ (1.732) in a rhombohedral structure and the deviation from this ratio describes the monoclinic distortion of the unit cell.[141] What these Pawley fits show is that the distortions in both monoclinic and tetragonal structures are relatively small, resulting in the pseudocubic diffraction patterns typical of relaxor ferroelectrics.

	NBT-BT	BA2	BA4	BG2	BG4	BI1	BI2
Сс							
a	9.5424(1)	9.592(2)	9.586(4)	9.522(11)	9.525(7)	9.599(4)	9.598(2)
b	5.4995(1)	5.419(3)	5.417(3)	5.484(1)	5.519(1)	5.415(4)	5.478(3)
с	5.5211(1)	5.537(2)	5.536(3)	5.565(8)	5.673(5)	5.531(3)	5.568(3)
β	124.93(1)	124.35(3)	124.33(4)	125.160(91)	124.905(60)	124.512(44)	124.329(73)
a _m /b _m	1.7351	1.7695	1.7696	1.7370	1.7257	1.7725	1.7519
P4bm							
a	5.5277(1)	5.5136(2)	5.5115(2)	5.5171(3)	5.5171(2)	5.5202(2)	5.5237(3)
С	3.9005(1)	3.9041(3)	3.9028(2)	3.9060(4)	3.9059(3)	3.9097(3)	3.9112(4)
c/a	0.99789	0.99861	0.99858	0.99892	0.99879	0.99838	0.99862
R _{wp} (%)	2.481	2.202	2.135	2.159	1.986	2.099	1.963

Table 2-6: Pawley fit data table.

While Rietveld refinements were performed on the neutron data, full structural models were inconclusive due to unstable models that could not be identified as absolute minima. Many factors lead to the challenging assessment of the average structure: a tetragonal phase with small, broad peaks; negative thermal displacement parameters for a few oxygen sites, and local distortions that lead to a large amount of diffuse scattering. Additional cations introduced into the NBT-BT system in this study further increase disorder, which manifests itself with an average pseudocubic structure that is typical of relaxors, but notoriously difficult to model. [14, 17, 96, 142] Our refinements were similar to the results by Ge et al., where an example refinement can be found one the next page (Table 2-7 and Figure 2-12).[134] However, in the case of both NBT-BT and its substituted constituents, the extent of disorder prevents a clear description of the structure with diffraction data alone.

Table 2-7: Example atomic positions, lattice parameters, and atomic displacement parameters of a neutron Rietveld refinement of NBT-BT-BA2.

	Сс			P4bm					
<i>a,b,c,</i> (Å)		9.594(1)	5.415(1)	5.5424(9)		5.5170(2)	5.5170(2)	3.8999(3)	
β(°)		124.53(1)				-			
Na/Bi/Ba	x,y,z,B	0	0.25	0	1.56(16)	0	0.5	0.53(1)	4.76(27)
Ti/Al	x,y,z,B	0.269(3)	0.255(3)	0.809(2)	-0.11(1)	0	0	0	0.97(7)
01	x,y,z,B	0.017(3)	0.184(3)	0.581(2)	0.62(12)	0	0	0.514(7)	2.73(14)
O2	x,y,z,B	0.237(3)	0.518(2)	0.010(3)	0.07(6)	0.277(1)	0.222(1)	0.026(2)	1.95(3)
O3	x,y,z,B	0.268(3)	-0.003(3)	0.0207(1)	1.26(23)	-	-	-	
R _{wp}	4.877								



Figure 2-12: Example neutron Rietveld refinement of two phase, *Cc* + *P4bm*, NBT-BT-BA2.

2.3.4.2 Poled/Unpoled

X-ray diffraction data was collected on poled samples of the two compositions with the highest strain response, NBT-BT-BG2 and NBT-BT-BA4, to further understand the origin of their strain mechanisms. This diffraction data will provide more information about the nature of any electric field induced structural changes. Recall that the BG2 composition shows a large strain while the d_{33} remains similar to that in the parent compound, while the BA4 composition demonstrates properties inherent to an incipient piezoelectric where the strain increases dramatically while the d_{33} decreases sharply. We show that NBT-BT-BA4 is an incipient piezoelectric that shows a reversible transition with a high strain only at high electric fields, while the other compositions behave like NBT-BT where a phase transition upon poling results in increased long-range ferroelectric ordering and high piezoelectric strain.

The poled NBT-BT-BG2 diffraction data in Figure 2-13 shows a clear structure change compared to the unpoled sample. Splitting of the $(111)_M$ is indicative of the formation of a more highly distorted monoclinic phase from the more symmetric, pseudocubic phase. The peak-splitting observed for the monoclinic $(111)_M$ peak shows an increase in the long-range

ferroelectric ordering that emerges from the applied electric field.[99] The lack of significant changes in the (200)_T peak implies little change in the tetragonal phase upon poling. We hesitate to comment further about what the specific changes occur to both phases upon poling as this diffraction data was collected on a laboratory based XRD. To understand the structural mechanism of poling, both neutron diffraction data, which is sensitive to oxygen positions, and high energy X-ray diffraction data, which allow for better peak resolution, should be collected and analyzed. The poled structure of NBT-BT was not fully understood to show changes in both phases until neutron diffraction was performed.[143-145] Therefore, for now we can only say that there is a clear structural transition after poling in the BG2 composition. This structural change as a function of electric field is supported by strong FE polarization-electric field measurements as well as piezoelectric strain curves with large negative strain indicating ferroelectric switching.



Figure 2-13: Laboratory X-ray diffraction data for crushed pellets of a) NBT-BT-BG2, unpoled and poled and b) NBT-BT-BA4, unpoled and poled. Inset expands the $(111)_M$ and $(200)_T$ reflections which can demonstrate monoclinic and tetragonal splitting, respectively.

In contrast, there is no discernable difference in the XRD patterns of poled and unpoled NBT-BT-BA4. In Figure 13b, there is clearly no splitting or peak shifts in the featured $(111)_{M}$

and $(200)_T$ peaks. As discussed previously, the strain originates from the ferroelectric phase that is induced at high electric fields, but reverses back to the pseudocubic structure when the electric field is removed. Near room temperature, the material is dominated by its paraelectric-ergodic nature which is demonstrated by the low T_{R-F} of this composition. As the boundary between the non-ergodic and ergodic phases is approached, the long-range ferroelectric domains cannot be achieved as a permanent phase transition as a function of electric field. The high field ferroelectric domains relax back to their PNR states when the field is removed and therefore do not display a structural change after poling. This structural description is supported by the lack of direct strain (d_{33} , Figure 2-5a), the lack of negative strain in the bipolar strain curves (Figure 2-8d), and the polarization-electric-field measurements (Figure 2-9).

2.4 Conclusion

When considering the dielectric, ferroelectric, and piezoelectric properties, no obvious trends can be described down the group in the periodic table as the third component of the phase diagram changed from BiAlO₃ to BiInO₃. The BI and BG systems behaved similarly to the parent compound NBT-BT where the mechanism for a large strain and d_{33} come from an electric-field induced phase transition where the long-range ferroelectric ordering is increased. In the Al system, a large strain and high field d_{33} were observed, but showed a significant decrease in the macroscopic ferroelectric properties and the low field d_{33} . The strain mechanism in the Al system is very different from that observed in all the other compositions and is derived from incipient piezoelectricity. In this case, a reversible phase transition which increases ferroelectric ordering at high fields results in a large strain and high-field d_{33} . When the field is removed, the long-range ordering relaxes back into a pseudocubic structure resulting in

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diminished macroscopic properties. Unfortunately, the applied field necessary to achieve the high strain (~ 70 kV/cm) is likely too high for long term, reliable usage. However, this example shows how non-polar groups with an incipient piezoelectric strain mechanism could be useful in applications if the applied electric field to achieve the giant strains is reasonable.

2.5 References

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Chapter 3 - Structure and property relationships in lead-free piezoelectric solid solution (x)NaNbO₃ – (1-x)BaZrO₃

3.1 Introduction

Novel ferroelectric compounds are needed for a variety of reasons. Firstly, they attempt to improve on hindrances or solve problems with the current leading materials, such as lead zirconate titanate (PZT), potassium sodium niobate (KNN), etc. For an example, PZT, due to the high lead content, is environmentally regulated and needs an exception to continue to be used.[3] In addition, KNN is prone to density issues and difficulty in poling making it too costly and inconsistent for industrial use.[146] Secondly, current issues are only taken into account, therefore new understandings may be necessary for future applications. Thus, developing an understanding for the use of a non-traditional piezoelectric mechanism for improving the electromechanical properties could lead to a new and deep phase space for the synthesis of new materials. Currently, to surpass PZT, the majority of potential replacement materials attempt to leverage the mechanism of polarization rotation at a morphotropic phase boundary (MPB) in order to drastically increase the piezoelectric response.[147]

The MPB is a region of structural instability where one structure acts as a transition between two other phases caused by a flattening of the free energy profile (Figure 3-1), which allows for a low energy transition between structures upon a change in composition. Its name, polarization rotation, is due to the rapid change in the direction of the polarization vector which is allowed to rotate between the various states. For PZT in particular, it has been shown that the polarization vector is allowed to rotate through the (110) plane of a monoclinic pseudocubic structure. (Figure 3-2) In PZT, this is usually found at around a 50 % substitution of zirconium, but could also be present in a variety of other material systems with phase transitions between three separate and unique polar phases (Figure 3-3).



Figure 3-1: Shows the phase diagram for the PZT solid solution. Also displays the flattening of the Gibbs free energy near the MPB. P₁, P₂, and P₃ correspond to the polarization directions, x, y, and z respectively. For example, since the dipole for the rhombohedral structure is oriented in the [111] direction P₁=P₂=P₃. Whereas for the cubic structure polarization is zero, thus P₁=P₂=P₃=0.Figure adapted from Damjanovic.[30]



Figure 3-2: Displays the rotation of the polarization direction within PZT at the MPB through the 110 plane between the [111] and [100] family of directions. Figure adapted from Ogino et al.[29]



Figure 3-3: Displays the increase in the piezoelectric response near the MPB composition for PZT. Figure adapted from Chen et al.[148]

Attempting to find solid solutions with morphotropic phase boundaries (MPBs) caused by polarization rotation is the current research standard. However, ferroelectric materials can display a different mechanism that could also improve the electromechanical properties called polarization extension. It can be seen in most piezoelectric materials, but it is typically seen at a certain temperature (rather than composition for polarization rotation), and it is the main basis why properties see a sharp increase at the Curie temperature (T_C). Polarization extension is denoted by the polarization vector extending, or contracting, when switching from a polar to a nonpolar phase and vice versa, with one such example being BaTiO₃ (Figure 3-4). However, in most materials, this mechanism is temperature dependent, thus they are only viable in a narrow temperature range around the Curie temperature, and not desirable for industry. Therefore, this research attempts to take the normally temperature-dependent polarization extension and make it compositionally dependent. This has been theorized to be potentially viable if there exists a small ferroelectric MPB linking ferroelectric and paraelectric phases causing both polarization rotation and extension, one at each side of the morphotropic phase boundary (MPB) in the phase diagram. (Figure 3-5)



Figure 3-4: Displays the increase in properties seen at the polymorphic phase transition (PPT) between ferroelectric and paraelectric phases for BaTiO₃.[149]


Figure 3-5: Describes a theoretical phase diagram that could display polarization extension.[30]

In an attempt to accomplish this goal, a sodium niobate - barium zirconate solid solution was synthesized. The first end member is sodium niobate (NN), NaNbO₃, and it crystallizes in the orthorhombic space group *Pbcm*. (Figure 3-6) This structure is an antiferroelectric phase, but previous structure studies have shown that sodium niobate has a rhombohedral ferroelectric (*R3c*) local structure distortion or phase coexistence at room temperature.[150] In addition, once any small substitution is made to pure NN there is commonly a transition to the previously mentioned ferroelectric structure. Due to NaNbO₃ being used extensively in other lead-free attempts, mainly through the potassium sodium niobate (KNN) family of materials, it appeared to be a good starting point and endmember.[59, 151] BaZrO₃ crystallizes with a cubic non-polar structure (*Pm-3m*) and fulfills the paraelectric requirement. Barium zirconate (BZ) has also colloquially been called the perfect perovskite due to its tolerance factor being almost exactly 1. These compounds were likewise chosen, due to the similarities in size between zirconium and niobium, to try and minimize the b-site compositional strain. Previous research has shown that compositional ordering and antiferroelectric coordination has led to relaxation properties in lead-based materials.[152]



Figure 3-6: Shows a phase diagram for NaNbO₃ using different structural identification techniques.[153]

3.2 Experimental

3.2.1 Synthesis

Samples of (1-x)NN - (x)BZ solid solutions were prepared from x=0.05-0.2 using standard solid-state methods. The precursor oxides and carbonates were combined in stoichiometric amounts, along with 7.5 % mol excess sodium to ease volatility concerns, and ground in an agate mortar and pestle. The precursors used were Na₂CO₃ (Millipore Sigma 99.5 %), Nb₂O₅ (Millipore Sigma 99.99 %), BaCO₃ (Millipore Sigma 99 %), and ZrO₂ (Millipore Sigma 99 %). The mixed powders were first ball milled for 6 h at 350 rpm (10 min on, five minutes rest, and 10 min in the reverse direction) in a Planetary Ball Mill (Fritsch Pulverisette) with 25 mL of ethanol and eight, 10 mm diameter, yttria-stabilized zirconia balls. They were then dried overnight and calcined at 1050 °C for 2 hours. The resulting powders were then milled a second time for 25 hours using the same rotation timings at 350 RPM in the ethanol media. The resulting powder was then used to sinter dense ceramic pellets. The powder was dried and mixed with a 3 wt. % polyvinyl butyral (PVB, Butvar B-98, Sigma Aldrich) binder/ethanol solution. The powder was then pressed in a Carver uniaxial press at 8000 lbs using a die to form pellets with a diameter of 13 mm and thickness of ~ 1.5 mm. The resulting pellet was then placed in the cold isostatic press, CIP, for a secondary pressing at 25 MPa. The pellets were placed inside alumina crucibles with sacrificial powder of the same composition. Sacrificial powder means loose powder of the same composition of the pellet was added on top of and below the pellet essentially covering the pellet in loose powder. This is done to increase the vapor pressure of the volatile elements within the crucible by having the loose powder volatilize first which in turn should lower the loss of the volatile elements within the pellet. The material was then sintered utilizing a one-step sintering process. This includes heating at 450 °C for 30 minutes with a 10 °C/minute ramp rate as a binder burnout stage, then continuing at a ramp rate of 3 degrees a minute to sintering temperature of 1250 °C – 1300 °C for 2 hours and then ramping down also at 3 °C/minute until room temperature. All physical properties were measured on pellets with densities greater than 90% of their crystallographic value as determined by a Mettler Toledo Archimedes kit.

3.2.2 Ceramic preparation

Ceramic pellets for physical property measurements were carefully polished to appropriate thicknesses of ~1 mm for dielectric measurements and <0.5 mm for strain (*S*-*E*) and polarization (*P*-*E*) measurements as a function of electric field. The pellets were polished to a

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mirror finish using a LaboPol-5 (Struers) with #800, #1200, and #4000 SiC foils (Struers) sequentially. For *S*-*E* and *P*-*E* measurements, electrodes of silver conductive paint (SPI Supplies) were applied to the parallel faces of each pellet before the pellet was heated to 600 °C for 30 min to cure the silver electrodes.

3.2.3 Physical properties measurements

Dielectric permittivity was measured using a ModuLab XM MTS, a NorECsAS ProbostatTM, and a Carbolite tube furnace. The measurements were performed on unpoled samples during cooling as a function of temperature and frequency from 1 kHz to 1 MHz and from 300 °C down to room temperature. Strain vs. electric field (*S-E*) and polarization vs. electric field (*P-E*) measurements were performed on a Radiant Precision Premier II, at a frequency of 1 Hz, with the sample pellet submerged in an insulating silicone oil. The *S-E* measurements were run using 2 loops with the final average being used as the final data set. The strain measurements utilized an optical displacement sensor (MTI-2100). Poling was performed on the ModuLab XM MTS by applying a DC bias to the sample at 70 kV/cm for 30 minutes. The direct piezoelectric effect was measured on a Berlincourt-type d_{33} meter (APC International, Ltd. YE2730A).

3.2.4 X-ray and Neutron diffraction

Phase purity of each sample was verified using X-ray diffraction (XRD) on a Rigaku Miniflex 600 using Cu K α radiation ($\lambda = 1.541862$ Å) and scanning a 2 θ range from 10 to 60° at a rate of 5° degrees per minute. Longer scans were also taken from 10-90° with a step size of 0.02 degrees per minute. Neutron diffraction data was collected at Oak Ridge National Laboratory on the POWGEN diffractometer. Approximately 6 grams of each sample was loaded into vanadium cans and one-hour scans were performed at room temperature using a wavelength of 1.066 Å. Pawley and Rietveld refinements were performed using Topas Academic software.[74]

3.3 Results and Discussion

3.3.1 Dielectric Permittivity

Starting with the dielectric permittivity, the solid solution undergoes a drastic change in samples above 5 % addition of barium zirconate (BZ). As seen in Figure 3-7, for the .975 and .95 NN samples, there is little frequency dependence in the relative permittivity (ε_r), a unitless value calculated by the ratio of the permittivity of a material (ε) and the permittivity of free space (ε_0), and the profile shows one main peak and one distinct shoulder, with the shoulder moving closer to the main peak with increased substitution. Interestingly, as seen in the dielectric loss, here denoted as tan δ and is a ratio between the imaginary and real permittivity (Equation 17), there is only a single frequency independent peak located at the same temperature as the shoulder. This frequency independent peak, where the loss decreases with increasing frequency, is indicative of the presence of a structural phase transition.[107] Meaning energy is lost for atomic reorientation upon transition to the new structure, increasing the imaginary permittivity, creating the aforementioned peak in tan δ .



Figure 3-7: Left: Temperature dependence of the relative permittivity of unpoled NN-BZ samples. Top Right: Temperature dependence of the relative permittivity and tanδ of the .975NN composition. Bottom Right: Temperature dependence of the relative permittivity and tanδ of the .90NN composition. Figure shows the increase in relaxor character as more BZ is added.

Composition	Er at Tm	$T_{\rm m}$ (°C)	Er at RT	$\tan \delta$	
.975 NN	2750	260	400	0.0086	-
.95 NN	3250	220	500	0.0089	
.925 NN	4100	180	600	0.0210	
.90 NN	5800	100	3500	0.0333	
.85 NN	2600	25	2600	0.0255	

Table 3-1: Summary of dielectric properties for a range of (1-x)NN-(x)BZ compositions.

In this case, the ferroelectric and dielectric data point toward this being a transition from a ferroelectric to relaxor material. Thus, the second peak represents the temperature of maximum permittivity, $T_{\rm m}$. This can be inferred because traditional relaxor materials do not have a Curie temperature, as there is no corresponding phase change at $T_{\rm m}$ to a paraelectric structure, unlike traditional ferroelectric materials. As more BZ is added past the 5 % value, the profile shows a drastic change. These compositions lose all ferroelectric character, changing to a fully diffuse and frequency peak indicative of relaxor ferroelectrics. The degree to which a sample becomes a relaxor can also be seen utilizing a modified version of the Curie-Weiss law, shown below.

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_m} = \frac{\left(\frac{1}{T} - \frac{1}{T_m}\right)^{\gamma}}{C}$$
19

Where $\varepsilon_{\mathbf{r}}$ is the relative permittivity, $\varepsilon_{\mathbf{m}}$ is the maximum relative permittivity, **T** is the measured temperature, $T_{\mathbf{m}}$ is the temperature of maximum permittivity, γ is the degree of relaxation, and **C** is the Curie-Weiss constant. This is in comparison to the traditional Curie Weiss law (Equation 20) which sees a deviation from a straight line at the Curie-Weiss temperature (T_{CW}):

$$\varepsilon_r = \frac{C}{\left(\frac{1}{T} - \frac{1}{T_{cw}}\right)}$$
 20

The modified Curie Weiss law is useful for relaxor materials which show a deviation much earlier at the Burns temperature. This modified equation on the other hand is able to determine the degree of deviation utilizing the slope where in Equation 17, traditional ferroelectrics have γ values close to 1, with relaxor materials being closer to 2. As seen in Figure 3-8, as more BZ is added, the γ values increase further, thus confirming increased relaxor character with increased substitution. (Table 3-2) The 0.85 value is lower than expected due to the maximum permittivity being measured at room temperature. As such, the true maximum could be located slightly below RT, which causes the slightly lower than expected values. The T_m , as more BZ is added, decreases drastically with .975 NN having a T_m of 250 °C while 0.85 NN falls below room temperature. The lowering of T_m can be attributed to the weakening of the spontaneous polarization caused by local deformation with increased substitution.[154] This is far lower than even KNN's T_C at 350-450 °C. With the exception of the .85 NN sample, this material shows increased maximum permittivity with increased substitution raising from 3000 to around 6000, although this maximum is lower than other common relaxor ferroelectric materials in this temperature range which will commonly range above ten thousand.[19, 155, 156] This leads to some advantages compared to traditional ferroelectric materials in that because of the diffuse transition, the maximum permittivity is reachable over a larger temperature range. The fully relaxor compositions also show higher room temperature permittivity due to the increased compositional and structural strains present in relaxor ferroelectrics.



Figure 3-8: The plot of log $(1/\epsilon - 1/\epsilon_m)$ as function of log $(T-T_m)$ at 1 kHz for (1-x) NN–(x) BZ ceramics.

 Table 3-2: Measurement of the slope from the modified Curie-Weiss law, determining degree of relaxor ferroelectric character.

Composition	γ	
.975 NN	1.60	
.95 NN	1.55	
.925 NN	1.785	
.90 NN	1.84	
.85 NN	1.63	

3.3.2 Piezoelectric Coefficient (d_{33})

The indirect piezoelectric response at high field, d_{33}^* , was determined by calculating the maximum strain divided by the applied field within the unipolar *S-E* data, while the direct piezoelectric response at low field, d_{33} , was measured by poling the sample under field and measuring the piezoelectric response with a Berlincourt meter. As shown in Figure 3-9, the high field d_{33}^* is consistently higher than the low field response. This is indicative of strain present within the sample, whether that strain is compositional or structural is only able to be accessed under field. This could be potentially caused by an electric field induced phase transition as in Bi_{0.5}Na_{0.5}TiO₃-BaTiO₃-K_{0.5}Na_{0.5}NbO₃ solid solutions.[55, 120, 157]



Figure 3-9: Piezoelectric coefficients, d_{33} and $d_{33}*(d_{33}*=S_{\text{max}}/E_{\text{max}})$, for all compositions.

This increased high field response, as well as traditional piezoelectric response, is lost at .825 NN which agrees with the previous permittivity data. This data showed that the $T_{\rm m}$ for the .85 NN composition was located near room temperature, and if the trend follows upon further substitution, the $T_{\rm m}$ for the .825 NN composition would be below room temperature. This would indicate that room temperature is higher than the Burns temperature, which is where the PNRs for the majority of relaxor materials disappear and will react as a paraelectric. Also seen in the above figure, at .875 NN, the low field d_{33} drops to 0 but still shows a response under electric field, which can indicate a nonergodic to ergodic relaxor transition. In ergodic relaxors, the PNRs are smaller and mobile, and while under an electric field, the material will still show a net polarization, but when the field is removed, the PNRs are no longer able to interact with each other and the response is lost. Thus, the compositions between .90 and .95 NN which show relaxor character in the permittivity data but can be poled are designated as a nonergodic relaxor. In this region, the PNRs are large and stable, allowing the net dipole moment and polarization to remain when the field is removed. As for the magnitude of the piezoelectric coefficients, the maximum value for the low field d_{33} is around 50 pC/N, which is far lower than other contemporary materials, such as PZT and KNN, which are around 300 and 250 pC/N respectively, depending on dopant.

3.3.3 Polarization vs Electric Field Hysteresis

The polarization vs electric field response shows three distinct shapes in the loops, as seen in Figure 3-10. For .95-.975 NN, the samples were unable to saturate as they broke down at high fields, shorting the pellet. The shape of the loops still suggest that the material is a

ferroelectric because the slope of each loop changes with voltage, thus indicating domain wall motion.[158] Even with the slope changing, the maximum polarization is extremely low, with a maximum of 4 μ C/cm² at 70 kV/cm. This could be indicative of a material containing many defects or large amounts of strain, preventing easy domain wall motion and saturation.



Figure 3-10: Polarization vs. electric field hysteresis loops for each composition.

This data agrees with the dielectric data, showing little to no frequency dispersion as well as a fairly sharp transition, thus indicating ferroelectric character. The .90 and .925 NN samples on the other hand, show full saturation with a maximum polarization of 20 μ C/cm². Even in this small range, the addition of BZ displays a large impact on the resulting hysteresis loops, lowering both the remanent polarization and coercive field, and increasing the relaxor character. Within this range, the material is acting as a non-ergodic relaxor, while after .90 NN, the hysteresis loop loses all remanent polarization, indicating the progression to an ergodic relaxor. In the ergodic region, the material is no longer able to stay poled after the applied field is removed. The dielectric loss for .90 NN also agrees with the non-ergodic to ergodic transition seen in the *P-E* loops. In the .85 NN composition, the T_m is at room temperature, meaning the diffuse peak in the loss has shifted to below room temperature. The .85 NN composition also displays a high field strain response, which falls to zero when the field is removed, indicating small and mobile PNR's. Upon the addition of more BZ, after .85 NN, the loop completely flattens to a straight line and acts like a linear dielectric, as can be seen in the .80NN loop. This agrees with the permittivity data, with the real permittivity showing a maximum at room temperature, and with further substitution following the trend and shifting to below room temperature. The polarization maximum only reaches around 20 μ C/cm², with a remanent polarization of 15 μ C/cm², for the composition with the highest response. Similar to the piezoelectric coefficients, these values are low compared to its contemporaries such as PZT (40 μ C/cm²).

Composition/	<i>P</i> m/	$P_{\rm r}$ /	<i>E</i> c/	Strain/	<i>d</i> ₃₃ /	<i>d</i> ₃₃ * /
x	μC/cm²	μC/cm²	kV/cm	%	pC/N	pm/V
.975 NN	5	3	30	-	48	110
.95 NN	8	5	30	.05	45	78
.925 NN	18	15	30	.055	50	72
.90 NN	18	12.5	20	.07	50	113
.875 NN	-	-	-	.03	0	50
.85 NN	8	0	0	.02	0	37
.825 NN	5	0	0	0	0	0

Table 3-3: Summary of ferroelectric and piezoelectric properties for a range of (1-x)NN-(x)BZ compositions.

3.3.4 Strain vs. Electric Field Hysteresis

The strain response relates well with the polarization vs electric field data, which shows the material losing all strain response at .825 NN. (Figure 3-11) This corresponds to the materials acting similar to a linear dielectric material past the Burns temperature. Upon removing BZ, the material begins to show a strain response while under field, although it shows little strain hysteresis and only reaches a maximum of around 0.02 % strain. This is indicative of an ergodic relaxor, where the PNRs are small and mobile thus leading to low hysteresis. The .90 NN composition starts to display increased hysteresis and additionally shows the largest strain response at 0.07 % strain. After this composition, the hysteresis increased drastically while the maximum lowered to around 0.05 % strain. The .90 NN composition, showing the drastic increase, is indicative of an ergodic to nonergodic relaxor transition, which has been seen previously in literature, and mirrors the transitions seen in the ferroelectric hysteresis data seen previously. The higher percentage sodium niobate (NN) samples in the solid solution continue to show increased strain hysteresis and have a response similar to traditional ferroelectric materials.



Figure 3-11: Strain vs. electric field hysteresis loops for each composition.

While the majority of materials display polarization extension near the Curie temperature, this is a temperature dependent phenomenon, and as such is a hinderance for industrial use. While the original goal was to discover a compositionally dependent phase change, the end material showed a ferroelectric to relaxor transition. To that end, there are a multitude of relaxor materials with interesting electrical properties to compare to, such as PMN (Lead Magnesium Niobate), PZN (Lead Zinc Niobate), and PSN (Lead Scandium Niobate), with PMN in particular being one of the first observed relaxors discovered by Smolenskii and Agranovskaia in 1958.[14, 159, 160] Structurally, PMN also displays a pseudocubic structure, having a T_m slightly below room temperature, with ferroelectric properties similar to the .80 NN composition. Dielectric permittivity however is much higher, ranging from 10,000 – 15,000 depending on frequency used.[161] This lowering of the permittivity for NN-BZ could be caused by the mixed phases present due to less availability for domain reorientation under field.

These traditional relaxor materials are mixed into solid solutions to improve the end properties. For most of these materials, the most common end member chosen is lead titanate with PMN-PT being particularly well studied due to excellent properties.[13, 45, 162] Similarly to NN-BZ, PMN-PT undergoes a relaxor to ferroelectric phase transition, with the change occurring at around .36 PT. At this composition, the T_m is around 175 °C with very little frequency dispersion in the permittivity data. The maximum permittivity also increases to 30,000, which is far higher than the 3,500 seen at the relaxor to ferroelectric transition at .95 NN. This points to an interesting difference between NN-BZ and PMN-PT, where upon with increasing ferroelectric character, the maximum permittivity increases for the PMN-PT solid solution, while the opposite occurs in NN-BZ. This could potentially indicate an increase in the percentage of paraelectric character at .95 NN, even though there exists a ferroelectric response in the permittivity and hysteresis data, causing a lowering of the maximum. The ferroelectric properties near this MPB for PMN-PT are also much higher than their NN-BZ counterparts, with the d_{33} reaching the 6-700 pC/N range while also having a higher maximum polarization with a lower coercive field.[163] The complicated nature seen in the electromechanical measurements is continued throughout the structural data.

3.3.5 Diffraction Measurements

All sintered ceramics were first ground then structurally characterized utilizing a benchtop X-ray diffractometer. Upon measurement, the addition of BZ changes two main things about the diffraction profile. (Figure 3-12) First, there is a general shift towards lower 2-theta upon continued substitution. This shows lattice expansion understandably from substituting the

much larger barium onto the sodium A-site. Secondly, as more BZ is added, the profile changes to a pseudocubic structure. This can be seen where the peak separation (present in the .975 NN profile) comes together into single peaks, with the superstructure peaks present between 35 and 40 degrees disappearing almost entirely after .90NN. Analyzing pseudocubic structures can be particularly difficult to solve utilizing X-ray data alone due to subtle differences in oxygen positions of related space groups. Thus, to obtain more information about distortion of the oxygen ion positions and other subtle structural effects, neutron data was acquired for the area of interest between .85 NN and .975 NN.



Figure 3-12: X-ray diffraction data for the NN-BZ samples. The red inset displays a close-up of 31-33 $^{\circ}$ 2 θ and the change from two distinct reflections to a single pseudocubic reflection. The blue insert displays a zoom in of the 35-41 $^{\circ}$ 2 θ super structure peaks which decrease in intensity with increased substitution of BZ.

The neutron diffraction data shows that the solid solution undergoes large structural changes with increased substitution of BZ that cannot be observed using X-ray diffraction. When the diffraction patterns are laid on top of each other, specific differences can be seen involving the appearance and disappearance of superstructure peaks, which can be easily seen in the d-spacing between 2.0 and 3.0 Å. (Figure 3-13)



Figure 3-13: Comparison of neutron diffraction data for NN-BZ samples. Inset displays closeups of the 2.0 - 3.0 Å area in the d-spacing where superstructure peaks are visible.

As mentioned previously, NN displays a very complex phase diagram which has been extensively discussed.[150, 153, 164] Starting with the simplest composition, .85 NN has the highest symmetry. Pawley and then Rietveld refinements were performed using the structures that each of the end members crystallize in. These space groups included *P4/mbm*, *Ccmm*, *Pnmm*, *Pmnm*, *Pbnm*, *Pbcm*, *R3c*, and *Pm-3m*. None of these structures provided an accurate model and fit to the final data, with the majority of space groups adding extra reflections not found in the measured data. (Table 3-4)

Structure	Mismatched Intensities	Non-physical Thermal Parameters	Missing or extra reflections
Pm3m			X
Pnma	X		X
R3c	X		X
Pmmn	X	Х	X
P4/mbm	X		X
P4/nmc	X	Х	X
I4/mmm		Х	X
Стст		Х	X
Im3-	X	Х	X
Pbcm + Pmc21	X	Х	X

Table 3-4: Attempted Rietveld refinements for the .85 NN - .15 BZ composition and reason for inaccuracy.

The highly symmetric Pm-3m on the other hand, shows a model where there are missing peaks compared to the original data. Pm-3m was the closest to fitting without adding any extra peaks, which is understandable considering that this composition has the highest amount of BZ, which displays a Pm-3m structure throughout the temperature range. Comparing the measured data to the calculated Pm-3m profile, two broad reflections are missing with d-spacing values of around 2.5 and 1.5 Å. (Figure 3-14) With the X-ray data showing the absence of any large impurity, this indicated that there were possibly multiple phases present with one being a structural distortion of the cubic unit cell, which gives rise to these additional reflections. Further analysis was needed to accurately determine which structural distortions from the cubic superstructure in particular gives rise to these super-reflection peaks.



Figure 3-14: Example neutron Rietveld refinement of *Pm-3m*, .85NN.

In order to determine which distortions are occurring, another approach is necessary, as traditional Rietveld refinements focus on the changes in atomic positions instead of particular distortions. Distortion mode analysis gives a more granular look at the possible distortions of the parent cubic perovskite unit cell and how they would manifest in the resulting diffraction data. Distortion mode analysis represents the symmetry elements for each space group as an irreducible representation relating back to the Brillouin zone of the parent unit cell. Simply, when a parent structure distorts, the symmetry lowers to make a subgroup of the parent space

group. Rather than refining the atomic positions, as in a traditional Rietveld refinement, a distortion mode analysis refines the amplitude of a chosen distortion mode, which in turn moves the atoms in the unit cell. This analysis was done utilizing the ISODISTORT and ISOVIZ software.[80, 81] To start, a cubic parent structure of each composition in the solid solution was created and the possible displacement modes were then chosen. The most common modes chosen in any refinement relate to atomic displacements and strain, although other modes can be chosen, such as occupancy and magnetism. Four different methods are possible to calculate the distorted structures, but this work only utilizes two methods, 1) searching over all special k points and 2) the general method which involves searching specific k-points. As denoted in previous literature, there are three main irreducible representations depending on the centering method you choose, that are commonly present in non-centrosymmetric structures and those are the Γ_4^- , M_4^+ , and R_4^+ which represent non-centrosymmetricity due to cation displacement, inphase octahedral rotations, and out of phase rotations respectfully.[39, 165, 166] Some of these distortion modes were additionally chosen based on property measurements showing ferroelectricity which will be described further in an upcoming section. After the space group, kpoint, and distortion modes are chosen, the data is then exported to whichever refinement program is utilized, in this case TOPAS Academic.[74] The data then goes through a simulated anneal with the amplitude of the distortion modes refined, thus making a model of the end structure.

As an example, the .85NN data shows an anomalous peak at a d-spacing of 2.5 Å. Of those three representations the R distortions place a superstructure peak at 2.35 Å, which can be seen in the lower doped materials, while the M representation places a pair of peaks with one occurring at 2.5 Å but the other is at 2.1 Å which is not present in the .85NN data. This second

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reflection can also be seen in the lower substituted compositions. This leaves the gamma irreducible representation, which places a single peak at 2.5 Å and thus the best match of these options. This particular distortion mode relates to cation distortion leading to a non-centrosymmetric structure, while the absence of R and M distortion peaks indicate a lack of octahedral rotation. Gamma, R, and M however are just the simplest distortions to observe without accounting for strain modes, Additionally, this also assumes only one primary distortion which might not be true for complex structures.

The .975 NN diffraction pattern is one of these more complex structures and does not solely show peaks at 2.1 Å, 2.4 Å, and 2.5 Å, meaning that both in and out of phase rotations are present, with the possibility of cation distortions occurring as well. This can be reconciled either by trying to find a single structure with all three of those distortions present or by mixing two phases together which will sum to the correct structure As for the first option, *Pbcm, P4₂mc, Pmc2₁, Pm2₁, Pca2₁, Pna2₁, and Pnma were all attempted although all failed with major intensity mismatches or resulted in non-physical thermal parameters, leading to the potential conclusion that this composition might have multiple phases. (Table 3-5)*

Structure	Mismatched Intensities	Non-physical Thermal Parameters	Missing or extra reflections
Pnma			Х
Pbcm			Х
Pna21	X		Х
Pmn21	Х	Х	Х
Pmc21	Х		Х
Pca21	Х	Х	Х
P42mc	Х	Х	Х
Pmc21 + Pm3m	Х	Х	Х
Pbcm + Pnma	Х	Х	
Pbcm + Pmc21	X	Х	
Pbcm + Pna21	X	Х	Х
Pbcm + Pmn21	X	X	
Pbcm + P42mc	X	X	X

Table 3-5: Attempted Rietveld refinements for the .975 NN - .025 BZ composition and reason for inaccuracy.

The second technique was used for Figure 3-15, which utilized a mixed phase refinement between the *Pbcm* parent phase for NN and *Pmc2*₁, a subgroup of *Pnma* containing a polar distortion. The reason why the structures with a polar distortion was used is reflected in the ferroelectric data provided earlier, where upon a ferroelectric to relaxor transition was seen at 95NN. This technique also attempted mixing *Pbcm* with other ferroelectric active phases such as *Pna2*₁, *Pmn2*₁, and *P4*₂*mc*. The two-phase attempts did fit the data better than the single phase attempts, however all still led to non-physical thermal parameters or intensity mismatches. Therefore, further techniques are necessary for complete structural analysis in order to differentiate the possible ferroelectric distortions. Some possible techniques for further analysis include selected area electron diffraction and attempting to grow a single crystal of the final composition for single crystal X-ray diffraction.



Figure 3-15: Example neutron Rietveld refinement of two phase, $Pbcm + Pmc2_1$, .975 NN.

With the attempt to remove lead from electrical devices in recent years, lead free relaxors have grown in popularity and also display fascinating electrochemical properties. The most common involve solid solutions based on sodium bismuth titanate (NBT)[167, 168] and potassium sodium niobate (KNN).[50] NBT, also first discovered by Smolenskii et al.[9], is particularly interesting because the material also has a very complex structure and undergoes a diffuse phase transition between rhombohedral and tetragonal structures, between 200 and 320 °C. NBT has a T_m at 320 °C with a piezoelectric coefficient of around 70 pC/N, both higher than NN-BZ. As for the ferroelectric properties, NBT has a major drawback of having a high coercive field of 70 kV/cm, which makes it difficult to saturate under field, but does show a high remanent polarization of 38 μ C/cm². Upon addition of most dopants, such as barium titanate, the ferroelectric properties are also commonly drastically improved. This is especially true for the extremely commonly studied NBT-BT solid solution which displays an MPB near .06 BT where the piezoelectric coefficient more than doubles and the coercive field is basically cut in half. One negative though, is the drastic lowering of the depolarization temperature from 200 to around 100 °C reducing the potential applications to only room temperature ones.

KNN, on the other hand, is a traditional ferroelectric material also with a complex structural diagram with multiple MPBs and PPTs. It has been studied intensively due to promising electromechanical properties, although processing concerns and difficulties necessitated multiple advances before usable devices were possible. As for relaxor materials, KNN has been doped with SrTiO₃ (STO), SrZrO₃ (SZO), CaTiO₃, and even NBT.[169-172] The best dielectric properties of these solid solutions belong to the strontium dopants, which have dielectric constants ranging from 3000 for STO addition and 5000 for SZO. These maximums are similar to the 90NN composition, although at least for the STO solid solution the piezoelectric coefficient ranges, depending on STO, addition from around 50 to 200, which is almost four times higher than the maximum for the entire NN-BZ solid solution, while also showing better dielectric aging after annealing than comparable lead containing relaxors. This mix of promising properties make them highly useful for energy storage applications.[173]

3.4 Conclusion

To determine whether the theory of polarization extension can be utilized in an attempt to synthesize novel ferroelectric materials, the solid solution (1-x) NaNbO₃ – (x) BaZrO₃ (NN-BZ) was used as a test solid solution. Unfortunately, there was no evidence of the structural changes that would lead to polarization extension for this particular solid solution. The X-ray diffraction

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results show with increasing BZ content, there is a corresponding increase in pseudocubic character. Furthermore, the material showed very complex structural changes throughout, necessitating the use of high-resolution neutron diffraction in an attempt to determine the full structure. Rietveld refinements were performed on the resulting data although an accurate model was not found. When traditional analysis was unable to determine the structure, distortion mode analysis was attempted. Utilizing k-space, it was discovered that for the majority of solid solutions, multiple distortion modes were present, thus creating a very difficult problem to solve. As such, more techniques will be necessary to further narrow down an appropriate space group.

The dielectric permittivity indicates a ferroelectric to relaxor transition at 5% substitution of BZ. This is noticeable in the drastic change from a sharp to diffuse permittivity profile indicating the appearance of polar nano regions, with the diffuse profile being caused by each PNR having a different relaxation time due to the varying sizes of the PNRs. The ferroelectric data also displayed a transition within this compositional range, and although the .95 NN sample did not show high properties, there was still domain wall motion, as indicated in the changing slope of the hysteresis loop. The composition which displayed the highest properties in the d_{33} , *P-E*, and Strain tests was the .90NN material. The .90NN sample had a P_r of 15 μ C/cm² and a E_c of around 20 kV/cm, with a strain percentage of around .07 % and a d_{33} and d_{33} * of 50 pC/N and 110 pm/V, respectively. This increase in properties is likely due to being near the ergodic to nonergodic relaxor transition, which is indicated by the .875 NN composition losing the ability to hold a poling charge when not under an electric field, which can be seen in the piezoelectric data. This is corroborated by the P-E and S-E loops losing most hysteresis and having a very low remanent polarization. In the end, the material properties compare unfavorably to contemporary materials, but further study could be done on the complex structural changes.

As for future work opportunities, a full measurement of the microstructure is necessary to determine any drastic changes which could impact the properties between the compositions. This is particularly important due to sodium niobate showing difficulty in densification and abnormal grain growth.[146, 174] Both of which can have a drastic impact on the end properties. Also, considering niobium and zirconium were chosen due to being similar in size in order to try and lower the possibility of turning into a relaxor, it should be investigated whether the relaxor character is caused by ordering or clustering on the a-site. The structural work can also be continued by utilizing electron diffraction in order to give another point of comparison with the neutron data. The local structure can also be investigated to see if the solid solution also displays a local rhombohedral structure similar to sodium niobate.

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Chapter 4 - Synthesis and Characterization of a New Ferroelectric with Low Lead Content, a High Curie Temperature, and a High Piezoelectric Response

4.1 Introduction

Piezoelectric materials convert between mechanical and electrical energy and vice versa as such, they are used in a plethora of electronic devices for sensor and actuator applications including cell phones, sonar equipment, engine knock sensors, pressure sensors, diesel fuel injectors, medical devices, and many more. [6, 175] One of the developing applications is to utilize these materials as energy harvesting devices to capture the energy from natural repetitive motions generated by vibrations in machinery, vehicles, or human movement to then power devices, such as wireless sensor networks in remote locations, wearable biomedical devices, or mobile electronics. The most highly utilized piezoelectric material is currently the perovskite $Pb(Zr_{1-x}Ti_x)O_3$, (PZT), due a morphotropic phase boundary (MPB) that causes an enhancement of d_{33} , the piezoelectric response at x ~ 0.5, and its ability to be easily doped to tune the material for a wide range of applications. [27, 28] However, PZT contains 60 wt. % lead, which is a toxic element, and has a low operating temperature due to a phase transition at its Curie temperature $(T_{\rm C})$ of 350 °C. This prevents it's use in high temperature applications such as structural health monitoring in harsh conditions, pressure sensors, and other high temperature, high power transducer applications.

This study replaced the end member PbZrO₃ (PZ) with BiFe_{2/8}Ti_{3/8}Mg_{3/8}O₃ (BFTM), with the goal to increase the operating temperature of piezoelectric devices. BFTM is unique in that it is one of just three perovskites with only bismuth on the A-site that can be synthesized under ambient conditions.[158] Generally, the Bi-cation is too small to stabilize the perovskite phase when it is the sole A-cation and therefore can only be synthesized at high pressures. However, in BFTM, the B-site cations have +3, +4, and +2 oxidation states, creating a flexible O-framework that more easily allows the Bi-coordination environment to be satisfied. BFTM was chosen to replace PbZrO₃ (PZ) in the PZT solid solution due to BFTM having a high $T_{\rm C}$ of 730 °C. With PT having a $T_{\rm C}$ of 495 °C, the $T_{\rm C}$ of the resulting solid solution is expected to fall somewhere in between its end members. This contrasts with PZ, which has a lower $T_{\rm C}$ than PT, resulting in a phase transition temperature of ~350 °C at the MPB of PZT. Additional benefits of using BFTM as an end member is that it decreases the amount of lead in the material. Bismuth, like lead, also has a lone pair of electrons which helps to maintain long-range ferroelectric ordering, rather than shifting to a relaxor ferroelectric with short range polar nanodomains, as is often observed when making substitutions with a variety of cations that prefer different coordination environments.[176] In this study, we synthesized solid solutions of (1-x)BiFe_{2/8}Ti_{3/8}Mg_{3/8}O₃-(x)PbTiO₃, (BFTM-PT) which has a morphotropic phase boundary, a much lower wt. % of lead (22 % in BFTM-PT compared to 60 % in PZT), a higher phase transition temperature of ~650 °C for use in high temperature applications, and high d_{33} value compared to most materials with a similar $T_{\rm C}$.

4.2 Experimental

4.2.1 Synthesis

Samples of (1-x)BFTM- $(x)PbTiO_3$ solid solutions were prepared from x=0.1-0.5 using standard solid-state methods. The precursor oxides and carbonates were combined in stoichiometric amounts and ground in an agate mortar and pestle. The precursors used were Bi₂O₃ (Sigma Aldrich 99 %), Fe₂O₃ (Sigma Aldrich 99 %), TiO₂ (Sigma Aldrich 99 %), Magnesium carbonate hydroxide hydrate ($C_4Mg_4O_{12} \cdot H_2MgO_2 \cdot xH_2O$) (Sigma Aldrich 99 %), and PbCO₃ (Sigma Aldrich 99 %). The mixed powders were first ball milled for 30 hours at 350 rpm (15 minutes on, five minutes rest, and 15 minutes in the reverse direction) in a Planetary Ball Mill (Fritsch Pulverisette) with 25 mL of ethanol and eight, 10 mm diameter, yttriastabilized zirconia balls. The resulting powder was used to sinter dense ceramic pellets. The powder was dried and mixed with a 3 wt % polyvinyl butyral (PVB, Butvar B-98, Sigma Aldrich) binder/ethanol solution. The powder was then pressed in a Carver uniaxial press using a die to form pellets with a diameter of 10 mm and thickness of ~ 1.5 mm. The pellets were placed inside alumina crucibles with sacrificial powder of the same composition and sintered utilizing a two-step sintering process. This includes heating at 300 °C for one hour with a 10 °C/minute ramp rate as a binder burnout stage, continuing to the first holding temperature of 1100 °C for 5 minutes, ramping down also at 10 °C/minute until a second holding temp of 800 °C for 6 hours, and then setting the box furnace to ramp down again at 10 °C/minute until room temperature but due to relying on atmospheric temperature for cooling the lower the temperature the longer each degree will take to cool. All physical properties were measured on pellets with densities greater than 95 % of their crystallographic value as determined by a Mettler Toledo Archimedes kit.
4.2.2 Ceramic preparation

Ceramic pellets for physical property measurements were carefully polished to appropriate thicknesses of ~1 mm for dielectric measurements and <0.5 mm for strain (*S*-*E*) and polarization (*P*-*E*) measurements as a function of electric field. The pellets were polished to a mirror finish using a LaboPol-5 (Struers) with #400, #800, #1200, and #4000 SiC foils (Struers) sequentially. For *S*-*E* and *P*-*E* measurements, electrodes of silver conductive paint (SPI Supplies) were applied to the parallel faces of each pellet before the pellet was heated to 600 °C for 30 minutes to cure the silver electrodes. Platinum paint (SPI Supplies) was applied to the pellets used in the dielectric measurements and sintered to the polished pellets at 350 °C for 1 hour with a ramp rate of 1 degree Celsius per minute, then ramped at 5 degree per minute up to 1000 °C and then cooled to room temperature.

4.2.3 Physical properties measurements

Dielectric permittivity was measured using an HP 4192A LF Impedance Analyzer, a NorECsAS ProbostatTM, and a Carbolite tube furnace. The measurements were performed on unpoled samples during cooling as a function of temperature and frequency from 1 kHz to 1 MHz and from 800 °C down to room temperature. Strain vs. electric field (*S-E*) and polarization vs. electric field (*P-E*) measurements were performed on a Radiant Precision Premier II, at a frequency of 1 Hz, with the sample pellet submerged in an insulating silicone oil. The *S-E* measurements, utilizing an optical displacement sensor (MTI-2100), were run using two loops with the final average being used as the final data set. Poling was performed on the Radiant Precision Premier II by applying a DC bias to the sample at 100 kV/cm for 30 minutes. The direct piezoelectric effect was measured on a Berlincourt-type d_{33} meter (APC International, Ltd. YE2730A). The depolarization temperature measurements were performed on a poled pellet which was subsequently heated to and held at each corresponding temperature for 30 minutes, then left to cool to room temperature before measuring the direct piezoelectric effect.

4.2.4 X-ray diffraction

Phase purity of each sample was verified using X-ray diffraction (XRD) on a Rigaku Miniflex 600 using Cu K α radiation ($\lambda = 1.541862$ Å) and scanning a 2 θ range from 10 to 60 ° at a rate of 5 ° per minute. Synchrotron powder X-ray diffraction data was also collected at Argonne National Laboratory on the 11BM beamline using their mail-in program. The 11BM beamline utilized a .458165 Å wavelength scanning from .5 to 50 degrees (2 θ) with a step size of .001 degrees and .01 seconds per step. Pawley refinements to determine lattice parameters were performed using Topas Academic software. [74]

4.3 Results and Discussion

X-ray diffraction measurements indicate this material to be a solid solution with no impurities in any of the compositions synthesized. The diffraction patterns can be seen in Figure 4-1, showing that there are multiple phase transitions present. Figure 4-1b displays the full range of structural phase transitions. The Bi-rich side starts off in rhombohedral (R) R3c, which is the structure of BFTM, and is indicated by the splitting of the (104) and (2-10) peaks as well as the (202) and (006) peaks. As more PT is added, a mixture of R3c and monoclinic (M) Cm occurs, and between x=0.30-0.35, a single phase of Cm can be observed. SEM images taken at this composition do not indicate a mixed phase structure, as seen in Figure 4-2. On the Pb-rich side of this structure, two phases are again detected, Cm and tetragonal (T) P4mm, then as PT is approached, the structure changes to single phase P4mm, which is noted by the splitting of the (101) and (110) peaks. The polarization direction varies in each of these structures going from

the [111] direction in *R3c* on the Bi-rich side, to the [001] direction in *P4mm* on the Pb-rich side of the MPB. The M structure has a polarization of [110], which provides a bridge between the R and T phases, and the movement of the polarization direction between these states is often referred to as polarization rotation.[30, 177] This structural sequence of phase transitions is somewhat similar to PZT where the PZ end starts in the antiferroelectric, orthorhombic *Pbam* phase, then changes to *R3c* before reaching the MPB, where monoclinic *Cm* is observed, and finally transforming to *P4mm* on the Pb-rich side of the MPB.[28] Because the transition sequence in BFTM-PT and PZT is similar, the structural data of BFTM-PT suggests that the *Cm* structure found between 0.30-0.35 could be an MPB, a region of the phase diagram with enhanced piezoelectric and ferroelectric properties. While BFTM-PT and PZT are structurally similar, their dielectric, ferroelectric, and piezoelectric properties are different, especially in terms of the Curie temperature, which is rather low in PZT at ~350 °C, and therefore limits its use in high temperature applications.



Figure 4-1: a) Synchrotron X-ray patterns for BFTM-PT at and around the MPB region showing no impurity phases present and b) (104)+(2-10)/(101)+(110) diffraction peaks showing the progression of phases in the solid solution. The red ticks display the (T) *P4mm* phase, the green ticks mark the (R) *R3c* phase, and the black ticks denote the *Cm* phase.



Figure 4-2: a) SEM picture taken of the .325 PT composition indicating primarily single phase material with a normal single distribution of grain sizes b) SEM micrograph of La doped NBT with an impurity phase showing a distinct bimodal distribution of grain sizes. Figure b adapted from Eaksuwanchai et al.[178]

Although much of the synthesis follows traditional solid state synthesis techniques, a single step sintering process was substituted for a two-step process. As seen in Figure 4-3, this involved a binder burnout step, a rapid heat to a high temperature, and then a rapid cooling and hold for a longer time at a lower temperature to complete densification. This version of two-step sintering was first popularized by Wang et al. (2006) on yttrium oxide and barium titanate.[179, 180] The theory behind two-step synthesis is two fold, whereupon the initial high temperature provides enough energy for atomic diffusion, while the lower holding temperature allows for densification while hindering abnormal grain growth, commonly seen in crystals held at high temperatures. For certain materials such as KNN, this abnormal grain growth can hinder densification efforts greatly.[146] Since both bismuth and lead are volatile at elevated temperatures, with the majority of the sintering occurring at the lower temperature, there is in theory a lower possibility for vacancies and other defects, thus improving the density of the end product. Two-step sintering has been seen to be a low-cost alternative to spark plasma sintering and therefore used in a variety of solid solutions.[181]



Figure 4-3: Diagram showing the differences between a one-step and two-step sintering techniques.

Electrical properties of BFTM-PT were measured on dense ceramic pellets (>95 %). Figure 4-4 shows the temperature dependent dielectric permittivity and loss data, where a sharp phase transition from a ferroelectric to paraelectric state is observed between 630-650 °C depending on the composition. These $T_{\rm C}$ values lie between those of the end members BFTM at 730 °C and PT at 495 °C. Table 4-1 displays a summary of the permittivity and loss data for the compositions x=0.25-0.40. The room temperature permittivity exhibits a trend at 1 kHz, where x=0.25 on the Bi-rich end has a value of 357, which increases to 758 at x=0.35, then decreases to 598 at x=0.40. The loss values at the same temperature and frequency vary from 0.029-0.096, depending on the composition. They show no trend that corresponds to the permittivity data, but these loss values are typical for ferroelectric materials. At higher temperatures near $T_{\rm C}$, the loss increases significantly and varies from 0.158-0.295. This large increase indicates that the material is likely conductive at high temperatures, due to the volatile A-cations and/or the tendency for iron to change oxidation state, leading to A-site or oxygen vacancies. These dielectric properties contrast with PZT, which has a $T_{\rm C}$ of 350 °C. PZT can be easily tailored and shows a range of $T_{\rm C}$ values from 300-400 °C through doping,[182, 183] but it still cannot maintain the polar structure up to the $T_{\rm C}$ values found for BFTM-PT. The $T_{\rm C}$ of BFTM-PT can also be compared to other well-known PZT competitors. One well studied lead-free piezoelectric K_{0.5}Na_{0.5}NbO₃ has a $T_{\rm C}$ that falls between that of PZT and BFTM-PT and ranges from 350 to 450 °C, depending on the dopant incorporated into the structure.[57, 58] Other ferroelectrics such as BiFeO₃-BaTiO₃ (BF-BT) solid solutions[48, 62, 184, 185] and the family of bismuth Aurivillius phases (Bi₂O₂)(A_{n-1}B_nO_{3n+1}) (where n = the number of perovskite blocks between bismuth oxide layers) have $T_{\rm C}$ values that range from 550-750 °C which is similar to what is observed in BFTM-PT.[60, 186, 187]



Figure 4-4: a) Dielectric permittivity and loss as a function of temperature for three select compositions with different room temperature structures and b) Curie temperature as a function of composition, laying out the phase diagram.

Composition	Er 1kHz	Er 1MHz	Tan ð	Tc	Er 1MHz	Tan ð
x	@RT	@RT	@RT	°C	@T _C	@ T C
0.25	357	319	0.0296	640	10212	.1638
0.275	522	436	0.0435	625	12691	.2315
0.30	578	478	0.0474	645	13094	.2951
0.325	650	524	0.0505	650	10226	.2173
0.35	758	598	0.0542	635	10639	.2198
0.375	666	641	0.0956	635	8230	.1239
0.40	598	529	0.0426	630	10088	.1584

Table 4-1: Summary of dielectric properties for a range of (1-x)BFTM-(x)PT compositions.

The polarization (P) and strain (S) were measured as a function of electric field (E) on dense ceramic pellets to determine the ferroelectric and piezoelectric properties. A summary of the ferroelectric and piezoelectric properties can be found in Table 4-2. The composition in the R region of the phase diagram (Bi rich end) does not have a saturated *P*-*E* loop, seen in Figure 4-5a, and is similar to what is observed in the parent compound BFTM.[158] This loop is common for ferroelectric materials that have a high $T_{\rm C}$ and/or high coercive field. When moving into the two-phase region of R and M phases and through to the T phase on the Pb-rich side, all those loops became saturated, indicating an alignment of all the dipoles. The property summary in Table 4-2 shows that both the maximum polarization (polarization at saturation), $P_{\rm m}$, and remanent polarization (polarization that remains after the field is removed), $P_{\rm r}$ increase up through x=0.325, then slightly decreases as more PT is added. The values for $P_{\rm m}$ and $P_{\rm r}$ at this composition are 39 μ C/cm² and 26 μ C/cm², which are on par with what is found in PZT.[182, 188] The coercive field (E_c) of BFTM-PT is fairly high, varying between 38-54 kV/cm,

designating these materials as hard ferroelectrics. Hard ferroelectrics more readily retain longrange ordering and are more difficult to switch, making these materials suitable for applications that require high levels of electrical excitation and/or mechanical stress such as high voltage or high power generators and transducers.[6, 47] This is typically caused by oxygen defects which under field undergo defect-dipole rotation stabilizing the domain structure.[189] Materials with a lower $T_{\rm C}$ typically have a lower $E_{\rm c}$ value as well, as such, undoped PZT shows an expected lower $E_{\rm c}$ of ~20 kV/cm.[26] Doping can change the $E_{\rm c}$ of PZT in addition to its $T_{\rm c}$, where soft dopants, consisting of electron donors decrease the $E_{\rm c}$ and hard dopants consisting of electron acceptors, increase $E_{\rm c}$. This easy tunability of PZT has been developed over decades through the use of dopants (hard vs soft) and mechanical synthesis techniques, which implies that these techniques could also be utilized to alter the properties of BFTM-PT and tailor it for specific applications. [4, 190-193]

Both bipolar and unipolar loops, *S-E*, were measured to determine the electromechanical strain properties as seen in Figure 4-5b and 4-5c. Figure 4-5b shows bipolar strain vs electric field loops. These loops demonstrate ferroelectric back-switching as indicated by a negative strain component and they also show an increased strain percentage within the MPB region. The strain response was also studied under unipolar electric field cycling to investigate its potential use for actuator applications. (Figure 4-5c) The highest strain achieved is 0.19 % in the x=0.325 composition, which is consistent with the observed excellent dielectric and ferroelectric properties of this composition. This value is a large increase compared to the strain in other BFTM based materials (0.04 - 0.08 %), [176, 194] and even displays a slight increase compared to PT (0.15 %) [182] indicating, along with the dielectric and ferroelectric data, the presence of a

morphotropic phase boundary (MPB) in this region of the phase diagram. The strain values are comparable to some doped compositions of PZT (0.15-0.3 % on average),[183] although due to the vast amount of research on strain engineering and dopants on the properties of PZT, they can display a wide range of values.[182, 195-197] As mentioned previously, Bi-based Aurivillius phases show a $T_{\rm C}$ similar to BFTM-PT, but their strain values are not typically measured due to the Aurivillius structure [187] only being a two dimensional ferroelectric. Therefore, the traditional method of measuring the piezoelectric response along the c-axis usually results in values an order of magnitude smaller.

Composition/	<i>P</i> m/	$P_{\rm r}$ /	<i>E</i> c/	Strain / %	<i>d</i> ₃₃ /	<i>d</i> ₃₃ * /
x	µC/cm²	µC/cm²	kV/cm		pC/N	pm/V
0.25 PT	16	7	38	.06	60	60
0.275PT	31	19	48	.075	70	75
0.30 PT	36	23	47	.12	85	120
0.325 PT	39	26	51	.19	100	190
0.35 PT	38	24	49	.17	75	170
0.375 PT	38	25	54	.15	145	150

Table 4-2: Summary of ferroelectric and piezoelectric properties of BFMT-PT solid solutions.



Figure 4-5: a) Polarization vs electric field b) bipolar strain vs electric field and c) unipolar strain vs electric field for six compositions both within and near the morphotropic phase boundary.

The indirect piezoelectric response at high field, d_{33}^* , was determined by calculating the maximum strain divided by the applied field within the unipolar *S-E* data while the direct piezoelectric response at low field, d_{33} , was measured by poling the sample and measuring the response with a Berlincourt meter. As shown in Figure 4-6, there is an increase in both the high field and low field piezoelectric response around x=0.325. At this composition, the d_{33} value is 100 pC/N and the d_{33}^* value is 190 pm/V. In the monoclinic region, the d_{33} and d_{33}^* diverge,

with the d_{33}^* becoming significantly higher than d_{33} which could potentially occur due to an electric field induced phase transition as in Bi_{0.5}Na_{0.5}TiO₃-BaTiO₃-K_{0.5}Na_{0.5}NbO₃ solid solutions.[55] Electric-field induced phase transitions have large d_{33}^* values and a suppressed d_{33} . If this type of phase transition is indeed present within the monoclinic region of the phase diagram only, and the d_{33} values are lowered because of this phenomenon, that could explain why the d_{33} is the highest in the x=0.375 composition. At x=0.375, the d_{33} and d_{33}^* values converge again which indicates that there would not be an electric-field induced phase transition in this region. Another theory for why the d_{33} of x=0.375 could be higher than in the monoclinic region is due to this composition being mixed phased and therefore having a contribution from each phase.

The piezoelectric response, d_{33} , is typically inversely proportional to $T_{\rm C}$, hence materials with $T_{\rm C}$ values around room temperature can have very high d_{33} values – on the order of 600-1000 pC/N while materials with high $T_{\rm C}$ (>500 °C), typically have a very low piezoelectric response, with d_{33} values less than 50 pC/N.[60, 186] The temperature stability for the .325 composition was also measured as seen in Figure 4-7. This measurement showed fairly poor temperature stability, with consistent loss in the dielectric constant above 100 °C until the value hit 0 at 500 °C. This loss is most likely caused by conductivity at elevated temperatures. Ferroelectrics have to be insulating in order to get charge displacement instead of charge flow which will disturb the long-range ferroelectric ordering. The d_{33} values in BFTM-PT are much higher than typically seen for materials with a similar $T_{\rm C}$ as shown in Figure 4-8. The piezoelectric response in BFTM-PT is on par with recent high $T_{\rm C}$ materials found in the literature BF-BT,[48, 62, 184, 185] but significantly higher than the well-known piezoelectric Aurivillius phases such as Bi₄Ti₃O₁₂ and PbBi₄Ti₄O₁₅, which have d_{33} values in the range of 10-30 pC/N.[60, 186, 187] The reason for the differences in the piezoelectric response between the Aurivillius materials and the perovskites BFTM-PT, BF-BT, BF-PT, [46, 198] BScO₃-PT[63] is that the Aurivillius materials are not a solid solution, so there is no MPB present to enhance the piezoelectric response compared to the bismuth-based perovskite materials. Therefore, in order to maximize the piezoelectric response in high $T_{\rm C}$ materials, it is imperative to design a solid solution with an MPB such as BFTM-PT in this study.



Figure 4-6: High and low field piezoelectric coefficients for BFTM-PT.



Figure 4-7: Change of d_{33} for the .325 PT composition with varying annealing temperature indicating poor thermal stability.



Figure 4-8: A demonstration of the inverse relationship between piezoelectric effect and Curie temperature. Figure adapted from Yu Z, Zeng J, Zheng L, et al.[48]

This study is not the first to use BFTM as an end member in a solid solution to attempt to replicate or even improve upon the properties of PZT. The first solid solution synthesized was BFTM – BaTiO₃ (BFTM-BT),[176] which similar to BFTM-PT, has R3c and P4mm end members, representing the structures of PZT on either side of its MPB. While the solid solution of BFTM-BT has end members with the same structure as BFTM-PT, the electromechanical properties are different. In BFTM-BT, the structure changes from R3c to a pseudocubic R3mstructure extending from x=0.95 to 0.05, therefore not technically an MPB that typically occurs over a very narrow composition range. The properties of BFTM-BT are between that of a ferroelectric and a relaxor ferroelectric. Relaxors are a subset of ferroelectrics, where the longrange ferroelectric ordering is disrupted by local disorder, forming regions of electric dipole ordering in polar nano domains (PNRs), where those PNRs are not correlated to each other. This phenomenon results in distinct properties compared to traditional ferroelectrics and therefore are used in alternate applications such as energy storage.[199, 200] One notable feature of BFTM-BT is the permittivity as a function of temperature. The data shows two peaks, one broad peak at lower temperatures and a second sharper peak at a higher temperature. The study suggests that the high temperature peak is from a phase transition while the low temperature peak is from the dielectric relaxation due to the reorientation of the polarization direction within the PNRs caused by thermal fluctuations. In addition, the ferroelectric and piezoelectric properties of BFTM-BT are very poor with the origin of this behavior coming from the different preferred cation environments of bismuth and barium. Bismuth has a lone pair of electrons, resulting in a distorted polyhedral environment where barium prefers a symmetric coordination environment,

thus causing a structural strain which disrupts the long-range ferroelectric ordering and causes the onset of relaxor behavior.

The next study on BFTM investigated the ternary solid solution BFTM-LaFeO₃-La(Mg_{0.5}Ti_{0.5})O₃ (BFTM-LF-LMT).[201] LF was used as it has been known to improve the piezoelectric properties of BiFeO₃, however, iron often results in lossy dielectric behavior, hence why LMT was added to counterbalance the increased loss. In the phase diagram for the solid solution, several compositions displayed a new ferroelectric phase with the *Pmc2*₁ structure, which is rarely found from a perovskite structure. This space group has a complex set of displacements, but overall shows a ferroelectric properties, but the d_{33} values were small, ~0.25 pC/N. Unfortunately, between the ferroelectric phase of the BFTM end member and the new *Pmc2*₁ structure, there is a range of compositions where phase separation occurs, resulting in a mixed phase perovskite and Aurivillius structure. As in BFTM-BT, there is no MPB present with an enhancement of the piezoelectric response.

Solid solutions between BFTM-CaTiO₃ (BFTM-CT) were able to successfully bridge the gap between the ferroelectric phases observed in the BFTM-LF-LMT system.[194] The BFTM-CT solid solution showed a structural transition from the parent R3c structure to a wide mixed phase region (x =0.05-0.20) of R3c and orthorhombic $Pna2_1$ in what can be defined as the MPB. On the CT rich side of the MPB, the structure was single phase $Pna2_1$. Additionally in this solid solution, there is no bridging polarization direction as in PZT and BFTM-PT, and the polarization changes from the [111] direction in the R phase directly to the [001] direction in the O phase. The electromechanical properties demonstrate that the mixed phase region can be considered an MPB. The ferroelectric hysteresis loops were able to be fully saturated, showing

well developed loops with the best recording maximum and remanent polarizations of 49 and 44 μ C per cm² respectively. This can be compared to BFTM-PT with values of 39 and 26 μ C per cm², with this region of the phase diagram in BFTM-CT displaying an enhanced piezoelectric response, a *d*₃₃ value of around 50 pC/N of which is lower than that found in BFTM-PT. BFTM-CT also has a higher *T*_C of 840 °C, thus the lower *d*₃₃ is not unexpected. The piezoelectric response in BFTM-PT is largely due to the inverse relationship between *T*_C and *d*₃₃, as described above. The *T*_C values within the BFTM-CT MPB are actually higher than that of BFTM because the other end member CaTiO₃ stabilizes in the *Pnma* space group which is centrosymmetric and therefore does not display ferroelectricity. By replacing non-ferroelectric CT, with ferroelectric PT, which also has a lower *T*_C than BFTM, the piezoelectric response within the MPB of BFTM-PT is larger.

BFTM-PT displays electric properties comparable to one of the primary lead-free competitors, potassium sodium niobate (KNN). KNN was first discovered in the late 1950's by Bell Labs and was primarily used for ultrasonic applications.[202] It wasn't thought of as a competitor to PZT until the mid 2000's when Saito et al. doped the pure KNN compound with lithium, tantalum, and antimony drastically improving the piezoelectric properties.[147] Pure KNN when first synthesized had a piezoelectric constant of around 80 pC/N although with improved sintering as well as processing techniques that value has been raised to around 160 pC/N over the years.[151] The Curie temperature has stayed consistent at 400 °C. As previously mentioned, Saito et al. were able to raise the piezoelectric coefficient to 300 pC/N with the textured version reaching 400 pC/N, but this also drastically lowered the Curie temperature to only 250 °C. The remanent polarization was also only around 10 μ C/cm² and had a coercive field of around 20 kV/cm. Additionally, the strain also showed similar values to PZT with 0.15 %

strain values. All in all, while KNN has a larger d_{33} compared to BFTM-PT, the Curie temperature is drastically lower along with the remanent polarization and strain response. There are structural reasons why KNN has not been adopted over PZT, which does not affect BFTM-PT.

The KNN solid solution has a very complicated phase diagram with KN having the ferroelectric orthorhombic *Amm2* phase, the NN crystal structure showing multiple polymorphs with the most commonly accepted space group being antiferroelectric orthorhombic *Pbcm*.[57, 151] For pure KNN, around 50-50 KN-NN, previous research suggested there was an MPB between two different orthorhombic phases although current research has not shown any changes in symmetry.[203, 204] KNN also shows multiple temperature dependant phase transitions changing from a rhombohedral phase to orthorhombic *Amm2* at ~0 °C to tetragonal *P4mm* at ~ 200 °C. These transitions being purely temperature dependant are classified as polymorphic phase transitions (PPTs). As for the improved doped KNN, multiple studies have shows that the doping lowered the orthorhombic to tetragonal phase transition moving it close to room temperature causing the increase in properties compared to pure KNN.[205] PPTs though are much less desirable compared to MPBs due their low temperature stability for industrial applications.

There has been additional promising research done on other lead free solid solutions involving bismuth iron oxide and barium titanate (BF-BT).[48, 62, 184, 185] These materials, depending on dopant and barium titanate amount, sees a rhombohedral to pseudocubic transition caused by the addition of barium onto the A-site. Very recently, co-doping of chromium and manganese near this R-Pc transition led to discovering a rhombohedral to tetragonal transition similar to PZT and BFTM-PT.[62] At this transition, the piezoelectric coefficient and Curie

temperature are very similar to BFTM-PT with the maximum and remanent polarization being slightly lower with the BF-BT sample having a $P_{\rm m}$ of around 30 µC/cm² and a $P_{\rm r}$ of 16 µC/cm² compared to 39 and 26 µC/cm² respectively for BFTM-PT. The thermal stability of the piezoelectric coefficients is improved compared to BFTM-PT although both show constant degradation over increasing temperatures. To that end, co-doping could provide an avenue for further research into improving BFTM-PT with both lowering the dielectric loss and improving thermal degradation.

4.4 Conclusion

Overall, it appears that the crystal structure of the non-BFTM end member has little effect on the piezoelectric properties in all these BFTM systems. BFTM-BT and BFTM-PT both have end members with the same space groups as in PZT, but BFTM-BT forms more of a relaxor-type ferroelectric because of the strain created by the large size difference and coordination environment variance between Ba^{2+} and Pb^{2+} . There is a phase separation between the ferroelectric structures in BFTM-LFO-LMT likely due to the increased amount of Fe³⁺, which typically distorts along the [111] direction, perhaps restricting the accessible ferroelectric structures in this solid solution. In BFTM-CT, the CT end member is isostructural to LFO, but Ti⁴⁺ has been shown to displace locally along multiple directions that are not necessarily coordinated to the A-cation. Thus, increasing the possible ferroelectric structures, which allowed for the formation of an MPB despite CT having a centrosymmetric structure. BFTM-PT and BFTM-CT both display MPBs despite Ca²⁺ and Pb²⁺ having different coordination environments. However, the d_{33} value of BFTM-CT is much lower. This is partly due to the differences in $T_{\rm C}$, but the chemistry could also be a contributing factor. Perhaps the different coordination environments of Bi³⁺ which has a lone pair of electrons and Ca²⁺ which does not, so while both solid solutions show ferroelectric ordering, on a local scale that might be beginning to break down. BFTM-CT is likely to have weaker long-range ferroelectric ordering compared to BFTM-PT. This ordering is important to the enhancement of domain wall motion, which is an extrinsic mechanism of piezoelectric strain.[206, 207] With Bi³⁺ and Pb²⁺ having similar preferred coordination environments, the strong long-range ordering can enable more domain wall motion, therefore increasing the extrinsic effects on the measured piezoelectric strain, resulting in a high d_{33} .

As for future work, the microstructure for each composition should be looked at to see if there are large differences, which could have a large impact on the end properties. This experiment also uses a two-step sintering technique for increased density with lower volatility, as such the microstructure with this technique should be compared to materials sintered with a traditional one-step technique as well as a quench. Due to the thermal stability issues and indications of conductivity at elevated temperatures, in-situ experiments should be conducted looking for changes occurring at high temperatures. This could include domain wall motion, oxidation state changes, and conductivity measurements. Doping experiments should also be attempted with a particular focus on donor doping which has been shown to lower the conductivity and coercive field in PZT.[4, 175] Another avenue involves looking at possible cation ordering in the original solid solution as well as upon addition of dopants. Currently, the three cations on the b-site have large differences in size, oxidation state, and only titanium is second order Jahn Teller active. These differences can all raise the potential of ordering which upon addition of dopants can be increased even further.

4.5 References

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Chapter 5 - Conclusion

In the end, this thesis presents three attempts to synthesize ferroelectric solid solutions in order to further elucidate structure and property relationships using the perovskite structure for development of a viable replacement material for PZT. The first involves the NBT-BT system doping in group 13 elements onto the B-site in order to improve the ferroelectric properties. In order, aluminum had the largest impact on the ferroelectric stability with gallium and indium inducing lower amounts of disorder. When measuring using X-rays, these solid solutions formed a pseudocubic phase, therefore the use of neutron diffraction was needed in order to look deeper at the oxygen distortions and elucidate the complete structure. Upon measurement, the mixed phase P4bm and Cc fit the data most accurately with increased P4bm percentage with larger dopant amounts. On the properties side, the trend follows with indium doping showing the smallest change in the electromechanical properties compared to the parent NBT-BT, while aluminum shows the largest changes. This is particularly noticeable in the piezoelectric coefficients and strain data which indicates the formation of an incipient piezoelectric at 4 % substitution. This is evident from the drop in the d_{33} from 144 pC/N with 2 % Al to only 20 pC/N at 4 % Al. The high field strain, d_{33}^* , over this range increases drastically from around 200 pm/V to nearly 700 pm/V. This is echoed in the strain vs electric field hysteresis loops where the 4 % Al is sprout shaped as compared to the butterfly shaped loop seen in the 2 % Al material. These large strain increases indicate a field induced phase transition occurring which drastically increases the strain response present at the 4 % Al doped material. NBT-BT also undergoes an induced phase transition but unlike the parent material it is not permanent.

As mentioned previously, the piezoelectric and ferroelectric properties for PZT are increased in an area of lowered free energy called the morphotropic phase boundary (MPB) where the dipole is allowed to rotate between similar energy states in multiple ferroelectric phases. One experiment attempted to see if the theory of polarization extension is possible and an MPB could form between paraelectric and ferroelectric phases through compositional changes. The solid solution $(1-x)NaNbO_3 - (x)BaZrO_3$ (NN-BZ) was synthesized and the electromechanical properties were measured in order to see if there was in increase in the piezoelectric response. The resulting solid solution showed very complex structural changes throughout, and therefore involved X-ray diffraction looking pseudo-cubic throughout the range and additional need for the use of neutron diffraction in order to further clarify the structural changes. The neutron data indicated a mixed phase structure throughout with multiple orthorhombic phases present throughout the range, which caused severe peak overlap leading to difficulties in completely solving the structure. As for the properties, starting with the dielectric permittivity, a ferroelectric to relaxor transition was observed at around 5 % substitution of BZ. This transition is best seen in the drastic change from a sharp to diffuse permittivity profile with the $T_{\rm m}$ lowering drastically with increased substitution. The best piezoelectric properties can be seen in the 0.90 NN sample which displayed a d_{33} of 50 pC/N and a d_{33} * of around 110 pm/V. This increase in properties compared to the rest of the solid solution is likely due to being near the ergodic to nonergodic relaxor transiton as seen in the change in the *P*-*E* and *S*-*E* data. Compared to other contemporary lead-free materials such as KNN this shows a far lower piezoelectric response with some textured KNN materials showing around 300 pC/N for d_{33} while also having a higher $T_{\rm C}$, 250 °C to a $T_{\rm m}$ of 100 °C for the .90 NN sample. For the polarization vs electric field measurements, the .90 NN sample had a P_r of 15 μ C/cm² and a E_c of

around 20 kV/cm, a slight upgrade on the parent KNN. Upon further substitution the .85 NN sample loses all remanent polarization and can no longer be poled as seen in the d_{33} data, which indicates a full transition to an ergodic relaxor regime. In the end, the solid solution was deemed to be nonviable for further study due to the extremely poor electromechanical response and complex mixed phase structure.

Finally, with the first two experiments resulting in relaxor materials, the third experiment attempted to synthesize a ferroelectric solid solution that improves on PZT's Curie temperature. Thus, a new solid solution (1-x) Bi(Fe_{2/8}Ti_{3/8}Mg_{3/8})O₃ – (x) PbTiO₃ (BFTM-PT) was synthesized, and the electromechanical properties were measured. Unlike the previous experiments, a MPB similar to PZT was seen, utilizing X-ray diffraction, with phase transitions from rhombohedral to tetragonal. The system demonstrates ferroelectric hysteresis throughout the solid solution, where x=0.325 displays the best properties with a maximum polarization of 39 μ C/cm² and a remanent polarization of 26 μ C/cm². At this composition, the d_{33} value is 100 pC/N while the d_{33}^* value is 190 pm/V, and all of the piezoelectric response measurements within the MPB region show a discrepancy between the high and low field d_{33} values. This discrepancy could potentially occur due to an electric field induced phase transition, as seen in Bi_{0.5}Na_{0.5}TiO₃-BaTiO₃-K_{0.5}Na_{0.5}NbO₃ solid solutions, or could also be caused by differing contributions from multiple phases within this region. The range of compositions also have high Curie temperatures ($T_{\rm C}$), as seen as a single sharp peak in the dielectric permittivity data, ranging from 625-650 °C. The solid solution displays high loss, especially at elevated temperatures, thus indicating poor thermal stability. As such, further research is being conducted looking at in-situ electric field measurements trying to quantify the intrinsic and extrinsic contributions to the piezoelectric response. Dopants can also be attempted in order to improve the conductivity and

thermal stability concerns. To that end, these experiments show how broad traditional synthesis of ferroelectrics can be, creating valuable learning opportunities through experiment successes and failures.

Appendix A (Dopants not included in the manuscript for chapter 4)



Figure A-1: Series of X-ray diffraction profiles displaying the current maximum amount of aluminum able to be added to base composition without impurities.



Figure A-2: Series of X-ray diffraction profiles displaying the current maximum amount of gallium able to be added to base composition without impurities.



Figure A-3: Series of X-ray diffraction profiles displaying the current maximum amount of indium able to be added to base composition without impurities.



Figure A-4: Series of X-ray diffraction profiles displaying the current maximum amount of niobium excess able to be added to base composition without impurities.



Figure A-5: Series of X-ray diffraction profiles displaying the current maximum amount of manganese oxide able to be added to base composition without impurities.

Pure phase doped materials were also synthesized utilizing techniques discussed in the previous sections. Of the aforementioned materials if there are three sections the top picture is the current maximum pure material. The second section shows a composition above the solubility limit of the dopants forming a secondary impurity phase, denoted by stars in the above patterns. The third pane shows the pure phase composition the structure is closest to. If there are only two sections the solubility limit has not been currently reached.