MAXIMIZING STRAIN BEHAVIOR AND MINIMIZING LOSSES IN
TEXTURED PIN-PMN-PT PIEZOELECTRIC CERAMICS

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ABSTRACT

PbTiO$_3$-based perovskite ceramics represent a premier class of state-of-the-art materials used for piezoelectric applications such as actuators, high-power transducers, resonators, and ultrasonic motors. The high strain behavior and dielectric tunability of these materials also makes them highly competitive for sensor and hydrophone applications as well. The chemistries of next-generation materials are complex and their properties are highly sensitive to changes in processing which makes fabrication difficult. The greatest challenges to date are designing and processing materials that have high strain behavior as well as low dielectric and mechanical losses. In this document, new approaches to simplifying the manufacturing process, strategies for tailoring chemistry to reduce losses, and crystallographic texturing of ceramics for enhancing strain behavior are explored and discussed in detail. Finally, the intrinsic and extrinsic contributions to piezoelectricity of high-strain behavior textured ceramics are explored, setting the stage for a discussion of the development of the next-generation of high-performance piezoelectric ceramics.

The effects of CuO-doping on perovskite phase formation and reactive sintering of 28Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-40Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-32PbTiO$_3$ ceramics were investigated, and the densification kinetics were compared with conventionally sintered ceramics. CuO-doping was observed by in situ x-ray diffraction to accelerate perovskite and suppress pyrochlore formation. The 0.5 mol% CuO-doped PIN-PMN-PT ceramics sintered to $\geq$95% density at temperatures as low as 790 °C. Comparable densification kinetics were observed with both conventional and reactive sintering. In the final stage of sintering, reactive sintering reduced the activation energy from 616 kJ/mol to 382 kJ/mol due to formation of a uniform 26-33 nm crystallite size microstructure that formed in situ at the onset of densification.
Annealed reactively sintered ceramics also demonstrated equivalent ferroelectric behavior to conventionally sintered ceramics. The results demonstrate that reactive sintering is a novel approach to minimize material volatility during ceramic processing, an avenue for exploring co-firing with electrodes, as well as improved manufacturability through elimination of the perovskite powder synthesis step.

Relationships between sintering temperature and annealing atmosphere on microstructure and dielectric, ferroelectric, and piezoelectric properties of reactively sintered CuO-doped Pb(In\(_{1/2}Nb_{1/2}\))O\(_3\)-Pb(Mg\(_{1/3}Nb_{2/3}\))O\(_3\)-PbTiO\(_3\) (PIN-PMN-PT) ceramics were investigated. Uniform 2-3 μm grain size, dense CuO-doped PIN-PMN-PT ceramics were obtained when oxygen sintered versus a bimodal grain size microstructure when sintered in air. Oxygen sintered ceramics have excellent properties including piezoelectric coefficient \((d_{33})\) of 300-315 pC/N, coercive field \((E_C)\) of 7.7–8 kV/cm, and dielectric loss \((\tan \delta)\) < 1.5%. The MPB region was mapped for ternary compositions doped with 0.5 mol% CuO and sintered in O\(_2\). MPB 25PIN-40PMN-35PT demonstrated the maximum piezoelectric properties with \(d_{33}\) of 565+/−23 pC/N and \(k_p\) of 0.64+/−0.01. Sintering from 1050 °C to 1200 °C increased \(E_C\) from 8.5 to 11.5 kV/cm and reduced \(\tan \delta\) from 1.8% to 0.8% by facilitating diffusion of CuO into the lattice and creating domain wall pinning defect dipoles as evidenced by an increase in the internal field bias of \(P-E\) loops.

The effects of acceptor-doping with manganese as either MnO\(_2\) or MnNb\(_2\)O\(_6\) (MnN) with CuO on the dielectric, ferroelectric, and piezoelectric properties of PIN-PMN-PT ceramics were investigated. The 2% MnNb\(_2\)O\(_6\)-doped PIN-PMN-PT (6Pb(Mn\(_{1/3}Nb_{2/3}\))O\(_3\)-25Pb(In\(_{1/2}Nb_{1/2}\))O\(_3\)-34Pb(Mg\(_{1/3}Nb_{2/3}\))O\(_3\)-35PbTiO\(_3\)) ceramics possessed hard properties such as high coercive field \((E_C)\) of 11.7 kV/cm, low dielectric loss \((\tan \delta)\) of 0.7%, and
high electromechanical quality factor \((Q_M)\) of 1011. These properties were diminished in MnO\(_2\)-doped ceramics because of lower oxygen vacancy defect concentration, and exaggerated grain growth resulted in \(>20\) micron grain size. Co-doping with 2 mol\% MnNb\(_2\)O\(_6\) and 0.5 mol\% CuO retained hardened properties such as high \(E_C\) of 9.6 kV/cm, low \(\tan \delta\) of 0.6\%, and high \(Q_M\) of 1029. MnNb\(_2\)O\(_6\)-doped and MnNb\(_2\)O\(_6\)+Cu co-doped ceramics display excellent figures of merit for resonance and off-resonance applications as well as high energy conversion efficiencies which make them promising candidates for high-power transducer elements.

Mn-doped PIN-PMN-PT ceramics with 90\% [001]\(_C\) texture were textured by reactive templated grain growth (RTGG) with 5 vol\% high aspect ratio BaTiO\(_3\) microplatelets. The 2 mol\% Mn-doped textured ceramics possess hardened properties such as high coercive field \((E_C)\) of 14 kV/cm, low dielectric loss \((\tan \delta)\) of 0.37-0.66\%, and high \(Q_M\) of 496. Texturing suppressed permittivity variation near the TR-TT transition, and Mn-doping increased the \(T_C\) of textured PIN-PMN-PT from 212 °C to 219 °C relative to undoped PIN-PMN-PT. Textured Mn-doped ceramics have two times greater strain and low-field \(d_{33}^*\) of 846 pm/V than random ceramic. Rayleigh analysis of textured PIN-PMN-PT ceramics shows that Mn-doping reduces the extrinsic contribution of the piezoelectric response to the strain behavior from 38\% to 18\% (at 4 kV/cm) by reducing irreversible domain wall motion. Reduced irreversible domain wall motion is attributed to the formation of \(\text{Mn}_{Nb}^l - \text{V}_O^{*}\) defect dipoles that pin ferroelectric domains. Under low field conditions, domain pinning significantly reduced strain hysteresis from 29\% to 9\%. Mn-doping reduced the overall strain response of PIN-PMN-PT, but crystallographic texturing increased the intrinsic piezoelectric response of the lattice as evidenced by the increase in
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CHAPTER 1: Introduction

1.1 Statement of the Problem

The unique properties of piezoelectric ceramics, such as electric field-dependent strain behavior and the ability to interconvert electrical and mechanical energy, make them key components in complex applications involving precision actuation,\(^1\) acoustic transduction,\(^2\) and energy harvesting.\(^3, 4\) Early developments in piezoelectric materials focused on compositional and property exploration of PbZrO\(_3\)-PbTiO\(_3\) (PZT) ceramics, which have been standards in the field, and used reliably for civilian and navy SONAR applications.\(^5, 6\) Compositional exploration over several decades yielded many advances in state-of-the-art properties such as the emergence of solid solution chemistries of relaxor-ferroelectric Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) with PZT (PMN-PZT ceramics),\(^7\) and the development of single crystal compositions, such as Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PMN-PT),\(^8\) which have exceptional electromechanical properties. Ternary single crystal compositions, such as Pb(In\(_{1/2}\)Nb\(_{1/2}\))O\(_3\)-Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PIN-PMN-PT)\(^9\) and Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbZrO\(_3\)-PbTiO\(_3\),\(^10\) have improved single crystal performance by increasing low rhombohedral-tetragonal phase transition \(T_{R-T}\) and Curie \(T_C\) temperatures to \(\geq 90\, ^\circ\)C and \(\geq 180\, ^\circ\)C, respectively, and thus increase the temperature usage range and prevent depoling.

The relaxor-based single crystals, such as PMN-PT, PIN-PMN-PT, and PMN-PZT, set the standard in terms of maximum dielectric and electromechanical properties. High piezoelectric charge coefficients \(d_{33}\),\(^1\) > 1500 pC/N and high-strain behavior are observed for [001]\(_C\) poled single crystal compositions situated on the rhombohedral side of the
morphotropic phase boundary (MPB) region and at the MPB. High longitudinal electromechanical coupling coefficients \(k_{33} > 0.85\) are also observed due to the nature of the perfect crystal lattice which contributes to high energy conversion efficiencies. The significant property enhancements of single crystal technologies originate from the high degree of crystallographic anisotropy which maximizes non-centrosymmetric properties along the polar axis of the crystal.\(^1\)\(^{11}\) Despite the advancements in property developments, single crystal technology faces several significant challenges such as a lack of compositional uniformity, geometrical restrictions for devices, poor mechanical properties leading to chipping or cracking, and high cost of fabrication. Transducer devices fabricated with single crystals often require techniques such as “tiling” of multiple crystals together. This often necessitates growing multiple crystals because Ti\(^{4+}\) segregation along the length of the boule results in significant variation in dielectric, ferroelectric, and piezoelectric properties which makes material fabrication expensive.\(^{12}\)\(^{14}\)

Polycrystalline ceramics offer solutions such as improved compositional uniformity of powder batches, machinability for complex shapes, more robust mechanical properties, and significantly lower cost of fabrication than single crystals. However, the functional properties of randomly oriented polycrystalline ceramics are significantly lower than single crystals of the same composition due to the random orientation of grains in 3D space. For example, PIN-PMN-PT ceramic disks have piezoelectric charge coefficients \(d_{33}\) that range from 150 – 550 pC/N and planar electromechanical coupling factors \(k_p\) that range from 0.20 to 0.67 which are much lower than single crystals.\(^{15}\)\(^{17}\) Due to the random grain orientation distribution, the properties of ceramics are maximized by compositional tailoring around the MPB region (Figure 1-1) because the coexistence of
multiple crystal structures facilitates enhanced polarization rotation under an applied field, and as a result, improved electromechanical properties.\textsuperscript{18}

![Figure 1-1. Ternary PIN-PMN-PT phase diagram comprised of Pb(In\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3} (PIN), Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PMN), and PbTiO\textsubscript{3} (PT) perovskite ceramic components. The green line represents the approximate location of the morphotropic phase boundary (MPB) region which is estimated from the MPB end-member compositions of 63PIN-37PT and 68PMN-32PT as well as experimental data provided in the literature.\textsuperscript{15–17}}](image)

Crystallographic grain orientation, or texturing, is a proven solution to enhance the strain behavior and electromechanical coupling of bulk ceramics.\textsuperscript{19, 20} Ceramics are textured by controlling alignment along a common polar axis, known as fiber texture, through a process called templated grain growth (TGG).\textsuperscript{21} TGG technology takes advantage of the benefits of polycrystalline ceramics (i.e. low cost high volume production) while maximizing electromechanical properties. Textured PMN-PT ceramics have two
times improvement in strain behavior with high-field $d_{33}$ ($< 5$ kV/cm) ranging from 1150 to 1600 pm/V and electromechanical coupling factors ($k_p$) ranging from 0.75 to 0.85 which is a significant improvement relative to ceramic properties.\textsuperscript{22–24} Three important approaches to improve the piezoelectric properties of textured ceramics include careful compositional selection relative to the MPB, maximizing texture fraction, and improving the alignment quality.\textsuperscript{19}

While property enhancements quite obviously correlate with increased texture fraction and texture quality, significant processing challenges arise due to high temperatures ($> 1150$ °C) and long hold times ($> 5$ h) required for densification and grain growth. High temperature sintering leads to PbO volatility which makes controlling grain boundary and bulk chemistry significantly challenging and limits production of multilayered actuators requiring expensive electrode material.\textsuperscript{25–27} Cu-doping of PZT-based ceramics,\textsuperscript{26} PMN-PT,\textsuperscript{28} and PIN-PMN-PT\textsuperscript{29, 30} has been demonstrated by several authors to reduce the sintering temperature to $\leq 1050$ °C and enhance grain growth through liquid-phase sintering mechanism by formation of a PbO-CuO eutectic.\textsuperscript{31} However, sintering these ceramics to high densities and maximizing properties still involves extensive milling and calcination steps to fabricate fine perovskite powders which makes processing lengthy, expensive, and time consuming.

Despite the significant improvements in strain behavior and electromechanical coupling of polycrystalline ceramics through texture enhancements, controlling heat generation during piezoelectric actuation or ultrasonic drive at high vibration velocities remains a significant challenge.\textsuperscript{32, 33} Heat is generated during vibration as a result of dielectric and mechanical losses during piezoelectric drive which problematically depoles
the piezoelectric ceramic elements if the temperature rise of the transducer exceeds the Curie temperature of the elements. The two most widely studied strategies to address this issue involve (1) increasing the phase transition temperatures of materials through compositional modification and (2) reducing the amount of dissipated vibrational energy through chemical doping strategies by increasing the electromechanical quality factor ($Q_M$) and reducing dielectric loss ($\tan \delta$).\textsuperscript{34, 35} Furthermore, a high coercive field ($E_C$) is also required to minimize domain wall movement at high electric fields which reduces domain motion-related losses.\textsuperscript{36}

Acceptor-doping with manganese is one of the most widely studied methods to reduce $\tan \delta$, increase $Q_M$, and increase $E_C$; an approach termed piezoelectric hardening.\textsuperscript{37–40} The mechanism by which piezoelectric properties are hardened via manganese doping involves aliovalent substitution of Mn$^{2+}$ or Mn$^{3+}$ for higher valence cations on the $B$-site of the perovskite (i.e. Zr$^{4+}$, Ti$^{4+}$) which results in oxygen vacancy formation ($V_O^{**}$) for charge compensation.\textsuperscript{41} The oxygen vacancies are mobile and diffuse to the ferroelectric domain walls forming $Mn^{2+}_B - V_O^{**}$ defect dipoles that pin domain walls and raise the energy barrier to domain switching.\textsuperscript{42, 43} While acceptor doping effectively decreases dielectric losses, the contribution of domain wall motion to the piezoelectric response is lower leading to decreased strain behavior ($d_{33}$) and electromechanical coupling.\textsuperscript{35, 44}

Texturing of Mn-doped PMN-PT ceramics has been demonstrated as an effective method to increase the $d_{33}$ to $\geq 500$ pm/V, reduce dielectric loss ($\tan \delta$) $\leq 0.5\%$, and increase the electromechanical quality factor ($Q_M$) to $\geq 700$ which is necessary for achieving high vibration velocities in resonance applications.\textsuperscript{24} However, the relatively low rhombohedral-tetragonal phase transition temperature ($T_{R-T}$) of $\sim 75$ °C and Curie
temperature \((T_C)\) of \(~130\ \degree \text{C}\) of textured Mn-doped PMN-PT presents a significant risk to property degradation during temperature rise. Texturing of Mn-doped PMN-PZT ceramics improved the Curie temperature \((T_C > 200\ \degree \text{C})\), however, the coercive field \((E_C)\) is still relatively low \(<8\ \text{kV/cm}\).\textsuperscript{45,46} Textured PIN-PMN-PT ceramics have high strain behavior of \(d_{33} > 800\ \text{pC/N}\), improved \(E_C\) of \(>8\ \text{kV/cm}\), \(T_{R-T}\) of \(120\ \degree \text{C}\), and \(T_C\) of \(200\ \degree \text{C}\), however, dielectric loss is still high \((\tan \delta > 1\%)\) which limits their use for applications involving high vibration velocities.\textsuperscript{30,47}

Advancing the state-of-the-art in performance of high-power transduction and resonant vibration applications requires developing novel materials that possess multiple characteristics such as high phase transition temperatures over \(200\ \degree \text{C}\), high strain behavior of \(d_{33}^* \geq 800\ \text{pm/V}\), low \(\tan \delta \leq 1\%\), high \(Q_M \geq 500\), and high \(E_C \geq 10\ \text{kV/cm}\). The greatest challenge to pushing the boundary in materials properties lies in balancing strain behavior with loss mitigation and heat production. This dissertation presents a systematic approach to addressing this challenge by utilizing enhanced polarization rotation behavior near the MPB to enhance strain behavior, Mn/Cu doping and co-doping strategies to minimize dielectric and mechanical losses, and texture to enhance grain orientation to maximize electromechanical properties. Furthermore, processing routes are established that mitigate exposure of lead-based electroceramics to high temperature and simplify the manufacturing process of complex perovskite ceramics.
1.2 Scientific Approach

The Pb(In½Nb½)O₃-Pb(Mg½Nb²/₃)O₃-PbTiO₃ composition was selected for this dissertation work because it represents a current generation of piezoelectric ceramics being commercially produced for acoustic transduction applications, possesses high $T_{R-T} > 100$ °C and $T_C > 200$ °C, and excellent electromechanical properties in ceramic and single crystal form. Reactive sintering was explored to simplify the processing of PIN-PMN-PT ceramics by eliminating the perovskite powder synthesis step. The feasibility of this approach was investigated using the following approach:

- Elucidating the phase formation pathway and effect of CuO-doping on phase formation during reactive sintering of PIN-PMN-PT ceramics.
- Investigating the sintering behavior, grain growth, and microstructure development as a function of temperature, time, and atmosphere.
- Comparing the dielectric, ferroelectric, and piezoelectric properties of reactively sintered PIN-PMN-PT against conventionally sintered perovskite powders.

The effects of compositional variation of PIN-PMN-PT ceramics relative to the MPB on dielectric, ferroelectric, and piezoelectric properties were explored to identify promising compositions with high electromechanical properties for acceptor-doping.

- Identifying promising new chemistries near the MPB with enhanced electromechanical properties.
- Identifying the relationship between processing conditions, defect chemistry, and properties ($P_R$, $E_C$, tan δ, and $d_{33}$) of CuO-doped PIN-PMN-PT ceramics.
The PIN-PMN-PT composition with maximum electromechanical properties at the MPB was selected to:

- Explore effects of Mn-doping and Mn/Cu co-doping on key electrical properties.
- Investigate the relationship between the method in which acceptor dopant is introduced into the lattice (i.e. MnO$_2$ vs MnNb$_2$O$_6$) and defect chemistry.
- Assessing the figure-of-merit (FOM) of acceptor-doped PIN-PMN-PT ceramics for resonance and off-resonance applications as well as energy conversion efficiency.

The acceptor-doped PIN-PMN-PT composition with the highest FOM for resonance applications and greatest enhancement in key properties such as phase transition temperatures, strain behavior, $E_C$, tan $\delta$, and $Q_M$ was selected for reactive templated grain growth study to:

- Establish the effects of Mn-doping on ferroelectric properties, dielectric properties, and losses in PIN-PMN-PT ceramics
- Explore the effect of texture on strain behavior and electromechanical properties of Mn-doped PIN-PMN-PT ceramics.
- Quantify the effect of texture on the intrinsic contribution and Mn-doping on the extrinsic contribution of piezoelectricity to the strain response via Rayleigh analysis.
1.3 Organization of Dissertation

Reactive sintering of CuO-doped PIN-PMN-PT ceramics is discussed in Chapter 2. Since reactive sintering is a coupled process between phase formation and densification, the effects of CuO-doping on PIN-PMN-PT perovskite formation are discussed. Sintering kinetics are explored isothermally and via dilatometry experiments and are compared to conventional sintering of PIN-PMN-PT perovskite powder. The relationship between annealing time and key ferroelectric properties is also discussed.

Chapter 3 explores the densification and properties of oxygen sintered CuO-doped PIN-PMN-PT ceramics. The reactive sintering kinetics are shown to be enhanced in oxygen atmosphere. The effects of annealing time and atmosphere on microstructure development as well as dielectric, ferroelectric, and piezoelectric properties are also discussed. The changes in dielectric, ferroelectric, and piezoelectric properties with composition variation relative to the MPB were explored in detail. Finally, defect chemistry effects of copper substitution on the B-site of the perovskite lattice are discussed in terms of internal field bias and related effects on $E_C$, tan $\delta$, and $d_{33}$.

The effects of Mn and Mn/Cu-doping of PIN-PMN-PT ceramics on key properties for high-power transducer applications are discussed in Chapter 4. The implications of doping with MnO$_2$ or MnNb$_2$O$_6$ (where manganese is site balanced in the perovskite structure) are discussed in terms of crystallography, microstructure development, and electrical properties. The temperature and frequency dependence of dielectric loss is compared and discussed for undoped and Mn-doped chemistries. The applicability of
acceptor-doped PIN-PMN-PT chemistries for resonance and off-resonance conditions is also discussed and compared to PZT ceramic standards.

Chapter 5 investigates the effects of texture on the strain behavior of Mn-doped PIN-PMN-PT ceramics. Undoped and Mn-doped PIN-PMN-PT ceramics were templated using anisotropically shaped tetragonal BaTiO$_3$ microplatelets. Microstructure development during reactive templated grain growth is discussed, and the effect of platelet alignment on texture fraction is shown. Strain behavior was characterized and compared for undoped and Mn-doped compositions. Dielectric, ferroelectric, and electromechanical properties were investigated in detail and demonstrate that textured Mn-doped PIN-PMN-PT ceramics are promising candidate materials for high-power transduction, high frequency, and resonance applications. Finally, the different intrinsic and extrinsic contributions of the piezoelectric response to the strain behavior of textured ceramics are determined via Rayleigh analysis and discussed.

1.4 References


K. Song, Z. Li, H. Guo, Z. Xu, and S. Fan, “Compositional segregation and electrical properties characterization of [001]- and [011]-oriented co-growth Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ single crystal,” *J. Appl. Phys.*, 123 154107 (2018).


Y. Hosono, Y. Yamashita, H. Sakamoto, and N. Ichinose, “Dielectric and Piezoelectric Properties of Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$–Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ Ternary


29 J. Wu, Y. Chang, B. Yang, X. Wang, S. Zhang, Y. Sun, X. Qi, J. Wang, *et al.*, “Densification behavior and electrical properties of CuO-doped Pb(In$\frac{1}{2}$Nb$\frac{1}{2}$)O$_3$-Pb(Mg$\frac{1}{3}$Nb$\frac{2}{3}$)O$_3$-PbTiO$_3$ ternary ceramics,” *Ceram. Int.*, 42 [6] 7223–7229 (2016).

30 Y. Chang, B. Watson, M. Fanton, R.J. Meyer, and G.L. Messing, “Enhanced texture evolution and piezoelectric properties in CuO-doped Pb(In$\frac{1}{2}$Nb$\frac{1}{2}$)O$_3$-Pb(Mg$\frac{1}{3}$Nb$\frac{2}{3}$)O$_3$-PbTiO$_3$ grain-oriented ceramics,” *Appl. Phys. Lett.*, 111 [23] (2017).


Y. Chang, J. Wu, Y. Sun, X. Wang, S. Zhang, B. Yang, G.L. Messing, and W. Cao, “Enhanced electromechanical properties and phase transition temperatures in [001] textured Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ ternary ceramics,” *Appl.


CHAPTER 2: Low Temperature Reactive Sintering of CuO-doped PIN-PMN-PT Piezoelectric Ceramics

2.1 Introduction to Piezoelectric Ceramic Chemistries & Sintering

Ternary relaxor-based ferroelectrics, such as Pb(In\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}-Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3} (PIN-PMN-PT), are leading candidates for next-generation piezoelectric applications. The higher rhombohedral-tetragonal phase transition temperature ($T_{r-t} > 100$ °C) and Curie temperature ($T_C > 180$ °C) of the ternary PIN-PMN-PT system makes it better suited than binary systems, such as Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3} (PMN-PT), for applications where in-service electromechanical property degradation due to heating is an issue.\textsuperscript{1,2} While there has been considerable improvement in the properties of PIN-PMN-PT through compositional exploration along the rhombohedral side of the morphotropic phase boundary (MPB) region, lead-based electroceramics still face considerable materials processing challenges due to high temperature sintering requirements. For example, sintering requires temperatures as high as 1250 °C and hold times as long as 6 h to achieve dense ceramics and desirable electromechanical properties.\textsuperscript{3} Sintering at temperatures $\geq$1050 °C results in PbO volatilization (~0.5 – 1 wt%),\textsuperscript{4} which increases substantially at temperatures $\geq$1250 °C (~3 – 5 wt%),\textsuperscript{5} which makes controlling the bulk and grain boundary chemistry problematic. High sintering temperatures also limit the development of multilayer actuators because only expensive platinum electrodes can be used. Furthermore, sintering of perovskite powders requires complex and time-consuming powder synthesis steps involving separate calcination and milling to prepare sub-micron
particle size, phase pure perovskite powder. Because of the high temperature and long calcination times, stoichiometry control can be challenging due to PbO volatilization.

Copper oxide doping has been shown to reduce the sintering temperature of lead-based perovskite ceramics. Corker et al. first demonstrated that the sintering temperature of PZT (commercial composition near the MPB region) was reduced from 1260 °C to 850 °C by addition of ~4.5 mol% (3 wt%) of Cu$_2$O/PbO with the eutectic ratio (1:4 molar ratio of Cu$_2$O to PbO) to a 1.1 μm median particle size PZT powder. The significant reduction in sintering temperature was attributed to the formation of a Cu$_2$O-PbO eutectic liquid at 680 °C. However, a residual copper oxide/lead oxide rich grain boundary phase reduced the electromechanical properties of the sintered PZT.$^6$ CuO has been demonstrated to reduce the sintering temperature by as much as 300 °C in several other lead-based perovskite systems such as 85Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$-2Pb(Mg$_{0.33}$Nb$_{0.67}$)O$_3$-13Pb(Zn$_{0.33}$Nb$_{0.67}$)O$_3$, $^7$ 65Pb(Zr$_{1-x}$Ti$_{x}$)O$_3$-35Pb(Ni$_{0.33}$Nb$_{0.67}$)O$_3$, $^8$ and 26Pb(In$_{0.5}$Nb$_{0.5}$)O$_3$-40Pb(Mg$_{0.33}$Nb$_{0.67}$)O$_3$-34PbTiO$_3$. $^3$ The reduction in sintering temperature in these systems was linked to the eutectic liquid formed between PbO and CuO (i.e. 78 mol% PbO and 22 mol% CuO) at ~ 790 °C. $^9$ From TEM microstructural studies of 10 mol% CuO-doped 65Pb(Zr$_{0.42}$Ti$_{0.58}$)O$_3$-35Pb(Ni$_{0.33}$Nb$_{0.67}$)O$_3$, Kim et al. proposed that a PbO/CuO-rich grain boundary phase formed during sintering at 900 °C and they showed that nanosize monoclinic CuO precipitates on the grain boundaries during cooling.$^{10}$ Wu et al. observed that the sintering temperature of 26PIN-40PMN-34PT ceramics was reduced from 1250 °C to 960 °C with 4 mol% (1 wt%) CuO dopant, and the grain size decreased as dopant concentration increased. The greatest enhancement in the ferroelectric and electromechanical properties of CuO-doped 26PIN-40PMN-34PT ceramics was observed
with 1 mol% (0.25 wt%) CuO. When applied to textured 28PIN-40PMN-32PT ceramics, Chang et al. found that CuO-doping increases densification, grain growth, and texture fraction, and that maximum ferroelectric and electromechanical properties (except for $k_p$) were observed for 0.5 mol% (0.125 wt%) CuO.11

Reactive sintering, which involves starting with the constituent metal oxides, is a well-known approach to lower the sintering temperature. A major advantage of reactive sintering is that calcination and re-milling steps to synthesize the final phase are eliminated because both phase transformation and densification occur in the same sample. Kwon et al. showed that reactive sintering decreases the sintering temperature of PMN-PT by the in situ formation of a very fine, high driving force perovskite powder.12 Reactive sintering has been demonstrated in other materials systems such as YAG (Y$_3$Al$_5$O$_{12}$) where Kupp et al. demonstrated that the starting particle size of the individual metal oxides has a significant effect on both in situ phase transformation and densification kinetics.13 During reactive sintering of lead-based perovskites, it is also important that in situ phase formation results in 100% perovskite. Swartz et al. demonstrated that adverse pyrochlore phase formation can be mitigated in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ with the Columbite process in which MgNb$_2$O$_6$ (Columbite) is used as a reactant instead of the individual metal oxides.14

The motivation for this investigation is to demonstrate that the manufacturability of bulk-processed lead-based piezoelectric ceramics can be simplified by reactive sintering. We explored the effects of combining CuO-doping and reactive sintering to lower the sintering temperature of 0.28Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-0.40Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.32PbTiO$_3$ (28PIN-40PMN-32PT) ceramics and compare these results to conventional sintering. The 28PIN-40PMN-32PT was studied because it resides on the rhombohedral side of the morphototropic
phase boundary (MPB) and has been shown to possess excellent electromechanical properties. Since phase formation and densification are coupled processes in reactive sintering, the effects of CuO-doping on PIN-PMN-PT perovskite phase formation are first presented. Samples were doped with 0.5 mol% (0.125 wt%) and 1 mol% (0.25 wt%) CuO because these concentrations result in the maximum ferroelectric and electromechanical properties and significantly reduced the sintering temperature of CuO-doped 28PIN-40PMN-32PT ceramics. We show that CuO promotes PIN-PMN-PT perovskite phase formation and suppresses pyrochlore formation during reactive sintering and reduces the activation energy for sintering. Reactive sintering of CuO-doped PIN-PMN-PT perovskite powders resulted in slightly higher densities (98.1 +/- 0.3% dense) than conventional sintering (97.2 +/- 0.4% dense) as well as faster sintering rates and greater total shrinkage. Reactively sintered and annealed ceramics have comparable ferroelectric property performance as conventionally sintered ceramics of the same composition while providing the advantage of eliminating the powder synthesis step.

2.2 Materials and Methods

We investigated the effect of CuO addition on the phase formation of PIN-PMN-PT perovskite in mixtures of simple metal oxides, MgNb$_2$O$_6$ and InNbO$_4$. InNbO$_4$ powder was synthesized by mixing and vibratory milling In$_2$O$_3$ (median particle size $D_{50} \sim 50$ nm, 99.99%, Santech Materials, Changsha, Hunan, China) and Nb$_2$O$_5$ ($D_{50} \sim 100$ nm, 99.9%, H.C. Starck, Newton, MA) in ethanol for 72 h using a 1:1:1 mass ratio of spherical 3 mm, 5 mm, and 10 mm diameter YSZ media. Powder mixtures were dried, crushed, ground, and calcined at 925 °C for 3 h to produce phase pure InNbO$_4$ with a $D_{50}$ of 300 nm. Powder
mixtures of the composition 28PIN-40PMN-32PT were prepared by mixing PbO(II) (D$_{50}$ ~ 7 μm, 99.9%, Alfa Aesar, Ward Hill, MA), InNbO$_4$ (D$_{50}$ ~ 300 nm), MgNb$_2$O$_6$ (D$_{50}$ ~ 400 nm, 99.9%, H.C. Starck, Newton, MA), TiO$_2$ (D$_{50}$ ~ 25 nm, 99.5%, Evonik Aeroxide P25, Addison, IL), and CuO (D$_{50}$ ~ 40 nm, 99.99%, Sigma Aldrich, Milwaukee, WI) in ethanol and vibratory milling for 96 h. The milled powder mixtures were dried, ground in a mortar and pestle, and sieved to <88 μm (~170 mesh sieve).

Phase formation was studied \textit{in situ} using a Siemens D5000 diffractometer with CuK$_\alpha$ radiation and a calibrated high temperature stage to investigate the reaction pathway as a function of temperature. Samples for \textit{in situ} diffraction were prepared by mixing the reactive powder mixture with ethanol and then dispensing the powder suspension onto a 1.5 x 1.5 cm$^2$ alumina substrate to create a several hundred micrometers thick sample. Scans were first collected at 30 °C, and then the samples were heated to 500 °C at 60 °C/min in air using a hot stage and diffraction scans were collected from 500 °C to 775 °C in intervals of 25 °C, followed by a final scan at 30 °C after cooling. The 2θ range of the XRD scans was limited to 26 - 34° to capture the primary peaks of the constituent metal oxides and the primary peaks of the perovskite phases.

We studied the effect of CuO on conventional sintering (C.S.) of PIN-PMN-PT perovskite powder using linear dilatometry (Shimadzu TMA-50 Thermomechanical Analyzer) to establish a baseline for comparison with the reactively sintered (R.S.) powders of the same composition. Powders chosen for conventional sintering included an undoped 28PIN-40PMN-32PT composition, (D$_{50}$ = 0.3 μm, Penn State Applied Research Lab, Freeport, PA) and a 0.5 mol% CuO-doped 28PIN-40PMN-32PT composition fabricated in-house from mixed metal oxides as previously described (D$_{50}$ = 0.4 μm). The powder
was vibratory milled 48 h, calcined at 750 °C for 2 h, vibratory milled 48 h, and sieved to <88 μm (-170 mesh sieve). Samples were prepared by uniaxially pressing undoped and CuO-doped perovskite and reactive powder mixtures into green body pellets at 60 MPa followed by cold isostatic pressing at 200 MPa. The perovskite powders pressed to relative green densities of 55 ± 2%, and reactive powder mixtures pressed to relative green densities of 45 ± 4%. The relative density of the reactive powder samples was calculated using a theoretical density of ~7.34 g/cm³ as calculated from the densities and volume fractions of the metal oxide components (PbO, InNbO₄, MgNb₂O₆, TiO₂). Cylindrical samples of 6 mm in diameter by 3 mm tall were placed between platinum foils for TMA experiments.

Samples for isothermal studies were prepared by uniaxially pressing perovskite and reactive powder mixtures into discs of approximately 13 mm in diameter by 1 mm at 10 MPa and then cold isostatic pressing at 200 MPa to green densities of 58 ± 3%. The green density was determined from the geometry of the pressed pellets. Samples were placed on a powder bed of 1 – 2 μm PIN-PMN-PT embedding powder and heated in separate 54 x 38 x 20 mm alumina crucibles. Samples heated for > 8 min were covered with alumina lids to minimize lead volatility, and samples heated for less than 8 min were left uncovered to allow for rapid temperature equilibration. Sintering kinetics were monitored by heating samples in a box furnace at 10 °C/min in air from 700 °C to 900 °C for up to 18.3 h before thermal quenching. Pellets were lightly polished and analyzed by x-ray diffraction (XRD, PANalytical™ Empyrean Xpert Pro MPD diffractometer, The Netherlands). Grain size analysis was performed using linear intercept rule according to ASTM E112-10 standard
2.3 Results and Discussion

2.3.1 Phase Formation

XRD patterns of the undoped PIN-PMN-PT precursor powder are shown as a function of temperature from 500 °C to 775 °C in Figure 2-1 where the first and last scans are room temperature diffraction scans taken before and after heating, respectively. At room temperature, the diffraction peaks correspond to the initial reactant powders. From 500 °C to 600 °C intermediate phases and disordered perovskite phases nucleate and form phases with overlapping, broad diffraction peaks. By 650 °C a high PbTiO$_3$-content tetragonal PIN-PMN-PT perovskite phase forms, as indicated by the (101)/(110) splitting at 31.2 and 31.8° 2θ. By 700 °C the residual PbO and Columbite precursor phases (i.e. InNbO$_4$ and MgNb$_2$O$_6$) have completely reacted as judged by XRD. The result is a mixture of pyrochlore and perovskite phases that subsequently reacts at 725 °C to form a single-phase PIN-PMN-PT perovskite powder which shifts from a tetragonal to rhombohedral crystal structure. A minor amount of a pyrochlore (Pb$_3$Nb$_2$O$_8$) phase remains until 775 °C as indicated by the small peak at 29.0° 2θ.
In the final stage of the perovskite formation reaction, the observed tetragonal to rhombohedral structural transition is controlled by the diffusion path distance of the cations which is dependent on the sizes of the initial reactant powders. In situ diffraction of the formation of the PIN-PMN-PT perovskite shows that the PIN component readily forms, along with a tetragonal perovskite structure, and as the PIN phase content diminishes, the perovskite crystal structure phase gradually becomes rhombohedral. Assuming homogeneous distribution of the oxides, the large size difference between the 300 nm InNbO$_4$ and 400 nm MgNb$_2$O$_6$ powders compared to the 25 nm TiO$_2$ powder suggests that as interdiffusion occurs between the different oxides and PbO, compositionally and structurally graded particles may form. Continued heating results in complete reaction of the rhombohedral perovskite phase.
The diffraction patterns of the 0.5 mol% CuO-doped powder are shown Figure 2-2. When CuO is added to the system, the perovskites begin to form at \( \sim 575 \, ^\circ C \), or 25 \( ^\circ C \)-50 \( ^\circ C \) lower than in the undoped powder. By 625 \( ^\circ C \) the precursors are consumed, resulting in a mixture of pyrochlore, PIN, and PIN-PMN-PT. At 650 \( ^\circ C \) the (110) peak of the PIN phase decreases, and the powder consists of tetragonal PIN-PMN-PT and a residual pyrochlore phase. Further heating shifts the structure of the perovskite solid solution from tetragonal to rhombohedral at 700 \( ^\circ C \), and the pyrochlore phase is eliminated by 750 \( ^\circ C \). CuO effects the reaction pathway by first stabilizing the tetragonal structure of the PIN-PMN-PT perovskite at a lower temperature (650 \( ^\circ C \)) which undergoes a structural transition to the rhombohedral phase by 700 \( ^\circ C \). XRD patterns shown in Figure 2-3 show that CuO-doping decreases the concentration of second phase pyrochlore relative to undoped PIN-PMN-PT at 725 \( ^\circ C \) and eliminates pyrochlore by 750 \( ^\circ C \). A small peak at 28.08° 2\( \theta \) at 750 \( ^\circ C \) corresponds to low concentration of residual PbO.
Figure 2-2. In situ x-ray diffraction of 0.5 mol% CuO-doped PIN-PMN-PT during heating at 60 °C/min from 500 °C to 775 °C in air.
Figure 2-3. *In situ* XRD of undoped and 0.5 mol% CuO-doped PIN-PMN-PT powder heated at 725 °C (Top) and 750 °C (Bottom). The diffraction patterns show that CuO-doping decreases the concentration of second phase pyrochlore during heating.

The x-ray diffraction spectra provide a good overall depiction of the phase development, but a more quantitative analysis is needed to better determine the impact of CuO-doping on the formation of complex perovskites. Rietveld refinement provides an
approach to quantitatively determine the concentration of phase fractions as a function of temperature as well as the lattice parameters of the developing phases for undoped and CuO-doped PIN-PMN-PT powders. However, the highly disordered nature of the intermediate structures and the unknown site occupancies of the A-site and B-site cations made it exceedingly difficult to perform the Rietveld refinement. Additional information such as the compositions of the intermediate phases is needed to compliment the structural information to enable a more quantitative analytical comparison to further understand the effects of CuO on phase development.

While it is not currently known why CuO increases the reactivity of the precursors, it is possible that during solid state reaction the CuO has a similar effect as excess MgO in accelerating the pyrochlore to perovskite conversion during calcination.\textsuperscript{14,16} During the calcination of PMN and PMN-PT below 800 °C, PbO and the mixed metal oxides react to form lower density (~7.58 g/cc), B-site deficient compounds such as pyrochlores (Pb\textsubscript{3}Nb\textsubscript{2}O\textsubscript{8}). Pb\textsubscript{3}Nb\textsubscript{2}O\textsubscript{8}-type pyrochlores have a lower-density arrangement of cations on the B-site of the pyrochlore crystal structure than B-site rich pyrochlores such as Pb\textsubscript{3}Nb\textsubscript{4}O\textsubscript{13}. Cations, such as Mg\textsuperscript{2+}, are then capable of diffusing through regions created by low atomic packing on the B-site and relatively large interatomic separation distances between the niobium and oxygen atoms. With increasing MgO content the rate of pyrochlore to perovskite conversion increases indicating the final perovskite concentration is kinetically controlled by the local packing arrangement of metal oxides supplying B-site cations during the reaction. Since Mg\textsuperscript{2+} and Cu\textsuperscript{2+} have similar atomic radii of 0.072 nm and 0.073 nm, respectively, it is reasonable to expect that Cu\textsuperscript{2+} acts similar to Mg\textsuperscript{2+} during the lower temperature solid state reaction of PIN-PMN-PT.
2.3.2 Conventional Sintering of PIN-PMN-PT Perovskite Powder

Samples were heated at 10 °C/min to 750 °C and held for 1 min before applying different heating rates because this is the temperature at which perovskite formation is complete in the reactively sintered samples. The linear shrinkage at 20 °C/min in Figure 2-4-(a), was converted to the relative density data in Figure 2-4-(b) using Equation 2-1 where $\rho(t)$ is the density as a function of time, $\rho_f$ is the final sintered density, $L(t)$ is the sample length as a function of time, and $L_f$ is the final sample length. The data for the reactively sintered samples in Figure 2-4-(b) are presented for >750 °C because that is when the samples are 100% perovskite and thus the theoretical density is known.

$$\rho(t) = \left(\frac{L_f}{L(t)}\right)^3 \rho_f$$

Equation 2-1.
Figure 2-4. (a) Linear dilatometry and (b) relative density as a function of temperature during conventional sintering (C.S.) of undoped and 0.5 mol% CuO-doped PIN-PMN-PT perovskite powder and reactive sintering (R.S.) of undoped, 0.5 mol% CuO-doped, and 1 mol% CuO-doped PIN-PMN-PT heated at 20 °C/min in air.

During conventional sintering of undoped PIN-PMN-PT perovskite powder, only samples heated at 20 °C/min resulted in >95% dense ceramics. The lower heating rate data is shown in Figure 2-5 for conventional sintering of undoped and 0.5 mol% CuO-doped perovskite powders, and in Figure 2-6 and Figure 2-7 for reactive sintering of undoped, 0.5
mol%, and 1 mol% CuO-doped powders. Figure 2-4-(b) shows that the perovskite powder does not sinter well below 1000°C and requires \( \geq 1100 \) °C to achieve closed porosity (~92% density). All samples sintered to 96.1 +/- 1.7% density by 1150 °C. Slower heating rates (5 °C/min) (Figure 2-5) led to greater shrinkage at lower temperatures, but when the ceramics reached ~77% density the densification rate decreased. The reduced densification rate in the intermediate and final stages of sintering may be a result of reduced driving force for sintering because of powder coarsening under slower heating conditions.\(^{17}\) Above 80% density, faster heating rates (20 °C/min) led to faster shrinkage rates and increased relative densities of 98% density for 20 °C/min and 94% density for 5 °C/min.
Figure 2-5. (a) Linear dilatometry and (b) relative density as a function of temperature and heating rate during conventional sintering (C.S.) of undoped and 0.5 mol% CuO-doped PIN-PMN-PT perovskite powder in air.
Figure 2-6. (a) Linear dilatometry and (b) relative density as a function of temperature and heating rate during reactive sintering (R.S.) of undoped and 0.5 mol% CuO-doped PIN-PMN-PT in air.
Figure 2-7. (a) Linear dilatometry and (b) relative density as a function of temperature and heating rate during reactive sintering (R.S.) of 1 mol% CuO-doped PIN-PMN-PT in air.

The addition of 0.5 mol% CuO significantly enhanced the densification kinetics during conventional sintering. The average temperature at which 0.5 mol% CuO-doped
perovskite powder sintered to 92% density was 870 °C +/- 11 °C, or 235 °C lower, compared to 1105 °C +/- 22 °C for conventional sintering of the undoped perovskite powder. Conventionally sintered CuO-doped ceramics sintered to 97.2 +/- 0.4% density by 1150 °C. The densification behavior during conventional sintering was less sensitive to heating rate with CuO, however slower heating rates (5 °C/min) led to slightly reduced kinetics entering the final stage of sintering. Isothermal sintering kinetics shown in Figure 2-8-(a) demonstrate the enhanced kinetics at lower temperatures where CuO-doped perovskite powder samples sintered to 96% density at 790 °C after 6.7 h. The SEM micrograph in Figure 2-9-(a) shows that there is limited grain growth at low temperatures when sintered at 790 °C for 18.3 h.
2.3.3 Reactive Sintering of PIN-PMN-PT

All reactively sintered samples expanded as a result of the internal phase formation whereas no expansion was seen for the C.S. sample. In Figure 2-4-(a), the undoped R.S. sample expands by 8.6%. The onset of expansion corresponds to the formation of pyrochlore and disordered perovskite intermediate phases of low theoretical densities (i.e.
larger specific volume). The onset of shrinkage at ~720 °C is coincident with the completion of PIN-PMN-PT perovskite phase formation.

The reactively sintered perovskite powder (Figure 2-4-(b)) sintered to 92% density by 1095 °C +/- 12 °C on average for different heating rates. Final sintered densities of 93.8 +/- 0.3% were obtained at 1150 °C. These densities are lower than the conventionally sintered perovskite powder and is likely a result of the lower green density of the sample due to the volumetric expansion during the phase transformation. Sintering kinetics of the undoped reactively sintered perovskite are plotted in Figure 2-8-(b) for isothermal temperatures of 790 °C, 825 °C and 900 °C. Samples were only 90% dense when reactively sintered at 900 °C for 6.7 h (Figure 2-9-(b)).
Figure 2-9. SEM images of intergranular fracture surfaces of (a) 0.5 mol% CuO-doped PIN-PMN-PT conventionally sintered at 790 °C for 18.3 h (96% dense), and reactively sintered (b) undoped PIN-PMN-PT at 900 °C for 6.7 h (90% dense), (c) 0.5 mol% CuO-doped PIN-PMN-PT at 790 °C for 18.3 h (95% dense), (d) 0.5 mol% CuO-doped PIN-PMN-PT at 900 °C for 20 min (95% dense), and (e) 0.5 mol% CuO at 900 °C for 6.7 h (95% dense).
2.3.4 Reactive Sintering of CuO-doped PIN-PMN-PT

Doping with 0.5 mol% CuO reduced the expansion during phase formation relative to the undoped powder to 4.6%, and the onset temperature for densification was reduced from 720 °C to 675 °C. On average for all heating rates, 0.5 mol% CuO-doped PIN-PMN-PT ceramics reactively sintered to 92% density at 912 °C +/- 15 °C, which is a reduction in sintering temperature of 183 °C compared to the reactively sintered undoped perovskite powder. The average temperature at which ceramics reactively sintered to 92% density was 42 °C higher than conventional sintering of 0.5 mol% CuO-doped perovskite powder, however reactive sintering resulted in faster sintering rates and greater total shrinkage than conventional sintering. Unlike conventional sintering, slower heating rates did not appear to significantly impact the sintering rate with reactive sintering. Furthermore, final sintered densities of 98.1 +/- 0.3% were achieved by 1150 °C for all reactively sintered 0.5 mol% CuO-doped PIN-PMN-PT ceramics, which is slightly greater than the densities achieved by conventional sintering of the same composition.

During isothermal reactive sintering of 0.5 mol% CuO-doped PIN-PMN-PT the sintering kinetics were dramatically increased at lower temperatures compared to undoped PIN-PMN-PT (Figure 2-8-(c)). The length of time before the observed onset of densification for 0.5 mol% CuO-doped ceramics was greater for reactive sintering than conventional sintering at the same temperatures, however faster densification rates were observed during reactive sintering. Reactively sintered PIN-PMN-PT doped with 0.5 mol% CuO reached 95% density in as little time as 20 min at 900 °C and after 18.3 h at 790 °C. Figure 2-9-(c) shows that the 0.5 mol% CuO-doped PIN-PMN-PT reactively sintered at 790 °C for 18.3 h was 95% dense with a 1.4 μm grain size.
When the dopant level was increased to 1 mol% CuO, the expansion associated with perovskite phase formation was slightly greater (~5.5%) than the expansion observed for 0.5 mol% CuO. 1 mol% CuO-doped ceramics reactively sintered to 92% density at 886 °C +/- 22 °C and to 98.7 +/- 0.5% density by 1150 °C. PIN-PMN-PT densification kinetics were further enhanced relative to the 0.5 mol% CuO R.S. sample when doped with 1 mol% CuO as seen in Figure 2-8-(d) where closed porosity is rapidly achieved after only 1 min at 900 °C, and in 6.7 h at 790 °C. Previous investigations on the sintering of CuO-doped PIN-PMN-PT perovskite powder reported that ≥1 wt% (4 mol%) CuO is needed to lower the sintering temperature below 1000 °C. Here we have shown that the sintering temperature can be reduced to as low as 790 °C by combining reactive sintering and CuO-doping.

The average grain size, as determined by linear intercept, is plotted in Figure 2-10 as a function of relative density for samples sintered at 790 °C, 825 °C, and 900 °C. The undoped perovskite powder formed in situ coarsened from <0.5 μm to 2.5 μm and did not sinter above 90% density. In all CuO-doped cases, limited grain growth was observed during reactive sintering of PIN-PMN-PT. The limited grain growth may be a result of a CuO-based grain boundary phase that retarded grain growth by a solute drag mechanism.
The faster densification rates during reactive sintering is related to the size of the perovskite crystallites that form \textit{in situ} during heating. The Scherrer equation (Equation 2-2) was used to calculate the crystallite size ($d$) of the perovskite phase, where $\lambda$ is the wavelength of incident x-rays, $\beta$ is the FWHM of the (110) perovskite peak (the 100% peak for PIN-PMN-PT), $\theta$ is the Bragg angle, and $K$ is a shape factor assumed to be $\sim 1$.\textsuperscript{18,19} The x-ray diffraction patterns used in the analysis indicate that the perovskite formation reaction is complete, therefore we do not expect contributions from micro strain to the peak broadening due to thermal expansion mismatch of multiple phases. Furthermore, in the absence of an applied field, no contributions from ferroelastic domain walls due to differences in domain orientation with respect to spontaneous strain are expected.

\[
d = \frac{K \lambda}{\beta \cos \theta}
\]

Equation 2-2

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Figure 2-10. Grain size-sintered density trajectories for reactively sintered undoped, 0.5 mol% CuO-doped, and 1 mol% CuO-doped PIN-PMN-PT. Grain sizes reported within 95% confidence interval.
The average crystallite sizes for undoped and 0.5 mol% CuO-doped PIN-PMN-PT are 26 and 33 nm at the temperature at which the perovskite solid state reaction is complete, respectively. The crystallite size of the perovskite powder used for conventional sintering is also 26 nm. In contrast, SEM of the starting powder shows that the D50 particle size is ~300 nm which indicates that the powder particles are polycrystalline. This data suggests that the *in situ* formation of the perovskite phase during reactive sintering results in a uniform nanocrystalline microstructure at the onset of densification, while during conventional sintering the microstructure is initially composed of submicrometer polycrystalline particles with larger interparticle pores. Furthermore, the fine grain size in the presence of a liquid at high temperature can explain why reactive sintering of CuO-doped powders resulted in faster sintering rates and higher final densities than conventional sintering of the same composition despite the expansion that occurred during *in situ* formation of the perovskite phase.

### 2.3.5 Activation Energy Analysis

The activation energies for sintering were determined from the slope of an Arrhenius plot of $T \frac{d\rho}{dT}$ as a function of 1/T for different heating rates ($\dot{T}$) in Figure 2-11. The densification rate $\frac{d\rho}{dt}$ was determined as a function of temperature by plotting isodensity data for 90% relative density versus 1/T. This density was chosen to avoid contributions from particle rearrangement to the sintering shrinkage values that occur at <74% density. The activation energy for conventional sintering of 0.5 mol% CuO-doped PIN-PMN-PT perovskite powder is 616 kJ/mol as seen in Figure 2-11-(a), and reactive
sintering of the same composition reduced the activation energy to 382 kJ/mol as seen in Figure 2-11-(c). The activation energy for reactive sintering of undoped PIN-PMN-PT is 690 kJ/mol at 90% density (Figure 2-11-(b)) because grain growth reduces the driving force for densification as indicated by the 2.5 μm grain size at 90% density in Figure 2-10. Increasing the dopant concentration to 1 mol% CuO further reduced the activation energy for reactive sintering to 320 kJ/mol. Based on previous investigations of CuO-doped lead-based ceramics, we believe that CuO forms a liquid grain boundary phase below 800 °C due to the PbO-CuO eutectic at 790 °C that enhances mass transport.\(^3,9,10,11\) The lower activation energies with CuO-doping are attributed to the faster diffusion in the liquid grain boundary phase that forms between CuO and PbO and fine grain size retained into the final stages of sintering of PIN-PMN-PT. Grain growth in CuO-doped samples was suppressed presumably as a result of solute drag by the CuO-doped liquid.

It should be noted that the apparent activation energy, or Q value, should be viewed more as a “fitting parameter,” but is valuable in this case for comparative purposes.\(^20\) The data fit for reactively sintered undoped and 1 mol% CuO-doped PIN-PMN-PT in Figure 2-11(b) and Figure 2-11(d), respectively, had the highest R\(^2\) values of 0.95 indicating good fits to the data. The conventionally sintered 0.5 mol% CuO-doped perovskite powder in Figure 2-11(a) has an R\(^2\) value of R\(^2\) = 0.75 and the reactively sintered 0.5 mol% CuO-doped powder in Figure 2-11(c) is R\(^2\) = 0.88. It is assumed that the activation energy depends on only 1 mechanism, however, it may be possible that the deviation from linearity is a result of the different mechanisms active during slower heating rates. Slower heating exposes the samples to lower temperatures for much greater times. If different densification mechanisms are active in lower temperature regimes explored in this study, then this may
explain the nonlinearities observed here in the Arrhenius plot. Additionally, only one sample per composition per heating rate was measured. To improve the accuracy of the analysis, it is recommended that multiple data points be collected for each heating rate.

Figure 2-11. Arrhenius plots to estimate the activation energies at 90% density for (a) conventional sintering of 0.5 mol% CuO-doped PIN-PMN-PT perovskite powder, and reactive sintering of (b) undoped, (c) 0.5 mol% CuO-doped, and (d) 1 mol% CuO-doped PIN-PMN-PT.
Even though CuO doping significantly enhances the sintering kinetics of PIN-PMN-PT ceramics, it is unclear whether the copper and lead cations that form the eutectic liquid (~1:4 molar ratio of CuO:PbO) remain at the grain boundary or diffuse into the lattice. According to the \textit{in situ} diffraction data, there is either no free PbO left by 775 °C, or it is present in nearly undetectable amounts. This is not surprising because the powders used in this investigation were not prepared with excess PbO. However, if densification is facilitated by a PbO-CuO or PbO-Cu$_2$O eutectic in the absence of excess free PbO, then the Cu$^{1+/2+}$ is likely reacting with local A-site cations or possibly Pb$^{2+}$ cations terminating at the grain boundary. Therefore, the densification rate would be controlled by the rate of PbO and CuO dissolution or precipitation at the grain boundary. Furthermore, if the densification is assisted by a eutectic liquid, then the liquid would likely accumulate at the grain boundaries and triple pockets in the final stages of sintering. A more detailed analysis of grain boundary chemistry by HRTEM and/or x-ray photoelectron spectroscopy is needed to test this hypothesis.

\textbf{2.3.6 Ferroelectric Properties of Reactively Sintered Ceramics}

Ceramic disk samples of 0.5 mol% CuO-doped PIN-PMN-PT were prepared for ferroelectric property measurements by dry pressing, isothermally sintering in air, and polishing such that the diameter to thickness ratio was 10:1. Dupont 6160 silver paste was painted on the sample faces, air dried at 75 °C, and fired at 750 °C for 30 mins. Polarization versus electric field loops (P-E) were measured with a modified Sawyer-Tower circuit. The 0.5 mol% CuO-doped PIN-PMN-PT ceramics reactively sintered at temperatures as low as
790°C displayed ferroelectric behavior, however annealing steps were critical to tailoring the properties as seen in Figure 2-12. The coercive field \((E_c)\) when sintered at 790 °C for 18.3 h was 5.1 kV/cm, but increased to 7.0 kV/cm when annealed at 1050 °C for up to 8 h. Annealing also resulted in substantial increases in the remnant polarization \((P_r)\) to 32.8 μC/cm\(^2\). Annealing facilitates further enhancements in densification, diffusion of the elements, and removal of defects which all contribute to further enhancement in the ferroelectric properties.

Figure 2-12. Coercive field and remnant polarization of samples that were reactively sintered at 790 °C for 18.3 h and then annealed at 1050 °C for various times.

Figure 2-13 shows the polarization as a function of field for 0.5 mol% CuO-doped PIN-PMN-PT ceramics that were conventionally and reactively sintered at 1050 °C for 8 h. The coercive field is 7.9 kV/cm for reactively sintered ceramics and 8.3 kV/cm for conventionally sintered ceramics. The ferroelectric loops of ceramics sintered by these two methods are nearly equivalent which demonstrates that functional ceramics can be obtained.
by reactive sintering and have comparable ferroelectric property performance to ceramics fabricated by conventional sintering.

![Figure 2-13. Polarization as a function of applied electric field of 0.5 mol% CuO-doped PIN-PMN-PT ceramics that were conventionally and reactively sintered at 1050°C for 8 h.](image)

While conventional sintering and reactive sintering of CuO-doped PIN-PMN-PT ceramics have comparable densification kinetics and ferroelectric properties, additional factors must be considered when investigating the electrical property performance of these materials. As shown in the literature, many strategies have been reported for other ceramic lead-based perovskites for controlling stoichiometry and defect chemistry, such as PbO-doping and atmosphere control. Therefore, further investigation into the effect of annealing temperature and atmosphere on dielectric, ferroelectric, and piezoelectric properties are necessary to understand how to maximize properties in reactively sintered ceramics.
2.4 Conclusion

Reactive sintering of CuO-doped PIN-PMN-PT ceramics is a viable, one-step method for reducing the sintering temperature required for fabricating dense ceramics. CuO-doping facilitates rhombohedral perovskite phase formation in PIN-PMN-PT and reduces the formation of an intermediate pyrochlore second phase. The densification kinetics observed during reactive sintering were comparable to conventional sintering of the same composition and resulted in high sintered densities (97-98% dense). The faster sintering rates of reactive sintering of PIN-PMN-PT ceramics were attributed to the in situ formation of a nanocrystalline structure of 26-33 nm crystallites at the onset of densification that results in a high driving force for sintering. The addition of CuO reduces the activation energy for reactive sintering of PIN-PMN-PT ceramics presumably by forming a eutectic liquid phase with PbO that increases mass transport, retains a fine grain size into the final stage of sintering, and enhances densification kinetics at temperatures as low as 790°C. Reactive sintering provides a means to sinter ceramics at low temperatures and reduce exposure of the high surface area powder to high sintering temperatures and thus limit vaporization of volatile lead compounds. The ferroelectric properties of reactively sintered ceramics were also demonstrated to be equivalent to conventionally sintered ceramics, and when ceramics were reactively sintered at low temperatures the ferroelectric properties were comparable to those of conventional sintering after a post-processing thermal anneal. This is a remarkable finding because it provides a method for minimizing material volatility, an avenue for exploring co-firing with electrodes, and
improved manufacturability. Elimination of the calcination and re-milling steps also result in significant time, cost, and energy savings for the fabrication of this class of ceramics.

2.5 References


7. X. Chao, D. Ma, R. Gu, and Z. Yang, “Effects of CuO addition on the electrical responses of the low-temperature sintered Pb(Zr0.52Ti0.48)O3-Pb(Mg1/3Nb2/3)O3-Pb(Zn1/2Nb2/3)O3 ceramics,” J. Alloys Compd., 491, 698–702 (2010).


CHAPTER 3: Densification and Properties of Oxygen

Sintered CuO-doped PIN-PMN-PT Ceramics

3.1 Introduction

Lead-based electroceramics are an important class of functional materials used for piezoelectric actuators and ultrasonic drive applications because of their high strain behavior. One of the challenges in these applications is heat generation during drive which degrades functional properties and possible depoling of the active piezo elements. Several generations of materials have emerged to address this challenge by increasing the tolerance of functional properties to temperature rise by altering the solid solution chemistry to raise the phase transition temperatures.\textsuperscript{1, 2} One such example is the PIN-PMN-PT system which has higher rhombohedral-tetragonal phase transition temperatures ($T_{R-T} > 100 \, ^\circ C$) and Curie temperatures ($T_C > 200 \, ^\circ C$) than observed with binary PMN-PT. The ternary PIN-PMN-PT compositions also demonstrate higher coercive fields ($E_C > 7 \, kV/cm$) while maintaining comparable electromechanical performance (i.e. $d_{33} > 500 \, pC/N$, $k_p > 0.6$) to its binary counterpart.\textsuperscript{1, 3, 4}

Lead-based electroceramics require sintering temperatures of $\geq 1100 \, ^\circ C$ which results in volatility of certain constituents, such as PbO. Approaches to lower sintering temperature include the use of liquid phase additives/dopants such as Li$_2$O, CuO, or excess PbO.\textsuperscript{5–7} Several recent papers reported that CuO provides mutual benefits of enhanced sintering kinetics and improved ferroelectric properties by increasing the coercive field through Cu substitution on the B-site of the perovskite lattice. These enhancements were
observed at < 1 mol% CuO which avoided segregation of CuO on the grain boundaries and thus did not compromise ferroelectric and piezoelectric properties of the ceramics.8–10

Reactive sintering is another approach to reduce the sintering temperature of lead-based ceramics.11, 12 In a recent paper we reported that heating powder compacts of mixed metal oxides leads to the in situ nucleation of a nanocrystalline perovskite particles that have a high driving force for sintering and effectively eliminates the need to synthesize perovskite powder.13 Building on these findings, it is important to further understand the complex processing-structure-property relationships observed within CuO-doped ternary PIN-PMN-PT ceramics. This paper shows how sintering and annealing dense ceramics in air and oxygen affects microstructure development and the dielectric, ferroelectric, and piezoelectric properties. Since compositional selection relative to the morphotropic phase boundary (MPB) region is a necessary strategy for achieving high strain behavior for actuators and transducers,3 this paper also shows how the properties change with composition and structure relative to the MPB.

3.2 Materials and Methods

Powders of composition (60-x)PIN-40PMN-xPT where x = 32-37 were prepared for reactive sintering (RS) from simple metal oxides and columbite (MgNb2O6 and InNbO4) powders. The simple metal oxide powders included PbO (D50 ~ 7 μm, 99.9%, Alfa Aesar, Ward Hill, MA), and TiO2 (D50 ~ 25 nm, 99.5%, Evonik Aeroxide P25, Addison, IL). All compositions in this study contained 0.5 mol% CuO (D50 ~ 40 nm, 99.99%, Sigma Aldrich, Milwaukee, WI) to enhance sintering kinetics and electrical
properties, and 1 wt% excess PbO to compensate for PbO volatility during sintering. The
columbite powders (InNbO$_4$ ($D_{50} \sim 0.3$ μm) and MgNb$_2$O$_6$ ($D_{50} \sim 0.4$ μm) were each
prepared by vibratory milling In$_2$O$_3$ ($D_{50} \sim 50$ nm, 99.99%, Santech Materials, Changsha,
Hunan, China), MgO ($D_{50} \sim 0.6$ μm, Mallinckrodt Chemicals, Dublin, Ireland), and Nb$_2$O$_5$
($D_{50} \sim 100$ nm, 99.9%, H.C. Starck, Newton, MA) for 24 h in ethanol and calcined at 925
°C for 3 h and 1000 °C for 6 h, respectively. Matrix powder batches were vibratory milled
for 48 - 60 h in a 1 L Nalgene bottle with a 1:1:1 mass ratio of 3 mm, 5 mm, and 10 mm
YSZ ball media. Phase pure perovskite powders for conventional sintering (CS) were
prepared by calcining crushed powder batches of mixed metal oxides at 750 °C for 2 h. All
powders were crushed in a mortar and pestle and sieved to < 106 μm (-140 mesh).

The effect of sintering atmosphere on shrinkage was investigated using linear
dilatometry (Shimadzu TMA-50 Thermomechanical Analyzer). Cylindrical samples of 6
mm diameter by 3 mm tall were uniaxially pressed (40 MPa) followed by cold isostatic
pressing at 200 MPa. Green bodies were 58 +/- 0.5% dense for perovskite powders and 60
+/- 0.8% dense for reactive powders. For dilatometry experiments, samples were placed
between platinum foils and heated at 20 °C/min in air or oxygen (50 ml/min flow rate).

Samples were prepared for grain growth experiments by uniaxial pressing powders
into green bodies of 11 mm diameter by 2 mm thickness at 40 MPa and cold isostatic
pressing at 200 MPa for 3 mins. Samples were embedded in a closed alumina crucible with
twice the sample mass in 0.5 mol% CuO-doped PIN-PMN-PT embedding powder to
mitigate lead and copper loss. The effects of oxygen atmosphere on grain growth were
explored by sintering samples at 1050 °C in a tube furnace under 0.25 L/min flowing
oxygen. The effects of annealing in a quasi-static atmosphere environment were explored
by sintering in oxygen until fully dense (~12 mins at 1050 °C) and subsequently annealing in air in a box furnace for times ranging from 20 min to 5 days followed by air quenching. Average grain sizes were measured using line intercept rule and ImageJ analysis of scanning electron microscope (FEI Quanta 250 ESEM, ThermoScientific, Hillsboro, OR) images of fracture surfaces. Structure was characterized with x-ray diffraction (XRD, PANalytical Empyrean Xpert Pro MPD diffractometer, The Netherlands).

For electrical property measurements, sintered ceramics were polished with SiC grit paper to a diameter to thickness ratio of > 10:1. Samples were sonicated in acetone and methanol for 30 sec, air dried, and painted with silver electrodes using Dupont 6160 paste. Electrodes were air dried at 85 °C for 30 min and fired at 750 °C for 30 min. Samples were DC poled at 20-30 kV/cm for 15 mins at room temperature and aged for 24 h. Ferroelectric measurements were performed with a modified Sawyer-Tower circuit equipped with a Stanford Research Systems Model SR830 DSP Lock-In Amplifier. The piezoelectric coefficient (d_{33}) was measured on a Berlincourt d33 PiezoMeter System (Piezotest, UK) at 10 N at 110 Hz. Planar electromechanical coupling factor (k_p) and electromechanical quality factor (Q_m) were calculated from electrical impedance spectra measured using an Agilent 4294A Precision Impedance Analyzer. Dielectric measurements of poled samples were performed using an Agilent 4284A Precision LCR meter.

3.3 Results and Discussion

3.3.1 Effect of Atmosphere on Sintering

Sintering conditions were first analyzed by performing constant heating rate dilatometry under static air and 50 ml/min O_2 at 20 °C/min. Figure 3-1 compares the
shrinkage (Figure 3-1(A)) and densification (Figure 3-1(B)) for conventional sintering (CS) of 0.5 mol% CuO-doped PIN-PMN-PT perovskite powder and reactive sintering (RS) of mixed metal oxides. The onset of shrinkage for the perovskite powder begins at 600 °C, and the sintering rate decreases significantly at 815 °C when the powder compact reaches 90% relative density (% R.D.). The reactively sintered powder compacts expand at 600 °C as a result of the formation of low density (7.58 g/cc) pyrochlores (Pb$_3$Nb$_2$O$_8$) and disordered intermediate perovskites of PIN, PMN, and PT. The complete consumption of pyrochlores and intermediate perovskites by 700 °C indicates that the PIN-PMN-PT perovskite solid solution formation reaction is complete, and the onset of shrinkage is observed.$^{13}$ The relative density as function of temperature is only shown for temperatures > 700 °C when the PIN-PMN-PT perovskite phase formation is complete. Thus, the relative density of ceramics above 700 °C was determined relative to the theoretical density of 8.198 g/cc.
Figure 3-1. The effect of sintering atmosphere on (A) shrinkage and (B) densification during conventional and reactive sintering of 0.5 mol% CuO-doped 28PIN-40PMN-32PT ceramics. The highest final relative densities were observed when samples were sintered in flowing oxygen.
In all cases, oxygen sintering enhanced the sintering kinetics during final stage densification and increased final sintered densities. The effects of atmosphere on final densities were more pronounced during reactive sintering (96% R.D. in oxygen versus 94% R.D. in air in dilatometry experiments). Only a single sample was measured for the dilatometry experiments, however, isothermal sintering of 3-5 samples at 1050 °C for ≤30 min resulted in 99 +/- 0.7% dense ceramics in 0.25 L/min O₂ and 96 +/- 0.3% dense ceramics in air. The enhanced densification kinetics in oxygen is hypothesized to be the result of the removal of gas species such as nitrogen that have low diffusivity into the perovskite lattice in the final stage of sintering, thus pore closure in oxygen sintered samples is driven by diffusion of oxygen species and vacancies which ultimately resulted in higher sintering rates and densities >95% density.¹⁴ If pore closure is dependent upon elimination of gaseous species with low diffusivity into the lattice, then transitioning from air to oxygen upon entering the final stage of sintering should also enhance the final sintered densities. Further investigation is needed to test this hypothesis.

### 3.3.2 Grain Growth

Grain growth of conventionally and reactively sintered 0.5 mol% CuO-doped 28PIN-40PMN-32PT ceramics are shown in Figure 3-2 as a function of annealing time in air and oxygen. Samples were initially sintered in a tube furnace in 0.25 L/min flowing oxygen at 1050 °C for 12 min, and all samples were >99% of theoretical density. Both conventionally and reactively sintered ceramics have initial average grain sizes of 2-3 μm (Figure 3-3) and display similar grain growth behavior during the air anneal, however two different grain growth behaviors were observed during the microstructural evolution. The
kinetics data in Figure 3-2 can be divided into 2 distinct growth trends that correspond to the growth of equiaxed fine grains and a population of abnormally large, cubic shaped, and faceted grains that rapidly coarsen with time. After the initial sintering step, the volume fraction of large faceted grains is quite small but is 3 - 4x larger than the average matrix grain size. After annealing, the fine grains display normal grain growth behavior according to $G \sim t^{1/n}$, with grain size kinetics exponents ranging from $n = 3.8$ to $n = 4$, however, the growth rate of the large grains is much more rapid ($G \sim t^{1/3}$ to $\sim t^{1/2}$). SEM micrographs in Figure 3-3 show that after 2.5 h of annealing in air, the growth of abnormally large cubic grains dominates microstructure development. When ceramics were reactively sintered in oxygen and annealed in oxygen, only normal grain growth behavior was observed. Grain growth rates were significantly reduced in oxygen and increased according to $G \sim t^{1/12}$ with no signs of abnormal grain growth during the entirety of the thermal process as seen in Figure 3-3 (E) of ceramics annealed at 1050 °C for 10 h.
Figure 3-2. Grain growth kinetics for conventionally and reactively sintered powders show the difference in grain sizes and grain growth behavior between a population of equiaxed fine matrix grains and abnormally large faceted cubic grains. Abnormal grain growth behavior was not observed in samples sintered in oxygen.
Figure 3-3. SEM micrographs of 0.5 mol% CuO-doped 28PIN-40PMN-32PT ceramics that were (A) conventionally sintered and (B) reactively sintered at 1050 °C for 12 min in oxygen to 99% relative density with no anneal. (C) Conventionally sintered ceramics and (D) reactively sintered ceramics annealed in air for 2.5 h show the growth of abnormally large faceted grains with cuboidal morphology. (E) Reactively sintered ceramics annealed in oxygen for 10 h show a uniform grain structure with no abnormal grain growth.

The abnormal growth of matrix grains has been observed in other systems such as tungsten carbides, and PMN-PT. Recent work on the sintering of PZT\textsuperscript{15} and ferrites\textsuperscript{16} with
liquid phase additives has also shown bimodal grain size distributions or discontinuous grain growth behavior. In these cases, the authors attributed the difference in grain sizes to a heterogeneous distribution of the liquid phase. Early work by Yoon et al. on tungsten carbide ceramics observed that the conditions controlling normal grain growth of finely sized, equiaxed grains and abnormal grain growth (AGG) of large faceted grains in a cobalt liquid phase depends on the grain surface structure. In systems with a high volume fraction of liquid, faceted surfaces that undergo defect-assisted nucleation of step ledges grow rapidly to complete the ledge when the rate-limiting step to grain growth is controlled by the interface reaction.\textsuperscript{17} Similar results were observed by Wallace et al. in the sintering of PMN-PT ceramics with excess PbO liquid phase.\textsuperscript{18} Kang et al. summarized the thermodynamics and experimental work for interface control of grain growth. They showed that the grain growth rate can be divided by the driving force into linear (normal grain growth) and non-linear (abnormal grain growth) growth regimes. They attributed the change in growth behavior from normal grain growth to abnormal grain growth to the difference in the critical driving force for grain growth (\(\Delta g_c\)) and the maximum driving force (\(\Delta g_{\text{max}}\)) for growth of the largest grain.\textsuperscript{19}

The difference between the maximum and critical driving forces depends on the step free energy or the energy required to nucleate new atomic sites. Grain boundary energy has previously been discussed as being altered by a liquid phase, however dopants may also play a significant role. Seo and Yoon observed non-linear grain growth behavior in the sintering of MgO-doped PMN-PT ceramics. Their work showed that 0.5 wt\% excess MgO addition to PMN-35PT ceramics initiated abnormal grain growth, while no excess MgO addition resulted in normal grain growth. All ceramics were sintered in oxygen in
their work. In the absence of a liquid phase, growth of large cuboidal faceted grains was observed and attributed to MgO dopant altering the grain boundary surface energy.20

In our case, abnormal grain growth was observed when annealing in static air conditions, not oxygen. Diffraction spectra of the conventional and reactive as-sintered samples Figure 3-4 show a rhombohedral perovskite structure with a minor amount of PbO which corresponds to the 1 wt% excess PbO added to the powder batch during milling. The PbO remains after the sintering process, however, it disappears with 20 min anneal in air but not after 30 min in O2. This suggests that the rate of PbO volatility is greater in static air than in oxygen. PbO volatility in static air diminishes the number of A-sites in the perovskite structure, and as a result the associated B-site cations will not have sufficient charge and site balance to remain in the perovskite lattice. The reduction in Pb2+ filled A-sites will occur preferentially at the grain boundary, resulting in an accumulation of cations on the grain boundary that can no longer remain in the lattice. The segregation of B-site cations and metal oxide phases on the grain boundary alters the grain boundary surface energy and the presence of a CuO-based liquid phase enhances mass transport along the grain boundary leading to enhanced grain growth. PbO volatility drives local differences in perovskite chemistry that create a nonequilibrium process and sets the conditions for rapid growth of a small volume fraction of large grains grows at the expense of smaller grains. The CuO-based liquid at the grain boundary provides the mechanism by which rapid growth of the large grains occurs. It should also be noted that the growth of the large grains is nonuniform and may be related to the heterogeneous distribution of the CuO dopant. If the concentration of CuO is increased > 0.5 mol%, then it should increase the number of abnormal grains growing in the microstructure. The changing state of the grain
boundary has implications for dielectric, ferroelectric, and piezoelectric properties which will be described later. When annealing in oxygen, PbO volatility is suppressed which explains why normal grain growth was observed during the oxygen anneal.

Figure 3-4. XRD of 0.5 mol% CuO-doped 28PIN-40PMN-32PT ceramics reactively sintered and annealed in air and oxygen at 1050°C. The diffraction patterns shown that PbO is still present in the O\textsubscript{2} annealed samples however when samples were annealed in air no PbO was detected.

While the volatility of PbO creates a non-equilibrium state that drives the observed abnormal grain growth behavior, the onset of the abnormal grain growth is delayed by the presence of a liquid phase at the grain boundary. The presence of a liquid creates a solute drag effect that dominates grain growth kinetics early in the process, and the initial slow growth of faceted interfaces suggests that grain growth is controlled by the rate of diffusion
of cations through the liquid to perovskite lattice sites. As a faceted grain grows and increases its grain boundary surface area, the number of possible atomic sites for creating a new step ledge increases resulting in greater reactivity of the grain boundary. The increase in the interface reaction and step ledge growth at the grain boundary results in rapid growth of these large grains and substantially diminishes the total grain boundary surface area. This type of growth leads to a heterogeneous distribution of liquid that accumulates in local areas and restricts the growth of a smaller subset of grains resulting in bimodal grain growth behavior. While this explanation is plausible and based on the literature, a detailed TEM analysis is needed to test these ideas.

While the abnormal grain growth behavior is likely due to atmospheric related suppression of PbO volatility, the influence of additional constituents or contamination should not be ignored. Adair et al. showed that barium carbonate, formed during the processing of BaTiO$_3$ in water, leads to abnormal grain growth. The proposed mechanism is that incongruent dissolution of Ba$^{2+}$ from the surface of BaTiO$_3$ particles creates Ti-rich particle surfaces, and removal of CO$_3^{2-}$ species during sintering creates local BaO rich regions which create a liquid phase that enhances grain growth.$^{21}$

In this investigation, all processing was performed under nonaqueous conditions, however, static atmosphere conditions during sintering do contain low concentrations of CO$_2$ (~400 ppm). Furthermore, the ethanol solvent that the powder is milled in may leave trace carbon on the surface of the powder particles. If we consider the decomposition reaction of PbCO$_3$ $\leftrightarrow$ PbO + CO$_2$, Le Chatlier’s principle indicates that CO$_2$ present in the atmosphere will inhibit the decomposition of lead carbonate to PbO. If the conversion of lead carbonate to lead oxide is inhibited, then the supply of A-site cations to the perovskite
will be decreased and will inhibit the incorporation of B-site cations, such as copper, into the lattice. If liquid phase formers, such as copper, remain on the grain boundary, then the continuous presence of the liquid phase may promote abnormal grain growth. However, Ciomartan et al. determined experimentally using XRD, thermogravimetric analysis, and Raman spectroscopy that PbCO$_3$ decomposes fully to tetragonal PbO at > 400 °C even in static air.$^{22}$

While it is unlikely that carbon contamination from the milling process is unlikely to contribute to the abnormal grain growth observed in this study, several key experiments may be conducted to isolate any contribution of carbonate formation. If abnormal grain growth of PIN-PMN-PT is related to carbonate formation or retention due to CO$_2$ in the static air, then increasing the CO$_2$ during the static air anneal from ambient conditions (~4 x 10$^{-4}$ atm) to 0.01 or 0.1 atm should result in increased abnormal grain growth. If the nonaqueous milling conditions contribute to significant carbonate formation, then sintering and annealing in static O$_2$ should increase the abnormal grain growth relative to an environment of flowing O$_2$ because the concentration of CO$_2$ in the static environment will gradually increase.

### 3.3.3 Effect of Annealing Atmosphere on Dielectric, Ferroelectric, and Piezoelectric Properties

The dielectric, ferroelectric, and piezoelectric properties of reactively and conventionally sintered CuO-doped 28PIN-40PMN-32PT ceramics are shown in Figure 3-5 as a function of annealing time in air and oxygen at 1050 °C. The properties are
summarized in Table 3-1. Since samples annealed in air show abnormal grain growth after 2.5 h of annealing and the rate of change in properties is significantly lower, the properties of all samples annealed between 2.5 h and 10 h were averaged together for comparison. The properties of as-sintered ceramics display relatively “soft” properties such as relatively high piezoelectric coefficients and high dielectric loss. RS and CS as-sintered ceramics (no anneal) have piezoelectric coefficients \(d_{33}\) of 311 and 282 pC/N and dielectric loss (tan \(\delta\)) of 2.2 and 2.1%, respectively. RS and CS as-sintered ceramics also display comparable remnant polarization \(P_R\) of 34.6 and 34.1 μC/cm\(^2\) and coercive field \(E_C\) of 7.1 and 7.0 kV/cm, respectively. When ceramics were annealed in air, the remnant polarization, coercive field, piezoelectric coefficient, and dielectric loss decreased. RS and CS ceramics disks annealed in air for 2.5 to 10 h possessed average \(P_R\) of 31.5 and 31.9 μC/cm\(^2\), \(E_C\) of 6.2 and 6.3 kV/cm, \(d_{33}\) of 243 and 248 pC/N, and tan \(\delta\) of 1.8 and 1.7%, respectively. When ceramics were annealed in oxygen, no change was observed in \(P_R\) or \(d_{33}\) relative to the as-sintered state, however, the average \(E_C\) increased from 7.1 to 7.8 kV/cm and the dielectric loss of 1.5% was the lowest measured.
Figure 3-5. Change in (A) piezoelectric coefficient ($d_{33}$) and dielectric loss ($\tan \delta$) and (B) remnant polarization ($P_R$) and coercive field ($E_C$) as a function of annealing time and atmosphere at 1050 °C for reactively and conventionally sintered 0.5 mol% CuO-doped 28PIN-40PMN-32PT powders. Oxygen sintering and annealing of ceramics yields high $d_{33}$, suppresses $\tan \delta$, maximizes $P_R$, and increases $E_C$. 
Table 3-1. Properties of CuO-doped 28PIN-40PMN-32PT ceramics that were reactively sintered (RS) and conventionally sintered (CS) and annealed at 1050 °C in different atmospheres. Properties of air and O₂ annealed samples were averaged from all samples annealed between 2.5 and 10 h.

<table>
<thead>
<tr>
<th>Sintering Method</th>
<th>Anneal Conditions</th>
<th>$P_R$ ($\mu$C/cm$^2$)</th>
<th>$E_C$ (kV/cm)</th>
<th>$d_{33}$ (pC/N)</th>
<th>tan δ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive</td>
<td>No Anneal</td>
<td>34.6</td>
<td>7.1</td>
<td>311</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>31.5</td>
<td>6.2</td>
<td>243</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>34.5</td>
<td>7.8</td>
<td>307</td>
<td>1.5</td>
</tr>
<tr>
<td>Conventional</td>
<td>No Anneal</td>
<td>34.1</td>
<td>7.0</td>
<td>282</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>31.9</td>
<td>6.3</td>
<td>248</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Variation in the electrical properties when annealing in air can be explained by the observed bimodal grain growth behavior and heterogeneous microstructure development. In contrast, there is no abnormal grain growth when annealed in O₂ and the uniform microstructure minimizes property variation over the course of the anneal. The nature of the change in the properties when annealing in static air conditions is related to a reduction in B-site cation stability in the local perovskite structure at the grain boundary. When annealed in air, PbO volatility from the grain boundary reduces charge and site balance of the B-site cations in the perovskite structure. The reduction in B-site cation stability results in accumulation of cations at the grain boundary and promotes abnormal grain growth behavior. The growing grains accrue a type of “core-shell” structure in which the inner core of the grain maintains the stoichiometric perovskite chemistry. However, the shell of the growing grains is composed of an unstable perovskite lattice containing lead vacancies and enriched with B-site cations that prevents the CuO sintering aid from diffusing into the lattice and acting as an acceptor dopant. The result is a decrease in overall polarization due to reduction in Pb$^{2+}$, lower coercive field, lower piezoelectric coefficient, and greater dielectric losses due to the increased disorder.
Phase field modeling studies of polycrystalline materials showed that dielectric grain boundary phases “soften” the ferroelectric and electromechanical properties, and piezoelectric coefficients decreased as the grain boundary thickness decreased. When a grain boundary phase is present, such as PbO, a discontinuity in polarization is created at the non-ferroelectric grain boundary between two adjacent grains. The discontinuity results in a polarization gradient, or depolarization field, from within the bulk to the grain boundary. The depolarization field lowers the coercive field and enhances the piezoelectric coefficient by lowering the energy barrier to domain nucleation under an applied field.\textsuperscript{23}

The depletion of PbO from the grain boundary due to volatility during thermal anneal in air reduces the grain boundary thickness and associated depolarization field which rapidly diminishes the $d_{33}$. A TEM study of the grain boundaries of sintered PZN-based ceramics confirmed that an annealing process is sufficient to eliminate the dielectric PbO grain boundary phase, however annealed samples showed an increase in $d_{33}$ after anneal which the authors attributed to lead vacancies enhancing domain motion. Nevertheless, the authors demonstrated that Pb$^{2+}$ deficiency of 1 mol\% or greater is associated with significant reduction in piezoelectric coefficients of $\geq 30\%$.\textsuperscript{24} Studies of polycrystalline PZT films also suggest that diffusion of Pb$^{2+}$ cations to the grain boundary and corresponding diffusion of lead vacancies ($V_{Pb}^{\prime\prime}$) into the bulk at 600°C contributes to the formation of electric double layers near grain boundaries that partially pin domains and reduce the overall switchable polarization ($P_R$).\textsuperscript{25} This explains why after 1 h of anneal, the decline in $d_{33}$ slows and the $E_C$ and $P_R$ decline faster as PbO volatilizes from the from the bulk of the grains.
In contrast, when samples are annealed in oxygen the volatility of PbO is suppressed and $d_{33}$ over 300 pC/N are maintained. Maintaining the perovskite chemistry at the grain boundary provides a pathway for the aliovalent substitution of Cu$^{2+}$ cations into the lattice. The 6-fold coordinated B-site cations and their ionic radii ($r_i$) include Cu$^{2+}$ ($r_i = 0.073$ nm), Mg$^{2+}$ ($r_i = 0.072$ nm), In$^{3+}$ ($r_i = 0.080$ nm), Nb$^{5+}$ ($r_i = 0.064$ nm), and Ti$^{4+}$ ($r_i = 0.061$ nm). Based on relatively similar ionic radii of Cu$^{2+}$ and Mg$^{2+}$ and slightly smaller ionic radii of Cu$^{2+}$ than In$^{3+}$, it is reasonable to assume that copper will substitute onto the B-site of the perovskite lattice for magnesium and indium. Studies of CuO-doping of BaTiO$_3$ ceramics have also shown using electron paramagnetic resonance that Cu$^{2+}$ substitutes for Ti$^{4+}$ as well. Aliovalent substitution into the lattice for higher valence cations such as In$^{3+}$ and Ti$^{4+}$ creates oxygen vacancies for charge compensation that enhance the degree of “hard” piezoelectric properties which is why the coercive field increases and dielectric loss decreases. The remnant polarization is greater because of the reduced PbO volatility, and the uniform microstructure and mitigated accumulation of B-site cations on the grain boundary are why the properties are maximized when annealing in oxygen. Clearly, further analysis is needed to investigate the mechanisms that govern properties when annealed in different atmospheres.

In addition to changes in the grain boundary chemistry, the grain size of the microstructure may also play a role in piezoelectric property variation. Previous studies of PZT ceramics observed varying trends in grain size-property relationships where $d_{33}$ increased with grain size because the extrinsic piezoelectric response was maximized by increasing the domain size. However, the grain sizes investigated in these studies ranged from submicron to $< 10 \mu m$, and in contrast, some studies in BaTiO$_3$ ceramics with
grain sizes > 1 μm show a decreasing trend with increasing grain size.\textsuperscript{30,31} The reasons for the different observations are unclear but may be due to effects of space charge accumulation on the grain boundary, mechanical stresses, or chemistry/impurity effects of the precursor powders used for investigations.\textsuperscript{32} In addition to grain size changes, rapid growth of a small subset of grains ≥20 μm over the initial course of the annealing process (≤ 2.5 h) leads to redistribution of liquid grain boundary phases, and any grain boundary species present may effect significant changes in local polarizability, polarization rotation, and dielectric loss mechanisms. The variation in properties with annealing atmosphere and processing time at high temperature highlights the necessity to thoroughly understand how to control the grain size, grain boundary chemistry, and overall microstructure development of complex perovskite materials to maximize property performance.

Lead deficiency is often correlated with a reduction in dielectric losses and a crystallographic shift toward the tetragonal structure,\textsuperscript{33} however, x-ray diffraction analyses shown in Figure 3-6 suggest that PbO-deficiency related structural shifts are not contributing to changes in the properties in this study. After 20 min annealing in static air, the PbO is no longer detectable by XRD. The ceramics retain the rhombohedral perovskite structure when annealed for > 20 min. Since the c/a axis of the air-annealed remains unchanged, structural variations cannot account for the monotonic decrease in polarizability and electromechanical properties of the ceramic with annealing time in air. However, comparison of the (100) peaks indicate that the FWHM of the (002) peak decreases with anneal time indicating that microstructural variation results in increases in domain size when annealing in air and may be related to the associated increase in grain size.\textsuperscript{34}
Figure 3-6. XRD of 0.5 mol% CuO-doped 28PIN-40PMN-32PT ceramics conventionally (C.S.) and reactively (R.S.) sintered at 1050°C and annealed for 10 h in air. The diffraction spectra show no change in the crystal structure with annealing besides the removal of PbO.

### 3.3.4 Effects of Composition on Properties

In complex ternary perovskite materials, compositional selection relative to the morphotropic phase boundary is key for achieving desirable dielectric, ferroelectric, or piezoelectric properties. Compositional targeting on the rhombohedral ($R$) side of the MPB is desirable for achieving the $4R$ domain configuration which enhances polarization rotation, extension and ultimately improved electromechanical properties. PIN-PMN-PT compositions close to the MPB,\textsuperscript{35-37} and the sintering and electrical properties of CuO-
doped 26PIN-40PMN-34PT, which is on the rhombohedral side of the MPB, have been reported. However, due to the structural effects of acceptor-doping, the compositional space of CuO-doped PIN-PMN-PT ceramics was mapped to further understand how dielectric (T_{R-T} and T_C), ferroelectric, and piezoelectric properties change as a function of composition relative to the MPB. Since the $d_{33}$, $E_C$, and $P_R$ values were maximized when sintered and annealed in oxygen, all ceramics were sintered at 1050 °C for 30 min in flowing oxygen.

Figure 3-7 shows x-ray diffraction spectra of 0.5 mol% CuO-doped (60-x)PIN-40PMN-xPT ceramics where x = 32 – 37. When x = 32, the single peak at 45° 2θ represents the (002) peak of the perovskite structure indicating that the structure is rhombohedral. When the PbTiO_3 content is increased to x = 34 the (002) peak broadens as the composition approaches the MPB from the rhombohedral side of the phase boundary. At x = 35, the peak width increases substantially and begins to split as a result of the appearance of tetragonal structure which indicates that this is the MPB composition. The structure shifted toward the tetragonal side of the MPB when the PbTiO_3 content decreased to x = 36 and x = 37.
Figure 3-7. (A) XRD spectra of reactively sintered 0.5 mol% CuO-doped (60-x)PIN-(40)PMN-xPT ceramic compositions across the MPB where x = 32 – 37. (B) Enlarged view of the 45° 2θ peak of the diffraction spectra showing the peak splitting that occurs as the composition is shifted from the rhombohedral side (x = 32) to the tetragonal side (x = 37) of the MPB.

The shift in crystal structure with composition effects changes in the ferroelectric behavior as demonstrated by the polarization versus field (P-E) loops shown in Figure 3-8. It should be noted that the P-E loops were only measured up to 20 kV/cm because samples that were primarily of the tetragonal structure, such as 24PIN-40PMN-36PT and 23PIN-40PMN-37PT, experienced breakdown when $E > 20$ kV/cm. The coercive field ($E_C$) increased from 7.0 kV/cm at $x = 32$ PT to 10.5 kV/cm at $x = 37$ PT. The enhancement in coercivity is a result of the increase in the tetragonal PbTiO$_3$ concentration moving across the MPB. The remnant polarization ($P_R$) is greatest on the rhombohedral side and at the MPB and ranges from 33.3 μC/cm$^2$ to 35.8 μC/cm$^2$. When the structure is primarily
tetragonal, the $P_R$ decreases to 32.8 $\mu$C/cm$^2$ at $x = 36$ and 29.7 $\mu$C/cm$^2$ at $x = 37$. The difference in $P_R$ is explained by the fewer number of polarization directions along the $<001>$ in tetragonal and rhombohedral structures.\textsuperscript{38}

![Figure 3-8](image_url)

Figure 3-8. Ferroelectric loops of reactively sintered 0.5 mol% CuO-doped (60-x)PIN-40PMN-xPT ceramics as a function of Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$ and PbTiO$_3$ content where $x = 32$ - 37. $E_C$ increases with PbTiO$_3$ content as the composition becomes increasingly tetragonal.

Dielectric properties of poled samples are shown in Figure 3-9(A) as a function of temperature and composition. The tetragonal 23PIN-40PMN-37PT composition displays no significant changes in permittivity with temperature until the Curie temperature at $T_C = 226$ °C. When $x = 36$, the permittivity fluctuates at 100°C indicating the appearance of a rhombohedral-tetragonal phase transition ($T_{R-T}$) temperature and the Curie temperature decreases to $T_C = 225$ °C due to the minor rhombohedral phase present as the composition shifts toward the MPB. As the PbTiO$_3$ content decreases and the structure becomes
increasingly rhombohedral, the $T_{R-T}$ and $T_C$ gradually increase and decrease, respectively, to $T_{R-T} = 139 \, ^\circ C$ and $T_C = 207 \, ^\circ C$ at $x = 32$. The changes in structural phase transition and Curie temperatures are shown as a function of composition in Figure 3-9(B). As the amount of rhombohedral phase increases, the $T_{R-T}$ also becomes significantly more pronounced as a greater volume fraction of the material experiences large changes in overall polarizability during the transition to the tetragonal structure with heating. The MPB composition at $x = 35$ displayed the largest relative permittivity maximum $\varepsilon_{max}$ as well as the lowest dielectric losses which are effects of the enhanced polarizability as well as lower barrier to polarization rotation at the MPB. The dielectric and ferroelectric properties are summarized as a function of composition in Table 3-2.

Table 3-2. Ferroelectric and dielectric properties of 0.5 mol% CuO-doped PIN-PMN-PT compositions near the MPB. As the PIN/PT ratio decreases, the structure shifts toward the tetragonal side of the ternary phase diagram resulting in higher coercive field, greater relative permittivity, and increased Curie temperature.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$P_R$ (μC/cm²)</th>
<th>$E_C$ (kV/cm)</th>
<th>$\varepsilon/\varepsilon_0$</th>
<th>$\tan \delta$</th>
<th>$T_{R-T}$ (°C)</th>
<th>$T_C$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28PIN-40PMN-32PT</td>
<td>33.3</td>
<td>7.0</td>
<td>1115</td>
<td>0.022</td>
<td>139</td>
<td>207</td>
</tr>
<tr>
<td>27PIN-40PMN-33PT</td>
<td>35.8</td>
<td>7.4</td>
<td>1399</td>
<td>0.027</td>
<td>133</td>
<td>210</td>
</tr>
<tr>
<td>26PIN-40PMN-34PT</td>
<td>33.6</td>
<td>8.0</td>
<td>1848</td>
<td>0.025</td>
<td>119</td>
<td>213</td>
</tr>
<tr>
<td>25PIN-40PMN-35PT</td>
<td>35.8</td>
<td>8.5</td>
<td>2146</td>
<td>0.018</td>
<td>103</td>
<td>219</td>
</tr>
<tr>
<td>24PIN-40PMN-36PT</td>
<td>32.8</td>
<td>9.3</td>
<td>2444</td>
<td>0.022</td>
<td>100</td>
<td>225</td>
</tr>
<tr>
<td>23PIN-40PMN-37PT</td>
<td>29.7</td>
<td>10.5</td>
<td>3065</td>
<td>0.021</td>
<td>--</td>
<td>226</td>
</tr>
</tbody>
</table>
Figure 3-9. (A) Permittivity as a function of temperature for reactively sintered 0.5 mol% CuO-doped (60-x)PIN-40PMN-xPT ceramics as a function of Pb(In_{1/2}Nb_{1/2})O_3 and PbTiO_3 content where the ratio was varied by $x = 32 - 37$. (B) Change in phase transition temperatures as a function of composition showing that when the PbTiO_3 content decreases and the composition becomes more rhombohedral, the $T_{R-T}$ increases and the $T_C$ decreases.
The electromechanical properties of poled reactively sintered 0.5 mol% CuO-doped PIN-PMN-PT ceramics were measured using 3 – 4 samples per composition and are shown in Figure 3-10. On the rhombohedral side of the MPB at $x = 32$, the $d_{33} = 302 \pm 3.6$ pC/N and $k_p = 0.48 \pm 0.02$. The electromechanical properties increase closer to the MPB and were maximum ($d_{33} = 565 \pm 23$ pC/N and $k_p = 0.64 \pm 0.01$) at the MPB composition where $x = 35$. As the PbTiO$_3$ content increased to $x = 36$ and $x = 37$ the electromechanical properties began to decrease slightly but remained quite high. This indicates that there is a relatively wide range of compositional space near the MPB in which excellent electromechanical properties are measured with high strain behavior and electromechanical coupling ($d_{33} \geq 500$ pC/N and $k_p > 0.55$). The origin of the electromechanical enhancements near the MPB is attributed to increased polarization rotation and extension behavior facilitated by the coexistence of both rhombohedral and tetragonal phases. Based on the higher PbTiO$_3$ content of PIN-PMN-PT ceramics studied by Wu et al., increasing the PbTiO$_3$ content to $x > 37$ shifts the composition to the tetragonal side of the MPB and leads to adverse effects such as lower $d_{33}$ and $k_p$. Thus, the MPB composition provides superior electromechanical performance, and CuO-doping of near-MPB compositions effectively widens the composition space in which excellent properties are achieved which has not yet been reported in the literature.
Figure 3-10. Variation in $d_{33}$ and $k_p$ for 0.5 mol% CuO-doped (60-x)PIN-40PMN-xPT samples when the PbTiO$_3$ concentration (x) varies from x = 32 to 37. (Averages and standard deviations are presented for at least 3 samples per composition.) Compositions close to the MPB exhibit excellent electromechanical properties and are maximum at the MPB composition where x = 35.

3.3.5 Effect of Sintering Temperature on Properties at the MPB

Piezoelectric properties such as $d_{33}$ and $k_p$ were observed to be maximal at the MPB composition of 25PIN-40PMN-35PT. Ceramic samples of the MPB composition were reactively sintered at temperatures ranging from 1050 °C to 1200 °C and for times ranging from 30 min to 5 h under flowing oxygen and allowed to furnace cool. Figure 3-11 shows SEM images of the microstructures of samples which were all $\geq 99\%$ dense. The microstructures remained uniform with a relatively small grain size ($GS_{ave} = 3 \mu m$) as the sintering temperature increased from 1050 °C to 1200 °C. When the sintering time at 1150 °C increased from 30 min to 5 h, the microstructure coarsened to 7 μm.
Figure 3-11. SEM images of 0.5 mol% CuO-doped 25PIN-40PMN-35PT ceramics reactively sintered in oxygen at (A) 1100 °C for 30 min, (B) 1150 °C for 30 min, (C) 1200 °C for 30 min, and (D) 1150 °C for 5 h. The microstructure remained uniform with increasing sintering temperature, and sintering for longer time increased the average grain size from 3 μm to 7 μm.

As the temperature increased from 1050 °C to 1200 °C, $d_{33}$ decreased from 589 pC/N to 491 pC/N, $E_C$ increased from 8.5 kV/cm to 11.5 kV/cm, tan δ decreased from 1.8% to 0.8%, and $Q_M$ increased from 69 to 134. The formation of an internal bias field ($E_i$) was also observed, where the $P-E$ loops were biased towards higher fields with increasing temperature. The internal bias fields ($E_i$) were calculated by $E_i = (E_C^+ + E_C^-)/2$ where $E_C^+$ and $E_C^-$ are the positive and negative x-intercepts, respectively, of the ferroelectric loops. The internal bias field is negligible at $E_i = -0.047$ kV/cm for samples sintered at 1050 °C.
However, when the sintering temperature is increased to 1200 °C the magnitude of the internal bias field increases by an order of magnitude to \( E_i = +0.41 \) kV/cm. During microstructural coarsening at high temperature (1150 °C), the \( d_{33} \) decreased slightly from 515 to 502 pC/N, \( E_C \) decreased from 11.3 to 10.2 kV/cm, \( P_R \) increased from 35.2 to 38.2 μC/cm\(^2\), and tan \( \delta \) increased from 0.8% to 1.1%. The \( E_i \) also decreased slightly from +0.34 kV/cm to +0.16 kV/cm with increased sintering time. The \( k_p \) values of all samples ranged from 0.63 to 0.65 regardless of sintering time or temperature.

Figure 3-12 shows the change in \( d_{33}, E_C, \) and tan \( \delta \) as a function of internal bias field (\( E_i \)). The shift from “soft” to “hard” piezoelectric properties with increasing sintering temperature is the result of a complex and dynamic interplay between diffusion of species at the grain boundary and formation of lattice defects that are represented by \( E_i \). Increasing the sintering temperature facilitates diffusion of the copper cations into the bulk of the grains from the grain boundary where they accumulated in the later stages of liquid phase sintering. Copper cation substitution onto the B-site of the perovskite for higher valence cations such as In\(^{3+}\) or Ti\(^{4+}\) results in the formation of charge compensating oxygen vacancies \( V_O^{**} \). The interaction of oxygen vacancies with the anionic oxygen sublattice of the perovskite structure creates defect dipoles that diffuse to the domain walls and create local internal fields (\( E_i \)) which raise the energy barrier to ferroelectric switching.\(^{40}\) It is reasonable to assume that increasing \( E_i \) increases the degree of “hard” piezoelectric character by pinning the domain walls.
Figure 3-12. Coercive field ($E_C$), piezoelectric coefficient ($d_{33}$), and dielectric loss ($\tan \delta$) for the MPB composition 25PIN-40PMN-35PT are shown as a function of internal bias field. Increasing the sintering temperature increases aliovalent substitution of Cu$^{2+}$ cations on the B-site of the perovskite that create charge balancing oxygen vacancies. These oxygen vacancies contribute to the formation of an internal bias field ($E_i$). Increasing the internal bias field increases the degree of “hard” piezoelectric character by pinning the domain walls which increases the field needed to switch domains (higher $E_C$), reduces $\tan \delta$, and lowers overall domain mobility (lower $d_{33}$).

Although the properties are still “hardened” relative to lower sintering temperatures (1050 °C), microstructural coarsening at high temperature (1150 °C) slightly reduces the $E_C$ and enhances the $P_R$ which can be understood by taking into account domain wall - grain boundary interactions. Uncompensated charges at the grain boundary alter local electric fields and contribute to electric and elastic stresses on local lattice structure which make domain reorientation more difficult. At small grain sizes, these effects are magnified. Grain growth decreases the total grain boundary surface area which reduces these stresses and it becomes easier to reorient domains (lower $E_C$) and enhances the
contribution of domain reorientation to overall polarization (higher $P_R$). The microstructure-property relationships observed here agree with similar findings in PZT.$^{28}$

3.4 Conclusions

Reactive sintering of CuO-doped PIN-PMN-PT ceramics in oxygen results in 99% dense ceramics with a uniform microstructure of 2 – 3 μm. Minimum dielectric loss (tan δ) of 1.5%, maximum piezoelectric coefficients ($d_{33}$) of 307 pC/N, and maximum ferroelectric properties ($E_C$) of 7.8 kV/cm and ($P_R$) of 34.5 μC/cm$^2$ were obtained for ceramics sintered in oxygen. Air sintering resulted in lower densities, a bimodal grain size distribution, and lower properties than oxygen sintered ceramics. Compositional selection along the MPB showed that ternary 0.5 mol% CuO-doped 25PIN-40PMN-35PT MPB ceramics had the maximum piezoelectric properties of $d_{33} = 565 +/- 23$ pC/N and $k_p = 0.64 +/- 0.01$. CuO doping imparts harder piezoelectric properties when ceramics were sintered $\geq$1100 °C in oxygen which were attributed to copper substitution into the perovskite lattice as evidenced by higher $E_C \geq 11$ kV/cm and the formation of an internal bias field $E_i$ ranging from +0.32 to +0.41 kV/cm.

3.5 References


24 F. Xia and X. Yao, “Role of PbO content on the dielectric and piezoelectric


CHAPTER 4: Mn and Mn/Cu-doped PIN-PMN-PT

Piezoelectric Ceramics for High-power Transducers

4.1 Introduction

One of the major challenges for acoustic transduction technologies is heat mitigation during high-power drive applications such as ultrasonic transducers and actuators. Dielectric and electromechanical energy losses during vibration are dissipated as heat which diminishes properties and reduces vibration velocity of the piezoelectric elements. To accommodate the effects of heating, transducers must be designed to dissipate heat to prevent depoling of ceramic or single crystal elements. For higher power applications, piezoelectric materials with lower losses and higher operating temperatures are needed.¹

Heat generation is modeled in terms of the rate (per second) of dissipation of vibrational energy \( H_{DVE} \) as shown in Equation 4-1 where \( \omega_0 \) is the resonant angular frequency, \( V_0 \) is the vibration velocity, \( M \) is the mass of the transducer, and \( Q_M \) is the electromechanical quality factor.² ³ Advances in ferroelectric theory, loss-measurement techniques, and piezoelectric materials research have identified that the dominant piezoelectric loss mechanisms contributing to heat generation are either intrinsic (i.e. lattice distortion) or extrinsic (i.e. domain wall motion) in nature.⁴

\[
H_{DVE} = \frac{\omega_0 M V_0^2}{2 Q_M}
\]

Equation 4-1.
Mn-doping is one of the most widely used strategies to address the challenge of heat generation. Manganese suppresses heat generation by reducing dielectric losses (tan \( \delta \)) and mechanical losses (1/\( Q_M \)) in piezoelectric ceramic elements under AC field drive\(^5\)–\(^8\) and has been explored in Generation III piezoelectric single crystal compositions such as \( \text{Pb(In}_{1/2}\text{Nb}_{1/2})\text{O}_3-\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3 \) (PIN-PMN-PT).\(^9\)–\(^11\) The primary mechanism for piezoelectric hardening (lower tan \( \delta \), higher \( Q_M \), higher \( E_C \)) arises from aliovalent substitution of Mn cations on the B-site of the perovskite lattice and associated formation of oxygen vacancies.\(^12\) The formation of \( Mn''_B - V'_{O} \) defect dipoles that pin domain walls has been verified with XPS and XAFS experiments on Mn-doped binary \( \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3 \) crystals.\(^13, 14\) Pinning of domain walls ultimately decreases the extrinsic piezoelectric contribution from domain motion and reduces the strain response (or \( d_{33} \)) in Mn-doped single crystals relative to undoped single crystals.\(^3, 15\)

Maximizing the strain behavior of Mn-doped single crystals is achieved by shifting the composition toward the MPB where exceptionally high piezoelectric coefficients (\( d_{33} \)) ranging from 800 to 1400 pC/N and electromechanical quality factors (\( Q_M \)) over 1000 are achieved. Mn-doped single crystals also display higher coercive fields (\( E_C = 8 – 9 \text{ kV/cm} \)) than undoped crystals (\( E_C = 5 – 6 \text{ kV/cm} \)).\(^5, 7, 16, 17\)

Relative to single crystals, ceramics possess advantages such as lower cost and fewer dimensional restrictions when fabricating piezoelectric elements for transducers. Mn-doped ceramics display low dielectric losses and high electromechanical quality factors comparable to single crystals and in some cases have \( E_C > 9 \text{ kV/cm} \) due to grain size and grain boundary effects. However, the strain behavior and piezoelectric coefficients
of Mn-doped ceramics are much lower than single crystals of the same composition due to the random distribution of grain orientations in three-dimensional space.\cite{18-20}

There are few studies on the effect of Mn-doping on PIN-PMN-PT ferroelectric properties. Qi et al. reported significant enhancements in hard piezoelectric properties for MnO$_2$-doped 24PIN-42PMN-34PT with the lowest dielectric losses and highest electromechanical quality factors for MnO$_2$ concentrations between 1 and 2 mol%. The authors attributed the piezoelectric hardening mechanism to oxygen vacancies and noted the formation of an internal bias field ($E_i$) with increasing MnO$_2$ dopant concentration.\cite{21,22}

In this study, we investigate the effects of Mn-doping by either MnO$_2$ or as a columbite (MnNb$_2$O$_6$) on the properties of PIN-PMN-PT. Previous work on Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbZrO$_3$-PbTiO$_3$ (PMN-PZT) and Pb(Zn$_{1/3}$Nb$_{2/3}$)-PbZrO$_3$-PbTiO$_3$ (PZN-PZT) suggests that MnO$_2$-doping causes the substituted B-site cations, such as Mg$^{2+}$ and Zn$^{2+}$, respectively, to accumulate on the grain boundaries and form piezoelectrically inactive second phase grains that diminish the ferroelectric and piezoelectric properties.\cite{23,24} Yan et al. showed that stabilizing manganese (Mn$^{2+}$) in a perovskite solid solution of Pb(Mn$_{1/3}$Nb$_{2/3}$)O$_3$ by incorporating Nb$^{5+}$ for site balance improved microstructural uniformity and substantially increased the degree of ferroelectric and piezoelectric hardening of Mn-doped PMN-PZT ceramics compared to doping with MnO$_2$ alone. Furthermore, manganese doping with MnNb$_2$O$_6$ columbite has been demonstrated to be an effective way to enhance electromechanical quality factors and reduce dielectric losses in PZT.\cite{25,26}
Based on prior work, it is reasonable to expect that Mn-doping with MnNb₂O₆ (MnN) columbite should improve ferroelectric and piezoelectric hardening by increasing the solubility of manganese in the PIN-PMN-PT lattice through adequate site balance of the perovskite structure. Cu-doping of lead-based piezoelectric ceramics has been shown to achieve similar effects of acceptor doping such as making domain reorientation more difficult and reducing dielectric losses. Copper oxide also forms a low temperature eutectic with lead oxide that lowers the sintering temperature of lead-based ceramics by a liquid phase sintering mechanism.²⁷–³² Therefore, we also investigated the combined effects of two acceptor-type dopants on the microstructure, crystallography, and key properties of PIN-PMN-PT for high-power transduction devices.

### 4.2 Experimental Procedure

25Pb(In[subscript 1/2]Nb[subscript 1/2])O₃-40Pb(Mg[subscript 1/3]Nb[subscript 2/3])O₃-35PbTiO₃ was chosen as the base composition for investigation because it resides on the MPB and possesses excellent electromechanical properties such as high piezoelectric coefficients and electromechanical coupling factors. In order to deconvolute the combined effects of multiple modifiers on structure and properties, several compositions were explored: 25PIN-40PMN-35PT with no copper or manganese (referred to as undoped PIN-PMN-PT), 6PMnN-25PIN-34PMN-35PT (referred to as MnN-doped PIN-PMN-PT), 0.5 mol% Cu-doped 6PMnN-25PIN-34PMN-35PT (referred to as MnN+Cu co-doped PIN-PMN-PT), and 2 mol% MnO₂ + 0.5 mol% Cu-doped 25PIN-40PMN-35PT (referred to as MnO₂+Cu co-doped PIN-PMN-PT). For all MnN-doped samples, the MnNb₂O₆ was substituted for MgNb₂O₆, therefore the
niobium in the manganese columbite is accounted for in the perovskite stoichiometry. Reactive powder mixtures were prepared from metal oxides including PbO (D\text{50} \sim 7 \mu m, 99.9\%, Alfa Aesar, Ward Hill, MA), InNbO\textsubscript{4} (D\text{50} \sim 0.3 \mu m), MgNb\textsubscript{2}O\textsubscript{6} (D\text{50} \sim 0.4 \mu m), and TiO\textsubscript{2} (D\text{50} \sim 25 \text{nm}, 99.5\%, Evonik Industries, Essen, Germany). Acceptor dopants included MnNb\textsubscript{2}O\textsubscript{6} (D\text{50} \sim 0.8 \mu m), MnO\textsubscript{2} (D\text{50} \sim 1.4 \mu m, 99.99\%, Sigma Aldrich, Milwaukee, WI), and CuO (D\text{50} \sim 40 \text{nm}, 99.99\%, Sigma Aldrich, Milwaukee, WI). The columbites (InNbO\textsubscript{4}, MgNb\textsubscript{2}O\textsubscript{6}, and MnNb\textsubscript{2}O\textsubscript{6}) were prepared by vibratory milling In\textsubscript{2}O\textsubscript{3} (D\text{50} \sim 50 \text{nm}, 99.99\%, Santech Materials, Changsha, Hunan, China), MgO (D\text{50} \sim 0.6 \mu m, Mallinckrodt Chemicals, Dublin, Ireland), or MnO\textsubscript{2} with Nb\textsubscript{2}O\textsubscript{5} (D\text{50} \sim 100 \text{nm}, 99.9\%, H.C. Starck, Newton, MA) for 24 h in ethanol. InNbO\textsubscript{4} was calcined at 925 \degree C for 3 h, and MgNb\textsubscript{2}O\textsubscript{6} and MnNb\textsubscript{2}O\textsubscript{6} were calcined at 1000 \degree C for 6 h. All powders were batched with 1 wt\% excess PbO to compensate for PbO volatility during reactive sintering. Matrix powder batches were vibratory milled for 48 - 60 h in a 1 L Nalgene bottle with a 1:1:1 mass ratio of 3 mm, 5 mm, and 10 mm YSZ ball media to mix the components and reduce the particle size.

Samples were prepared for reactive sintering by uniaxially dry pressing powder mixtures into disk shaped green bodies with diameter of 11 mm and thickness of 2 mm at 40 MPa and cold isostatic pressing at 200 MPa for 3 mins. To mitigate lead volatility during sintering, green bodies were embedded in two times the sample mass of stoichiometric powder which was calcined at 775 \degree C for 2 h and had a relatively coarse particle size of \sim 2 \mu m. Since the sintering kinetics of Mn-modified compositions were much slower without CuO, all samples were heated at 20 \degree C/min to 1150 \degree C and reactively sintered for 5 h in 0.25 L/min flowing oxygen. Samples were ground and polished to remove surface
pyrochlore phase. Microstructure was characterized by scanning electron microscopy (FEI Quanta 250 ESEM, ThermoScientific, Hillsboro, OR). Crystallographic structure was analyzed by x-ray diffraction (XRD, PANalytical Empyrean Xpert Pro MPD diffractometer, The Netherlands).

Ceramic disks were polished to a diameter to thickness ratio of > 10:1 with a thickness of ~1 mm and electroded with Dupont 7095 silver paste and fired at 575 °C for electrical property measurements. Ceramics were poled at 40 kV/cm for 15 min at room temperature for electromechanical and dielectric measurements and aged for 24 h before making small signal measurements. The piezoelectric coefficient ($d_{33}$) was measured using a Berlincourt d33 PiezoMeter System (Piezotest, UK) at 10 N at 110 Hz. Ferroelectric and strain behavior were characterized by measuring polarization and strain versus electric field ($P$-$E$, $S$-$E$) at 40 kV/cm at 1 Hz on a modified Sawyer-Tower circuit with a Stanford Research Systems Model SR830 DSP lock-in amplifier. Low-field $d_{33}^*$ was calculated from the decreasing portion of the unipolar $S$-$E$ curve (< 10 kV/cm) at 40 kV/cm maximum applied field. Strain hysteresis ($H_S$) was calculated from the strain differential at half of the applied field divided by the maximum strain. Planar electromechanical coupling factors ($k_p$) and electromechanical quality factors ($Q_M$) were calculated from the impedance spectra measured using an Agilent 4294A Precision Impedance Analyzer. Relative permittivity and dielectric loss were measured as a function of temperature and frequency with an Agilent 4284A Precision LCR meter. The rhombohedral-tetragonal phase transition temperature ($T_{R-T}$) was determined from the local minimum of the second derivative of the plot of permittivity as a function of temperature in the low temperature regime (< 200 °C), and the Curie temperature ($T_C$) was determined from where the first derivative equals zero.
4.3 Results and Discussion

4.3.1 Effect of MnN-doping

SEM images of the microstructures of sintered samples are shown in Figure 4-1. The undoped PIN-PMN-PT and MnN-doped PIN-PMN-PT ceramics sintered to 98.5 +/- 0.4% and 97.9 +/- 1% of theoretical density ($\rho_0 = 8.198 \text{ g/cc}$), respectively, and have relatively fine average grain sizes ($G_{ave} = 1.1 \mu m$ for undoped and $G_{ave} = 1.3 \mu m$ for MnN-doped). Some regions in the MnN-doped ceramics show slightly enhanced grain growth with periodic growth of 2-3 $\mu m$ which was not observed in the undoped ceramics. The slightly enhanced grain growth may be due to solid state diffusion of oxygen vacancies induced by elemental doping, and is similar to microstructural effects observed in MnN-doped PZT-based ceramics. There are also regions in the undoped and MnN-doped samples that contain residual closed porosity (dark regions) as a result of slower sintering kinetics in solid state sintering than in systems with a liquid phase. Some pores also appear to be anisotropic in shape which may be indicative of anisotropic particle packing in local regions of the microstructure. Due to the fine grain size of the microstructure in proximity to the pores, it is likely that further heating will result in gradual pore closure.
Figure 4-1. SEM images of fracture surfaces of (A) 25PIN-40PMN-35PT (undoped) and (B) MnN-doped ceramics. The microstructures of these samples have fine grain sizes of 1.1 – 1.3 μm and also show the presence of residual porosity (dark regions) as a result of being less than fully dense. SEM images of (C) MnN+Cu co-doped and (D) MnO$_2$+Cu co-doped ceramics reactively sintered at 1150 °C for 5 h in oxygen are also shown. Cu-doping increased the sintered densities, as evidenced by the absence of residual pores, and increased the grain growth of ceramics, and MnO$_2$+Cu co-doped ceramics display significantly enhanced grain growth.

XRD patterns of sintered samples in Figure 4-2(A) show that all compositions are perovskite. A minor pyrochlore (Pb$_3$Nb$_4$O$_{13}$) second phase was identified by the presence of the (222) peak at 29.2° 2θ in the x-ray diffraction pattern of MnN-doped PIN-PMN-PT. Figure 4-2(B) compares the change in shape of the (111) peak with doping and Figure 4-2(C) compares the change in symmetry of the {200} peaks. Undoped PIN-PMN-PT has a slightly asymmetrical (111) peak and a broadened (200) peak which indicate the
coexistence of rhombohedral and tetragonal structures and confirm the composition’s placement on the MPB. When ceramics were MnN-doped, the (111) peak symmetry increased relative to undoped PIN-PMN-PT, and the peak intensity ratio of the (200) peak at 45° 2θ to the (002)c peak at 44.6° 2θ increased as well. The increase in peak symmetry of the (111), increase in (200) peak intensity, and reduction in (002)c peak broadening relative to undoped PIN-PMN-PT indicate that manganese doping shifts the structure toward the rhombohedral side of the MPB. The effects of MnN-doping on structure observed here are consistent with observations of MnO$_2$-doped PZN-PZT\textsuperscript{18,23} and PMnN-PMN-PZT ceramics.\textsuperscript{24}

![XRD diffraction patterns](image)

**Figure 4-2.** XRD diffraction patterns of sintered PIN-PMN-PT ceramics doped with manganese or copper show how MnN-doping increased the (111) peak symmetry and (200) peak intensity indicating a rhombohedral structural shift. Cu-doping and MnO$_2$-doping induced a tetragonal structural shift as evidenced by the increase in (111) peak asymmetry, (002)c peak intensity, and (002)c/(200) peak splitting.
The ferroelectric properties are shown in Table 4-1. The ferroelectric and piezoelectric properties of undoped PIN-PMN-PT, such as the high polarization and strain behavior, are characteristic for soft compositions. Undoped PIN-PMN-PT has a relatively high remnant polarization \( (P_R) \) of 33.3 +/- 0.1 μC/cm² and coercive field \( (E_C) \) of 9.4 +/- 0.1 kV/cm as seen in Figure 4-3. Poled ceramics possessed excellent electromechanical properties such as high piezoelectric coefficients \( (d_{33}) \) of 559 +/- 5 pC/N and planar electromechanical coupling coefficients \( (k_p) \) of 0.57 +/- 0.01 which are listed in Table 4-2. The undoped composition had the greatest low-field strain behavior \( (d_{33}^*) \) of 597 +/- 24 pm/V measured at \( \leq 10 \) kV/cm and the highest maximum strain (0.174%) at 40 kV/cm shown in Figure 4-4. However, the electromechanical quality factor \( (Q_M) \) of 77 +/- 1 is too low and the dielectric loss \( (\tan \delta) \) of 1.8 +/- 0.1% is too high to be competitive as a material for high-power transducers.

MnN-doped PIN-PMN-PT displayed significantly harder properties than undoped PIN-PMN-PT such as lower dielectric losses, higher coercive fields, and greater electromechanical quality factors. MnN-doping increased the coercive from 9.4 to 11.7 +/- 0.2 kV/cm, increased the electromechanical quality factor by over 10x from 77 to 1011 +/- 78, and decreased dielectric losses from 1.8 to 0.7 +/- 0.03% (1 kHz). The piezoelectric coefficient \( (d_{33}) \) decreased by ~50% from 559 to 272 +/- 3 pC/N and planar electromechanical coupling decreased from 0.57 to 0.43 +/- 0.01 as a result of piezoelectric hardening. However, the maximum strain was reduced by only 28% from 0.174% to 0.125%, and consequently the low-field \( d_{33}^* \) only decreased by ~30% from 597 to 411 +/- 6 pm/V. These properties show that MnN-doped ceramics are promising candidates for high strain, low loss, and high frequency applications.
Table 4-1. Ferroelectric and dielectric properties of 25PIN-40PMN-35PT without dopants (undoped), MnN-doped, MnN+Cu co-doped, and MnO₂+Cu co-doped. All properties except phase transition temperatures were averaged from 3 samples per composition. Permittivity and loss values were measured at 1 kHz.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$P_R$ ($\mu$C/cm²)</th>
<th>$E_C$ (kV/cm)</th>
<th>$E_i$ (kV/cm)</th>
<th>tan $\delta$ (%)</th>
<th>$\varepsilon_{33}/\varepsilon_0$</th>
<th>$T_{R-T}$ (°C)</th>
<th>$T_C$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>33.3 +/- 0.1</td>
<td>9.4 +/- 0.1</td>
<td>-0.013 +/- 0.2</td>
<td>1.8 +/- 0.1</td>
<td>2168 +/- 28</td>
<td>100</td>
<td>222</td>
</tr>
<tr>
<td>MnN</td>
<td>23.8 +/- 0.8</td>
<td>11.7 +/- 0.2</td>
<td>1.4 +/- 0.1</td>
<td>0.7 +/- 0.03</td>
<td>1175 +/- 12</td>
<td>---</td>
<td>228</td>
</tr>
<tr>
<td>MnN+Cu</td>
<td>17.9 +/- 1</td>
<td>9.6 +/- 0.3</td>
<td>1.8 +/- 0.3</td>
<td>0.6 +/- 0.04</td>
<td>1299 +/- 23</td>
<td>---</td>
<td>222</td>
</tr>
<tr>
<td>MnO₂+Cu</td>
<td>32.6 +/- 0.8</td>
<td>9.4 +/- 0.1</td>
<td>0.49 +/- 0.2</td>
<td>1.2 +/- 0.6</td>
<td>1572 +/- 19</td>
<td>100</td>
<td>213</td>
</tr>
</tbody>
</table>

Table 4-2. Electromechanical properties and strain behavior of 25PIN-40PMN-35PT reactively sintered ceramics without dopants (undoped), MnN-doped, MnN+Cu co-doped, and MnO₂+Cu co-doped.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$d_{33}$ (pC/N)</th>
<th>$g_{33}$ ($\times 10^{-3}$ Vm/N)</th>
<th>$k_p$</th>
<th>$Q_M$</th>
<th>$d_{33}^*$ (pm/V)</th>
<th>$H_s$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>559 +/- 5</td>
<td>29 +/- 0.1</td>
<td>0.57 +/- 0.01</td>
<td>77 +/- 1</td>
<td>597 +/- 24</td>
<td>6.9 +/- 3</td>
</tr>
<tr>
<td>MnN</td>
<td>272 +/- 3</td>
<td>26 +/- 0.05</td>
<td>0.43 +/- 0.01</td>
<td>1011 +/- 78</td>
<td>411 +/- 6</td>
<td>15 +/- 0.3</td>
</tr>
<tr>
<td>MnN+Cu</td>
<td>212 +/- 12</td>
<td>18 +/- 1</td>
<td>0.37 +/- 0.01</td>
<td>1029 +/- 365</td>
<td>382 +/- 6</td>
<td>15 +/- 0.3</td>
</tr>
<tr>
<td>MnO₂+Cu</td>
<td>391 +/- 20</td>
<td>28 +/- 1</td>
<td>0.54 +/- 0.02</td>
<td>314 +/- 108</td>
<td>531 +/- 41</td>
<td>8.8 +/- 5</td>
</tr>
</tbody>
</table>
Figure 4-3. Ferroelectric loops (P-E) of reactively sintered PIN-PMN-PT ceramics doped with MnN-only, MnN+Cu, or MnO₂+Cu. MnN-doped ceramics provided the greatest enhancement in coercive field.

Figure 4-4. Unipolar strain versus applied field (S-E) behavior of PIN-PMN-PT ceramics. Undoped PIN-PMN-PT displayed the highest strain behavior. MnN doping increased strain hysteresis due to piezoelectric hardening and MnN+Cu decreased total strain response because of the increased acceptor dopant concentration.
Figure 4-5 shows the change in relative permittivity ($\varepsilon_{33}/\varepsilon_0$) and dielectric loss ($\tan \delta$) as a function of temperature. For undoped ceramics, the permittivity increases gradually with temperature, and then the rate of increase slows at $\sim$100 °C; the rhombohedral-tetragonal phase transition temperature ($T_{R-T}$). The wide breadth of the dielectric peak anomaly at the $T_{R-T}$ is characteristic of MPB compositions comprised of both rhombohedral and tetragonal structures which enhances polarizability and polarization rotation.\textsuperscript{35-37} The Curie temperature ($T_C$) was 222 °C. For MnN-doped ceramics the $T_{R-T}$ was not detectable, and the $T_C$ increased to 228 °C. Dielectric properties and phase transition temperatures are listed in Table 4-1.

![Figure 4-5](image)

Figure 4-5. Relative permittivity ($\varepsilon_{33}/\varepsilon_0$) and dielectric loss ($\tan \delta$) as a function of temperature for poled PIN-PMN-PT ceramics. MnN-doping reduced the dielectric loss, relative permittivity, and increased the Curie temperature. With MnO$_2$+Cu, the $T_{R-T}$ transition was more pronounced, and the $T_C$ was reduced.
Figure 4-6 shows dielectric losses as a function of frequency and temperature. Dielectric losses of undoped ceramics range from 1.6 to 2.4% at room temperature for 1 kHz and 100 kHz, respectively. A peak in tan $\delta$ was observed with initial temperature rise that increased with frequency which may be due to thermal activation of intrinsic dipoles and movement of space charges in the perovskite lattice. Dielectric loss steadily increases until the temperature exceeds the $T_{R\rightarrow T}$ transition at 100 °C, at which point the loss declines because the structure transitions from rhombohedral to tetragonal and domain switching becomes more difficult. Dielectric losses of MnN-doped ceramics were lower than undoped PIN-PMN-PT and displayed a strong frequency dependency. At 1 kHz, the room temperature loss is 0.7%, and the loss steadily increases with temperature and exceeds the losses of the undoped composition above 100 °C. At 10 kHz (Figure 4-5) the loss is reduced to 0.5% at room temperature and doesn’t exceed the losses of undoped ceramics until 150 °C. When the frequency is increased to 100 kHz, room temperature dielectric loss decreases significantly to 0.2%, and tan $\delta$ remains below 1% until the temperature exceeds 150 °C.
Figure 4-6. Dielectric loss as a function of temperature and frequency for undoped and MnN-doped PIN-PMN-PT ceramics. The dielectric losses of undoped ceramics did not change significantly with frequency below the Curie temperature. In contrast, MnN-doped ceramics possess significant frequency dependency of dielectric loss and display significantly lower loss at higher frequencies.

4.3.2 Mechanism of Piezoelectric Hardening by Manganese

Piezoelectric property hardening of MnN-doped ceramics is characteristic of acceptor-doped materials where mobile defects are created that diffuse to domain walls and pin them. Domain wall pinning makes ferroelectric domain reorientation difficult (higher $E_C$) which reduces the charge contribution to the overall polarization (lower $P_R$). Domain pinning results in lower extrinsic domain mobility and mobility-related losses but consequentially reduces electromechanical properties (lower $d_{33}$ and $k_p$).

The pores that were observed in the microstructure also have effects on the properties but should not be neglected. Uncompensated charges inside the pores may interact with the domains at the ceramic/pore interface and prevent domain switching from
contributing to the reversible polarization. It has also been suggested that the presence of pores may relax mechanical clamping of the grains and increase the domain response. The effects of the pores are also known to be anisotropic and depend on orientation with respect to the electric field.\textsuperscript{39} The implications of residual porosity on domain wall motion are complicated and difficult to determine but should not be ignored. Further investigations should be conducted to better understand the relationship between pore size, distribution, and orientation on the local domain switching effects to better understand how to maximize properties in this material system. Furthermore, future investigations which establish sintering conditions that eliminate residual porosity and prevent any contributions or effects of residual porosity on domain switching behavior may improve the accuracy of the interpretation of the effects of manganese doping on the properties.

The defects controlling the domain switching are likely oxygen vacancies that form for charge compensation when manganese is doped into the lattice. The ionic radius of manganese in 6-fold coordination ranges from 53 pm to 83 pm depending on valence and electronic spin state. The 6 fold coordinated B-site cations of the PIN-PMN-PT perovskite which include $\text{In}^{3+}$ ($r_i = 80$ pm), $\text{Nb}^{5+}$ ($r_i = 64$ pm), $\text{Mg}^{2+}$ ($r_i = 72$ pm), and $\text{Ti}^{4+}$ ($r_i = 61$ pm) may provide suitable atomic sites for substitution based on the relatively similar ionic radii.\textsuperscript{40} It has also been proposed that manganese may act as an amphoteric cation by entering the A-site and/or the B-site.\textsuperscript{41,42} However, due to the small size of manganese relative to $\text{Pb}^{2+}$ ($r_i = 119$ pm) and the excess A-site $\text{Pb}^{2+}$ cations provided by the PbO batched with the powder to mitigate lead volatility during sintering, only B-site substitutions are considered plausible.
Manganese is in the Mn$^{2+}$ state when doped in the form of MnNb$_2$O$_6$, but it is well known that processing conditions such as P$_{O2}$ and sintering temperature as well as local chemistry can alter the valence state of the manganese cation. In the high-spin electron state of Mn$^{2+}$ ($r_i = 83$ pm), the size of the manganese cation is close enough such that it may substitute for In$^{3+}$ forming Mn$^{I}_{In}$. As the valence increases to Mn$^{3+}$ ($r_i = 65$ pm) and Mn$^{4+}$ ($r_i = 53$ pm), the decreasing ionic radius leads to increased solubility in the lattice, however, only the Mn$^{2+}$ and Mn$^{3+}$ valence states are responsible for inducing oxygen vacancies since the average charge on the B-site of the $A$($B'B''$)O$_3$ perovskite structure is 4$^+$. Investigations using electron spin response (ESR) spectroscopy of Mn-doped PZT and x-ray absorption fine structure analysis (XAFS) of Mn-doped PMN-PT crystals show that manganese exists in the Mn$^{2+}$ state, even when the starting component is MnO$_2$ (Mn$^{4+}$) indicating that the cation changes valence state. Hennings et al. observed using electron spin resonance (ESR) that the valence state of the acceptor dopant in Mn-doped PbTiO$_3$ ceramics was particularly susceptible to P$_{O2}$ and sintering conditions. Mn$^{I}_{Ti}$ formation was observed to dominate at high P$_{O2}$ levels, while Mn$^{I}_{Ti}$ and Mn$^{II}_{Ti}$ were detected when samples were annealed in air. A study by Keeble et al. observed Mn$^{X}_{Ti}$ in Mn-doped PbTiO$_3$ single crystal. The valence state of the acceptor dopant on the B-site of Mn-doped BaTiO$_3$ ceramics is also strongly influenced by the processing conditions where Mn$^{II}_{Ti}$ forms in reducing conditions and Mn$^{I}_{Ti}$ in oxidizing conditions. Clearly, the multivalent nature of manganese in acceptor-doped perovskites severely complicates the path to understanding the relationship between processing conditions, local structure, defect chemistry, and properties and thus, merits further study.
The defect contribution to domain wall pinning is evidenced by the strength of the internal bias field \(E_i\) which is negligible for undoped ceramics at -0.013 +/- 0.2 kV/cm but with MnN-doping increased by 100x to 1.4 +/- 0.1 kV/cm. The defect dipoles create local internal fields which reduce overall polarizability which is also why relative permittivity \((\varepsilon_{33}/\varepsilon_0)\) decreased from 2168 +/- 28 for undoped ceramics to 1175 +/- 12 for MnN-doped ceramics.

These defects are sensitive to both applied field and frequency. The increase in strain hysteresis \((H_S)\) from 6.9% for undoped to 15% for MnN-doped ceramics indicates that domains move irreversibly when MnN-doped and require a critical applied field to reorient. The increase in dielectric loss for MnN-doped ceramics at low frequencies (1 kHz) occurs because the dielectric relaxation time of \(MnO_{\prime}\) - \(\cdot\cdot\cdot\) defect dipoles is less than the period of the frequency of the measurement.\(^{42,45}\) The time dependence of reorientation behavior and internal bias of acceptor-doped B-site defect dipoles has also been modeled for \((NiO_{\prime}\) - \(\cdot\cdot\cdot\)) complexes in Ni-doped BaTiO\(_3\) ceramics.\(^{38}\) This defect dipole reorientation behavior contributes to dielectric loss which scales with temperature because thermal vibration increases defect dipole mobility and shortens the dielectric relaxation time. With increasing frequency, the dielectric loss decreases because defect dipole reorientation and relaxation cannot keep up with the rapidly oscillating field. Since the resonant frequencies of the sintered ceramic disks are ~200 kHz, it is important to understand how dielectric behavior changes at high frequency and temperature since materials for high-power transducers are often used at resonance conditions.
4.3.3 Effects of MnN and Cu co-doping

All PIN-PMN-PT samples doped with Cu sintered to full density and had slightly larger grain sizes than samples without Cu. The microstructural SEM image of a sintered MnN+Cu co-doped sample shown in Figure 4-1 shows that the grain size is 2.3 μm. Addition of Cu also increased the (002) and (200)/(020) peak splitting as seen in the x-ray diffraction patterns (Figure 4-2(B)) indicating that Cu$^{2+}$ substitution shifts the perovskite structure slightly toward the tetragonal side of the MPB.

The structural effects of MnN+Cu co-doping are different from MnN-doping. Whereas a rhombohedral structural shift was observed with MnN-doped ceramics, a slight tetragonal shift is observed for MnN+Cu due to the lattice distortion caused by copper substitution. The ionic radius of Cu$^{2+}$ ($r_i = 73$ pm) is quite close to Mg$^{2+}$ and is smaller than In$^{3+}$ suggesting that Cu$^{2+}$ may substitute for these cations. Keeble et al. showed that for Cu-doped PbTiO$_3$ single crystal Cu$^{2+}$ substitutes for Ti$^{4+}$ in the octahedrally coordinated B-site, despite being a larger cation, resulting in formation of $V_O^{**}$. The substitution mechanism was later confirmed by a study conducted using ESR and DFT calculations. The effects of Cu-doping on crystallographic structural distortions observed in this study are consistent with observations made in the aforementioned studies as well as Cu-doped BaTiO$_3$ ceramic by Langhammer et al. The solubility limit of copper in the PIN-PMN-PT lattice has been experimentally determined to be between ~1 – 2 mol% CuO as evidenced by changes in fracture behavior and accumulation of copper at the grain boundaries. Since the copper concentration used in this study was only 0.5 mol%, it is assumed that all of the copper substitutes into the lattice.
MnN+Cu co-doped ceramics displayed hardened properties like MnN-doped ceramics such as low remnant polarization of $17.9 \pm 1 \mu C/cm^2$, low dielectric loss of $0.6 \pm 0.04 \%$, and very high electromechanical quality factor of $1029 \pm 365$. The coercive field $E_C$ of $9.6 \pm 0.3 \text{kV/cm}$ was not significantly affected, however the internal bias field $E_i$ of $1.8 \pm 0.1 \text{kV/cm}$ was the largest for all compositions indicating significant defect dipole generation. Compared to MnN-doped ceramics, the $d_{33}$ decreased from 272 to 212 $\pm 12 \text{pC/N}$ and $k_p$ decreased from 0.43 to 0.37 $\pm 0.01$ due to the higher acceptor dopant concentration. The $T_{R-T}$ transition was also not easily detectable, and the Curie temperature was $222 \, ^\circ\text{C}$. The permittivity maximum at the $T_C$ increased with Cu-doping from 11,490 to 14,800. The frequency dependent behavior of dielectric losses for MnN+Cu co-doped ceramics was nearly identical to MnN-doped ceramics.

4.3.4 Effects of MnO$_2$ and Cu co-doping

The SEM image of a MnO$_2$+Cu co-doped ceramic fracture surface in Figure 4-1 shows that the microstructure coarsened to an average grain size $> 20 \, \mu m$. The substitution of copper and manganese cations into the lattice resulted in the formation of MgO-rich grains of approximately 2 to 3 $\mu m$ in diameter primarily on the grain boundaries. The MgO was not detectable by XRD in Figure 4-2 due to the low concentration in the microstructure. EDS analysis shown in Figure 4-7 confirmed the second phase to be predominantly composed of magnesium and oxygen and thus it is likely MgO. EDS mapping of the other elements show a uniform signal. The formation of second phase grains has been observed in MnO$_2$-doped systems before.$^{20, 23, 24}$
Figure 4-7. (A) SEM image of fracture surface of MnO$_2$+Cu co-doped PIN-PMN-PT ceramic showing the formation of spherical particulate on the grain boundary. High Z-contrast of the backscatter SEM image indicate that the particulate is lower density than the surrounding grains. (B) and (C) Energy dispersive spectroscopy maps of the area show a strong magnesium and oxygen signal, respectively, originating from the particulate surface indicating that the particulate is primarily composed of Mg and O.

The enhanced grain growth with MnO$_2$-doping has previously been hypothesized to be driven by diffusion of manganese and oxygen vacancies,\textsuperscript{20} however, this increased
grain growth behavior was not observed when manganese was added in columbite form. Since the solubility limit of MnO₂ is known to be ~2 mol%,²¹ it is likely that the addition of 2 mol% MnO₂ and 0.5 mol% Cu exceeded the solubility limit of the lattice resulting in accumulation of dopants on the grain boundary. Reducing the solubility of copper in the lattice leads to liquid phase formation at the grain boundary which significantly enhances grain growth kinetics.²⁸

The difference between MnN+Cu and MnO₂+Cu co-doped ceramics in peak shape and splitting in Figure 4-2(B) and (C) indicates that the mechanism by which manganese is introduced to the lattice has a significant impact on the local crystal structure. The (111) peak asymmetry and (200) peak splitting were much more enhanced for MnO₂+Cu than for MnN+Cu. When Cu is added with MnN, the resulting crystal distortion is an average of the Jahn-Teller distortion effects of Mn³⁺ and Cu²⁺. However, when manganese is added as MnO₂, the further increase in relative peak intensity of the (002) C peak in MnO₂+Cu co-doped system suggests that the distortion and extension of the c-axis is enhanced. The increased extension of the c-axis of the crystal lattice may be because MnO₂+Cu inhibits the formation of Mn³⁺ ions, suppressing the rhombohedral structural distortion of Mn³⁺ and enhancing the tetragonal distortion of Cu²⁺. Studies of PIN-PMN-PT and PZT-based ceramics have shown that with MnO₂-doping there is no significant change in crystal structure,²⁰,²¹,⁴⁹ so the structural effects may also be dependent on other factors such as sintering temperature, atmosphere, or the local chemistry. Clearly, more work is needed to determine the true valence state of manganese cations and the relationship between oxidation state and doping effects on local distortions in the crystal lattice.
Despite having the same molar equivalent amount of manganese (2 mol%) as the MnN-doped compositions, MnO$_2$+Cu doped ceramics imparted only slight hardening effects on the properties. The $E_i$ of 0.49 +/- 0.2 kV/cm was the lowest of all doped compositions. Relative to undoped compositions, the $P_R$ and $E_C$ did not change significantly. Since only MgO-rich species were detected in local regions along the grain boundary, it is reasonable to assume that the acceptor dopants of manganese and copper are in the lattice on the B-site of the perovskite. Furthermore, if the acceptor-dopants, such as Cu$^{2+}$ or Mn$^{2+}$, substituted primarily for Mg$^{2+}$, then there is no net negative charge created which would require oxygen vacancy formation for charge compensation. If a net positive charge is created on the B-site, for example by Mn$^{4+}$, A-site vacancies ($V'_{Pb}'$) may form for charge compensation leading to a type of donor-doping effect, however, the A-site vacancies are immobile and will not contribute to ferroelectric hardening. There may also be more complex combinatory acceptor and donor-type effects depending on the nature of the net charge on each B-site and related compensation mechanisms, if any. Therefore, it is plausible that MnO$_2$+Cu co-doping has a decreased hardening effect on the properties due to a lower concentration of mobile oxygen vacancy defects in the lattice.

Compared to all doped compositions, MnO$_2$+Cu doped ceramics had the highest $d_{33}$ of 391 +/- 20 pC/N and $k_p$ of 0.54 +/- 0.02. However, the $Q_M$ of 314 +/- 108 was the lowest and dielectric losses of 1.2 +/- 0.6 % were the highest. It is well known that domain size scales with grain size, therefore a significant increase in grain size increases domain motion (higher $d_{33}$) but also increases domain motion related losses (higher tan $\delta$). In PZT ceramics, the $Q_M$ was also shown to have an inverse relationship with grain size. Since the grain size of MnO$_2$+Cu co-doped ceramics was over an order of magnitude larger...
than the grain sizes of the other acceptor-doped compositions, grain growth may explain the changes in piezoelectric coefficients and losses.

The relative permittivity of MnO$_2$+Cu co-doped ceramics is low at room temperature due to the tetragonal structural distortion and domain pinning oxygen vacancy defect dipoles induced by the manganese and copper. As the temperature increases, the relative permittivity exhibits similar changes in behavior as MnN-doped and MnN+Cu co-doped compositions. However, when temperature nears 100 °C, the permittivity abruptly increases and then levels off until the Curie temperature is reached at 213 °C. The rapid increase in permittivity near 100 °C indicates the appearance of sharp $T_{R\rightarrow T}$ transition behavior, which is in contrast to the broad transition observed for undoped PIN-PMN-PT. The appearance of a $T_{R\rightarrow T}$ transition indicates that MnO$_2$+Cu co-doped ceramics still are comprised of a minor amount of rhombohedral structure which transitions to the tetragonal state above 100 °C. Relative to undoped PIN-PMN-PT, the decrease in $T_C$ is due to the presence of second phase MgO in the microstructure, however, since the $T_{R\rightarrow T}$ temperature is the same then there may be regions in the lattice of MnO$_2$+Cu co-doped ceramics that are minimally affected by the dopants. The reasons for this may be due to a solubility limit of the dopants in the lattice structure which is ~2 mol% for MnO$_2$ in PIN-PMN-PT.$^{21}$ Furthermore, heterogeneous-distribution of the dopants in the microstructure may create pockets or defect clusters that behave independently. The multiple valence states of the Mn cation also complicate the relationship between defect chemistry, structure, and dielectric phase transition behavior. Clearly, the intricacies of the dielectric behavior observed here warrant further investigation.
4.3.5 Application Toward High-power Transduction

The effectiveness of piezoelectric ceramics for high-power transducer applications depends upon their ability to maximize vibration velocity while mitigating heat generation. The vibration velocity is directly related to the magnitude of \( Q_M \). When vibrating in off-resonance, the voltage and power generation is dependent upon the piezoelectric strain \( (d_{33}) \) and voltage \( (g_{33}) \) coefficients as well as dielectric loss. A figure of merit (FOM) for assessing the applicability of materials towards off-resonance applications is shown in Equation 4-2.\(^{53}\)

\[
FOM_{\text{off-res}} = \frac{d_{33} \times g_{33}}{\tan \delta} \\
\text{Equation 4-2.}
\]

Under resonance drive conditions, displacement and strain are very high. The FOM for resonance drive conditions is determined by the electromechanical coupling factors \( (k_{31}) \), electromechanical quality factor \( (Q_M) \), and the elastic compliance \( (s_{11}^E) \) tensors as shown in Equation 4-3.\(^{53}\) Therefore, power generation is dependent on maximizing electromechanical coupling while reducing mechanical loss. Materials with lower elastic compliance \( (s_{11}^E) \) will also have a higher power output during resonance drive. Since the elastic compliance is unknown and the impedance was studied in planar vibrational modes, for the purposes of simplifying the comparison, the FOM for resonance is discussed in terms of \( (k_p^2 \times Q_M) \), a dimensionless quantity.

\[
FOM_{\text{res}} = \frac{k_{31}^2 \times Q_M}{s_{11}^E} \\
\text{Equation 4-3.}
\]
As the material displaces during resonance drive, reducing mechanical losses and increasing electromechanical coupling increases the overall energy conversion efficiency during transduction and ensures that less vibrational energy is dissipated as heat. The energy conversion efficiency ($\eta$) can be approximated by Equation 4-4.\textsuperscript{54}

$$\eta = \frac{\frac{1}{Q_M} \frac{k^2}{2(1-k^2)}}{\frac{1}{1} \frac{k^2}{2(1-k^2)}}$$

Equation 4-4.

FOM’s for different compositions are shown in Table III. All ceramics doped with Mn show improved FOM which is due to the reduction in heat generation during room temperature piezoelectric drive. MnN-doped ceramics are among the highest FOM for resonance, off-resonance drive, and energy conversion efficiency due to the very high $Q_M$ and low $\tan \delta$. It can be clearly seen that even though manganese doping suppresses the $d_{33}$ and $k_p$, the improvements in FOM of manganese doped over the undoped PIN-PMN-PT underscores the importance of reducing losses for enhancing the performance of ceramics for high-power applications. Adding manganese as columbite improved the energy conversion efficiency and resonance FOM.
Table 4-3. Figures of merit and energy conversion efficiency ($\eta$) of undoped, MnN-doped, MnN+Cu co-doped, and MnO$_2$+Cu co-doped 25PIN-40PMN-35PT ceramic disks for high-power transducers. FOM’s for commercial PZT compositions are shown for comparison.

<table>
<thead>
<tr>
<th>Composition</th>
<th>FOM Off-Resonance ($\frac{m^2}{N} \times 10^{-12}$)</th>
<th>FOM Resonance (Dimensionless)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>996</td>
<td>25</td>
<td>94.9</td>
</tr>
<tr>
<td>MnN-doped</td>
<td>1600</td>
<td>190</td>
<td>99.1</td>
</tr>
<tr>
<td>MnN+Cu co-doped</td>
<td>1122</td>
<td>138</td>
<td>98.7</td>
</tr>
<tr>
<td>MnO$_2$+Cu co-doped</td>
<td>1615</td>
<td>72</td>
<td>98.3</td>
</tr>
<tr>
<td>PZT-8</td>
<td>1273</td>
<td>200</td>
<td>99.3</td>
</tr>
<tr>
<td>PZT-4</td>
<td>1242</td>
<td>168</td>
<td>99.2</td>
</tr>
</tbody>
</table>

If a process or application requires lower sintering temperatures to prepare low loss materials, Cu-doping may be used because all FOM’s and efficiencies were improved relative to the undoped composition. The reason that MnN+Cu did not have the highest FOM’s is because the $d_{33}$ and $k_p$ values were slightly reduced relative to MnN-doped ceramics because of the higher concentration of acceptor dopants. It is likely that if the MnN concentration is slightly reduced, then these electromechanical properties may be improved while still mitigating losses.

The FOM’s are compared with the military standard property data sets for PZT-4 ($\varepsilon_{33}/\varepsilon_0 = 1275$, $\tan \delta = 0.006$, $d_{33} = 290$ pC/N, $k_p = 0.58$, and $Q_M = 500$) and PZT-8 ($\varepsilon_{33}/\varepsilon_0 = 1025$, $\tan \delta = 0.004$, $d_{33} = 215$ pC/N, $k_p = 0.50$, and $Q_M = 800$). The FOM and energy conversion efficiency of MnN-doped and MnN+Cu compositions are comparable to PZT-8 and PZT-4, respectively, and are promising candidates for high-power transducer applications.
4.4 Conclusion

MnN-doping significantly hardens the ferroelectric and piezoelectric properties of PIN-PMN-PT ceramics. PIN-PMN-PT modified with MnN-only has a high coercive field $E_C = 11.7 \text{ kV/cm}$ and displays high strain behavior ($d_{33}^* = 411 \text{ pm/V}$). MnN-doped ceramics have low dielectric losses $\tan \delta \leq 0.7\%$, and high electromechanical coupling factors $Q_M \geq 1000$. MnN+Cu co-doping is an excellent way to process these materials at lower sintering temperatures, while maintaining material properties that are important for high-power acoustic transduction applications. Adding manganese in the columbite form (MnNb$_2$O$_6$) avoided second phase formation, substantially decreased dielectric and mechanical losses, and increased phase transition temperatures relative to MnO$_2$-doped ceramics. MnN-doped ceramics displayed very high FOM’s for resonance and off-resonance drive conditions as well as the highest energy conversion efficiency ($\eta = 99.1\%$) indicating this composition is highly promising for high-power transducer applications.

4.5 References


Y. Hosono, Y. Yamashita, K. Hirayama, and N. Ichinose, “Dielectric and Piezoelectric Properties of Pb[(In$_{1/2}$Nb$_{1/2}$)$_{0.24}$(Mg$_{1/3}$Nb$_{2/3}$)$_{0.42}$Ti$_{0.34}$]O$_3$ Single Crystals,” Jpn. J. Appl. Phys., 44 [9B] 7037–7041 (2005).


Y. Wang, E. Sun, W. Song, W. Li, R. Zhang, and W. Cao, “Improved thermal stability of [001]c poled 0.24Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-0.47Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.29PbTiO$_3$ single crystal with manganese doping,” *J. Alloys Compd.*, 601 154–157 (2014).


E. Sun, R. Zhang, F. Wu, B. Yang, and W. Cao, “Influence of manganese doping to the full tensor properties of 0.24Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-0.47Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.29PbTiO$_3$ single crystals,” *J. Appl. Phys.*, 113 [074108] 1–4 (2013).


X. Qi, E. Sun, J. Wang, R. Zhang, Bin Yang, and W. Cao, “Electromechanical properties of Mn-doped Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ piezoelectric ceramics,” *Ceram. Int.*, 42 15332–15337 (2016).

X. Qi, E. Sun, R. Zhang, B. Yang, S. Li, and W. Cao, “Effect of Mn-doping on dielectric relaxation behavior of Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ ferroelectric ceramics,” *Ceram. Int.*, 43 16819–16826 (2017).


30 X. Chao, D. Ma, R. Gu, and Z. Yang, “Effects of CuO addition on the electrical responses of the low-temperature sintered Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$-Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ ceramics,” *J. Alloys Compd.*, 491 698–702 (2010).


Y. Hosono, Y. Yamashita, H. Sakamoto, and N. Ichinose, “Dielectric and Piezoelectric Properties of Pb(In\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}–Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}–PbTiO\textsubscript{3} Ternary Ceramic Materials near the Morphotropic Phase Boundary,” Jpn. J. Appl. Phys., 42 [2A] 535–538 (2003).

D. Wang, M. Cao, and S. Zhang, “Phase diagram and properties of Pb(In\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}–Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}–PbTiO\textsubscript{3} polycrystalline ceramics,” J. Eur. Ceram. Soc., 32 433–439 (2012).

J. Wu, Y. Chang, B. Yang, S. Zhang, Y. Sun, F. Guo, and W. Cao, “Phase transitional behavior and electrical properties of Pb(In\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}–Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}–PbTiO\textsubscript{3} ternary ceramics,” J. Mater. Sci. Mater. Electron., 26 1874–1880 (2015).


CHAPTER 5: Textured Mn-doped PIN-PMN-PT Ceramics: Harnessing Intrinsic Piezoelectricity for High-power Transducer Applications

5.1 Introduction

High-power transduction devices such as actuators and ultrasonic projectors are designed to operate under resonance drive conditions where strain and displacement are maximal. Performance is improved by enabling higher vibration velocities ($v_{rms}$) of the active piezoelectric ceramic elements at resonance. The vibration velocity is proportional to the product of the piezoelectric coefficients ($v_{rms} \propto d_{ij} \times Q_{M}$) where $d_{ij}$ is the piezoelectric coefficient and $Q_M$ is the electromechanical quality factor (inverse of mechanical loss).\textsuperscript{1-4} At high vibration velocities, dielectric loss (tan $\delta$) contributes significantly to heating which degrades the piezoelectric properties and diminishes the vibration level. Therefore, materials with hard piezoelectric properties, such as high electromechanical quality factor ($Q_M$) and low dielectric loss (tan $\delta$), are desired to minimize heating of the ceramic elements. Materials with high coercive field ($E_C$) are also desired to reduced domain motion related losses under high AC field drive.\textsuperscript{5,6}

Perovskite single crystal compositions, such as Pb(Mg$\textsubscript{1/3}$Nb$\textsubscript{2/3}$)O$\textsubscript{3}$-PbTiO$\textsubscript{3}$ (PMN-PT) and Pb(In$\textsubscript{1/2}$Nb$\textsubscript{1/2}$)O$\textsubscript{3}$-Pb(Mg$\textsubscript{1/3}$Nb$\textsubscript{2/3}$)O$\textsubscript{3}$-PbTiO$\textsubscript{3}$ (PIN-PMN-PT), possess excellent electromechanical properties with exceptional piezoelectric coefficients ($d_{33}$) of $\geq 2000$ pC/N, electromechanical coupling factors of $k_{33} \geq 0.9$ and $k_p \geq 0.75$. However, these compositions are relatively soft as evidenced by low electromechanical quality factors ($Q_M$) $\leq 100$ and low coercive fields ($E_C \leq 7$ kV/cm) making them unsuitable for high-power applications.\textsuperscript{7-9}
Piezoelectrically hardened compositions with reduced dielectric and mechanical losses are often prepared by acceptor-doping with lower valence cations (i.e. Mn\textsuperscript{2+}/\textsuperscript{3+}, Fe\textsuperscript{3+}, and Cu\textsuperscript{2+}) on the $B$-site (i.e. Zr\textsuperscript{4+}, Ti\textsuperscript{4+}) of the perovskite crystal lattice.\textsuperscript{2, 3, 10–13} Of these chemistries, manganese is the most widely studied acceptor-dopant, and $[001]$c poled Mn-doped PIN-PMN-PT single crystal compositions on the rhombohedral side of the morphotropic phase boundary (MPB) and at the MPB region have high piezoelectric coefficients ($d_{33}$) $\geq$ 1000 pC/N and electromechanical quality factors ($Q_M$) $\geq$ 800.\textsuperscript{10, 14, 15} Since the average charge on the $B$-sites of the $A(B'B'')O_3$ perovskite structure is 4\textsuperscript{+}, aliovalent substitution of Mn\textsuperscript{2+} and Mn\textsuperscript{3+} cations create net negative charges on the $B$-site. The net negative charge is compensated by the formation of positively charged oxygen vacancy point defects ($V_O^{**}$). The interactions of oxygen vacancy defects with local charge imbalances result in the formation of $Mn_B^{'''} - V_O^{**}$ defect dipoles which pin the movement of domain walls. It is the interaction of defect dipoles with local polarization that increases the energy barrier for domain switching, and their mobility under ambient conditions which contribute to unique ferroelectric aging effects. The acceptor-dopant concentration and distribution dictate the defect concentration which effects changes in the domain size, structure, density, and mobility.\textsuperscript{16–18}

A drawback of acceptor-doping piezoelectric materials is the associated reduction in total strain because pinned ferroelectric domain walls reduce their collective motion (extrinsic response) under an applied alternating electric field.\textsuperscript{1, 2} For example, 2 mol\% Mn-doped 24PIN-42PMN-34PT ceramics have a low tan $\delta$ of 0.6\% and high $Q_M$ $>$ 2000 which make them promising for high-power transducer applications, however, the $d_{33}$ of 347 pC/N is relatively low and strain behavior is significantly suppressed by the acceptor
If a tradeoff in overall extrinsic response is the cost for obtaining hard piezoelectric properties, then maximizing the intrinsic piezoelectric response of the lattice and engineering the induced domain state may provide an approach for enhancing strain behavior for high-power transducers. The most effective approach to enhance the intrinsic piezoelectric response of the lattice of bulk ceramics is to crystallographically orient, or texture, piezoelectrically hard compositions. By harnessing the intrinsic anisotropy of the crystal lattice through grain orientation, then non-centrosymmetric properties of polycrystalline ceramics can approach those of single crystals.

The concept of textured ceramics, or grain-oriented ceramics, was first reported by Seabaugh et al. and has been extensively studied for maximizing piezoelectric properties in the Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)–PbTiO\(_3\) system. However, the base composition is inherently limited for high-power transduction by low rhombohedral-tetragonal (T\(_{R-T}\)) phase transition and Curie (T\(_C\)) temperatures ~75 °C and ~130 °C, respectively. Current developments in the state-of-the-art of textured ceramics have focused on materials with higher T\(_{R-T}\) > 100 °C and T\(_C\) ≥ 200 °C such as Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbZrO\(_3\)-PbTiO\(_3\) (PMN-PZT), Pb(In\(_{1/2}\)Nb\(_{1/2}\))O\(_3\)-Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PIN-PMN-PT), and Pb(Yb\(_{1/2}\)Nb\(_{1/2}\))O\(_3\)-Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PYN-PMN-PT). Yan et al. demonstrated that textured 1 mol% Mn-doped PMN-PZT ceramics have a high \(d_{33}\) of 720 pC/N, low dielectric loss (tan δ) of 0.3 %, and high \(Q_M\) of 403. Chang et al. showed that textured CuO-doped PIN-PMN-PT ceramics have excellent electromechanical properties such as \(d_{33}\) of 927 pC/N and planar electromechanical coupling factor \((k_p)\) of 0.87 which is important for energy conversion, however, the dielectric loss (tan δ) was > 1%. There are also new emerging ceramic compositions such as Pb(In\(_{1/2}\)Nb\(_{1/2}\))O\(_3\)-Pb(Zn\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-
PbTiO$_3$ (PIN-PZN-PT) which are pushing the limits of phase transition temperatures with high rhombohedral-tetragonal transition temperatures ($T_{R,T}$) of ~165 °C while maintaining high $d_{33}$ of 550 pC/N and high $E_C$ of 13 kV/cm.$^{37}$ However, there is still a need for materials that satisfy multiple key properties such as high phase transition temperature ($T_{R-T} > 100$ °C, $T_C > 200$ °C), high strain behavior ($d_{33} > 500$ pm/V), high electromechanical quality factors ($Q_M > 500$), low dielectric loss (tan $\delta \leq 0.5$ %), and high coercive field ($E_C > 10$ kV/cm). Significantly reducing dielectric and mechanical losses while maintaining high phase transition temperatures and electromechanical properties would constitute a significant advance in the development of textured piezoelectric ceramics for high-power transducer applications.

Mn-doping reduces the electromechanical properties of PIN-PMN-PT ceramics by decreasing the extrinsic contribution of domain motion to the piezoelectric response. However, if the intrinsic contribution of a [001]$_C$ crystallographically-oriented perovskite lattice can be harnessed by texturing then the strain behavior can be enhanced. In this paper we present conditions for fabricating [001]$_C$ oriented Mn-doped PIN-PMN-PT ceramics. The hardening effects of Mn-doping on the ferroelectric properties, dielectric properties, and losses of random and textured PIN-PMN-PT ceramics are also established. Rayleigh analysis of the low-field strain response of textured ceramics was used to isolate the reversible piezoelectric contribution of a crystallographically-oriented lattice from the irreversible motion of domain walls to quantify the effect of Mn-doping on extrinsic domain mobility. These materials are compared to state-of-the-art materials to highlight potential applications of Mn-doped textured PIN-PMN-PT ceramics.
5.2 Experimental Methods

The 25Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-40Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-35PbTiO$_3$ composition was selected as the base composition for this study because it was demonstrated to possess excellent electromechanical properties around the MPB. Two powder compositions were prepared for reactive templated grain growth studies: 25Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-40Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-35PbTiO$_3$ (referred to as undoped PIN-PMN-PT) and 6Pb(Mn$_{1/3}$Nb$_{2/3}$)O$_3$-25Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-34Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-35PbTiO$_3$ (referred to as 2 mol% Mn-doped PIN-PMN-PT). Manganese was added in the columbite form (MnNb$_2$O$_6$) because it avoids second phase formation.\textsuperscript{38, 39} BaTiO$_3$ was chosen as the platelet composition because it is chemically stable in the PIN-PMN-PT composition within the temperature regime explored in this study\textsuperscript{40} and has a small lattice parameter mismatch of 0.3% between the two materials making it suitable for epitaxial growth (pseudo cubic lattice parameters $a = 3.996$ Å for BaTiO$_3$, and $a = 4.008$ Å for 6PMnN-25PIN-34PMN-35PT calculated using Vegard’s Law\textsuperscript{41}).

Powders were prepared by vibratory milling metal oxides of PbO (D$_{50}$ ~ 7 μm, 99.9%, Alfa Aesar, Ward Hill, MA), TiO$_2$ (D$_{50}$ ~ 25 nm, 99.5%, Evonik Industries, Essen, Germany), and columbite powders (MgNb$_2$O$_6$, InNbO$_4$, MnNb$_2$O$_6$) to mitigate second phase pyrochlore formation.\textsuperscript{42} The columbite powders (InNbO$_4$ (D$_{50}$ ~ 0.3 μm), MgNb$_2$O$_6$ (D$_{50}$ ~ 0.4 μm), and MnNb$_2$O$_6$ (D$_{50}$ ~ 0.8 μm) were each prepared by vibratory milling In$_2$O$_3$ (D$_{50}$ ~ 50 nm, 99.99%, Santech Materials, Changsha, Hunan, China), MgO (D$_{50}$ ~ 0.6 μm, Mallinckrodt Chemicals, Dublin, Ireland), or MnO$_2$ (D$_{50}$ ~ 1.4 μm, 99.99%, Sigma Aldrich, St. Louis, MO) with Nb$_2$O$_5$ (D$_{50}$ ~ 100 nm, 99.9%, H.C. Starck, Munich, Germany) for 24 h in ethanol. InNbO$_4$ was calcined at 925 °C for 3 h, and MgNb$_2$O$_6$ and
MnNb$_2$O$_6$ were each calcined at 1000 °C for 6 h. All powder batches also contained 1 wt% excess PbO to mitigate lead loss due to volatility. All powder batches were vibratory milled for 60 h using a 1:1:1 mass ratio of spherical 3 mm, 5 mm, and 10 mm diameter spherical YSZ media. The milled powder mixtures were dried, ground in a mortar and pestle, and aggregates were removed using a < 106 μm (-140 mesh) sieve.

Tetragonal BaTiO$_3$ (BT) platelets were purchased from a commercial supplier (Entekno Materials, Inc., Eskisehir, Turkey) where they were fabricated by a topochemical microcrystal conversion process. Fine platelets with diameters that ranged from 5 – 10 μm and thickness on the order of ~1 μm were separated from the main batch by sedimentation.

Powders were ball milled with a non-aqueous formulation (Ethanol, xylenes, PVB, PAG, BBP, and menhaden fish oil) for 24 h in a 250 mL Nalgene bottle with spherical 5 mm YSZ ball media to prepare slurries for tape casting. BaTiO$_3$ platelets were dispersed separately in a mixture of the binder formulation by sonication and hand mixing and added to the ball mill for 15 min. Undoped and Mn-doped slurry compositions were adjusted to bring the BaTiO$_3$ platelet loading to 5 vol%. The slurry was strained into a Nalgene cup, the solids loading was adjusted to 18 vol%, and then mixed three times at 1500 RPM for 4 min using a FlakTech high speed mixer. Slurries were tape cast at a velocity of 50 cm/min under a 15.24 cm wide doctor blade with a gap height of 200 μm. The tape was dried on the bed at 35 °C for 2 h before removing for cutting and stacking. The tapes were cut, stacked, and laminated using a uniaxial laminator with an applied pressure of 15 MPa at 75 °C for 6 min. Laminated tapes were hydrostatically laminated at 200 MPa at 75 °C for 30 min. The binder was removed using the following burnout profile: ramp to 100 °C at 1 °C/min, ramp to 350 °C at 0.1 °C/min, holding at 350 °C for 9 h, ramp to 450 °C at 0.1
°C/min, holding at 450 °C for 4 h, and furnace cooled. Burned out tapes were vacuum sealed in latex bags and cold isostatically pressed (CIP) at 200 MPa to increase the green density to >50% relative density.

Green bodies were embedded in relatively coarse (~2 μm) stoichiometric PIN-PMN-PT embedding powder with 1 wt% excess PbO to mitigate the volatility of the constituents during high temperature sintering. Undoped and Mn-doped templated samples were sintered in a tube furnace at 1250 °C for 30 min to 10 h. Oxygen flow of 250 ml/min was maintained during firing to enhanced densification and grain growth. Random ceramics without templates were prepared by dry pressing powders at 40 MPa into 13 mm diameter by 1 mm thick green bodies, CIP at 200 MPa, and sintering at 1150 °C for 5 h in O₂.

Phase identification, crystallographic structure, and degree of preferred orientation were characterized with x-ray diffraction (XRD, PANalytical Empyrean Xpert Pro MPD diffractometer, The Netherlands). Texture fraction was calculated by Lotgering factor method. Microstructures were analyzed by scanning electron microscopy (SEM) (Quanta 250 ESEM, ThermoScientific, Hillsboro, OR) of fracture surfaces, and grain size was determined using line-intercept rule and ImageJ analysis software. Dense random and textured ceramic samples were prepared for electrical property measurements by preparing planar mode discs or square plates with > 10:1 diameter to thickness aspect ratio as specified by the IEEE Standards of Piezoelectricity. Samples were sonicated in acetone and methanol for 30 sec to clean the surface, dried at 85 °C, and painted with Dupont 7095 silver paste which was dispersed using α-terpineol, and dried at 125 °C for 30 min. Electrodes were fired at 575 °C for 15 min using a 15 °C/min ramp rate. Samples were DC
poled at 40 kV/cm for 15 min at room temperature and aged for 24 h. Ferroelectric and strain measurements were performed with a modified Sawyer-Tower circuit equipped with a Stanford Research Systems Model SR830 DSP Lock-In Amplifier. The quasi-static piezoelectric coefficient \(d_{33}\) was measured on a Berlincourt \(d_{33}\) PiezoMeter System (Piezotest, UK) at 10 N at 110 Hz. Low-field \(d_{33}^*\) was measured from the slopes of the decreasing portions of the unipolar \(S-E\) loops at \(\leq 5\) kV/cm and high-field \(d_{33}^*\) was calculated from the peak strain at 40 kV/cm. Strain hysteresis \(H_S\) was measured by the strain difference at half of the applied electric field divided by the maximum total strain. Electrical impedance spectra were measured using an Agilent 4294A Precision Impedance Analyzer and used to calculate electromechanical coupling factors \(k_p\) and electromechanical quality factors \(Q_M\). \(\varepsilon_{33}/\varepsilon_0\) of poled samples was measured as a function of temperature and frequency using an Agilent 4284A Precision LCR meter, and \(T_{R-T}\) transition was determined by calculating the minimum of the second derivative of the permittivity with respect to temperature.

5.3 Results and Discussion

5.3.1 Sintering and Reactive Templated Grain Growth of PIN-PMN-PT Ceramics

The conditions under which densification and grain growth are maximized for reactive templated grain growth (RTGG) of Mn-doped PIN-PMN-PT on \(\text{BaTiO}_3\) (BT) platelets were identified by examining fracture surfaces of sintered ceramics for changes in the microstructure. Figure 5-1 shows SEM images of random and textured ceramics.
Figure 5-1(A) shows that undoped PIN-PMN-PT random ceramic sintered at 1150 °C for 5 h is fully dense with a relatively fine average grain size of ~1 μm. Preliminary RTGG experiments demonstrated there was insufficient grain growth at 1150 °C for TGG with BT templates. Templated ceramics sintered at 1250 °C for 30 min (Figure 5-1(B)) consist of well-aligned BT templates with ~1.5 μm of oriented PIN-PMN-PT growth as evidenced by the elemental Z contrast between the Pb$^{2+}$ and Ba$^{2+}$ and a randomly oriented polycrystalline matrix of ~1.5 μm grain size. After 10 h at 1250 °C (Figure 5-1(C)), the microstructural growth of the templated PIN-PMN-PT consumed the matrix grains resulting in a textured microstructure. The templated grain size was difficult to determine but was ~8 – 15 μm based on the platelet interspacing.

SEM of 2% Mn-doped PIN-PMN-PT ceramic sintered at 1150 °C for 5 h (Figure 5-1(D)) shows a heterogenous microstructure with an average grain size of 1 μm and regions of ~2-3 μm grains. The grain size distribution may be related to heterogeneous distribution of multivalent elemental manganese creating oxygen vacancies that raise the grain boundary energy resulting in local regions of slightly enhanced grain growth. The microstructure development is similar to observations made in other Mn-doped PbTiO$_3$-based ceramics.\textsuperscript{39, 44, 45} Mn-doped PIN-PMN-PT ceramics templated with BT and sintered at 1250 °C for 30 min (Figure 5-1(E)) have similar templated growth and microstructure development as undoped PIN-PMN-PT. Heating at 1250 °C for 10 h resulted in fully textured Mn-doped PIN-PMN-PT (Figure 5-1(F)).
Figure 5-1. SEM images of reactive templated grain growth of PIN-PMN-PT (A) undoped random ceramic, (B-C) undoped textured ceramic sintered for different times, (D) Mn-doped random ceramic, and (E-F) Mn-doped textured ceramic sintered for different times. 

X-ray diffraction patterns of the undoped and Mn-doped random ceramics (r) in Figure 5-2 show that both compositions are perovskite. The (002) peak at 45° 2θ is significantly broadened because rhombohedral and tetragonal structures coexist. The peak
broadening is a typical effect for perovskite compositions located in the morphotropic phase boundary region.\textsuperscript{46, 47} When the ceramics templated with 5 vol\% BT platelets were sintered at 1250 °C for 10 h, the relative peak intensities of the (00l) peaks increased substantially as a result of oriented growth of PIN-PMN-PT on the [001]\textsubscript{c} aligned BT platelets. Undoped and Mn-doped PIN-PMN-PT textured ceramics (t) have texture fractions of 81\% and 90\%, respectively. The (002)c and (200)/(020) peaks at 45° 2θ are significantly broadened and split because of the residual stresses at the BT platelet/PIN-PMN-PT matrix interface that arises from the lattice parameter misfit between BT and textured PIN-PMN-PT.\textsuperscript{24, 48}

Figure 5-2. XRD of random (r) and textured (t) undoped and 2 mol\% Mn-doped PIN-PMN-PT ceramics. Textured undoped and Mn-doped ceramics have Lotgering factors of 0.81 and 0.90, respectively.
5.3.2 Ferroelectric Properties, Dielectric Properties, and Losses in Mn-doped PIN-PMN-PT

The purpose of Mn-doping is to decrease detrimental dielectric (\(\tan \delta\)) and mechanical \((1/Q_M)\) losses and thus mitigate heat generation at high vibration velocities. Undoped PIN-PMN-PT ceramics have excellent electromechanical properties for transducers but are particularly susceptible to heat generation because of their high \(\tan \delta\) of 1.8% and low \(Q_M\) of 77. The ferroelectric loops in Figure 5-3 show that the undoped ceramic has a relatively low \(E_C\) of 9.3 kV/cm. Figure 5-4 shows that the relative permittivity \((\varepsilon_{33}/\varepsilon_0)\) varies with temperature rise near the \(T_{R-T}\) transition at 100 °C and increases up to \(T_C\) at 222 °C. The variation in \(\varepsilon_{33}/\varepsilon_0\) with temperature rise is problematic because certain electromechanical properties are permittivity-dependent, such as the piezoelectric voltage coefficient \(g_{33} = d_{33}/(\varepsilon_0)\).\(^{49}\) The phase transition temperatures measured here are representative of similar PIN-PMN-PT ternary compositions\(^{46, 47, 50}\) and the high \(T_C\) makes this composition promising for studying acceptor-doping. The ferroelectric and dielectric properties are listed in Table 5-1.

![Table 5-1. Ferroelectric and dielectric properties of undoped and Mn-doped PIN-PMN-PT ceramics and textured ceramics. Dielectric loss and permittivity measured at 10 kHz.](image)

The 2 mol% Mn-doped PIN-PMN-PT ceramic possesses significantly lower losses as indicated by the \(\tan \delta\) of 0.52% and the \(Q_M\) of 1054. The \(E_C\) also increased to 11.8 kV/cm,
and because of ferroelectric hardening, the remnant polarization \( (P_R) \) decreased from 33.3 μC/cm\(^2\) to 24.5 μC/cm\(^2\) relative to undoped PIN-PMN-PT. An internal bias field \( (E_i) \) of 1.4 kV/cm was also determined from the shift in the \( P-E \) loops of Mn-doped ceramic \( (E_i = (E_C^+ + E_C^-)/2) \) in Figure 5-3. The large \( E_i \) is a measure of the defects introduced by acceptor-doping which increased the energy barrier to ferroelectric switching resulting in increased \( E_C \) and decreased \( P_R \).\(^{52,54,55}\) The room temperature \( \varepsilon_{33}/\varepsilon_0 \) decreased from 2198 to 1244 with Mn-doping and increased more slowly with the temperature rise than undoped PIN-PMN-PT. There was no discernable \( T_R-T \) transition for Mn-doped PIN-PMN-PT, and the \( T_C \) increased slightly from 222 °C to 228 °C. Properties are consistent with trends observed in previous investigations of Mn-doped PIN-PMN-PT ceramics.\(^{19,39}\)

Figure 5-3. Ferroelectric \( (P-E) \) loops of random \( (r) \) and textured \( (t) \) undoped and Mn-doped PIN-PMN-PT ceramics show that Mn-doping hardens the ferroelectric properties by increasing \( E_C \) and reducing \( P_R \). Textured ceramics also have higher \( E_C \) than the random ceramic analogs.
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Figure 5-4. Relative permittivity at 10 kHz as a function of temperature for random (r) and textured (t) undoped and Mn-doped PIN-PMN-PT ceramics.

The mechanism of ferroelectric hardening and decreased losses is related to the formation of oxygen vacancy defects following aliovalent substitution of Mn$^{2+}$ ($r_i = 83$ pm), Mn$^{3+}$ ($r_i = 65$ pm), or Mn$^{4+}$ ($r_i = 53$ pm) for higher-valence $B$-site cations of similar ionic radii such as In$^{3+}$ ($r_i = 80$ pm), Ti$^{4+}$ ($r_i = 61$ pm), or Nb$^{5+}$ ($r_i = 64$ pm). Although there is considerable debate regarding the amphoteric nature of manganese cations (i.e. $A$-site versus $B$-site substitution), the high $P_{O2}$ atmosphere and excess Pb$^{2+}$ $A$-site cations provided by excess PbO in the powder batches in this study is assumed to restrict manganese to $B$-site substitution. Hennings and Pomplun observed Mn$^{4+}$ formation in Mn$_2$O$_3$-doped PbTiO$_3$ ceramics by electron spin resonance spectroscopy under similar conditions. The authors also observed increases in the rate of PbO uptake by thermogravimetric analysis during high $P_{O2}$ and PbO vapor pressure atmosphere annealing and interpreted the results as manganese incorporation into the $B$-site and stabilization of
the perovskite lattice. Based on their findings, it is likely that manganese adopts the Mn$^{4+}$ valence state on the $B$-site in this study as well. Since Mn$^{4+}$ is smaller than Nb$^{5+}$ and there is a high concentration of niobium in the perovskite, it is plausible that manganese substitutes for niobium in the structure forming $Mn_{Nb}V_O^{**}$ defect dipoles that induce the hard ferroelectric properties observed in this study. Further analysis by ESR or XPS is required to verify the valence state as well as HRTEM and modeling to elucidate the site occupancy of manganese.

**5.3.3 Electromechanical Properties of Textured Mn-doped PIN-PMN-PT Ceramics**

In this section we explore the effect of crystallographic texture and grain alignment on the electromechanical behavior of textured Mn-doped PIN-PMN-PT ceramics, discuss the key properties for high-power transducers, and compare them to current state-of-the-art textured materials.

Table 5-2. Electromechanical properties of undoped and Mn-doped PIN-PMN-PT ceramics and textured ceramics.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$f$ (%)</th>
<th>$d_{33}$ (pC/N) (Berlincourt)</th>
<th>$g_{33}$ (x10$^{-3}$ Vm/N)</th>
<th>$d_{33}^*$ (pm/V)</th>
<th>$H_S$ (%)</th>
<th>$k_p$</th>
<th>$Q_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIN-PMN-PT</td>
<td>0</td>
<td>559</td>
<td>29.0</td>
<td>580</td>
<td>4.6</td>
<td>0.58</td>
<td>77</td>
</tr>
<tr>
<td>Mn-doped PIN-PMN-PT</td>
<td>81</td>
<td>521</td>
<td>25.1</td>
<td>1140</td>
<td>11</td>
<td>0.51</td>
<td>50</td>
</tr>
<tr>
<td>Mn-doped PIN-PMN-PT</td>
<td>90</td>
<td>341</td>
<td>32.2</td>
<td>846</td>
<td>22</td>
<td>0.53</td>
<td>496</td>
</tr>
</tbody>
</table>

Mn-doped PIN-PMN-PT ceramic has a piezoelectric charge coefficient ($d_{33}$) of 282 pC/N, piezoelectric voltage coefficient ($g_{33}$) of 26.2 $\times 10^{-3}$ Vm/N, and planar electromechanical coupling factor ($k_p$) of 0.44 as seen in the Table 5-2. Textured Mn-doped
ceramics possess enhanced piezoelectric properties such as the $d_{33}$ of 341 pC/N, $g_{33}$ of 32.2 $\times 10^{-3}$ Vm/N, and $k_p$ of 0.53. The increase in $g_{33}$ is a result of the higher $d_{33}$ and reduced relative permittivity. At high electric fields (40 kV/cm), a total bipolar strain of 0.32% and peak unipolar strain of 0.22% were measured in textured Mn-doped PIN-PMN-PT (Figure 5-5). The low-field $d_{33}$* of 846 pm/V and high-field $d_{33}$* of 613 pm/V are a 100% improvement relative to Mn-doped random ceramic and constitutes ~75% of the strain behavior of textured undoped PIN-PMN-PT (low-field $d_{33}$* = 1140 pm/V, high-field $d_{33}$* = 710 pm/V). The electromechanical properties of textured Mn-doped PIN-PMN-PT ceramics in this study are comparable to those reported for textured Mn-doped PMN-PT\textsuperscript{27} and textured Mn-doped PMN-PZT.\textsuperscript{35}
Figure 5-5. (A) Bipolar strain of and (B) unipolar strain (S-E) of random (r) and textured (t) undoped (LF = 0.81) and Mn-doped (LF = 0.90) PIN-PMN-PT ceramics. Textured ceramics display significantly enhanced strain behavior relative to random ceramics. Texture greatly enhanced the strain behavior of Mn-doped PIN-PMN-PT.
It should be noted that the $d_{33}$ measured by Berlincourt method for textured Mn-doped PIN-PMN-PT ceramics increased relative to the random ceramics whereas the $d_{33}$ decreased for textured undoped ceramics. It is likely that the decrease in $d_{33}$ measured by Berlincourt method for undoped PIN-PMN-PT is a result of the significant structural shift onto the tetragonal side of the MPB. Mn-doping shifts the structure toward the rhombohedral side of the MPB, resulting in a net shift toward the MPB for textured ceramics and may account for the greater $d_{33}$ in textured Mn-doped PIN-PMN-PT compared to random ceramic.

Strain hysteresis ($H_S$) of textured Mn-doped PIN-PMN-PT at high electric fields increased from 15% to 22% relative to random ceramic and was significantly more than the $H_S$ of textured undoped PIN-PMN-PT ($H_S = 11\%$). At high fields, acceptor-doped ceramics exhibit increased hysteretic strain behavior when internal interfaces and domain walls move irreversibly. At electric field strengths comparable to the $E_C$ of the material, the pinned domains decouple from the pinning defects and switch into the next low energy configuration, however, upon release of the field they remain in their new metastable configuration resulting in electromechanical hysteresis. Future work should be focused on better understanding how to decrease this hysteresis at high fields while maintaining low-loss characteristics and further improving electromechanical properties.
5.3.4 Rayleigh Analysis of Textured Mn-doped PIN-PMN-PT Ceramics

The Rayleigh law (Equation 5-1) provides an approach to isolate the intrinsic and extrinsic contributions of the piezoelectric response to the strain behavior. These contributions can be quantified by applying the Rayleigh law to the low-field strain response of materials.\(^{57}\) In Equation 5-1, \(d_{\text{int}}\) represents the intrinsic piezoelectric response which is composed of the reversible motion of the lattice in the zero-field condition and is determined by extrapolating the data to the y-axis. The product of \(\alpha E_0\) represents the extrinsic piezoelectric response and is interpreted as the irreversible motion of domain walls. The Rayleigh parameter, \(\alpha\), is the measure of the irreversibility of domain wall motion.\(^{58, 59}\) The converse piezoelectric coefficients \((d_{33}^*)\) of textured undoped and Mn-doped PIN-PMN-PT ceramics were calculated from the peak-to-peak bipolar strain of poled ceramics and is plotted in Figure 5-6 as a function of maximum applied field \((E_0)\). The Rayleigh parameters were used to calculate the strain behavior within the low-field region using Equation 5-2. Calculated strain loops show a good fit to the experimental loops plotted in Figure 5-7 which validates the Rayleigh law within this region.

\[
\begin{align*}
    d_{33}^* &= d_{\text{int}} + \alpha E_0 \\
    S(E) &= (d_{\text{int}} + \alpha E_0)E \pm \frac{\alpha(E_0^2 - E^2)}{2}
\end{align*}
\]

Equation 5-1.  
Equation 5-2.
Figure 5-6. Rayleigh analysis of the linear relationship between piezoelectric coefficient ($d_{33}$) and maximum applied electric field ($E_0$) for textured PIN-PMN-PT ceramics under low-field conditions. Mn-doping reduces the irreversible motion of domain walls ($\alpha E_0$) to the strain response by formation of $\textit{Mn}_B - V_{O}^{**}$ defect dipoles which increase the energy barrier to ferroelectric domain switching.

Figure 5-7. The agreement between the experimental strain and calculated strain demonstrate that the strain behavior can be predicted in the low-field region. Mn-doping significantly reduces strain hysteresis by reducing irreversible domain wall motion of textured PIN-PMN-PT ceramics.
The intrinsic responses \( (d_{\text{int}}) \) of the textured undoped and Mn-doped PIN-PMN-PT ceramics are 520 and 262 pm/V, respectively, and are relatively close to the \( d_{33} \) measured by Berlincourt meter for each composition which is determined by applying a low stress. It is worth noting that the difference between the \( d_{33} \) measured in the low-stress state of the quasi-static Berlincourt meter and zero-field extrapolation of Rayleigh analysis \( (d_{\text{int}}) \) is larger for textured Mn-doped ceramic (30%) than textured undoped ceramic (<1%). Although the Berlincourt meter method is a good assessment of the reversible intrinsic response of the lattice, the difference in piezoelectric coefficient may be due to the presence of elastic stresses at domain wall interfaces due to the lattice parameter mismatch of ferroelastic domain walls. In some cases, this can lead to enhanced piezoelectric response under applied stress due to 90° domain switching by altering the relative permittivity with applied stress as has been shown for hard PZT ceramics. In the case of textured Mn-doped PIN-PMN-PT, the larger difference in \( d_{33} \) and \( d_{\text{int}} \) may be attributed to electric field-induced stresses at domain wall interfaces related to the interaction of oxygen vacancy defects with manganese that enhanced the piezoelectric response under applied stress.

Table 5-3. Rayleigh coefficients and percentage of intrinsic (reversible) and extrinsic (irreversible) contribution of the piezoelectric response to the strain behavior of undoped and Mn-doped textured PIN-PMN-PT ceramics at low fields.

<table>
<thead>
<tr>
<th>PIN-PMN-PT Composition</th>
<th>Rayleigh Coefficients</th>
<th>Contribution at 1 kV/cm</th>
<th>Contribution at 4 kV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( d_{\text{int}} ) (pm/V)</td>
<td>( \alpha \times 10^{-17} \text{ m}^2/\text{V}^2 )</td>
<td>% Intrinsic</td>
</tr>
<tr>
<td>Undoped</td>
<td>520</td>
<td>78.5</td>
<td>87</td>
</tr>
<tr>
<td>Mn-doped</td>
<td>262</td>
<td>14.7</td>
<td>95</td>
</tr>
</tbody>
</table>
The Rayleigh parameter ($\alpha$) is $78.5 \times 10^{-17} \text{m}^2/\text{V}^2$ for the undoped ceramic and decreases to $14.7 \times 10^{-17} \text{m}^2/\text{V}^2$ for the Mn-doped ceramic. The fraction of the extrinsic contribution ($\alpha E_0/(d_{\text{int}} + \alpha E_0)$) of the piezoelectric response to the strain behavior of undoped PIN-PMN-PT that arises from irreversible motion of domain walls accounts for ~13% of the piezoelectric coefficient at 1 kV/cm and increases to ~38% at 4 kV/cm as seen in Table 5-3. The increase in extrinsic contribution with applied field reflects the low barrier to domain wall motion in textured undoped PIN-PMN-PT and is representative of relatively soft piezoelectric ceramics. In textured Mn-doped ceramics, the extrinsic contribution is ~5% at 1 kV/cm and increases to ~18% at 4 kV/cm. The lower extrinsic contribution of Mn-doped ceramics relative to undoped ceramics is a result of the piezoelectric hardening due to the doping effect. The analysis of the undoped composition agrees with Chang et al.’s analysis of textured CuO-doped 28PIN-40PMN-32PT ceramics where the barrier to irreversible domain wall motion is quite low and the extrinsic response was calculated to be ~13% at 1 kV/cm.\textsuperscript{61}

Strain hysteresis in Figure 5-7 measured at 0 kV/cm decreased from 29% in undoped to 9% in Mn-doped PIN-PMN-PT. The reduction in irreversible domain motion and hysteretic strain behavior in textured Mn-doped PIN-PMN-PT at low fields is also characteristic of hard piezoelectric materials.\textsuperscript{56, 58} Although the overall piezoelectric response of Mn-doped ceramics is lower than undoped ceramics, the lower hysteresis at low fields is a significantly beneficial effect of Mn-doping. Lower hysteresis means lower hysteretic losses and it also indicates that Mn-doping is a viable approach to exact more precise control over the strain behavior at low fields.
5.3.5 Frequency Dependency of Dielectric Loss in Mn-doped PIN-PMN-PT

A unique phenomena of acceptor-doped ceramics is the frequency dependency of the dielectric loss which is shown in Figure 5-8 for textured PIN-PMN-PT ceramics. Textured undoped ceramics display a slight increase in tan \( \delta \) with increase in frequency which ranges from 2\% to 3\% and is relatively independent of temperature. With Mn-doping, the dielectric losses change significantly with frequency and temperature. At low frequencies of 1 kHz, the room temperature tan \( \delta \) of 0.66\% steadily increases with increasing temperature and exceeds the dielectric loss of undoped ceramic (~2\%) above \(~135^\circ\)C. When the frequency is increased to 10 kHz, tan \( \delta \) remains below 1\% until the temperature exceeds 125 \(^\circ\)C and remains below undoped PIN-PMN-PT until \(~185^\circ\)C. At 100 kHz, the room temperature tan \( \delta \) decreases further to 0.37\% and remains below 1\% until the temperature increases above 165 \(^\circ\)C. The changes in tan \( \delta \) are not related to the low \( T_C \) of the BT templates because the same dielectric behavior has been observed in Mn-doped random ceramics.\(^{39}\)

The frequency dependency of dielectric loss is a characteristic of the dielectric relaxation behavior of the \( Mn_B^\prime - V_O^{**} \) defect dipoles. The dielectric relaxation time (\( \tau \)) of the oxygen vacancy defect dipoles is rapid enough that the defect dipoles can oscillate at low AC frequencies such as 1 kHz which results in dielectric loss. Thermal activation of defect dipoles and space charges reduces the dielectric relaxation time which is why the dielectric loss increases with temperature.\(^{62}\) As the frequency increases, the dielectric relaxation time exceeds the frequency period of the applied field and the defect dipoles do not have sufficient time to reorient at high frequencies of 10 kHz and 100 kHz so tan \( \delta \) decreases substantially. The relationship between temperature, frequency, and dielectric
relaxation time has been modeled with the Arrhenius function to explain the dielectric
frequency behavior and internal bias fields for defect systems such as $Ni_{Ti}''-V_{O}^{**}$ in Ni-
doped BaTiO$_3$ ceramics$^{62}$ and $Mn_{Ti}''-V_{O}^{**}$ complexes in Mn-doped PMN-PT single
crystal.$^{17}$ Although this explanation is plausible and based on the literature, further
investigation is needed to determine if conductivity is also contributing to the change in
frequency dependent dielectric loss behavior in Mn-doped ceramics.

![Figure 5-8](image.png)

Figure 5-8. Change in dielectric loss ($\tan \delta$) with frequency and temperature for textured
undoped and Mn-doped PIN-PMN-PT ceramics. Textured Mn-doped PIN-PMN-PT is a
low loss material with frequency-tunable $\tan \delta$.

5.3.6 Composite and Grain Size Effects of Textured PIN-PMN-PT Ceramics

Compared to random ceramics, all textured ceramics in this study have decreased
$P_R$ and larger $E_C$, and relative to all compositions in this study, textured Mn-doped ceramics
have the highest $E_C$ of 14.0 kV/cm. The high $E_C$ of textured Mn-doped PIN-PMN-PT is
the highest reported for textured ceramics and is comparable to high-coercive field textured
PYN-PMN-PT with \( E_C \) of 13.9 kV/cm\(^3\).\(^{34} \) Despite the enhancements in domain switching provided by larger grain sizes which enhances overall polarization in PbTiO\(_3\)-based ceramics,\(^{55, 63} \) the interfacial stresses at the platelet/matrix interface hinder domain switching in regions surrounding the BaTiO\(_3\) platelet. Piezoelectric force microscopy (PFM) studies of textured PIN-PMN-PT ceramics by Chang et al. show that fine 80 nm domains with higher domain wall density form near the BaTiO\(_3\) platelet/matrix interface in textured PIN-PMN-PT. Domain size increases with increasing distance from the platelet indicating that the platelet clamps the domain response.\(^{64} \) The clamped response explains why the \( P_R \) decreases and the \( E_C \) increases for textured ceramics with residual BT templates.

Textured Mn-doped PIN-PMN-PT possesses markedly improved temperature stability and reduced dielectric losses as evidenced by the reduced changes in dielectric properties with temperature shown in Figure 5-4. No \( T_{R-T} \) transition was observed, and the variation in relative permittivity decreased at low temperature. However, the \( T_C \) decreased from 228 °C to 219 °C in textured ceramic due to a composite effect of the low-\( T_C \) BaTiO\(_3\) templates.\(^{32, 65} \) Although no \( T_{R-T} \) was observed for textured Mn-doped PIN-PMN-PT in this study, Yan et al. showed that the electromechanical properties of \( d_{31} \) and \( k_{31} \) of textured Mn-doped PMN-PZT ceramics, which also show no \( T_{R-T} \), deviated with temperature rise > 100 °C. The authors attributed the deviation in electromechanical properties to the permittivity changes and structural transition near the Curie temperature of the BaTiO\(_3\) platelets.\(^{35} \) Therefore, it is recommended that a future study be conducted to investigate property variation of textured Mn-doped PIN-PMN-PT ceramics in the temperature regime of 100 – 150 °C.
The high $Q_M$ of 496 of textured Mn-doped PIN-PMN-PT is an order of magnitude higher than textured undoped ceramic but is 50% less than Mn-doped random ceramic ($Q_M = 1054$). Sakaki et al. showed that that $Q_M$ decreases with increasing grain size. Since the grains sizes of textured ceramics formed TGG are $>10 \, \mu m$, this may explain why $Q_M$ decreased by 50% relative to fine-grain size Mn-doped random ceramic. For application purposes, the relationship between template size, loading, and dispersion can be considered to tailor the grain size of textured ceramics for larger $Q_M$.\textsuperscript{21,48}

5.4 Conclusions

The 2 mol% Mn-doped PIN-PMN-PT ceramics were 90% textured by RTGG with 5 vol% BaTiO$_3$ templates. Mn-doping of PIN-PMN-PT induced significant enhancements in hardened ferroelectric, dielectric, and piezoelectric properties such as $E_C$ of 11.8 kV/cm, low tan $\delta$ of 0.52%, and high $Q_M$ of 1054. Crystallographically-textured Mn-doped PIN-PMN-PT has two times higher strain than untextured ceramic, and a low-field $d_{33}^*$ of 846 pm/V, $k_p$ of 0.53, and high $E_C$ of 14.0 kV/cm. The relative permittivity of textured Mn-doped ceramics varies less with temperature, and low tan $\delta$ ranging from 0.37% to 0.66% were measured. Textured Mn-doped PIN-PMN-PT ceramics have a higher Curie temperature of 219 °C than textured undoped ceramics. Rayleigh analysis revealed that Mn-doping decreased the extrinsic contribution of the piezoelectric response to the strain behavior from 38% to 18% at 4 kV/cm by limiting irreversible domain wall motion. The decreased irreversible domain wall motion due to Mn-doping significantly reduced the strain hysteresis ($H_S$) from 29% to 9% at low fields. Although the overall piezoelectric
response was reduced with Mn-doping relative to undoped ceramics, the increase in $d_{33}$ measured by Berlincourt meter from 283 pC/N in random ceramic to 341 pC/N in textured ceramic indicates that crystallographic texturing increases the intrinsic piezoelectric response of the lattice. Future work should be focused on improving the piezoelectric response of undoped and Mn-doped textured ceramics through compositional tailoring on the rhombohedral side of the MPB to induce 4R domain structure, improving the texturing fraction, and eliminating the residual BT templates to alleviate the residual interfacial stresses. Nevertheless, crystallographic texturing of hard Mn-doped PIN-PMN-PT ceramics makes these materials promising candidates for low loss, high frequency, and high-power transduction applications.

5.5 References


8 Y. Hosono, Y. Yamashita, K. Hirayama, and N. Ichinose, “Dielectric and Piezoelectric Properties of Pb[(In_{1/2}Nb_{1/2})_{0.24}(Mg_{1/3}Nb_{2/3})_{0.42}Ti_{0.34}]O_3 Single Crystals,” *Jpn. J. Appl. Phys.*, 44 [9B] 7037–7041 (2005).


X. Qi, E. Sun, J. Wang, R. Zhang, Bin Yang, and W. Cao, “Electromechanical properties of Mn-doped Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ piezoelectric ceramics,” *Ceram. Int.*, 42 15332–15337 (2016).

X. Qi, E. Sun, R. Zhang, B. Yang, S. Li, and W. Cao, “Effect of Mn-doping on dielectric relaxation behavior of Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ ferroelectric ceramics,” *Ceram. Int.*, 43 16819–16826 (2017).


S.F. Poterala, S. Trolier-mckinstry, R.J. Meyer, and G.L. Messing, “Processing,
texture quality, and piezoelectric properties of <001>C textured (1-x)Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3}) - xPbTiO\textsubscript{3} ceramics,” *J. Appl. Phys.*, **110** [014105] 1–9 (2011).


30 Y. Chang, J. Wu, Y. Sun, X. Wang, S. Zhang, B. Yang, G.L. Messing, and W. Cao, “Enhanced electromechanical properties and phase transition temperatures in [001] textured Pb(In\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}-Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3} ternary ceramics,” *Appl. Phys. Lett.*, **107** [082902] 1–6 (2015).


33 C. Duran, S. Cengiz, N. Ecebaş, S. Dursun, and E. Akça, “Processing and characterization of <001>-textured Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-Pb(Yb\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}-PbTiO\textsubscript{3} ceramics,” *J. Mater. Res.*, **32** [13] 2471–2478 (2017).


35 Y. Yan, K.-H. Cho, and S. Priya, “Piezoelectric properties and temperature stability of Mn-doped Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})-PbZrO\textsubscript{3}-PbTiO\textsubscript{3} textured ceramics,” *Appl. Phys. Lett.*, **100** (2012).

36 Y. Chang, B. Watson, M. Fantom, R.J. Meyer, and G.L. Messing, “Enhanced texture evolution and piezoelectric properties in CuO-doped Pb(In\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}-Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3} grain-oriented ceramics,” *Appl. Phys. Lett.*, **111** [23] (2017).

37 M.J. Brova, B.H. Watson, R.L. Walton, E. Kupp, M.A. Fanton, R.J. Meyer, and


Y. Chang, B. Watson, M. Fanton, R.J. Meyer, and G.L. Messing, “Enhanced texture evolution and piezoelectric properties in CuO-doped Pb(In\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}-Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3} grain-oriented ceramics,” *Appl. Phys. Lett.*, 111 [232901] 1–5 (2017).


**CHAPTER 6: Summary and Future Work**

### 6.1 Summary

In this dissertation, the effects of processing conditions, compositional variation, and Mn/Cu acceptor-doping on dielectric, ferroelectric, and electromechanical properties of PIN-PMN-PT ceramics were explored for transducer applications. The manufacturability of PIN-PMN-PT ceramics was first simplified using reactive sintering by eliminating the perovskite powder synthesis step. The effects of CuO-doping on phase formation during reactive sintering were explored and observed to suppress second phase pyrochlore formation. Processing conditions such as time, temperature, and atmosphere played a significant role in sintering kinetics, microstructure development, and key electrical properties for transducers such as $P_R$, $E_C$, $\tan \delta$, and $d_{33}$. Oxygen sintering of CuO-doped PIN-PMN-PT ceramics greatly enhanced densification and resulted in a uniform ceramic microstructure. Maximum electromechanical properties were measured for 0.5 mol% CuO-doped 25PIN-40PMN-35PT ceramics such as $d_{33}$ of 565 +/- 23 pC/N, $k_p$ of 0.64 +/- 0.1. Increasing the sintering temperature from 1050 °C to 1200 °C increased the $E_C$ from 8.5 to 11.5 kV/cm, reduced $\tan \delta$ from 1.8 to 0.8%, and reduced $d_{33}$ from 589 to 491 pC/N. The increase in sintering temperature and hard piezoelectric properties was directly correlated with formation of an internal bias field. The significant increase in piezoelectric hardening was attributed to oxygen vacancy formation as a charge compensation effect of aliovalent substitution of Cu$^{2+}$ cations for In$^{3+}$ and Ti$^{4+}$ on the B-site of the perovskite. Thus, tuning the processing conditions provided a way to directly tailor dielectric properties and domain switching behavior of CuO-doped PIN-PMN-PT ceramics.
Mn-doping of the MPB composition (25PIN-40PMN-35PT) with MnNb$_2$O$_6$ (MnN) rather than MnO$_2$ increased the degree of piezoelectric hardening by inducing formation of oxygen vacancy defect dipoles, retaining a fine grain size, and avoiding formation of non-ferroelectric second phase MgO-rich grains.\(^3\) The formation of manganese-oxygen vacancy defect dipoles was evidenced by the formation of large internal bias field of 1.8 kV/cm and strong frequency-dependency of dielectric loss which was not observed in undoped PIN-PMN-PT. Although the manganese was site balanced with niobium, the resulting internal defect dipole formation is presumed to be a result of interdiffusion of manganese with other B-site cations (In$^{3+}$, Ti$^{4+}$) and processing condition-related valence changes. MnN-doping increased the $E_C$ from 9.4 to 11.7 kV/cm, reduced the dielectric loss from 1.8 to < 0.6%, and enhanced the $Q_M$ to >1000. MnN-doped PIN-PMN-PT ceramics also displayed high energy conversion efficiency ($\eta$) of 99.1% and high figure of merit for off-resonance, resonance which were comparable to PZT-4 and PZT-8 compositions.

Textured Mn-doped PIN-PMN-PT ceramics with 90% texture fraction were fabricated and shown to have a high coercive field ($E_C$) of 14.0 kV/cm, enhanced strain behavior $d_{33}^*$ of 846 pm/V, low dielectric loss (tan $\delta$) of 0.5%, and high electromechanical quality factor ($Q_M$) of 496.\(^4\) Rayleigh analysis concluded that Mn-doping reduced the extrinsic response of domain wall motion and strain hysteresis under low field conditions because of domain wall pinning by oxygen vacancy defect dipoles. The improved electromechanical properties, low losses, and high Curie temperature of 219 °C make textured Mn-doped PIN-PMN-PT ceramics promising candidates for high-power transduction, high frequency, and resonance applications.
6.2 Future Work

6.2.1 Processing of Textured Ceramics

While reactive sintering and reactive templated grain growth simplify the processing of PIN-PMN-PT random ceramics and textured ceramics, there are several fundamental challenges and obstacles that must be overcome to further improve processing uniformity and property reproducibility. The large volumetric shrinkages experienced during reactive sintering of ~25-30 vol% make sintering large shapes and complex geometries challenging. Tape cast parts of thickness > 1 cm were difficult to make and, in some cases, exhibited cracking due to differential shrinkage from the outside toward the center of the green parts. Furthermore, densification of reactively sintered PIN-PMN-PT ceramics was impaired when using heating rates of < 10 °C/min. The densification rate and final sintered densities are less dependent on heating rate with a liquid phase present; however, it is still challenging to maintain a uniform thermal gradient and shrinkage across large parts. Further optimization of the sintering process or approaches to minimize the shrinkage would greatly benefit the reproducibility of these materials.

6.2.2 Electromechanical Properties of Textured Mn-doped PIN-PMN-PT Ceramics

Mn-doping decreased dielectric and mechanical losses, but compromised electromechanical properties due to reduction in extrinsic domain motion. The reduction in domain motion reduced hysteresis at low fields, however, Mn-doped ceramics have greater hysteresis at high fields due to irreversible domain motion. Further improvements to the piezoelectric properties should be focused on maintaining the low hysteretic behavior.
under low field conditions, but with greater overall strain behavior. Improving texture quality, such as higher texture fractions and improved quality of alignment with respect to the (001) axis, may provide significant enhancements in strain behavior as well. The composition may also be adjusted toward the rhombohedral side of the MPB, rather than on the MPB, to increase the 4R domain engineered state to account for the structural distortion induced by the BaTiO$_3$ platelets. Replacing the BaTiO$_3$ platelets altogether with a platelet composition, such as NBT-PT,$^5$ with a lower lattice parameter mismatch may also provide a method to further enhance the piezoelectric properties. Decreasing the interfacial stresses at the platelet/matrix interface may avoid domain clamping and increase the strain behavior which will be important for optimizing acceptor-doped compositions. Furthermore, selection of a platelet composition that enters solid solution with the matrix may provide improved compositional tunability relative to the MPB for further enhancements in piezoelectric properties.

Preliminary experiments were conducted in 2017 with the goal of texturing PIN-PMN-PT with (Na$_{1/2}$Bi$_{1/2}$)TiO$_3$-PbTiO$_3$ platelets, however, the NBT-PT platelets were unstable in the lattice and dissolved at temperatures as low as ~900 °C. The instability of NBT-PT platelets is currently believed to be a result of interdiffusion with the In$^{3+}$ or dissolution in the Cu$^{2+}$ liquid phase. Follow up experiments where long hold times of 1-4 h at temperatures below the PbO-CuO liquid eutectic were conducted to investigate nucleation of the perovskite on the NBT-PT platelet particles, however, the matrix coarsened and rapidly depleted the microstructure of the driving force needed for templated grain growth. There are approaches that may be worth investigating to minimize the requirement for high driving force for grain growth, such as (1) increasing the template
loading, or (2) depositing CuO via atomic layer deposition on NBT-PT platelets and pre-reacting the samples at lower temperatures ~750-850 °C where the templates were observed to be more stable. There may also be potential for texturing other compositions with NBT-PT as well, such as PMN-PZT or PYN-PMN-PT, that have higher Curie temperatures than PIN-PMN-PT. However, there is currently very little information available regarding the chemical stability of NBT-PT platelets in lead based perovskite systems. The potential benefits of a solid solution PbTiO₃ platelet are significant and merit future investigation.

6.2.3 Transducer Testing

Testing the performance of textured Mn-doped PIN-PMN-PT ceramics in transducer devices such as tonpilz elements or flexextensional transducers is a critical step in the next phase of this body of work. Data such as how textured Mn-doped PIN-PMN-PT affects source level, bandwidth, and transmitted voltage response would provide valuable feedback information to understanding the relationship between compositional selection relative to the MPB and key electromechanical properties. Optimized textured Mn-doped PIN-PMN-PT compositions should also be fabricated in other design geometries to investigate how hard piezoelectric properties such as QM vary between different vibration modes such as longitudinal and transverse mode.
6.3 References

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Vita

Beecher H. Watson, III

Beecher Hartley Watson, III was born in Richmond, Virginia on September 21, 1991 and grew up in Petersburg, VA. Beecher graduated from Maggie L. Walker Governors School in Richmond in 2010. He attended Pennsylvania State University in the fall of 2010. As an undergrad, Beecher was a member of the club wrestling and Olympic lifting teams, and competed several times in United States Strongman (USS) competitions in the 90 kg weight class. He is also a member of Sigma Tau Gamma Fraternity. He received his Bachelor of Science degree in Materials Science & Engineering and a minor in Biomedical Engineering from the Pennsylvania State University, University Park in August, 2015. He began his graduate studies on textured ceramics at the Pennsylvania State University in January, 2016 and was co-advised by Prof. Gary L. Messing and Prof. Richard J. Meyer, Jr.

List of Publications: