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PROCESSING AND PROPERTIES OF HIGH COERCIVE FIELD
TEXTURED PIEZOELECTRIC CERAMICS

A Dissertation in

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by

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Abstract

The current generation of textured piezoelectric ceramics are primarily limited in high power applications by low coercive fields (E_c), low tetragonal to rhombohedral phase transition temperatures (T_{π}), and low Curie temperatures (T_C). Over the past decade, numerous studies have shown that both $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PZN-PT) and $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PYN-PMN-PT) ceramics both have higher E_c 's and phase transition temperatures. However, random PIN-PZN-PT and PYN-PMN-PT ceramics show comparably low piezoelectricity compared to textured $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbZrO}_3\text{-PbTiO}_3$ ceramics. To realize high-strain textured piezoelectrics with coercive fields and phase transition temperatures that exceed those of the current generation, this dissertation explores the processing, templated grain growth, and electromechanical properties of random and textured PIN-PZN-PT and PYN-PMN-PT ceramics.

A major challenge in the development of textured PIN-PZN-PT ceramics is the synthesis of phase pure perovskite powder. The role of ZnO-doping was investigated in the phase formation of perovskite PIN-PZN-PT powder. ZnO dopant concentrations of 0.04 – 0.83 mol% increased the rate of perovskite formation and resulted in nearly phase pure powder. ZnO doping promoted perovskite formation by increasing the reactivity of an intermediate Zn-based pyrochlore phase by substituting on Nb^{5+} sites and forming oxygen vacancies. Because of the associated oxygen control, it is shown that phase pure powder can be achieved during synthesis.

The role of ZnO-doping was related to the densification and electromechanical properties of PIN-PZN-PT ceramics. ZnO-doping enhanced the rate and degree of sintering of PIN-PZN-PT due to the formation of oxygen vacancies. Incorporation of Zn^{2+} into the perovskite lattice increased the tetragonal character of PIN-PZN-PT, resulting in an increased Curie temperature and tetragonal splitting of the $\langle 200 \rangle$ peaks. Sintering in flowing oxygen reduced the solubility of Zn^{2+} into the perovskite lattice and resulted in the formation of rhombohedral PIN-PZN-PT perovskite. Oxygen sintering resulted in ZnO-doped PIN-PZN-PT ceramics with a large piezoelectric coefficient ($d_{33} \sim 550$ pC/N), large coercive field ($E_c \sim 13$ kV/cm), and high rhombohedral to tetragonal phase transition temperature ($T_{\text{rt}} \sim 165^\circ\text{C}$). It was determined that PIN-PZN-PT does not nucleate on barium titanate templates and thus texturing by TGG was not successful.

High PYN-content PYN-PMN-PT ceramics are challenging to texture due to limited grain growth. A PbO-CuO liquid phase was shown to promote the grain growth of 21PYN-41PMN-38PT ceramics barium titanate platelets, and thus enable templated grain growth of high E_c PYN-PMN-PT ceramics. Texturing increased the strain behavior by 83% compared to random 21PYN-41PMN-38PT ceramics. Textured 21PYN-41PMN-38PT had a high coercive field of 13.9 kV/cm and high T_c of 224°C .

The composition of textured high coercive field PYN-PMN-PT was related to electromechanical property enhancements. Increasing the rhombohedral character of PYN-PMN-PT increases the degree of intrinsic piezoelectricity, which reduces the strain hysteresis. Texturing the morphotropic phase boundary composition, 20PYN-46PYN-34PT, resulted in an 81% increase in peak strain to 0.18% while texturing tetragonal 20PYN-40PMN-40PT resulted in a 45% increase in peak strain to 0.16%. These results

reveal that ceramic composition and stresses associated with residual template particles are critical factors in the resulting electromechanical performance of texture-engineered ceramics.

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Chapter 1

Introduction

1.1 Motivation

Over the last two decades, the superior performance of relaxor-based ferroelectric single crystals, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZN-PT) (Gen. I), have had a major impact on research, design, and applications for piezoelectric devices such as sensors, actuators, and transducers.^{1,2} Although Gen. I single crystals possess large piezoelectric charge coefficients ($d_{33} > 1500$ pC/N) and high electromechanical coupling factors ($k_{33} > 0.9$), the range of applications – particularly high power applications – is severely restricted by the low coercive field ($E_c < 3$ kV/cm), low rhombohedral to tetragonal phase transition temperature ($T_{r-t} \sim 60\text{-}100^\circ\text{C}$), and Curie temperatures ($T_C < 150^\circ\text{C}$).³⁻⁵ To improve upon the shortcomings of PMN-PT, compositional modifications led to the development of ternary relaxor-based systems such as $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-Pb}(\text{Zr,Ti})\text{O}_3$ (PMN-PZT).^{4,5} This generation (Gen II.) of single crystals has similar d_{33} and k_{33} values as Gen. I crystals but with higher phase transition temperatures ($T_{r-t} \sim 100 - 130^\circ\text{C}$) and higher coercive fields (3 - 5 kV/cm).^{4,5} The subsequent generation (Gen. III) of crystals utilized dopants to further improve the coercive field (5 - 7 kV/cm), reduce loss and tailor other electromechanical properties such as mechanical quality factor (Q_m) of the ternary system.⁴⁻⁶ Table 1.1 shows comparison of the electromechanical properties of the different generations of crystals.

Table 1.1. General evolution of state-of-the-art piezoelectric crystals^{4,7,8}

Group	Single Crystal Composition	d_{33} (pC/N)	T_{r-t} (°C)	E_c (kV/cm)
Gen. I	PMN-PT, PZN-PT	> 1500	< 100	< 3
Gen. II	PIN-PMN-PT, PMN-PZT	> 1500	100 -130	3 - 5
Gen. III	Donor/acceptor doped: PIN-PMN-PT, PMN-PZT	> 1500	100 -130	4 - 7

The use of relaxor-based single crystals is also limited by practical reasons including high cost, limited range of achievable shape, poor machinability, and long growth times.^{9,10} The maximum size of lead-based single crystals is largely determined by compositional segregation during growth from the melt, and this processing challenge is further exacerbated by dopants.^{7,9} An alternative approach to next generation piezoelectrics are textured ceramics achieved by templated grain growth (TGG). Since the composition of the ceramic is retained during transformation to a textured ceramic by TGG, the scale is only limited by the size of the ceramic.¹¹ This benefit combined with the scalability of tape casting allows for the high-volume production of parts consisting of a greater range of sizes and shapes. Textured PIN-PMN-PT and PMN-PZT ceramics templated with barium titanate platelets show improved piezoelectric properties (600-850 pC/N) compared to their random counterparts (400-550 pC/N).^{12,13} While texturing improves the piezoelectricity of these materials, current generation textured ceramics are still limited because the E_c (~7-8 kV/cm), T_{r-t} (100-120°C), and low T_c 's (150-215°C) similar to the single crystal analogs because these properties are dominated by the material composition rather the final microstructure.⁹

The purpose of this dissertation is to develop and explore new textured piezoelectric ceramic compositions with improved E_c , T_{r-t} , and T_C . Specifically, this dissertation explores processing, doping, templated grain growth, and electromechanical properties of $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PZN-PT) and $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PYN-PMN-PT) ceramics. These compositions are chosen for their improved phase transition temperatures and coercive fields (> 10 kV/cm) compared to PMN-PZT and PIN-PMN-PT.^{14,15} They are additionally isostructural with barium titanate and have similar lattice parameters (4.030-4.045 Å) which indicates they are viable candidates for templated grain growth with barium titanate platelets.¹⁵⁻¹⁷

1.2 Templated grain growth

The electromechanical property enhancements achieved through texture engineering is dependent on the texture fraction.^{11,13,18} The most successful strategy for texturing engineering in terms of maximized texture fraction and cost effectiveness is templated grain growth (TGG).^{11,13,18} The first step of the TGG process is adding a small quantity of anisotropic template/seed particles to a tape casting formulation of the piezoelectric material (matrix powder). During tape casting, the shear field generated by the doctor blade aligns the anisotropic particles within the matrix powder.^{11,18} Upon sintering, the matrix material epitaxially grows on the surface of the template which leads to a crystallographically oriented matrix.^{11,13,18} For instance, highly anisotropic perovskite [001] BaTiO_3 platelets (BT) aligned during tape casting have been shown to readily allow for the epitaxial growth of oriented perovskite PMN-PT and PIN-PMN-PT.¹³ The size, geometric anisotropy, and morphology are important factors in both orienting the templates

during shear forming and establishing a driving force for epitaxial growth on the platelet surface.^{11,18,19}

There are three prerequisites for a successful TGG process. The first is that the matrix material and platelet material must have a similar crystal structure with a small lattice mismatch (< 15 %).^{11,13,18} PIN-PMN-PT can be templated on [001] BaTiO₃ platelets because PIN-PMN-PT has a lattice parameter of ~ 4.07 Å (a≈b) while BaTiO₃ has a lattice parameter of 3.9964 Å (a=b). The second requirement for successful templated grain growth is chemical compatibility between the matrix phase and template phase during sintering.^{11,20} It has been shown in some systems that high temperatures required to densify the ceramic result in a reaction between the matrix material and the template particle such that the template dissolves prior to texture development.^{11,20,21}

The third requirement for large degrees of templated grain growth is a sufficient solubility difference between the matrix grains and the template particles. The driving force behind TGG can be described by the Gibbs-Thompson equation:

$$S_m = S_0 \exp\left(\frac{2\sigma_m M}{\rho r_m RT}\right) \quad \text{Equation 1.1}$$

where S_m is the solubility difference between the matrix grains and S_0 is the equilibrium solubility of the material. The σ_m is the average surface energy of the matrix grains, M is the molecular weight, and ρ is the theoretical density. A critical factor in controlling the relative solubility of the matrix grains versus the template particles is the difference in size.^{11,18} Sufficient driving force for full green body conversion often necessitates template particles are at least > 1.5× larger than that of matrix particles.^{11,18} Several textured PMN-PT studies have shown complete texturing after using matrix particles that were 10× smaller

than the template particles.^{11,20,22} One additional method of increasing TGG during growth is the use of dopants, which increase matrix solubility. It has been shown that the PIN-PMN-PT system textured with barium titanate templates exhibits significantly enhanced template growth upon addition of CuO particles.^{13,23} The addition of CuO results in the formation of a PbO-CuO liquid which increased the solubility of PIN-PMN-PT matrix grains but does not lead to template dissolution.¹³ In addition to enhancing green body densification, the PbO-CuO liquid allows for growth at lower processing temperatures.¹³

1.2.1 Reactive templated grain growth

In the case of a matrix-platelet reaction, reactive templated grain growth (RTGG) has been shown to be an effective strategy for circumventing matrix template reactions and developing a textured microstructure.^{11,21} The major distinction between TGG and RTGG is that TGG uses matrix powder of the desired phase while RTGG uses unreacted matrix powder. In RTGG, the template interface allows for epitaxial nucleation of the matrix phase at a lower temperature than the platelet-matrix reaction temperature.^{11,21} The large template to matrix size ratio reduces the activation energy needed for both matrix phase nucleation and growth.²¹ The in situ formation of small particle size allows for densification and texture formation at lower temperatures than for TGG.^{11,21}

1.3 Morphotropic phase boundary

The large piezoelectric responses observed in Pb-based perovskite materials is due to the morphotropic phase boundaries (MPBs).^{10,24} Morphotropic phase boundaries are polymorphic phase boundaries that exist between ferroelectric phases with different

symmetries. Piezoelectric materials with MPB compositions exhibit substantially increased electromechanical and dielectric properties relative to their end member constituents. For example, the high electromechanical performance of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) ceramics is due to the MPB between rhombohedral PbZrO_3 and tetragonal PbTiO_3 .²⁴ Figure 1.1 shows the PbZrO_3 - PbTiO_3 phase diagram and the dielectric constant and planar electromechanical coupling factor (k_p) as a function of composition.²⁴ The MPB of PZT is 52 mol% PbZrO_3 and 48 mol% PbTiO_3 and corresponds to a peak in dielectric constant and electromechanical properties.²⁴

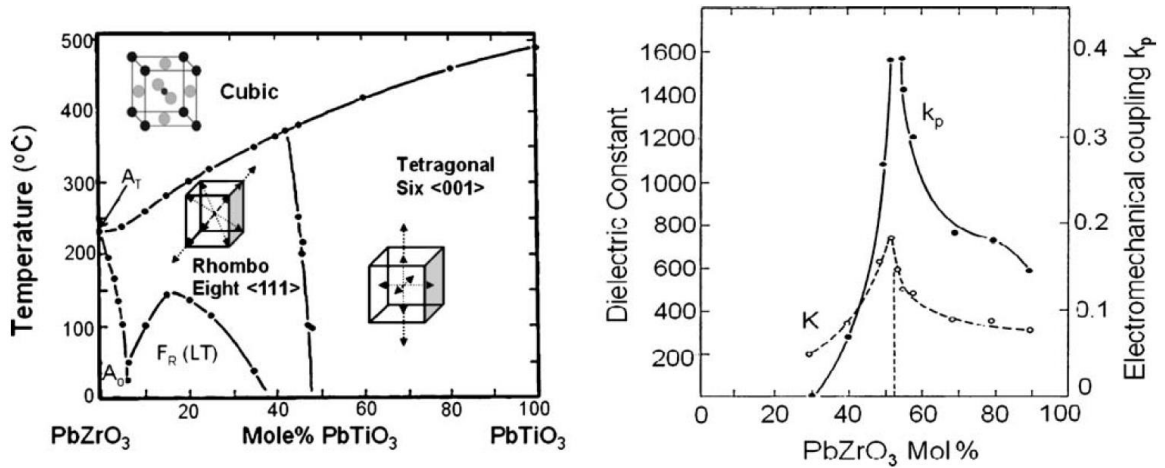


Figure 1.1. PbZrO_3 - PbTiO_3 phase diagram and the dielectric constant and planar electromechanical coupling factor (k_p) as a function of composition

It has been shown that PbTiO_3 forms MPBs with relaxor compounds such as PMN and PZN, and these compounds show increased piezoelectricity compared to PZT.^{9,25} However, relaxor-based materials are largely limited by their low transition temperatures and comparatively low coercive fields.^{7,10} Since electromechanical properties are maximized on, or close to, the MPB, secondary phases and dopants that affect the crystal structure can have large effects on the resulting electromechanical performance.^{6,7} This is

particularly important in textured piezoelectric ceramics since the template particle may impact the crystal structure by template dissolution or stresses arising from thermal expansion mismatch.²⁰

1.4 Domain engineering

The properties of texture-engineered ceramics are maximized as a result of domain engineering^{9,25,26}. While piezoelectricity in lead-based ferroelectric ceramics is typically dominated by domain reorientation (extrinsic contribution), piezoelectricity in lead-based ferroelectric single crystals is largely due to lattice strain (intrinsic).^{6,10,26,27} The large lattice strain observed in relaxor-based single crystals which is associated with maximized electromechanical properties, is generally attributed to polarization rotation (Fig 1.2). After poling in the [001] direction, the ferroelectric domains revert to the $\langle 111 \rangle$ directions which are symmetrically equivalent polarization states.^{6,10,26,27} The poled state is referred to as the 4R domain engineered state. Applying an electric field along the [001] direction causes the polarization vectors to “rotate” towards the [001] direction, and the resulting motion generates considerable lattice strain.^{6,10,26,27} [001]-poled single crystals with compositions near the rhombohedral side of the MPB maximize the effect of polarization rotation and the highest electromechanical properties (high d_{33} and k_{33}) are observed.⁶ Although other domain engineered states exist, the 4R state results in electromechanical properties best suited for transducer applications (high d_{33} , k_{33} , and Q_m) compared to other configurations.⁶ Texturing rhombohedral lead-based ferroelectrics in the [001] direction has been shown to give rise to the 4R domain-engineered state which results in the greatest improvement in piezoelectricity relative to the random ceramic counterpart.^{11,13}

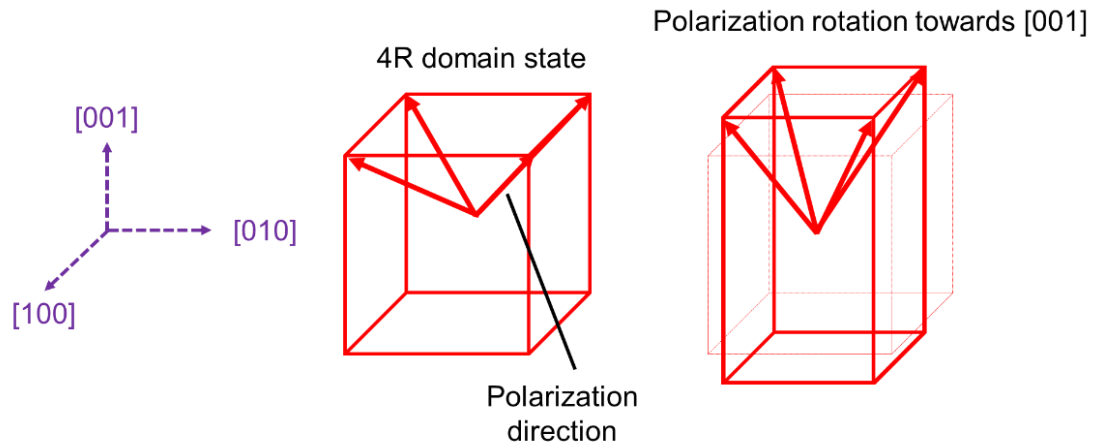


Figure 1.2. Schematic of lattice extension in the [001] under an applied electric field due to polarization rotation from the 4R domain engineered state.

1.5 PIN-PZN-PT ceramics

Li et al. demonstrated that $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PZN-PT) single crystals and ceramics have piezoelectric charge coefficients comparable to PIN-PMN-PT and PMN-PZT but possess much higher $T_{\text{r-t}}$ values of 150 - 170°C and coercive field values $> 10 \text{ kV/cm}$.²⁸ While PIN-PZN-PT single crystals have good properties for high power transducer applications, industrial implementation is greatly restricted by manufacturing factors including small maximum size, obtainable shape, high production cost, and long growth time.^{6,28} Although PIN-PZN-PT ceramics are a substantially less expensive alternative to single crystals, the random crystallographic nature of PIN-PZN-PT ceramics and other compounds such as PIN-PMN-PT and PMN-PZT results in a reduction of the piezoelectric charge coefficient by a factor of $\sim 3 - 4$.^{14,28}

1.6 Synthesis of PIN-PZN-PT ceramics

There are few reports about exists on the PIN-PZN-PT system due to the challenge of forming phase pure perovskite phase and avoiding pyrochlore. But excess ZnO has been shown to yield of perovskite single crystal PIN-PZN-PT and perovskite PIN-PZN-PT ceramics.^{17,28,28,29} Li et al. (2014) (Fig 1.3) showed that stoichiometric melts of PIN-PZN-PT resulted in zinc-based pyrochlore crystals, but the addition of 9 mol% excess ZnO results in phase pure single crystals. It was also demonstrated by Li et al. (2013) that 5 mol% excess ZnO stabilizes the formation of phase pure PIN-PZN-PT perovskite ceramics.^{28,29}

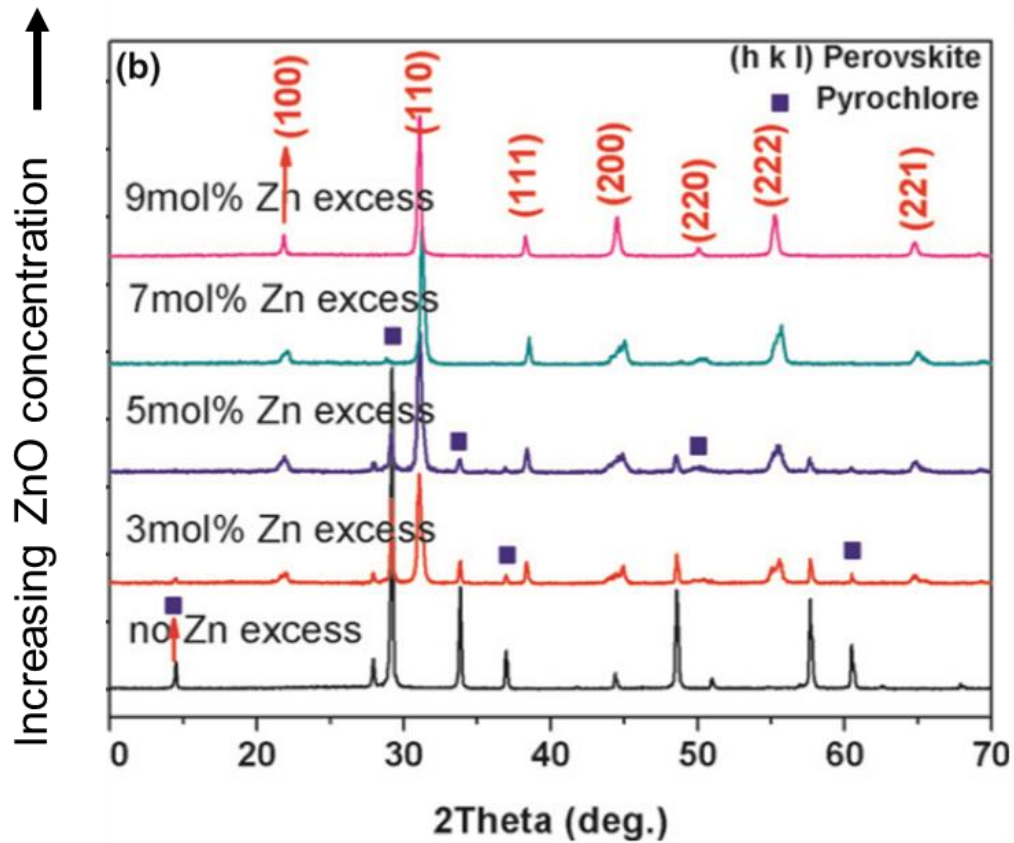


Figure 1.3. XRD of single crystal PIN-PZN-PT powders showing the effect of excess ZnO on the perovskite phase fraction.⁷

1.7 ZnO-doping in other lead-based ferroelectrics

ZnO-doping has been utilized as sintering aid in a wide range of lead-based ferroelectric systems.^{30–32} While in some cases it has been suggested the ZnO dopant forms a liquid phase with free PbO due to the ZnO-PbO eutectic at 861°C. Many studies report crystal structure and property modifications due to ZnO doping.^{31–33} For instance, ZnO-doping in both $\text{Pb}(\text{Zr,Ti})\text{O}_3\text{--Pb}(\text{Mn}_{1/3},\text{Sb}_{2/3})\text{O}_3\text{--Pb}(\text{Zn}_{1/3},\text{Nb}_{2/3})\text{O}_3$ and $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbZrO}_3\text{--PbTiO}_3$ decreased the sintering temperature and shifted the structure from pseudocubic to tetragonal.^{31,34} The change in crystal structure in both systems coincided with an increased T_c . Because ZnO doping altered the crystal structure, it was proposed in both cases that Zn^{2+} ions substituted onto the B-sites of the lattices which resulted in the formation of oxygen vacancies.^{31,34} In these studies, increasing ZnO content resulted in increasing coercive fields as a result of oxygen vacancies. In another study ZnO doping in relaxor 0.9PMN-1.0PT resulted in an increased coercive field, decreased sintering temperature, and decreased dielectric loss.³³ Furthermore, it was proposed that ZnO doping reduced the relaxor character and promoted polar order which increased the remnant polarization from $1.8 \mu\text{C}/\text{cm}^2$ in the undoped case to $17.6 \mu\text{C}/\text{cm}^2$ when doping with 11 mol% ZnO.³³

1.8 PYN-PMN-PT crystals and ceramics

The addition of $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PYN) to PMN-PT to form PYN-PMN-PT has been investigated as a strategy to improve the coercive field and phase transition temperatures of PMN-PT.^{15,35–37} Single crystals of PYN-PMN-PT containing 10 – 40 mol% PYN exhibit

an increased coercive field of 7 – 12 kV/cm and an increase in Curie temperature from 60 – 100°C to ~ 160°C.³⁵ These substantial property improvements are accompanied by a minor reduction in piezoelectricity compared to single crystal PIN-PMN-PT and PMN-PZT.⁹ While single crystal PYN-PMN-PT shows desirable electromechanical properties for high-power transduction, the commercial adoption of this material has been severely restricted due to substantial compositional segregation during single crystal growth.³⁵ This processing challenge limits the achievable sizes and shapes of single-crystal PYN-PMN-PT parts³⁵. Duran *et al.* (2017) investigated the templated grain growth of tetragonal 15.5PYN-46.5PMN-38PT ceramics and showed that texturing 15.5PYN-46.5PMN-38PT results in a peak strain of 0.33% compared to 0.21% in random 15.5PYN-46.5PMN-38PT ceramics.¹⁵ Textured 15.5PYN-46.5PMN-38PT also exhibits an E_c of 11.5 kV/cm; however, the coercive field could likely be further enhanced by increasing the PYN content of textured PYN-PMN-PT.³⁷ This work also showed that barium titanate templates are chemically stable in PYN-PMN-PT.¹⁵

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Chapter 2

ZnO-activated phase formation of phase pure perovskite PIN-PZN-PT powder

2.1 Introduction

Lead-based ferroelectrics are widely used as the active component of sensors, actuators, and transducers.¹ Complex perovskite ferroelectric compositions for piezoelectric applications are typically tailored around the morphotropic-phase-boundary (MPB), the composition boundary between two structurally dissimilar phases.¹⁻³ Binary relaxor-based MPB compounds such as $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZN-PT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) demonstrate high electromechanical properties but applications are primarily limited by relatively low rhombohedral to tetragonal phase transition temperatures ($T_{\text{r-t}} \sim 60\text{-}100^\circ\text{C}$) and low Curie temperatures ($T_{\text{c}} \sim 120\text{-}170^\circ\text{C}$).^{1,4,5}

The next generation of high performance piezoelectrics includes ternary MPB compositions with increased $T_{\text{r-t}}$ and T_{c} that also retain or improve upon binary MPB piezoelectric properties.⁵ The ternary system $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) has been explored in both single crystal and ceramic forms for high performance devices because of its higher temperature stability ($T_{\text{r-t}} \sim 110\text{-}180^\circ\text{C}$ and $T_{\text{c}} \sim 180\text{-}280^\circ\text{C}$) and higher coercive field relative to the binary PMN-PT system.^{5,6} In recent

years, the success of PIN-PMN-PT and other ternary systems such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Zr,Ti})\text{O}_3$ has led to the exploration of a PZN-PT ternary analogue, $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PIN-PZN-PT), in both single crystal and ceramic forms.⁷⁻¹⁰ Li et al. explored a variety of PIN-PZN-PT compositions around the predicted MPB and demonstrated maximum electromechanical properties between tetragonal 46PIN-21PZN-33PT and rhombohedral 51PIN-21PZN-28PT with piezoelectric charge constants as high as 660 pC/N.⁸ The high coercive field ($E_c = 15.7$ kV/cm) and high thermal stability ($T_{\text{r-t}} = 145^\circ\text{C}$, $T_c = 273^\circ\text{C}$) make PIN-PZN-PT a leading candidate for high power electromechanical applications.^{1,8,11,12} The substantially higher piezoelectric charge constant and a comparable Curie temperature make PIN-PZN-PT a promising candidate to replace Navy Type-VIII PZT which has been a staple for applications requiring hard piezoelectric materials.^{8,11}

PIN-PZN-PT is a solid solution between perovskite phases $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (rhombohedral), $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (rhombohedral), and PbTiO_3 (tetragonal).⁷ While it exhibits excellent properties, PIN-PZN-PT and other PZN-based MPB ferroelectric materials are challenging to synthesize in phase pure powder form due to the relative instability of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) perovskite; a result of the steric hindrance between the $6s^2$ lone pair on the A-site Pb^{2+} ion and the B-site Zn^{2+} ion.¹³⁻¹⁶ PIN-PZN-PT is more stable than PZN-PT due to the substantially reduced PZN content; however, synthesis of PZN-based perovskite powders and ceramics often results in large volume fractions of pyrochlore phases even when implementing the Columbite process.^{8,15,16} Residual pyrochlore in lead-based ceramics significantly reduces the ferroelectric and electromechanical properties.^{1,17} Excess ZnO has been shown to stabilize PZN-based

perovskites in both single crystal and polycrystalline ceramics.^{8,9,16,18,19} When growing PIN-PZN-PT single crystals, Li et al. demonstrated that a stoichiometric melt results in a large volume fraction of zinc-based pyrochlore, but single-phase perovskite crystals could be synthesized when 5-9 mol% excess ZnO was added to the melt.¹⁰ When fabricating sintered PIN-PZN-PT ceramics, Li et al demonstrated that 5 mol% excess ZnO resulted in phase-pure ceramics.^{8,9}

There is currently little understanding about how excess ZnO (doping) affects perovskite PIN-PZN-PT phase formation and how it stabilizes the perovskite phase. While ZnO doping is a factor in the stability of the perovskite, it has been shown that the stability of both perovskite and pyrochlore phases in other lead-based perovskites is also affected by the oxygen partial pressure.^{20,21} In this paper we analyze perovskite phase formation in the PIN-PZN-PT system as a function of ZnO doping and oxygen partial pressure to synthesize industry-ready perovskite powder.

2.2 Experimental Procedure

PIN-PZN-PT powders were prepared by a two-stage Columbite solid state reaction process to maximize perovskite phase fraction. The Columbite process has been shown to prevent the formation of pyrochlore phases by avoiding unintended reactions between binary oxides.^{8,9,17} This step included reacting ZnO with Nb₂O₅ to form ZnNb₂O₆, and reacting In₂O₃ with Nb₂O₅ to form InNbO₄ in order to prevent the direct reaction between PbO and Nb₂O₅.^{8,9,17} The binary oxides were synthesized by vibratory milling ZnO (99.7%, Inframat, Manchester, Connecticut, USA), Nb₂O₅ (99.9%, H.C. Starck, Munich, Germany), and In₂O₃ (99.9%, Santech Materials, Changsha, China) in ethanol for 24 h.

The milled powders were heated in air at 900°C for 4 h and 925°C for 4 h to synthesize 500 nm ZnNb_2O_6 and 400 nm InNbO_4 powders, respectively. Up to 0.83 mol% 30 nm ZnO dopant was added to stoichiometric mixtures of ZnNb_2O_6 , InNbO_4 , PbO (99.9%, Alfa Aesar Haverhill, Massachusetts, USA), and 20 nm TiO_2 (99.9%, Evonik Industries, Essen, Germany) corresponding to rhombohedral 50.5PIN-21PZN-28.5PT. The powder mixtures were vibratory milled in ethanol for 48 h, and subsequently dried. Zirconia milling media (3 mm diameter) was used in all milling processes. The resulting powder mixtures were loaded to ~ 0.4 mm thick beds (i.e. a bed to crucible height ratio of 0.01) in covered 20 mL alumina crucibles and heated in static air in a box furnace. The crucibles had a top inside diameter of 35 mm, bottom inside diameter of 24 mm, and height of 42 mm. Reaction kinetics were determined by removing crucibles from the furnace at specific times and temperatures and quenching in air. Additional reactions in covered crucibles were performed in a tube furnace under both flowing oxygen and argon to examine the relative stability of pyrochlore versus perovskite with respect to P_{O_2} . All reactions were performed with fill ratios, defined as the ratio of the powder bed height to the crucible height, ranging between 0.01 and 0.5. All powder samples were homogenized by grinding prior to x-ray diffraction.

The relative concentrations of PIN-PZN-PT perovskite phase content was approximated by x-ray diffraction (XRD, Xpert Pro MPD diffractometer, PANalytical, Inc., The Netherlands). Rietveld refinement of x-ray patterns to quantify perovskite phases was not possible due to the large multitude of phases, overlapping peaks, and lack of reference patterns for 50.5PIN-21PZN-28.5PT. Therefore, the approximate relative perovskite phase fractions was determined by comparing the intensity of the 100% peak

height (I) multiplied by the full width half maximum (FWHM) of each phase (Eq. 2.1).^{16,17,22}

$$\% \text{ perovskite} = 100\% * \frac{I_{\text{perovskite (110)}} * FWHM_{\text{perovskite (110)}}}{\sum (I_n * FWHM_n)} \quad (2.1)$$

Powder with no detectable secondary peaks, as determined by XRD, are considered 100% perovskite for the purposes of this work. The morphology and particle size of the reacted powders were observed by scanning electron microscopy (SEM, Phenom Pro, Phenom-World B.V., The Netherlands).

2.3 Results and Discussion

2.3.1 ZnO-doping effects

PIN-PZN-PT powder mixtures were doped with 0.04 mol% to 0.83 mol% ZnO and heated for 4 h at 800°C. As seen in Fig 2.1(a) as little as 0.04 mol% ZnO results in 98.0% perovskite, or 14.6 % more perovskite than undoped powder. Increasing the ZnO dopant concentration to 0.83 mol% increases the perovskite content to 99.8%. The minor second phase observed in the ZnO-doped samples was a cubic zinc-based pyrochlore ($\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$). Although pyrochlore formation is often attributed to PbO volatilization at high temperature (e.g. >880°C) that is not the reason for the very minor pyrochlore content in the doped powders since weight loss was <0.1% after heating for 4 h in all cases. The 0.12 mol% ZnO-doped perovskite powder shown in Fig. 2.1(b) is composed of unaggregated ~ 0.5 um diameter particles which was characteristic of all ZnO-doped perovskite powders heated at 800°C.

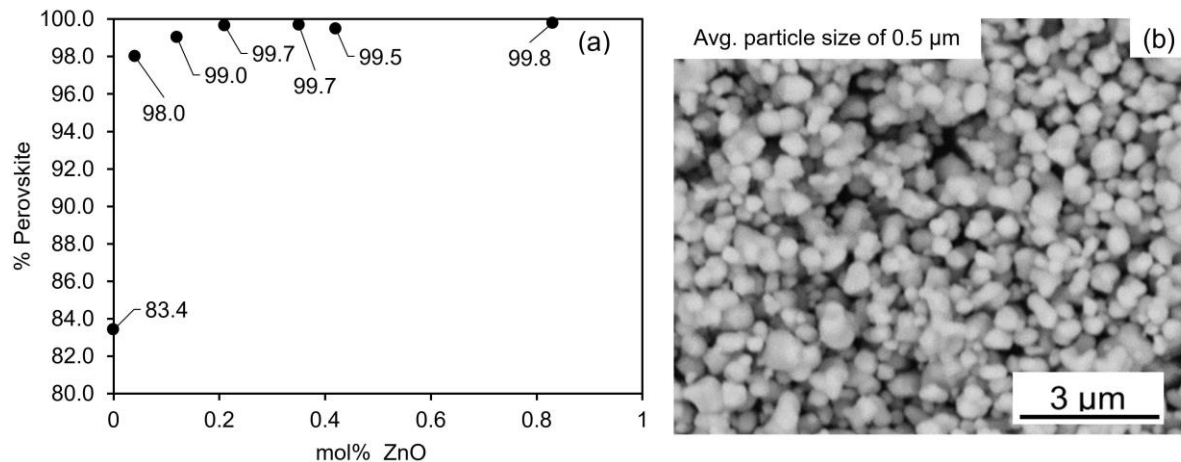


Figure 2.1. (a) Phase percentage of perovskite as a function of ZnO dopant concentration in 50.5PIN-21PZN-28.5PT powder heated at 800°C for 4 h in air. (b) SEM micrograph showing particle size of 0.12 mol% ZnO-doped PIN-PZN-PT powder. The powder fill ratio was 0.01, and the powders were heated in static air.

To further investigate the role of ZnO during PIN-PZN-PT perovskite formation, undoped and 0.12 mol% ZnO-doped powder mixtures were heated for up to 5 h between 700 and 800°C and then quenched at room temperature. Powders with > 0.12 mol% ZnO reacted too quickly to clearly observe the formation of perovskite and the stages of reaction pathway. Fig. 2.2 shows the relative phase fraction of PIN-PZN-PT perovskite formed at various times and temperatures for the undoped and 0.12 mol% ZnO-doped PIN-PZN-PT powders. Increasing the reaction temperature to 800°C increases PIN-PZN-PT perovskite content in both sets of powders, with > 98% perovskite formed in the 0.12 mol% ZnO-doped powder and only 83% perovskite in the undoped powder. There was no further reaction after ≤ 1 h in all ZnO-doped powders, and 100 min in the undoped powders. Heating the undoped powder above 800°C did not increase the perovskite content.

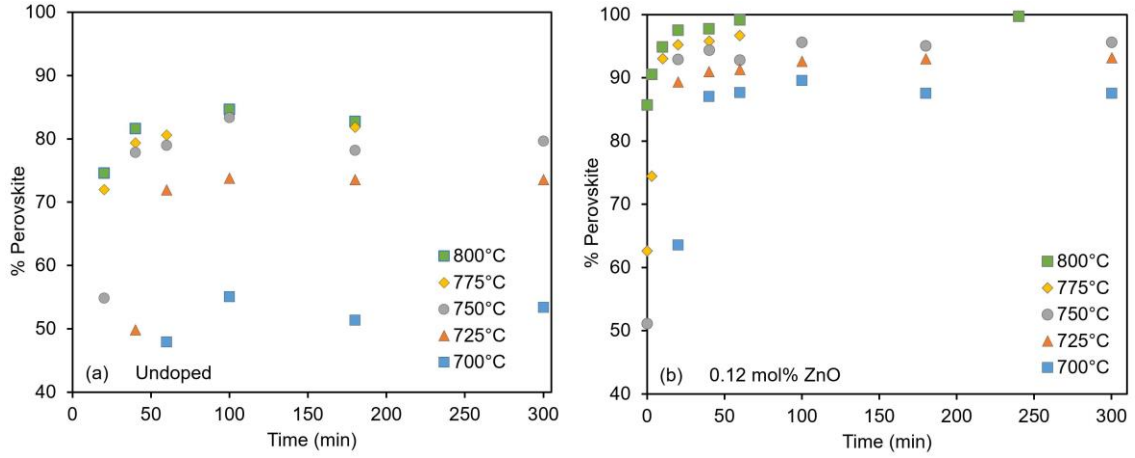


Figure 2.2. Phase percentage of perovskite as a function of time and temperature in (a) undoped and (b) 0.12 mol% ZnO-doped 50.5PIN-21PZN-28.5PT. The powder fill ratio was 0.01 and the powders were heated in static air.

To gain insight about the reaction path to perovskite formation, undoped and 0.12 mol% ZnO-doped PIN-PZN-PT powders were heated in air for 0 to 5 h at 750°C. Fig. 2.3 shows the x-ray diffraction patterns from 20 to 40° of the undoped (Fig. 2.3(a)) and 0.12 mol% ZnO-doped (Fig. 2.3(b)) powders. It is seen that after 0 min at temperature both undoped and doped powders consist of PbTiO_3 perovskite, $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ perovskite, $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore, and InNbO_4 . This indicates that PbO reacts with TiO_2 in the initial powder mixture to form PbTiO_3 perovskite and with InNbO_4 to form $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ perovskite. The presence of $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore shows that PbO also reacts with ZnNb_2O_6 to form the pyrochlore instead of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ perovskite.⁸ This result is similar to that observed during PMN phase formation in which the $\text{PbMg}_x\text{Nb}_{1-x}\text{O}_{3.5-x}$ pyrochlore phase is more thermodynamically stable than the perovskite phase, and thus the pyrochlore phase forms at a lower temperature than the perovskite phase.¹⁷ The amounts of $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore, PbTiO_3 perovskite, and $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ perovskite decrease and the PIN-PZN-PT perovskite phase fraction

increases after 20 min at 750°C in the ZnO-doped powder. The PIN-PZN-PT perovskite percentage increases in undoped powder heated at 750°C for up to 100 min, but after 100 min the $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore and In_2O_3 peak intensities increase concurrently suggesting that pyrochlore content increases due to the decomposition of $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$. In contrast, ZnO-doped powders show no In_2O_3 peaks and rhombohedral perovskite phase formation is nearly complete after 20 min at 750°C, and the phase composition remains constant when heated for up to 5 h. Because of the incomplete reaction in the undoped case, a rhombohedral perovskite composition, which is deficient in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, forms as evidenced by the increasing relative intensities of the tetragonal (002) and (200) peaks in Fig 2.3.

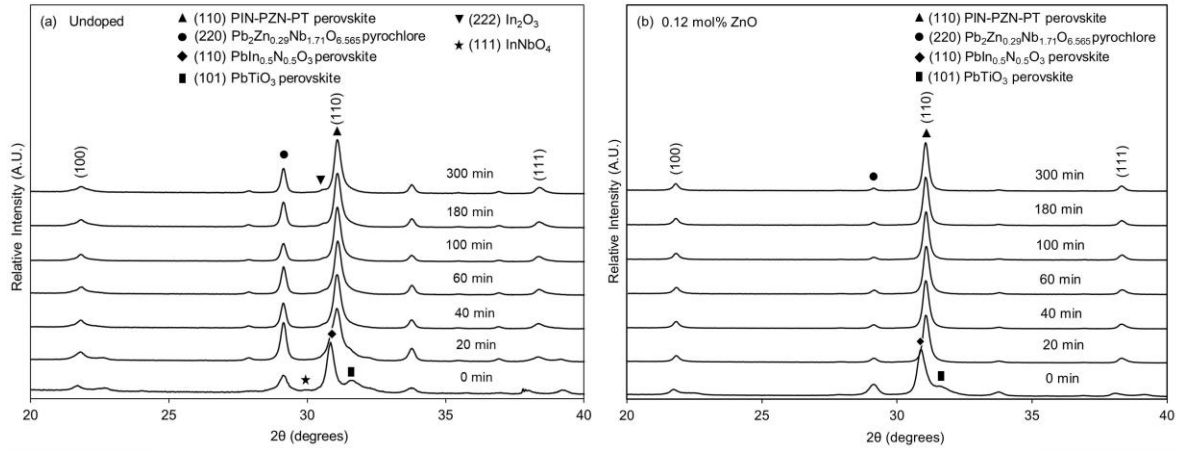


Figure 2.3. XRD patterns showing the reaction pathway of (a) undoped PIN-PZN-PT and (b) 0.12 mol% ZnO-doped PIN-PZN-PT at 750°C in air. The powder fill ratio was 0.01, and the powders were heated in static air.

To understand the effect of ZnO doping on the resulting phases, we examined the x-ray diffraction patterns from 20-60° of undoped and 0.35 mol% ZnO-doped PIN-PZN-PT powders after heating in air for 4 h at 800°C (Fig. 2.4). Calcining undoped PIN-PZN-PT powders at these conditions results in 83.4% perovskite, with secondary phases of $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore and In_2O_3 . ZnO doping (0.35 mol%) prevents the formation of In_2O_3 and increases the perovskite phase fraction to 99.7%. The minor secondary phase was $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore. The pyrochlore phase in both undoped and doped powders corresponds to cubic zinc-based pyrochlore ($\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$) which has been reported to have large solubility limits for both ZnO and Nb_2O_5 and has the general formula of $\text{PbZn}_x\text{Nb}_{1-x}\text{O}_{3.5-x}$.²¹

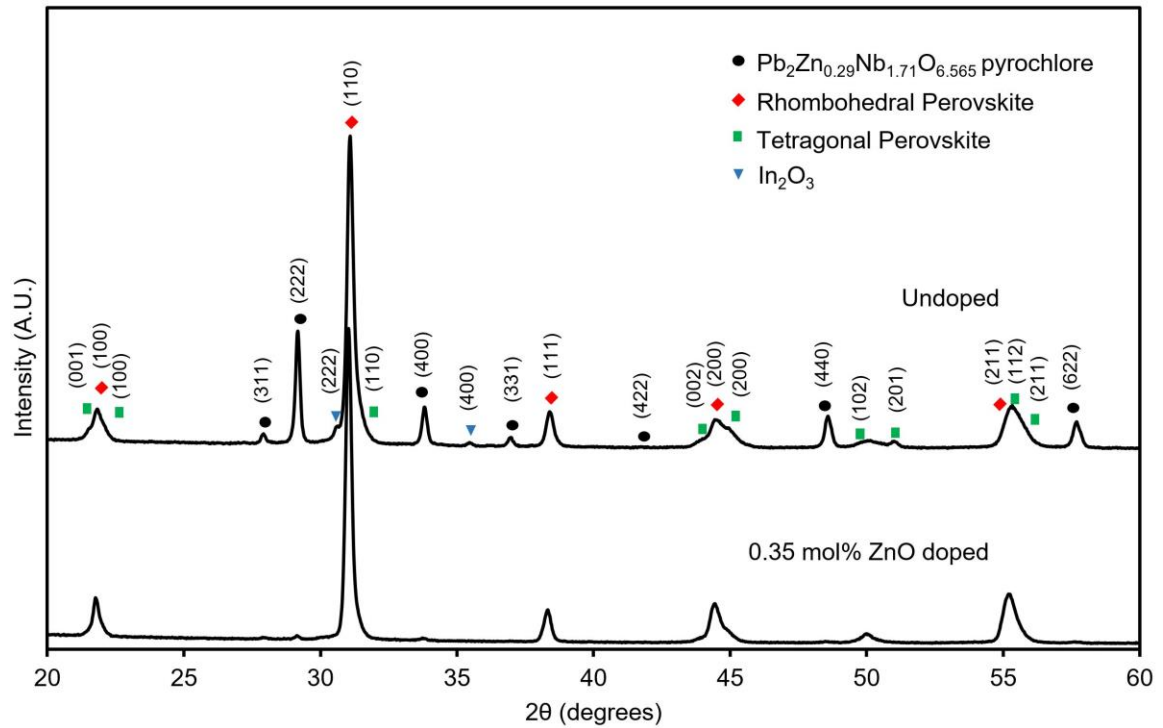
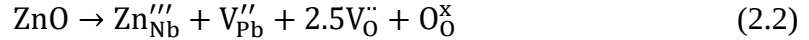


Figure 2.4. XRD patterns of (top) undoped and (bottom) 0.35 mol% ZnO-doped 50.5PIN-21PZN-28.5PT heated at 800°C for 4 h in air. The powder fill ratio was 0.01 and the powders were heated in static air.

The stability of cubic zinc-based pyrochlore ($\text{PbZn}_x\text{Nb}_{1-x}\text{O}_{3.5-x}$) is proposed to be a result of introduction of Zn^{2+} on Nb^{5+} sites in the pyrochlore lattice.^{21,23} From a stoichiometry standpoint, the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ component of the perovskite solid solution has a Zn^{2+} to Nb^{5+} ratio of 1:2, while the observed pyrochlore phase has a Zn^{2+} to Nb^{5+} ratio of $\sim 3:17$. By Le Chatelier's principle, increasing the zinc to niobium ratio promotes the formation of perovskite instead of lead zinc niobate pyrochlore. However, introduction of Zn^{2+} on Nb^{5+} sites in the pyrochlore and perovskite B-sites requires the formation of oxygen vacancies for charge balance as seen in Equation (2).^{21,24}



Lead vacancies form to maintain site neutrality within the pyrochlore phase, and no excess lead was used in this study to compensate for lead vacancies.

As shown in Fig 2.3, a necessary step to form the perovskite phase is the reaction between $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore, $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ perovskite, and PbTiO_3 perovskite. We hypothesize that Zn^{2+} doping on Nb^{5+} sites in $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ destabilizes the pyrochlore structure by changing the pyrochlore stoichiometry to be more “perovskite-like”. Thus, increasing ZnO content makes the ZnO-doped intermediate pyrochlore more reactive which enhances perovskite formation kinetics and results in a more complete reaction between pyrochlore and the intermediate perovskite phases.

2.3.2 Atmosphere effects

Based on the proposed defect model in Equation 2, it is clear that P_{O_2} can also influence the phase formation pathway of PIN-PZN-PT perovskite. That is, decreasing P_{O_2} favors oxygen vacancy formation in the intermediate pyrochlore phase which promotes perovskite formation. To investigate the effect of P_{O_2} on the formation of ZnO-doped PIN-PZN-PT, covered alumina crucibles were filled to powder bed depths ranging from 0.4 mm (fill ratio = 0.01) to 21 mm (fill ratio = 0.5) to change the diffusion distance of oxygen gas.

Fig. 2.5 shows XRD patterns of 0.12 mol% ZnO-doped PIN-PZN-PT powder heated at 800°C for 4 h in static air in 20 mL covered alumina crucibles with different fill ratios. Reacting ZnO-doped powder at a fill ratio of 0.01 results in 99.0% PIN-PZN-PT perovskite with 1.0% $Pb_2Zn_{0.29}Nb_{1.71}O_{6.565}$ pyrochlore. Increasing the powder fill ratio to 0.03 increases the resulting perovskite to 99.7% and $Pb_2Zn_{0.29}Nb_{1.71}O_{6.565}$ pyrochlore as the secondary phase. A powder fill ratio between 0.06 and 0.1 results in 100% PIN-PZN-PT perovskite. Increasing the powder fill ratio to 0.2 results in 100% powder that has a color gradient from yellow powder at the top of the crucible to red powder at the bottom of the crucible. SEM micrographs of powders heated with a fill ratio of 0.2 revealed equiaxed fine particles similar to those shown in Fig. 2.1. Rather than being attributed to particle size differences, this color change suggests a change in the defect chemistry of the perovskite.^{24,25} The crucible also had substantially more staining associated with PbO vaporization which was not observed in powders reacted with fill ratios < 0.2.

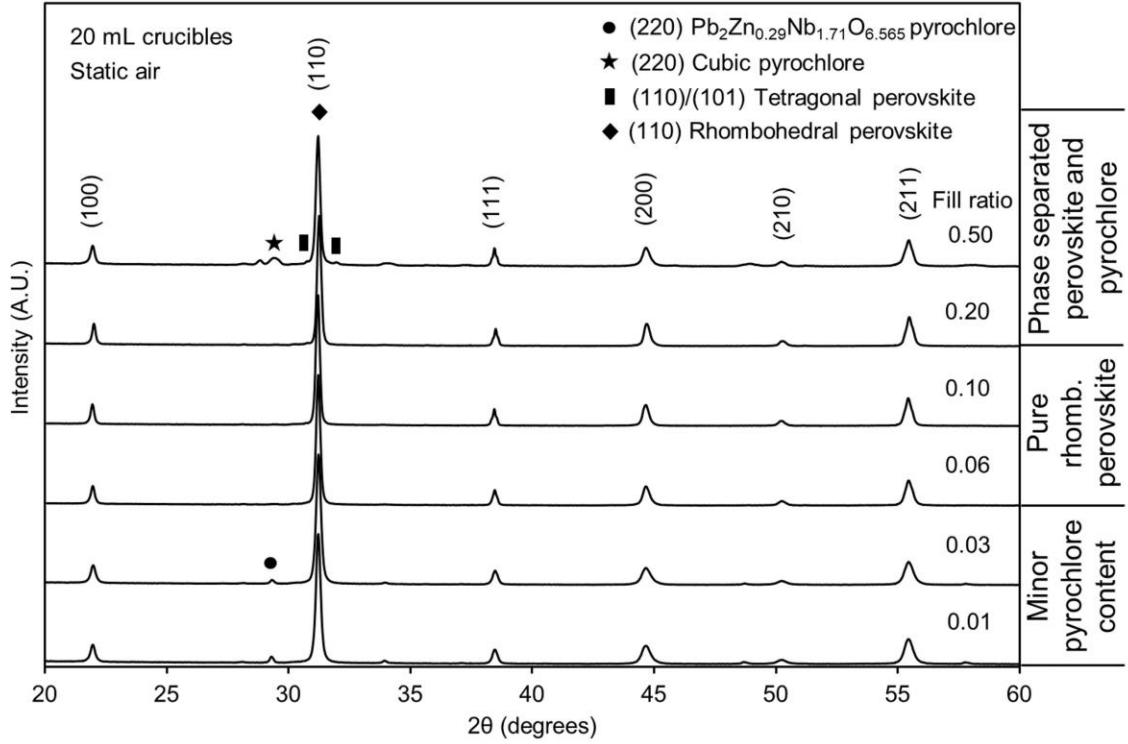


Figure 2.5. XRD patterns of 0.12 mol% ZnO-doped PIN-PZN-PT heated at 800°C for 4 h with different powder fill height ratios in static air.

Reacting powder at a fill ratio of 0.5 results in white powder in the top 90% of the crucible and a mixture of black and orange colored powder in the bottom 10% of the crucible. ZnO-doped powder samples were examined by XRD as a function of powder bed depth. Powder from the top 90% of the powder fill was 100% PIN-PZN-PT perovskite whereas powder from the bottom 10% of the crucible was composed of a tetragonal perovskite phase of unknown composition, a rhombohedral perovskite phase of unknown composition, and a pyrochlore structure. This result suggests that oxygen gas was unable to effectively diffuse to the bottom of the crucible due to the greater depth of the 0.5 fill ratio and thus PIN-PZN-PT perovskite separated into a tetragonal perovskite, rhombohedral perovskite, and pyrochlore due to excessive oxygen defects from both ZnO-

doping and the local reducing atmosphere at the bottom of the powder bed. Interestingly, 99.0% PIN-PZN-PT perovskite and 1.0% $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore formed when the powder produced at a fill ratio of 0.5 was spread to a fill ratio of 0.01 and heated for a second time at 800°C for 4 h in static air. Conversely, if the PIN-PZN-PT perovskite produced with a fill ratio of 0.01 was heated for a second time but with a fill ratio of 0.5, it phase separated into a tetragonal perovskite and rhombohedral perovskite phases, and a pyrochlore phase of unknown composition.

To study the effect of ZnO concentration on phase separation of PIN-PZN-PT calcined in static air at a fill ratio of 0.5, we examined the phase formation of PIN-PZN-PT powder doped with 0.12 mol% and 0.42 mol% ZnO after heating at 800°C for 4 h as shown in Fig. 2.6. Reacting powder doped with 0.12 mol% ZnO results in phase separation of PIN-PZN-PT into a tetragonal perovskite and rhombohedral phases, and a pyrochlore phase of unknown composition. Increasing the dopant concentration from 0.12 to 0.42 mol% ZnO increases the phase separation of PIN-PZN-PT as evidenced by the increase in peak intensity of the tetragonal perovskite phase. The increased phase separation seen with 0.42 mol% ZnO also coincided with the presence of PbO.

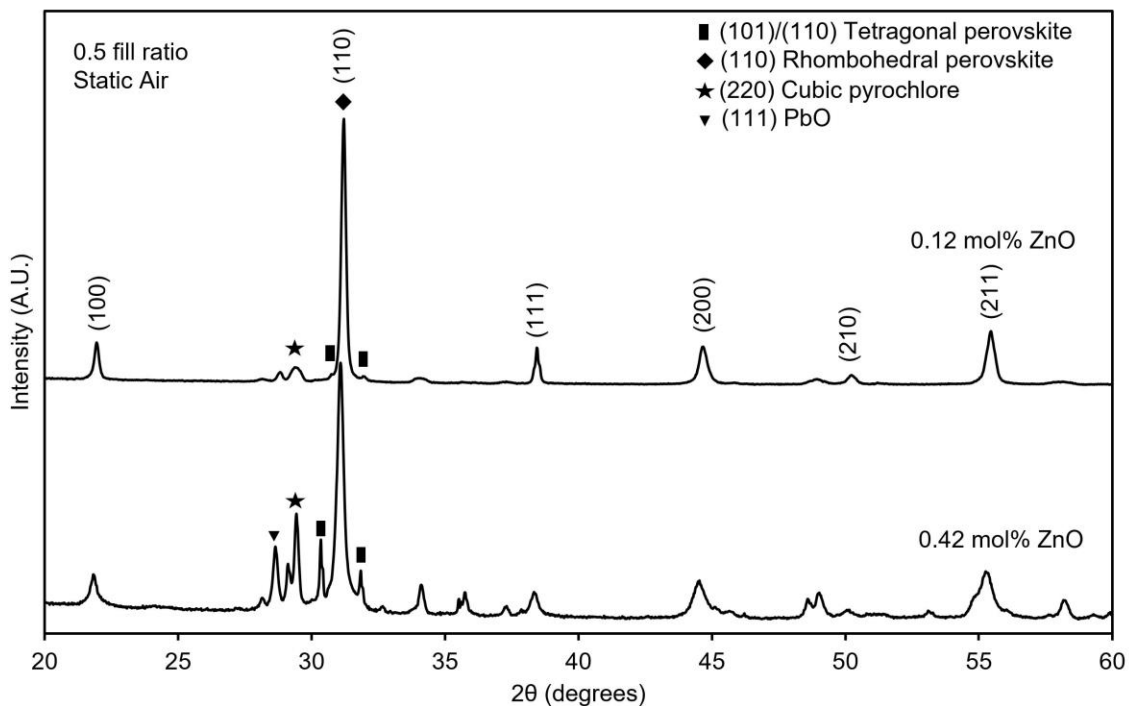


Figure 2.6. XRD patterns of 0.12 and 0.42 mol% ZnO-doped PIN-PZN-PT powder with a 0.5 fill ratio heated at 800°C for 4 h in static air.

To increase the achievable yield of 0.12 mol% ZnO-doped PIN-PZN-PT perovskite powder and to further understand the effect of P_{O_2} on phase formation, reactions were performed in a tube furnace under flowing oxygen and argon. Fig. 2.7 shows the XRD patterns of powders filled to a 0.5 fill ratio and heated at 800°C for 4 h at different oxygen flow rates, and argon at 20 mL/min. The resulting powders at all oxygen flow rates were 99.0% perovskite and 1.0% $Pb_2Zn_{0.29}Nb_{1.71}O_{6.565}$ pyrochlore. Heating with reduced P_{O_2} by flowing argon results in phase separated powder consisting of rhombohedral perovskite and tetragonal perovskite phases, and a pyrochlore phase of unknown composition. These results are consistent with those presented in Fig. 2.5.

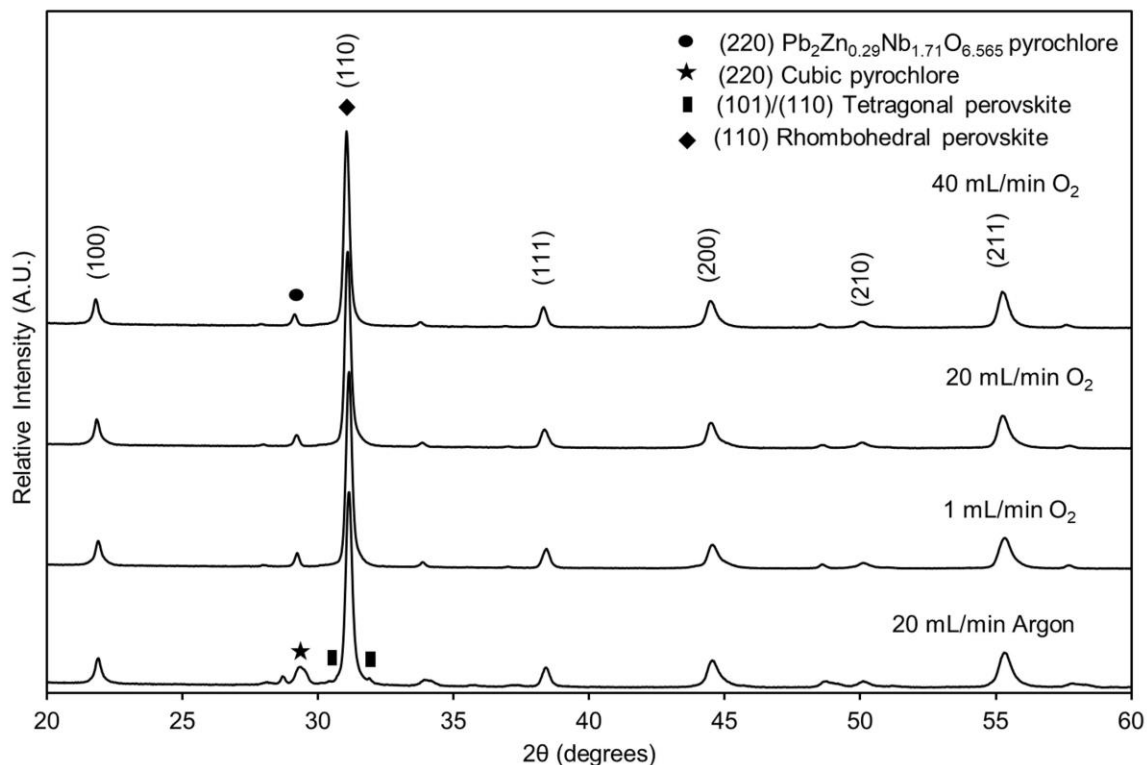


Figure 2.7. XRD patterns of 0.12 mol% ZnO-doped PIN-PZN-PT powder with a fill ratio of 0.5 heated at 800°C for 4 h under flowing oxygen and argon.

Several conclusions can be drawn from the results of the atmosphere experiments in the ZnO-doped case. With an intermediate P_{O_2} , 100% perovskite powder forms due to the increased reactivity of the ZnO-doped $Pb_2Zn_{0.29}Nb_{1.71}O_{6.565}$ pyrochlore. Heating powder in a higher P_{O_2} inhibits the incorporation of Zn^{2+} dopant into the $Pb_2Zn_{0.29}Nb_{1.71}O_{6.565}$ pyrochlore which prevents complete formation of perovskite. Heating powder in lower P_{O_2} destabilizes PIN-PZN-PT perovskite due to the formation of excessive oxygen vacancies which results in the formation of rhombohedral perovskite and tetragonal perovskite phases, and a pyrochlore. Increasing ZnO concentration increases the oxygen vacancy concentration which increases the required P_{O_2} needed to prevent perovskite phase

separation. Similar experiments in the undoped case show that phase formation is insensitive to P_{O_2} which further suggests the importance of oxygen vacancy formation by ZnO-doping.

2.4 Conclusions

This study demonstrated the effect of ZnO-doping on phase formation of PIN-PZN-PT perovskite powders by comparing the reaction pathway and kinetics of undoped and doped powders. In both cases, formation of PIN-PZN-PT perovskite was preceded by the formation of $PbTiO_3$ perovskite, $Pb(In_{1/2}Nb_{1/2})O_3$ perovskite, and $Pb_2Zn_{0.29}Nb_{1.71}O_{6.565}$ pyrochlore. These three intermediate phases then react to form PIN-PZN-PT perovskite phase. In the undoped case $Pb_2Zn_{0.29}Nb_{1.71}O_{6.565}$ pyrochlore is not sufficiently reactive to form 100% PIN-PZN-PT perovskite powder. In ZnO-doped powders, pyrochlore reactivity is substantially increased through Zn^{2+} addition on pyrochlore Nb^{5+} sites and the formation of oxygen vacancies to charge balance the structure. The formation of oxygen vacancies associated with ZnO-doping results in a processing sensitivity to P_{O_2} not found in the undoped case. At an intermediate P_{O_2} 100% PIN-PZN-PT perovskite can be readily achieved after heating at 800°C for 4 h. Heating ZnO-doped powder in higher P_{O_2} inhibits formation of oxygen vacancies whereas heating in a reduced P_{O_2} destabilizes the PIN-PZN-PT. This study showed the effect of P_{O_2} on the formation of ZnO-doped PIN-PZN-PT, but further work is needed to refine the P_{O_2} conditions needed to synthesize high purity perovskite powder.

2.5 References

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Chapter 3

Processing and electromechanical properties of high coercive field ZnO-doped PIN-PZN-PT ceramics

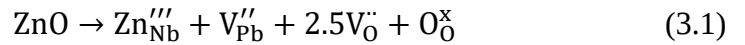
3.1 Introduction

Lead-based perovskite single crystals and ceramics are used in transducers and actuators because of their exceptional piezoelectric properties.¹ Lead-based relaxor piezoelectric single crystals such as $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZN-PT), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT), $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) show very high piezoelectric charge coefficients ($d_{33} > 2000$ pC/N) on the rhombohedral side of the morphotropic phase boundary (MPB) between tetragonal and rhombohedral phases.²⁻⁴ While relaxor-based single crystal piezoelectric materials demonstrate high piezoelectricity, adoption of these materials for high-power transducers is limited by low rhombohedral to tetragonal phase transition temperatures ($T_{r-t} \sim 60\text{-}130^\circ\text{C}$) and low coercive fields ($E_c < 7$ kV/cm).^{4,5}

In the past decade, there has been extensive research to find piezoelectric materials with high piezoelectricity and harder ferroelectric characteristics (i.e. high E_c , low loss).^{1,4} Li et al. demonstrated that $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PZN-PT) single crystals have high piezoelectric charge coefficients ($d_{33} \sim 2100$ pC/N) and substantially

improved T_{r-t} - 163°C and E_c - 14.3 kV/cm.⁶ In ceramic form, PIN-PZN-PT compositions between rhombohedral 51PIN-21PZN-28PT and tetragonal 46PIN-21PZN-33PT have good properties including a high piezoelectric charge coefficient (d_{33} - 660 pC/N), high thermal stability (T_{r-t} - 145°C), and high coercive field (E_c - 15.7 kV/cm).^{6,7} Thus, PIN-PZN-PT ceramics are strong candidates for use in the next generation of high power resonance devices.^{8,9}

Perovskite $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) based materials are challenging to synthesize due to perovskite phase instability.^{10,11} Attempts to synthesize single crystal PZN-based materials by melt growth, or as ceramics, commonly results in the formation of zinc-based pyrochlores.^{10,12} ZnO-doping enables the synthesis of phase pure perovskite PIN-PZN-PT single crystals and ceramics.^{6,7,13,14} Earlier, we reported that ZnO doping increases the reactivity of an intermediate zinc-based pyrochlore phase which enables increased reaction kinetics and formation of phase pure perovskite.¹⁴ Zn^{2+} was proposed to substitute on the perovskite B-site and form oxygen vacancies as shown in Equation (3.1).¹⁴



Interestingly, the formation of oxygen vacancies due to ZnO-doping led to an increased sensitivity of the perovskite phase stability to P_{O_2} such that phase pure perovskite could only be achieved in flowing oxygen.¹⁴

It is currently unknown how ZnO doping affects the densification and electrical properties of PIN-PZN-PT. It has been proposed for a variety of other lead-based piezoelectric systems that Zn^{2+} substitution on the B-site of the perovskite lattice promotes sintering by increasing the rate of bulk diffusion.¹⁵⁻¹⁷ In $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ and

$\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3\text{--Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3\text{--Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Zn^{2+} incorporation increases the perovskite's tetragonal character as evidenced by splitting of the (200) peak and an increased c/a lattice parameter ratio.^{15,16} The increased tetragonal character of these ZnO-doped perovskite ceramics resulted in a higher T_C relative to undoped ceramics.^{15,16} Li et al doped PIN-PZN-PT ceramics of various compositions with only one concentration of ZnO (~0.35 mol%), and thus it is unknown how the concentration of ZnO dopant affects the densification and electromechanical properties.¹³ In this paper we report how 0.0 - 0.35 mol% ZnO dopant and atmosphere affects densification of $50.5\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--}21\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}28.5\text{PbTiO}_3$ ceramics and consequent electrical properties. This composition was chosen for study because its rhombohedral structure would enable domain engineering in textured ceramics.^{18,19}

3.2 Experimental Procedure

ZnO-doped perovskite PIN-PZN-PT powders of 0.2-0.4 μm were prepared by the two-stage columbite solid state reaction process reported earlier.¹⁴ Raw materials included PbO (99.9%, Alfa Aesar Haverhill, Massachusetts, USA), In_2O_3 (99.9%, Santech Materials, Changsha, China), ZnO (99.7%, Inframat, Manchester, Connecticut, USA), Nb_2O_5 (99.9%, H.C. Starck, Munich, Germany), and TiO_2 (99.9%, Evonik Industries, Essen, Germany). No samples in this study were doped with excess PbO. Pellets of 1.75 cm diameter were uniaxially dry pressed at 35 MPa and subsequently cold isostatically pressed at 200 MPa. Green bodies were heated between 850°C and 1200°C for 0 to 2 h in closed alumina crucibles containing a perovskite PIN-PZN-PT embedding powder to minimize PbO,

In_2O_3 , and ZnO vaporization during sintering. Samples heated for 0 min were ramped to temperature and then immediately furnace cooled. To explore the effect of atmosphere on densification and electromechanical properties, pellets were densified in either air or flowing oxygen (25 mL/min) in a tube furnace.

The sintered densities were measured by Archimedes' method after a light polishing to remove surface pyrochlore. The phase compositions were characterized by XRD (Cu K_α radiation, 45kV, 45 mA, Xpert Pro MPD diffractometer, PANalytical, Inc., The Netherlands). All scans utilized a $1/8^\circ$ divergence slit, 4 mm incident beam mask, $1/2^\circ$ incident antiscatter slit, and $1/4^\circ$ receiving antiscatter slit. Scans were taken at a step size of 0.0525° with a time per step of 49.725 s. High counting statistic XRD scans were collected for select samples to evaluate whether low concentration second phases were present. These scans had a smaller step size of 0.0263° and a longer time per step of 25 min to increase the relative peak to noise intensity ratio. Microstructures and grain sizes of fracture surfaces were analyzed by scanning electron microscopy (SEM, Phenom Pro, Phenom-World B.V., The Netherlands).

Silver electrodes (DuPont 850, DuPont, Wilmington, DE) were fired on both faces of the samples by heating at 800°C for 30 min after application. Samples were poled in silicone oil at 100°C under 30 kV/cm for 15 min and were cooled to room temperature with the field still applied. Piezoelectric charge constants (d_{33}) were measured using a Berlincourt meter (d33 PiezoMeter System, Piezotest Ltd, Singapore) after aging for 24 h after poling. Capacitance (C) and dielectric loss ($\tan \delta$) were measured from poled samples at 1 kHz as a function of temperature ($30\text{--}300^\circ\text{C}$) using an LCR meter (Agilent 4284A, Agilent Technologies, CA, USA). The T_{r-t} temperatures were identified as the local minima

in the second derivative of the dielectric curves. Polarization vs. electric field loops were measured at 1 Hz using a custom Sawyer-Tower circuit.

3.3 Results and Discussion

3.3.1 Sintering in air

Fig. 3.1 shows the sintered density of PIN-PZN-PT ceramics as a function of ZnO dopant concentration and temperature. Heating undoped PIN-PZN-PT powder to 1200°C results in 83% relative density. Increasing ZnO dopant content increases the degree of densification and the maximum achievable density. Heating 0.35 mol% ZnO-doped PIN-PZN-PT powder to 1150°C results in ceramics of ~ 100% relative density. 0.35 mol% ZnO-doped PIN-PZN-PT powder shows a sharp increase in densification above ~1070°C. Fig. 3.2 shows microstructures of 0.35 mol% ZnO-doped PIN-PZN-PT ceramics after sintering for 0 min at 1075°C (Fig. 3.2a) and 1150°C (Fig. 3.2b). The powder densified to 85% at 1075°C and coarsened from 0.2 – 0.4 μm to 0.5 μm . When sintered at 1150°C for 0 min, 0.35 mol% ZnO doped perovskite PIN-PZN-PT powder results in dense microstructures with equiaxed 4 μm grains.

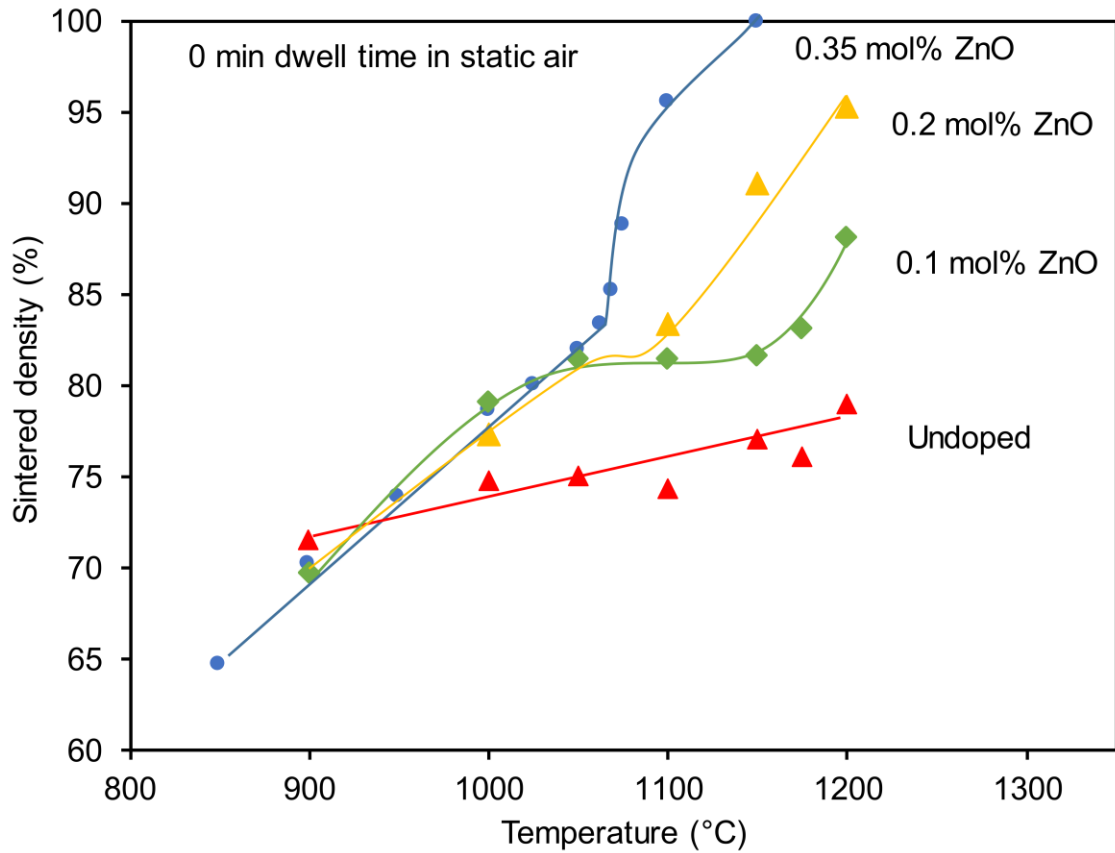


Figure 3.1. Sintered density as a function of ZnO dopant concentration and temperature of PIN-PZN-PT heated in air at 10°C/min. ZnO doping significantly improved PIN-PZN-PT densification relative to undoped samples, and 0.35 mol% ZnO resulted in 100% density after 0 min at 1150°C.

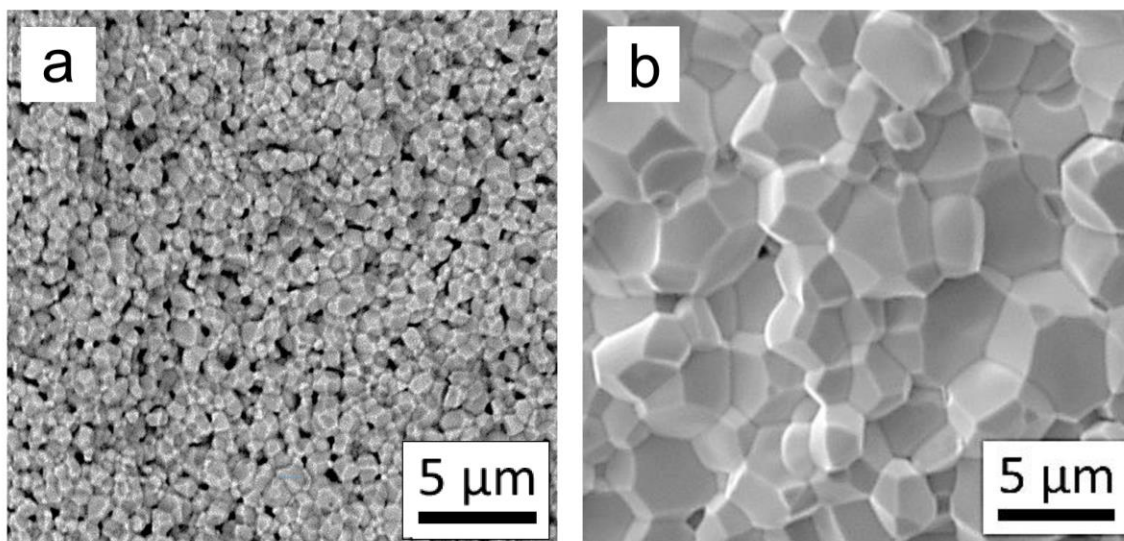


Figure 3.2. SEM micrographs of fracture surfaces of 0.35 mol% ZnO-doped PIN-PZN-PT heated in air to (a) 1075°C and (b) 1150°C for 0 min.

It was determined in the phase formation analysis of ZnO-doped PIN-PZN-PT perovskite powder that ZnO doping results in the formation of oxygen vacancies which are important to the phase stability.¹⁴ The increased sintering of ZnO-doped PIN-PZN-PT ceramics suggests that the increasing oxygen vacancy concentration increased the rate of bulk diffusion of perovskite PIN-PZN-PT. This result is consistent with increased densification observed in other ZnO-doped lead-based perovskite materials.^{15,20} An alternative hypothesis is that a PbO-ZnO eutectic (861°C) enhances sintering and grain growth by a liquid phase mediated process.²¹ This scenario is unlikely as the powders were not batched with excess PbO, and XRD did not show any reflections for free PbO at any stage of sintering. Additionally, accelerated sintering was only observed at temperatures well above the PbO-ZnO eutectic temperature.

Fig. 3.3 shows the sintering kinetics in air of 0.1 mol% ZnO-doped and 0.35 mol% ZnO-doped PIN-PZN-PT. Heating 0.1 mol% ZnO-doped PIN-PZN-PT powder at 1050°C for ≥ 15 min results in $\sim 86\%$ relative density while heating at 1150°C for ≥ 30 min results in relative densities $> 98\%$. Increasing the ZnO dopant concentration to 0.35 mol% increased the densification at all explored times and temperatures. Heating at 1100°C for ≥ 15 min resulted in ceramics with relative densities in excess of 95%. The difference in the sintering behavior of 0.1 and 0.35 mol% doped samples is consistent with the defect model in equation 3.1 in that oxygen vacancy concentration increased with ZnO doping level.

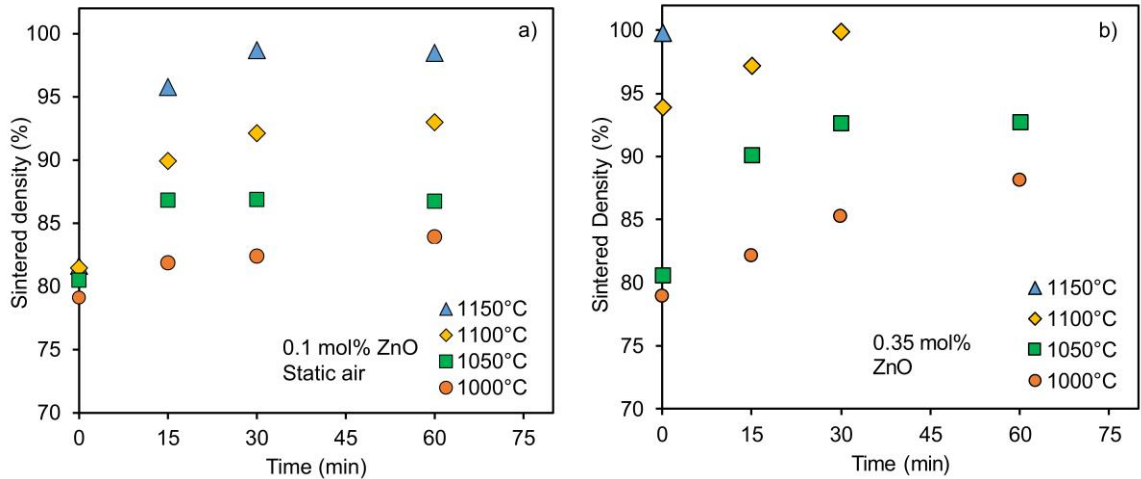


Figure 3.3. Sintering kinetics of (a) 0.1 mol% and (b) 0.35 mol% ZnO-doped PIN-PZN-PT ceramics heated in air. ZnO-doping significantly increased the densification of PIN-PZN-PT ceramics at all times and temperatures.

To determine the effect ZnO-doping on phase purity of PIN-PZN-PT ceramics, XRD was collected as a function of ZnO dopant concentration and sintering temperature. Fig. 3.4 shows XRD patterns of undoped and 0.1 mol% ZnO-doped PIN-PZN-PT ceramics after sintering from 900°C-1200°C for 30 min in static air. Sintering undoped PIN-PZN-PT

powder results in the formation of a minor amount of zinc-based pyrochlore and the majority rhombohedral PIN-PZN-PT perovskite phase at all explored temperatures. Heating 0.1 mol% ZnO-doped PIN-PZN-PT at 900°C resulted in a mixture of zinc-based pyrochlore and rhombohedral PIN-PZN-PT perovskite, but heating to $\geq 1100^\circ\text{C}$ resulted in the formation of phase pure rhombohedral PIN-PZN-PT perovskite. This result demonstrates that only 0.1 mol% ZnO is required to achieve phase pure 50.5PIN-21PZN-28.5PT perovskite ceramics which we earlier attributed to a reduction in the thermodynamic stability of pyrochlore phase relative to the ZnO-doped perovskite phase.^{14,22}

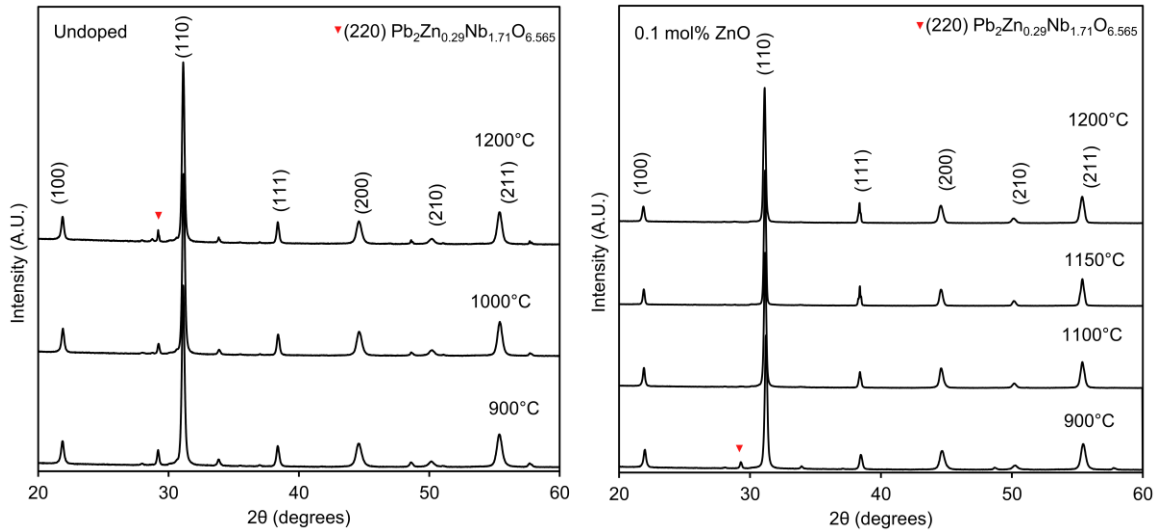


Figure 3.4. XRD patterns of undoped and 0.1 mol% ZnO-doped PIN-PZN-PT ceramics after sintering between 900°C and 1200°C for 30 min in static air. ZnO-doping results in formation of phase pure rhombohedral PIN-PZN-PT perovskite ceramics from 1100°C-1200°C.

3.3.2 Sintering in oxygen

Fig. 3.5(a) shows the sintered density of 0.35 mol% ZnO-doped PIN-PZN-PT ceramics after heating to various temperatures for 0 min in either static or flowing oxygen. Sintering in static air to 1150°C for 0 min resulted in 100% density, whereas sintering in flowing oxygen resulted in a relative density of 94.7%. The reduction in densification when firing in oxygen may be due to a reduction in the oxygen vacancy concentration. As suggested by equation 3.1, oxygen sintering should reduce the formation of oxygen vacancies and decrease the rate of bulk diffusion and densification. Figures 3.5(b) and 3.5(c) show the SEM microstructures after sintering 0.35 mol% ZnO-doped PIN-PZN-PT for 30 min in flowing oxygen or static air. Interestingly, sintering in either flowing oxygen or static air for 30 min resulted in similar grain morphology and size.

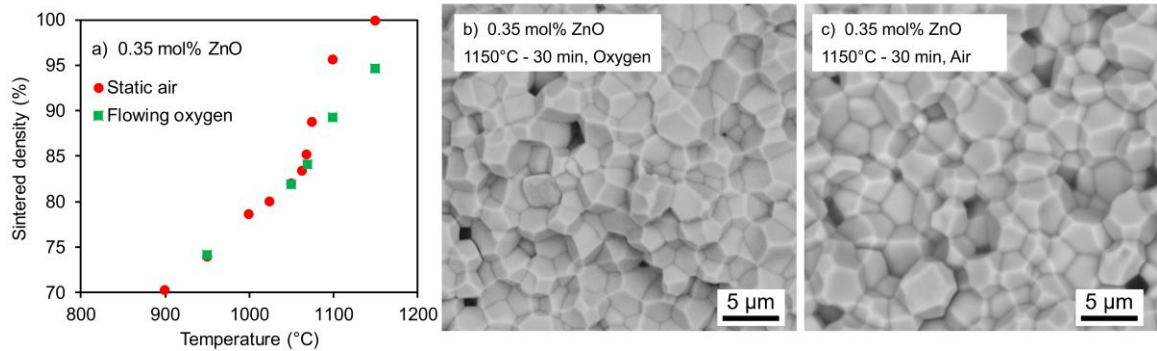


Figure 3.5(a). Density of 0.35 mol% ZnO-doped PIN-PZN-PT ceramics after sintering in either flowing oxygen or static air with 0 min dwell time. Sintering in oxygen decreased the rate of PIN-PZN-PT densification compared to sintering in air. SEM micrographs of 0.35 mol% ZnO-doped PIN-PZN-PT ceramics after sintering at 1150°C for 30 min in (b) flowing oxygen and (c) static air.

3.3.3 Perovskite structure and phase transition temperatures

The densification data shown in Fig. 3.5 suggests that the sintering atmosphere affects the solubility of Zn^{2+} in the perovskite B-site. In addition to increasing densification rates, Zn^{2+} incorporation into lead-based perovskite reportedly causes an increase in lattice tetragonality.^{16,23} Perovskite tetragonality is demonstrated by peak splitting of the rhombohedral/pseudocubic {100} reflections and is most commonly observed with the (200) peak at $\sim 44.5^\circ$.^{13,15,20,24} To explore how Zn^{2+} concentration affects the PIN-PZN-PT perovskite lattice, XRD was collected for samples with various dopant concentrations sintered in either flowing oxygen or static air.

Fig. 3.6 shows XRD scans of the (200) peak of 0.1, 0.2, and 0.35 mol% ZnO-doped PIN-PZN-PT ceramics sintered in (a) air and (b) flowing oxygen. Heating 0.1 mol% ZnO-doped PIN-PZN-PT in air results in a rhombohedral (200) peak. Increasing the ZnO concentration to 0.2 mol% results in peak broadening of the (200) peak, and further increasing the ZnO concentration to 0.35 mol% results in splitting of the rhombohedral (200) peak into tetragonal (200) and (002) peaks.^{17,20} Sintering 0.1 mol% ZnO-doped PIN-PZN-PT in flowing oxygen resulted in a rhombohedral (200) peak similar to the peak observed when sintering in air. However, increasing the ZnO concentration to 0.2 and 0.35 mol% resulted in slight peak broadening, but no peak splitting was observed when sintering in flowing oxygen. The sensitivity of phase composition with Zn^{2+} doping and sintering atmosphere can be explained in the following way. In accordance with equation 3.1, Zn^{2+} incorporation in the lattice results in the formation of oxygen vacancies and thus higher P_{O_2} suppresses the formation of oxygen vacancies. The change in crystal structure from

rhombohedral perovskite to tetragonal perovskite is due to differences in bonding character of the perovskite phase due to presence of additional Zn^{2+} and oxygen vacancies.^{17,20}

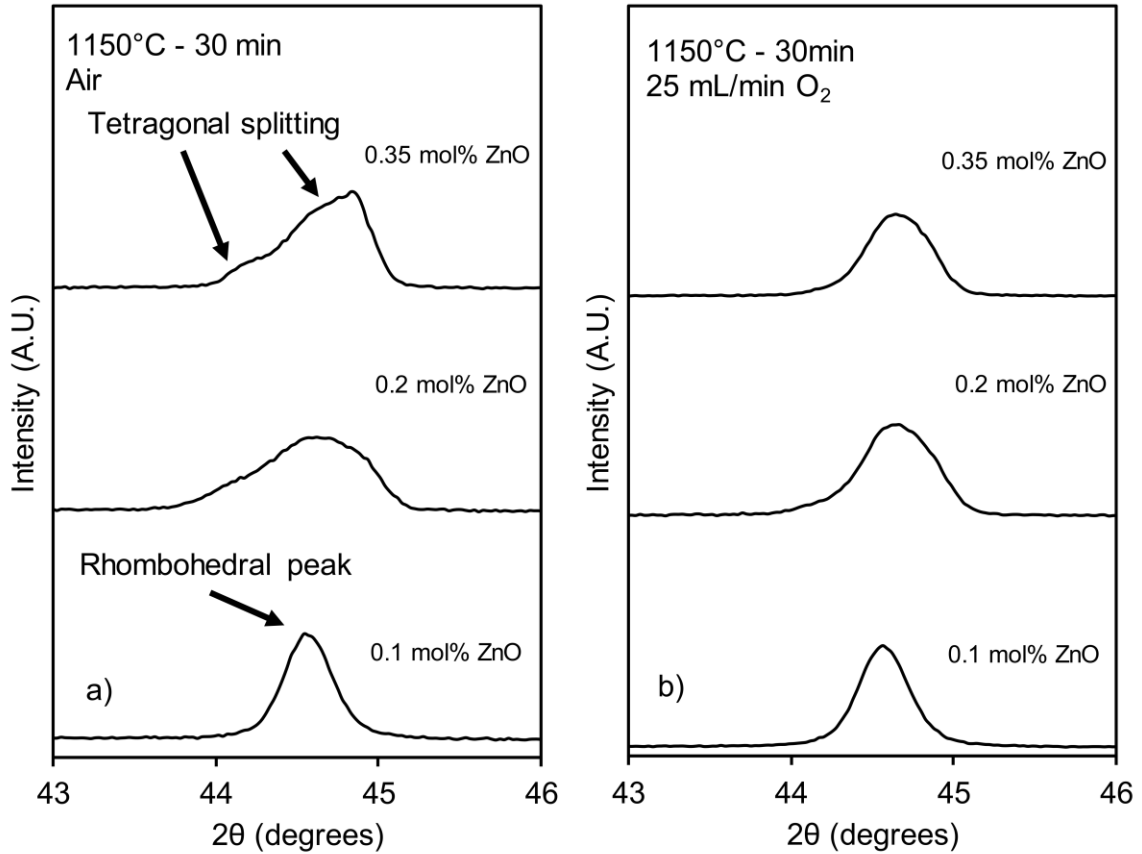


Figure 3.6. XRD of the (200) peak of 0.1, 0.2, and 0.35 mol% ZnO-doped PIN-PZN-PT ceramics sintered at 1150°C for 30 min (a) air and in (b) flowing oxygen. Sintering in flowing oxygen suppresses tetragonal peak splitting associated with ZnO doping.

Based on the results of Fig. 3.6 and equation 3.1, sintering in flowing oxygen should reduce the solubility of Zn^{2+} in PIN-PZN-PT and cause second phase formation. Fig. 3.7 shows high counting statistic XRD patterns of 0.35 mol% ZnO-doped PIN-PZN-PT

ceramics sintered at 1150°C for 30 min in static air and in flowing oxygen. As seen in Figure 3.7 sintering under flowing oxygen resulted in the formation ZnO precipitates whereas no ZnO peaks were observed in the air-fired sample. XRD of samples sintered in static air shows the presence of additional diffraction peaks of a secondary phase(s). These diffraction peaks do not correspond to a pyrochlore or perovskite phase, but this result further confirms that increased P_{O_2} relative to air is required to stabilize PIN-PZN-PT perovskite. It has been demonstrated that ZnO, MgO, and MnO₂ doping in other lead-based perovskite systems results in the formation of binary oxide precipitates because of insufficient dopant solubility.²⁶

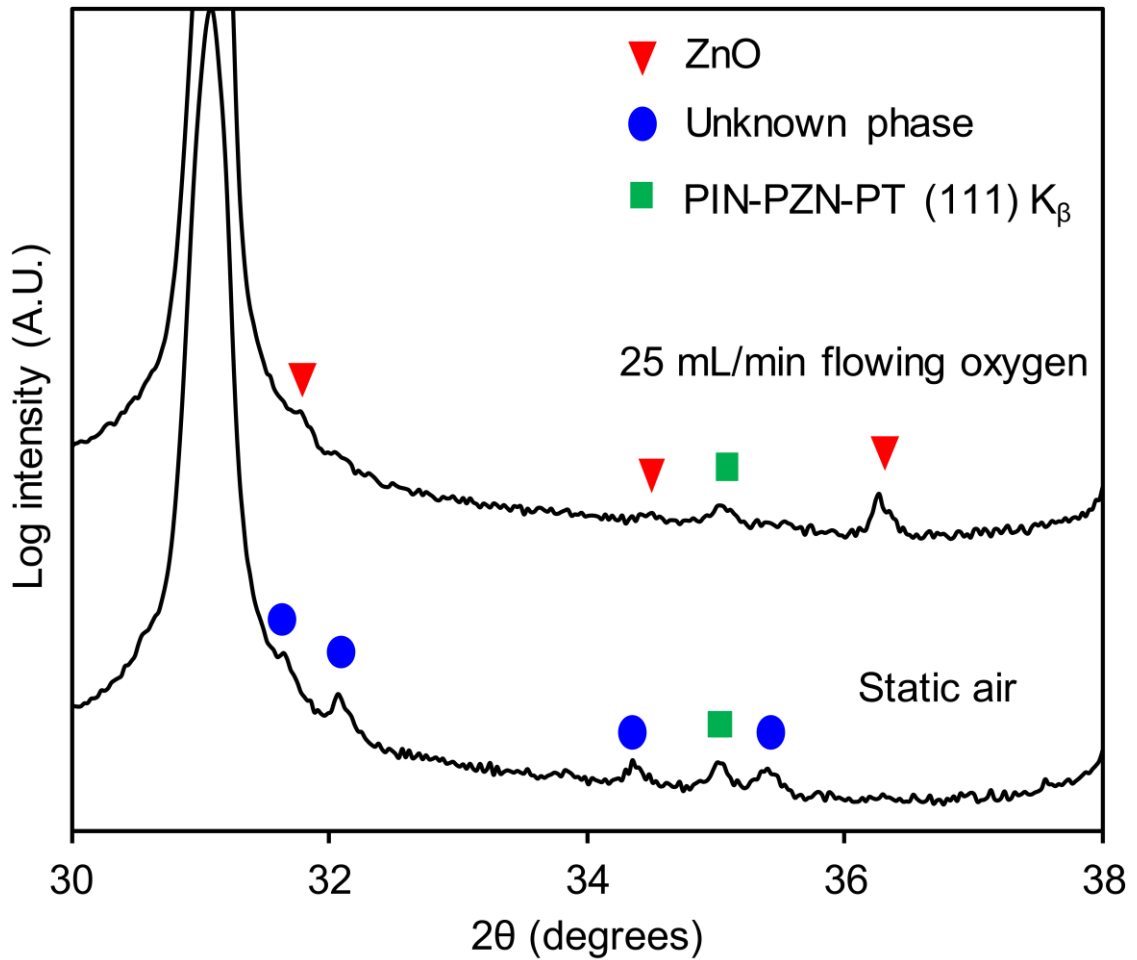


Figure 3.7. XRD of 0.35 mol% ZnO-doped PIN-PZN-PT ceramics sintered at 1150°C for 30 min in either static air or flowing oxygen. Sintering in flowing oxygen results in the formation of ZnO while sintering in static air results in the formation of an unidentified secondary phase at 31.6, 32.1, 34.3, and 35.4 degrees.

Fig. 3.8 shows the dielectric properties of >95% dense air-sintered PIN-PZN-PT ceramics as a function of ZnO dopant concentration and temperature. The 0.1 mol% ZnO-doped PIN-PZN-PT ceramic has a T_C of 259°C. Increasing the ZnO dopant concentration to 0.2 and 0.35 mol% ZnO increased the T_C to 265 and 270°C, respectively. The 0.1 mol% ZnO-doped PIN-PZN-PT ceramic has a T_{r-t} of 171°C and increasing the ZnO dopant concentration to 0.2 mol% and 0.35 mol% decreases the T_{r-t} to 161°C and 153°C, respectively. The simultaneous increase in the T_C and decrease in the T_{r-t} further suggests an increase in the tetragonal character of the perovskite structure which agrees with the XRD of the ZnO-doped PIN-PZN-PT ceramics shown in Figure 3.5. These results are consistent with reports for other ferroelectrics that increased tetragonality decreases the T_{r-t} and increases the T_C .^{13,17}

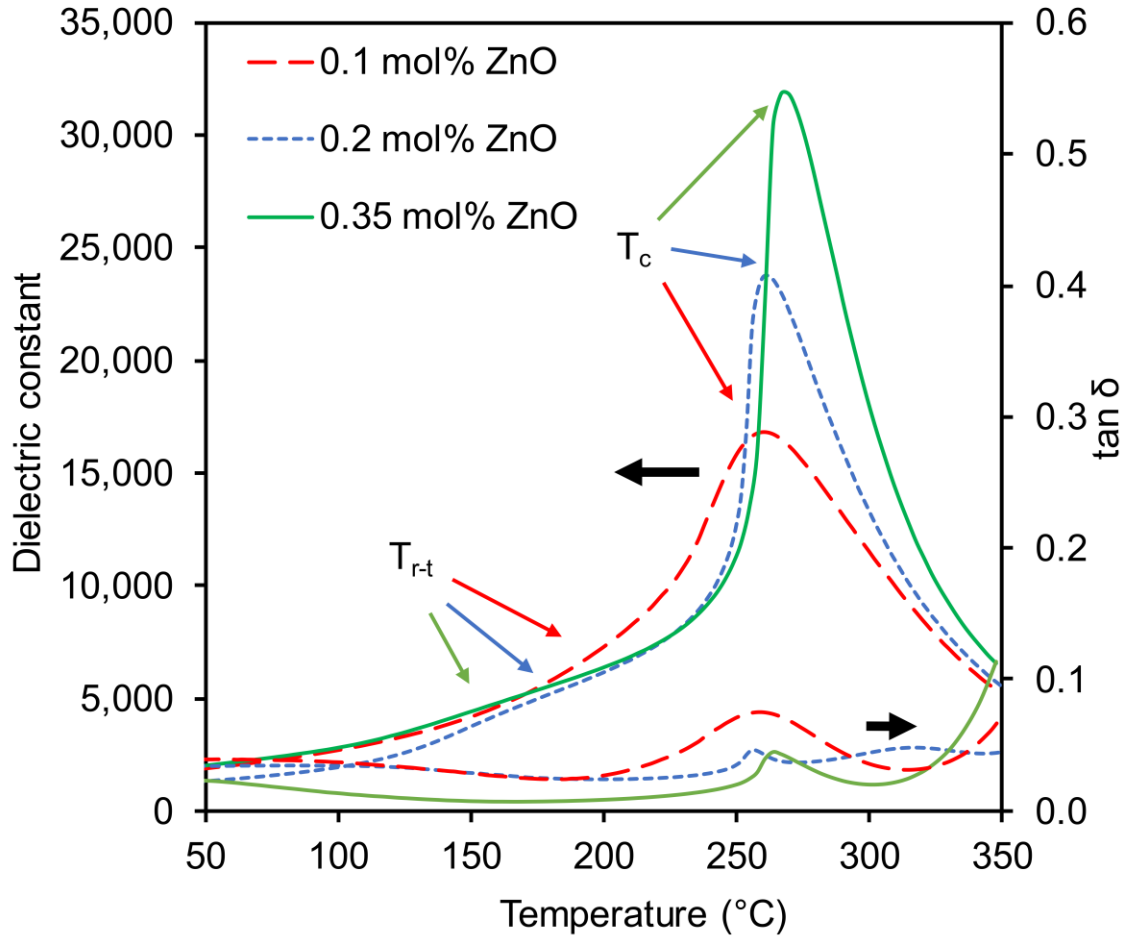


Figure 3.8. Dielectric constant at 100 kHz and dielectric loss of PIN-PZN-PT ceramics as a function ZnO-dopant concentration and temperature. These ceramics were sintered at 1150°C for 30 min in static air.

Fig. 3.9 shows the dielectric properties of (a) 0.1 mol% and (b) 0.35 mol% ZnO-doped PIN-PZN-PT ceramics sintered at 1150°C for 30 min as a function of sintering atmosphere. Sintering 0.1 mol% ZnO-doped PIN-PZN-PT in either static air or flowing oxygen resulted in a T_C of $\sim 260^\circ\text{C}$ and a T_{r-t} of approximately 172°C . Sintering 0.35 mol% ZnO-doped PIN-PZN-PT in air resulted in a T_C of 270°C and T_{r-t} of 153°C , but sintering in oxygen decreased the Curie temperature to 260°C and increased the T_{r-t} to 172°C . This peak shift

indicates that sintering 0.35 mol% ZnO-doped PIN-PZN-PT in oxygen results in a more rhombohedral perovskite structure than when sintered in air. These results are consistent with the XRD presented in Fig. 5 that showed that sintering 0.35 mol% ZnO-doped PIN-PZN-PT under flowing oxygen suppresses tetragonal peak splitting and promotes the formation of rhombohedral PIN-PZN-PT.

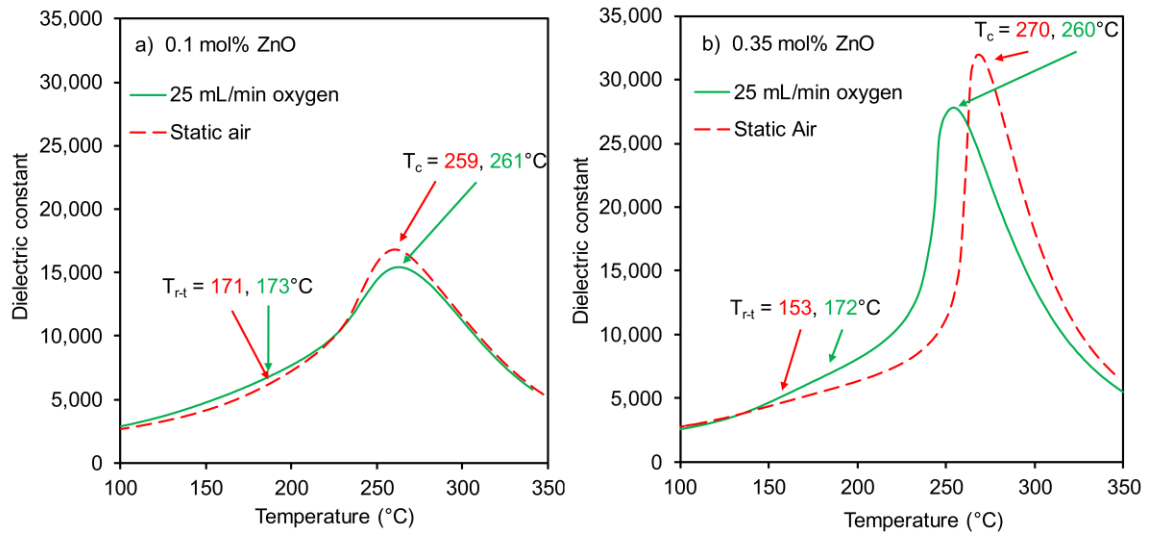


Figure 3.9. Dielectric constant at 100 kHz as a function of temperature of (a) 0.1 and (b) 0.35 mol% ZnO-doped PIN-PZN-PT ceramics sintered at 1150°C in air or oxygen. Increasing ZnO increases the sensitivity of T_C and T_{rt} as a function of sintering atmosphere.

3.3.4 Ferroelectric and electromechanical properties

Fig. 3.10 shows polarization-electric field (PE) loops as a function of sintering atmosphere of (a) 0.1 mol% and (b) 0.35 mol% ZnO-doped PIN-PZN-PT ceramics. Sintering 0.1 mol% ZnO-doped PIN-PZN-PT in either static air or flowing oxygen resulted in a coercive field (E_c) of ~ 11.7 kV/cm and remnant polarization (P_r) of $33.5 \mu\text{C}/\text{cm}^2$. The minimal differences in the properties of these two samples are likely because of the minor

crystallographic differences as shown in Fig. 3.6. Sintering 0.35 mol% ZnO-doped PIN-PZN-PT ceramics in static air results in an E_c of 9.4 kV/cm and P_r of 27.2 $\mu\text{C}/\text{cm}^2$, while sintering in flowing oxygen results in an E_c of 10.6 kV/cm and P_r of 34.2 $\mu\text{C}/\text{cm}^2$.

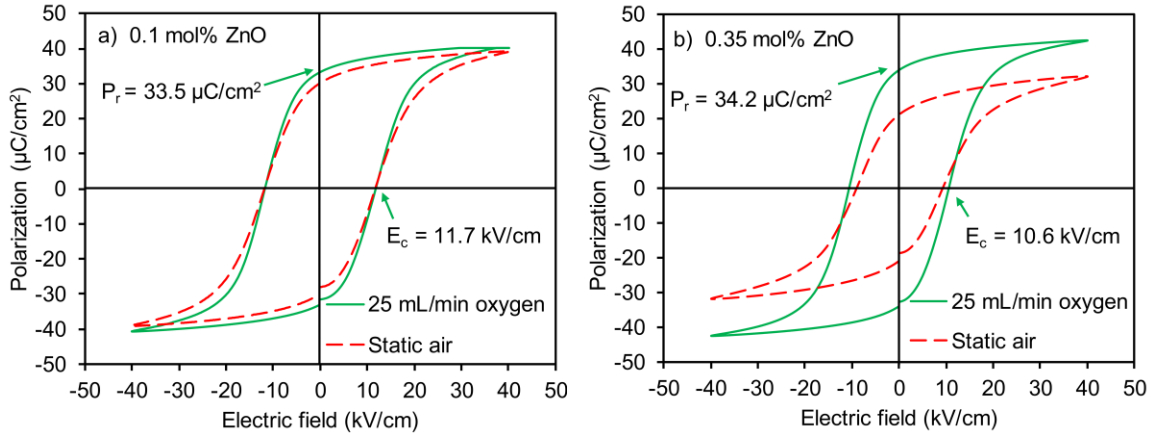


Figure 3.10. PE-loops of (a) 0.1 and (b) 0.35 mol% ZnO-doped PIN-PZN-PT ceramics sintered at 1150°C for 30 min in air or oxygen. ZnO concentrations > 0.1 mol% reduced both the polarization and coercive field in both static air and flowing oxygen.

In most lead-based piezoelectrics, increasing the tetragonal character of perovskite typically increases coercive field and remnant polarization.^{2,7,13} Furthermore, the formation of oxygen vacancies through acceptor B-site doping typically increases the E_c .^{1,2} Tetragonal PIN-PZN-PT was shown to form when sintering in air. The decrease in the ferroelectric properties may be due to the secondary phase formation shown in shown Figure 3.7. This result is similar to that of Yan et al. who observed 1 μm MgO precipitates as well as increased tetragonal splitting in the XRD when doping $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbZrO_3 - PbTiO_3 (PMN-PZT) with 2 mol% MnO_2 .²⁶ Mn^{2+} incorporation on the perovskite B-site was associated with decreased E_c and P_r which is comparable to the effects of ZnO

doping in this study.²⁶ Thus, while ZnO doping assists with PIN-PZN-PT densification and phase stability, only minimal ZnO-doping (0.1 mol%) is necessary for a high coercive field.

Because ZnO-doping and sintering P_{O_2} affect the structure of PIN-PZN-PT, the proximity of the ternary composition to the MPB is likely affected by the processing conditions. Since maximized coercive fields occurred when sintering in flowing oxygen, several (1-x)PIN-21PZN-(x)PT compositions with 0.1 mol% ZnO dopant were sintered in flowing oxygen to determine how ceramic composition near to the morphotropic phase boundary affects the d_{33} . Fig. 3.11 shows the d_{33} and E_c of (1-x)PIN-21PZN-(x)PT as a function of $PbTiO_3$ content. Increasing the $PbTiO_3$ content from 28.5 to 31% increases the coercive field from 9.4 to 13 kV/cm due to the increased tetragonality of PIN-PZN-PT. Increasing the $PbTiO_3$ content results in a maximum d_{33} of 550 pC/N at 31 mol% $PbTiO_3$ and then steeply drops to 300 pC/N at 32% PT. This d_{33} change indicates that the morphotropic phase boundary exists at 48PIN-21PZN-31PT. In contrast the MPB of PIN-PZN-PT ceramics with 5 mol% excess ZnO occurred at 50PIN-21PZN-29PT.^{7,13} These results indicates that the MPB composition changes slightly with different processing conditions and ZnO dopant levels.

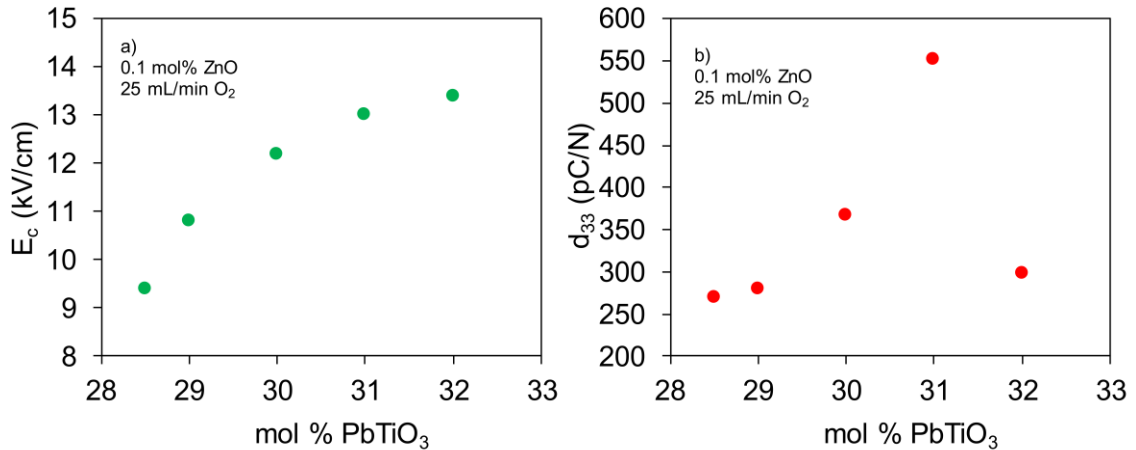


Figure 3.11. (a) Coercive field and (b) d_{33} of 0.1 mol% ZnO-doped (1-x)PIN-21PZN-xPT ceramics sintered at 1150°C for 30 min in oxygen.

In this investigation, it was determined that sintering 0.1 mol% ZnO-doped 48PIN-21PZN-31PT in flowing O_2 resulted in an excellent combination of electromechanical properties (Table 3.1). 0.1 mol% ZnO was sufficient to yield high density (>99%) ceramics relative to the undoped samples while also achieving excellent electromechanical properties. While ZnO-doping facilitates densification of PIN-PZN-PT ceramics, increasing ZnO concentration above 0.1 mol% greatly increases PIN-PZN-PT perovskite's sensitivity to P_{O_2} .

Table 3.1. Ferroelectric, dielectric, and piezoelectric properties of ZnO-doped 48PIN-21PZN-31PT ceramics sintered in flowing oxygen and static air at 1150°C for 30 min. Properties of undoped PIN-PZN-PT samples were not included because sintered densities were only ~75%.

Sintering atmosphere	ZnO (mol%)	d_{33} (pC/N)	T_c (°C)	T_{r-t} (°C)	E_c (kV/cm)	$\tan \delta$ (%)	ϵ_r	k_p (%)	Q_m
Flowing O_2	0.1	550	261	165	13	1.1	1683	59	70
	0.2	526	262	164	12.6	1.2	1714	-	-
	0.35	510	265	164	12.3	1.1	1652	-	-
Static air	0.1	511	262	163	12.7	1.2	1702	52	71
	0.2	487	265	151	11.6	1.3	1721	-	-
	0.35	465	274	143	10.3	1.1	1748	-	-

3.4 Conclusions

This study demonstrated the effects of ZnO-doping on the densification behavior, crystallographic structure, and electromechanical properties of PIN-PZN-PT ceramics. ZnO-doping greatly increased the densification rate of PIN-PZN-PT at all explored conditions due to the formation of oxygen vacancies associated with the substitution of Zn^{2+} ions on the perovskite B-site. Sintering ZnO-doped PIN-PZN-PT in both static air and flowing oxygen resulted in > 95% dense ceramics after heating to 1150°C for 0 min. Sintering ZnO-doped PIN-PZN-PT in high P_{O_2} conditions promoted the formation of rhombohedral PIN-PZN-PT ceramics and limited the solubility of Zn^{2+} in the perovskite lattice. Thus, the d_{33} and E_c were reduced due to the presence of ZnO inclusions at higher ZnO concentrations. Sintering in flowing oxygen with only 0.1 mol% ZnO resulted in substantially increased densities, elimination of pyrochlore, and an excellent combination of ferroelectric, piezoelectric, and dielectric properties.

3.5 References

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Chapter 4

Templated Grain Growth of High Coercive Field CuO-doped Textured PYN-PMN-PT Ceramics

4.1 Introduction

Ternary relaxor-based single crystals such as $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbZrO}_3\text{-PbTiO}_3$ (PMN-PZT) are the state of the art piezoelectric materials due to their exceptionally high piezoelectric charge coefficients ($d_{33} > 2000$ pC/N) and high electromechanical coupling factors ($k^2 > 90\%$).¹⁻³ The large electromechanical responses of these materials are due to their high electrostriction in conjunction with 4R domain engineering of $\langle 001 \rangle_c$ poled rhombohedral crystals.¹ While relaxor-based crystals possess exceptional piezoelectric properties relative to polycrystalline ceramics, their adoption for high-power sensing, actuation, and transducer applications has been severely restricted by their high production cost, limited size and shape, low compositional uniformity, low coercive field (E_c of 3-7 kV/cm), and low rhombohedral to tetragonal phase transition temperature ($T_{r-t} < 100^\circ\text{C}$).^{1,3,4} The coercive field is particularly important for preventing device depoling under high-drive

conditions. These limitations greatly reduce the scalability and range of possible applications of single crystal piezoelectrics.^{3,5}

Texturing ceramics through templated grain growth (TGG) is a substantially more cost-effective approach than single crystal growth for the production of high-performance piezoelectric materials.⁶⁻⁸ The TGG process allows for substantially improved compositional control relative to single crystal growth because growth retains the chemical homogeneity of the greenbody.⁶ This benefit, combined with the scalability of tape casting, enables high-volume production of compositionally-uniform parts of various sizes and shapes.⁷ Textured PIN-PMN-PT and PMN-PZT ceramics, templated with barium titanate platelets, show improved piezoelectric properties (600-850 pC/N) compared to their random counterparts (400-550 pC/N).⁸⁻¹¹ While texturing improves the piezoelectric properties, current generation textured ceramics are limited by the same low E_c (~7-8 kV/cm), T_{r-t} (100-120°C), and low T_C 's (150-215°C) as the single crystal analogs because these properties are dominated by material composition rather than the final microstructure.^{8,11}

$\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PYN) has been added to binary $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT) single crystals and ceramics in an effort to develop piezoelectric materials with higher phase transition temperatures and a greater coercive field.¹²⁻¹⁵ Single crystals of $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 with 15-40 mol% PYN have comparable piezoelectric coefficients to PIN-PMN-PT and PMN-PZT crystals but with improved T_{r-t} 's (~120-130°C) and substantially higher coercive fields (5-10 kV/cm).^{13,16} Unfortunately, increasing PYN in PYN-PMN-PT results in severe compositional segregation during single crystal growth (effective segregation coefficient $K_{\text{eff}}^{\text{Ti}} = 0.7-0.8$).^{13,16}

To avoid the processing challenges associated with single crystal growth of PYN-PMN-PT, Duran et al. explored templated grain growth of 15.5PYN-46.5PMN-38PT with barium titanate platelet (BT) particles.¹⁴ They showed that texturing 15.5PYN-46.5PMN-38PT with 5 vol% BT increased the peak strain from 0.21% (driven at 50 kV/cm) in the random ceramic to 0.33%. Textured 15.5PYN-46.5PMN-38PT ceramics have ~200% higher E_c of 11.5 kV/cm compared to 4-5 kV/cm of textured PMN-PT ceramics.¹⁴ The E_c of textured PYN-PMN-PT ceramics are also substantially higher than single crystal analogs.^{14,16}

Duran's work and the improved E_c 's of single PYN-PMN-PT crystals with 15-40 mol% PYN suggest that increasing PYN content in textured PYN-PMN-PT ceramics would result in textured ceramics with superior E_c 's. However, increasing PYN content to 10-30 mol% has been shown to significantly limit grain growth in random PYN-PMN-PT ceramics.¹² Chang et al. showed that CuO-doping of textured PIN-PMN-PT results in substantially increased template growth while also improving the ferroelectric, dielectric, and piezoelectric properties.⁸ This suggests that CuO-doping is an effective strategy for promoting templated grain growth in lead-based perovskites. In this paper we show CuO-doping with PbO promotes templated growth in PYN-PMN-PT and enables TGG with higher PYN content. Based on this preliminary analysis 21PYN-41PMN-38PT was selected for TGG and property evaluation.

4.2 Experimental Procedure

PYN-PMN-PT perovskite powders of various compositions were fabricated by a two-stage Columbite precursor method to maximize the formation of perovskite phase. The first stage included reacting MgO with Nb₂O₅ to form MgNb₂O₆, and reacting Yb₂O₃ with Nb₂O₅ to form YbNbO₄ in order to prevent the direct reaction between PbO and Nb₂O₅.^{12,17} The binary oxides were synthesized by vibratory milling MgO (99.9%, Mallinckrodt, Dublin, Ireland) with Nb₂O₅ (99.9%, H.C. Starck, Munich, Germany), and Yb₂O₃ (99.9%, Alfa Aesar, Massachusetts, USA) with Nb₂O₅ in ethanol for 24 h. The milled powders were heated in air at 1000°C for 6 h and 1100°C for 4 h to synthesize ~400 nm MgNb₂O₆ and ~400 nm YbNbO₄ powders. Mixtures of MgNb₂O₆, YbNbO₄, PbO (99.9%, Alfa Aesar Haverhill, Massachusetts, USA), and 20 nm TiO₂ (99.9%, Evonik Industries, Essen, Germany) were vibratory milled in ethanol for 24 h, and subsequently dried. All perovskite powders were batched with 1 mol% excess PbO to account for lead loss during sintering and to promote liquid phase sintering. The powder mixture was then heated in air at 750°C for 2 h and x-ray diffraction (XRD, Xpert Pro MPD diffractometer, PANalytical, Inc., The Netherlands) was used to confirm perovskite PYN-PMN-PT (with 1 mol% PbO) phase purity. The reacted perovskite powder was then vibratory milled for 24 h with various concentrations of CuO dopant (99.99%, Sigma Aldrich, St. Louis, Missouri, USA). Zirconia milling media (3 mm diameter) was used in all milling processes.

To evaluate the effect of PYN content on the epitaxial nucleation and growth of PYN-PMN-PT perovskite on barium titanate platelets, undoped PYN-PMN-PT of different compositions across the morphotropic phase boundary were mixed with barium titanate

platelet particles in a mortar and pestle and then dry pressed. Barium titanate templates were chosen for their high chemical stability during TGG of lead-based perovskites. The pellets were heated to 1150°C for 10 h and fracture surfaces were analyzed with scanning electron microscopy (SEM, Phenom Pro, Phenom-World B.V., The Netherlands). All PYN-PMN-PT parts were embedded in powder of the same composition to minimize PbO loss during sintering. After determining the PYN-PMN-PT compositions that nucleate on barium titanate in TGG, PYN-PMN-PT matrix powder with and without CuO and PbO dopants was ball milled for 24 h in an aqueous acrylic binder system (Polymer Innovations, Inc, California, USA). Barium titanate platelet particles were added to the mill jar for the final 30 min of milling. The resulting slurry was tape cast with a doctor blade height of 0.200 mm and a casting speed of 100 cm/min. The dried tape was cut, stacked, and compacted. The organic binder was removed by heating at 0.1°C/min to 370°C, and the parts were subsequently isostatically pressed at 200 MPa.

PYN-PMN-PT parts were embedded in powder of the same composition and then heated at various times and temperatures in flowing oxygen (25 mL/min). The sintered densities were measured by Archimedes' method after light polishing to remove surface pyrochlore. The phase composition and texture of the sintered samples was evaluated by XRD. The Lotgering factor of the <001> texture was calculated from the relative peak heights of diffraction patterns of templated and random PYN-PMN-PT ceramics.^{8,18}

Silver electrodes (DuPont 850, DuPont, Wilmington, DE) were fired on both faces of the samples by heating to 750°C for 30 min after application. Capacitance (C) and dielectric loss ($\tan \delta$) were measured as a function of temperature (30-300°C) using an LCR meter (Agilent 4284A, Agilent Technologies, CA, USA). Bipolar polarization vs electric field

loops were measured at 1 Hz using a custom Sawyer-Tower circuit. Samples were poled in silicone oil at 100°C under 30 kV/cm for 15 min, and piezoelectric charge constant and high field piezoelectric charge constants (d_{33} and d_{33}^*) were measured using a Berlincourt meter (d33 PiezoMeter System, Piezotest Ltd, Singapore) and Sawyer-Tower circuit after aging for 24 h after poling.

4.3 Results and Discussion

4.3.1 Growth of PYN-PMN-PT on BaTiO₃ templates

To determine the maximum amount of PYN possible in PYN-PMN-PT ceramics and still have templated growth on barium titanate, several compositions across the morphotropic phase boundary were heated with barium titanate platelet particles. The morphotropic phase boundary was estimated as a straight line between 67PMN-33PT and 50PYN-50PT (Figure 4.1(a)). Figures 4.1(b), (c), and (d) show micrographs of the interface between 21.5PYN-38PMN-40.5PT, 25PYN-33.5PMN-41.5PT, 28PYN-29.5PMN-42.5PT and barium titanate, respectively, after heating at 1150°C for 10 h. Compositions with $\leq$ 21.5 mol% PYN content resulted in uniform growth on barium titanate templates in a manner similar to what has been observed in textured PMN-PT ceramics, and the observed microstructures were found to be similar to what was observed in Fig. 4.1(b). Interestingly, 25PYN-33.5PMN-41.5PT exhibited regions of partial growth instead of a complete growth around the templates. Additionally, randomly oriented grains of 25PYN-33.5PMN-41.5PT can be observed in direct contact with the barium titanate template

suggesting no epitaxial growth in these regions. The lack of epitaxial growth present in these regions indicates non-wetting between some PYN-PMN-PT grains and barium titanate. There was no growth of 28PYN-29.5PMN-42.5PT on the surface of barium titanate, and the microstructures show randomly oriented grains in contact with barium titanate. The microstructure of 50PYN-50PT containing barium titanate templates was similar to that of Fig. 4.1(d). Additional experiments at different times, temperatures, and atmospheres showed that compositions with ≥ 28 mol% PYN do not result in epitaxial growth on barium titanate.

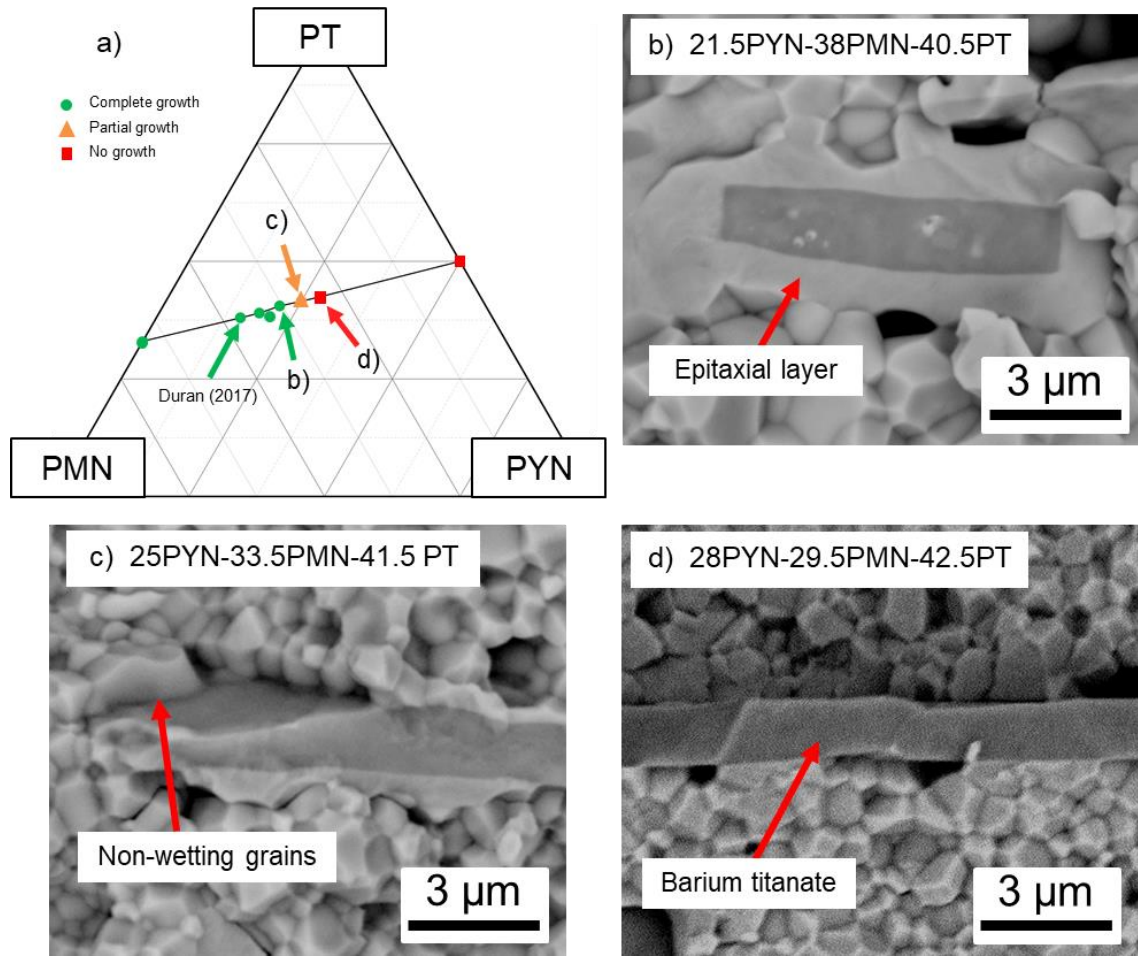


Figure 4.1(a) Phase diagram showing PYN-PMN-PT compositions evaluated for epitaxial growth on barium titanate. (b), (c), (d) SEM microstructures of interfaces of different PYN-PMN-PT compositions with barium titanate templates after heating at 1150°C for 10 h. Increasing PYN decreases the growth of PYN-PMN-PT on barium titanate.

A successful TGG process requires the initial formation of a terrace of matrix material on the surface of the template.^{6,19,20} The driving force behind this interaction is the overall reduction in interfacial energy which can be maximized by using isostructural materials with small lattice mismatch.^{6,19,20} Interestingly, 21.5PYN-38 PMN-40.5PT, 28PYN-29.5PMN-42.5PT, and barium titanate are all perovskite with cubic lattice parameters of 4.040 Å, 4.046 Å, and 4.036 Å, respectively. These small differences in lattice parameter suggest that all of the explored compositions should nucleate on barium titanate, but the absence of growth at >25 mol% PYN suggests there is an additional factor not related to the crystal structure that impacts templated grain growth or nucleation. Because both regions of growth and non-wetting grains appear in 25PYN-33.5PMN-41.5PT, the lack of nucleation is potentially due to local differences in chemistry at the template surface during sintering. Additional work is merited to elucidate the fundamental surface interactions between PYN-PMN-PT and barium titanate in TGG.

Based on the results shown in Fig. 4.1, 21PYN-41MN-38PT was chosen for texturing because higher PYN content was hypothesized to increase the coercive field of textured PYN-PMN-PT. 21PYN-41PMN-38PT powders containing 1 mol% excess PbO were milled with 0, 0.5 and 1.2 mol% CuO to explore the effect of the PbO-CuO liquid composition on template growth. Fig. 4.2 shows the effect of CuO concentration on the growth of PYN-PMN-PT on barium titanate after firing at 1050°C for 10 h. Sintering CuO-

free PYN-PMN-PT for 10 h resulted in $\sim 1 \mu\text{m}$ thick epitaxial film on the platelets. The addition 0.5 mol% CuO increased growth on the barium titanate templates from $1 \mu\text{m}$ to approximately $4 \mu\text{m}$. Increasing the CuO concentration to 1.2 mol% increased the template growth to approximately $6 \mu\text{m}$. The enhanced template growth in samples with the PbO-CuO liquid is attributed to increased solubility of the smaller sized matrix grains and deposition on the lower energy surface of the large template grains. Not surprisingly, increasing CuO concentration also increased the matrix grain growth. Templated grains in the PbO-CuO doped samples exhibit slight cuboidal morphology which indicates that the growth of templated grains during sintering may be limited or slowed by the growth of the $\{100\}$ planes of PYN-PMN-PT matrix grains.

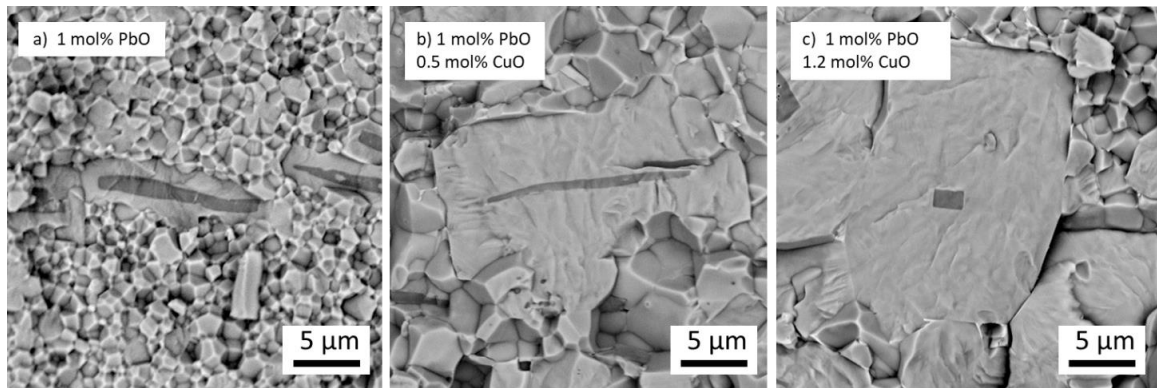


Figure 4.2. SEM micrographs showing the effects of CuO-doping on the template growth of 21PMN-41PMN-38PT after heating to 1050°C for 10 h. Increasing CuO content at 1 mol% PbO substantially increased template growth.

To further explore the role of the PbO-CuO liquid on the growth of templated PYN-PMN-PT, samples containing PbO and CuO were heated to 1050°C and immediately

cooled before substantial texturing and grain growth occurred. Fig. 4.3(a) shows evidence of a PbO-CuO rich grain boundary phase after sintering at 1050°C for 0 h. The high Z-contrast (brighter phase) of the grain boundary phase in Fig 4.3(a) indicates that it is PbO rich relative to the matrix phase. The presence of this phase is consistent with the hypothesis that a PbO-CuO liquid is responsible for PYN-PMN-PT growth on the BT template.

To determine if CuO must be on the grain boundary to promote texturing, samples were prepared by adding CuO to the PYN-PMN-PT precursor powder prior to powder calcination. Heating PYN-PMN-PT precursor powder with CuO likely results in Cu^{2+} entering the perovskite lattice because of its comparable ionic radii (73 pm) with the other B-site ions (60.5 – 86.8 pm).^{8,21} Fig. 4.3(b) shows an SEM micrograph of PYN-PMN-PT doped with 1.2 mol% CuO in the lattice and 1 mol% PbO sintered at 1050°C for 10 h. This sample shows substantially less growth compared to when PbO and CuO are added to perovskite powder (Fig 4.2(c)). This result shows that CuO must be distributed on the grain boundary in PYN-PMN-PT ceramics to form a PbO-CuO liquid. Because PYN-PMN-PT does not exhibit increased grain growth in samples with 1 mol% PbO alone, this result indicates that CuO addition to liquid PbO likely increases the solubility of PYN-PMN-PT.

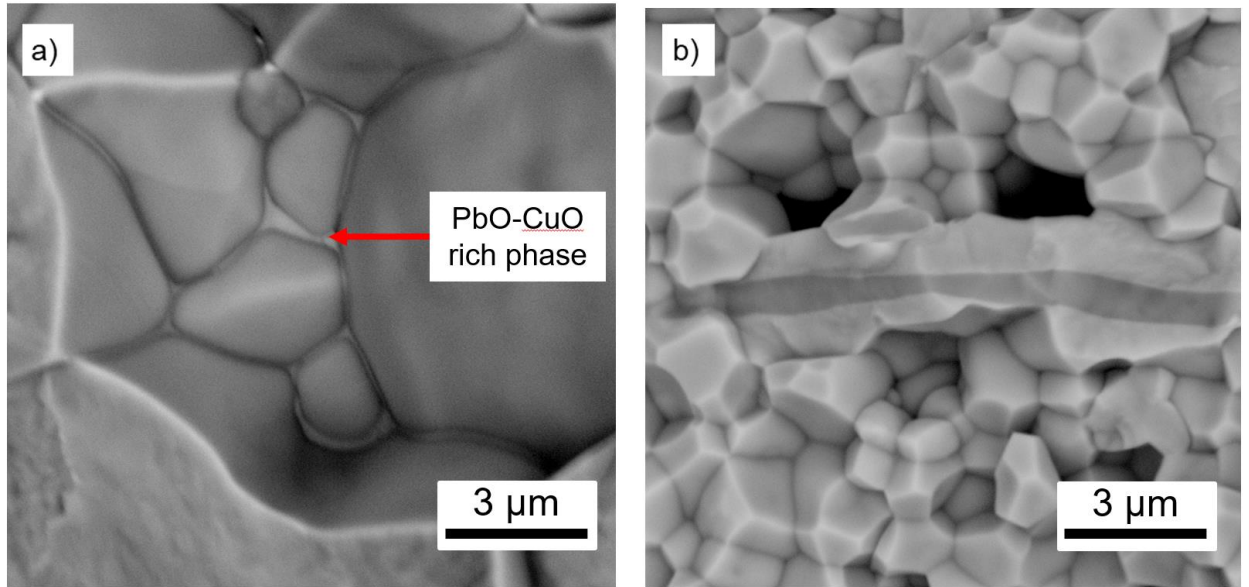


Figure 4.3(a). SEM micrograph of 1.2 mol% CuO-doped 21PYN-41PMN-38PT sintered at 1050°C for 0 h. A PbO-CuO rich phase can be seen at the grain boundaries. Fig. 4.3(b). SEM micrograph of 21PYN-41PMN-38PT doped with 1.2 mol% CuO (added before powder calcination) and 1 mol% PbO after sintering at 1050°C for 10 h.

To further explore the role of the grain boundary liquid composition in the templated grain growth of PYN-PMN-PT, perovskite powders were doped with either 1.2 mol% CuO or 3 mol% PbO. Fig. 4.4 shows an SEM micrograph of 21PYN-41PMN-38PT doped with 1.2 mol% CuO and 21PYN-41PMN-38PT doped with 3 mol% PbO after sintering at 1050°C for 10 h. Doping with 1.2 mol% CuO increased the growth of PYN-PMN-PT from ~ 1 to $2 \mu\text{m}$. This result suggests that free CuO at the grain boundary may form a liquid phase with PYN-PMN-PT that promotes TGG relative to undoped material. Similar systems such as PIN-PMN-PT have shown that doping with only CuO increases templated grain growth due to a liquid phase. It was observed that doping with only 3 mol% PbO increased matrix grain growth from 1 to $2.5 \mu\text{m}$. Doping with 3 mol% PbO changed the

morphology of the matrix grains from equiaxed to cuboidal. The appearance of faceted matrix grains suggests that PYN-PMN-PT growth in the PbO liquid is limited by the growth of the {100} planes. Furthermore, the increased size of the matrix grains relative to the template size reduced the driving force for TGG. Doping with either PbO or CuO was found to be far less effective at promoting TGG than doping with both PbO and CuO.

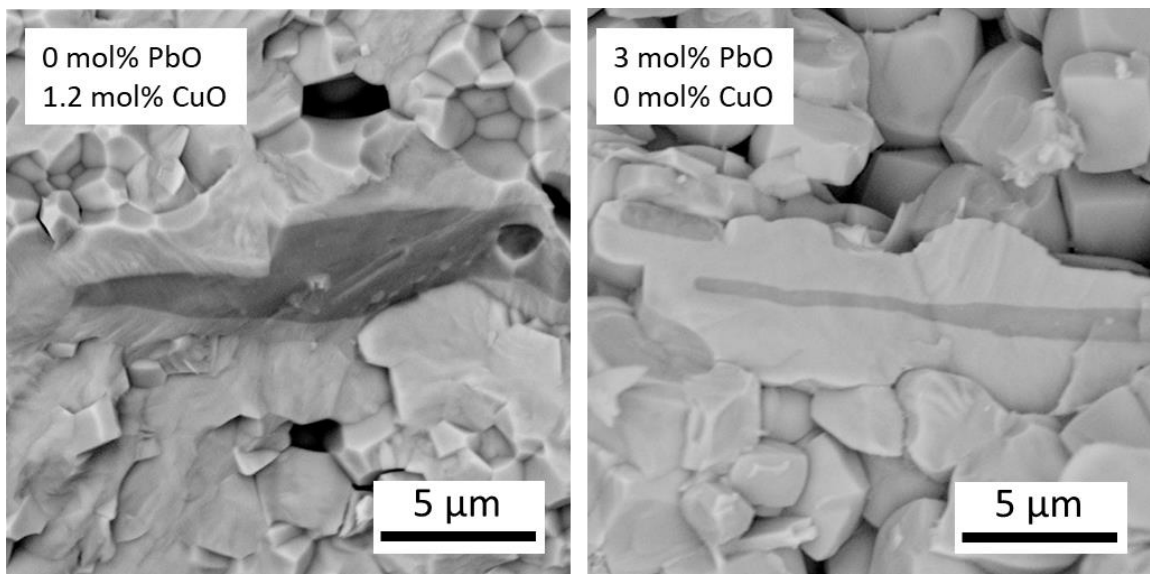


Figure 4.4. SEM micrograph of 1.2 mol% CuO-doped 21PYN-41PMN-38PT and 3 mol% PbO-doped 21PYN-41PMN-38PT after sintering at 1050°C for 10 h. Sintering CuO-doped powder without PbO resulted in a 2x increase in template growth compared to undoped PYN-PMN-PT. Doping PYN-PMN-PT with 3 mol% PbO resulted a 2x increase in template growth while the matrix coarsened from 2 to 3 μm.

4.3.2 Templated grain growth of PYN-PMN-PT ceramics

Fig 4.5 shows XRD patterns of tape cast 21PYN-41PMN-38PT ceramics with and without 5 vol% barium titanate templates after heating at 1050°C for 10 h. The addition of

5 vol% barium titanate to 1 mol% PbO-doped 21PYN-41PMN-38PT resulted in minor increases in the {001} peaks relative to random 21PYN-41PMN-38PT and a Lotgering factor of only 11% due to the limited growth layer around the barium titanate templates. Templated 21PYN-41PMN-38PT with 1.2 mol% CuO and 1 mol% PbO had substantially increased <001> fiber texture and a Lotgering factor of 93%. Texture did not increase after samples were heated at temperatures >1050°C for 10 h. Although 21PYN-41PMN-38PT lies on the compositional line directly tying PMN-PT and PYN-PT, the presence of both the (002) and (200) peaks in both random and textured samples indicates that 21PYN-41PMN-38PT is tetragonal. This result shows that the MPB is curved away from PbTiO₃ and that MPB PYN-PMN-PT compositions have less PbTiO₃ than predicted. Samples containing 1.2 mol% CuO and barium titanate showed a small increase in (200)/(002) peak splitting compared to the random ceramic. Since, BaTiO₃ has a different lattice parameter and thermal expansion coefficient than 21PYN-41PMN-38PT, the tetragonal splitting is likely more pronounced because of the stresses associated with the presence of the residual templates.

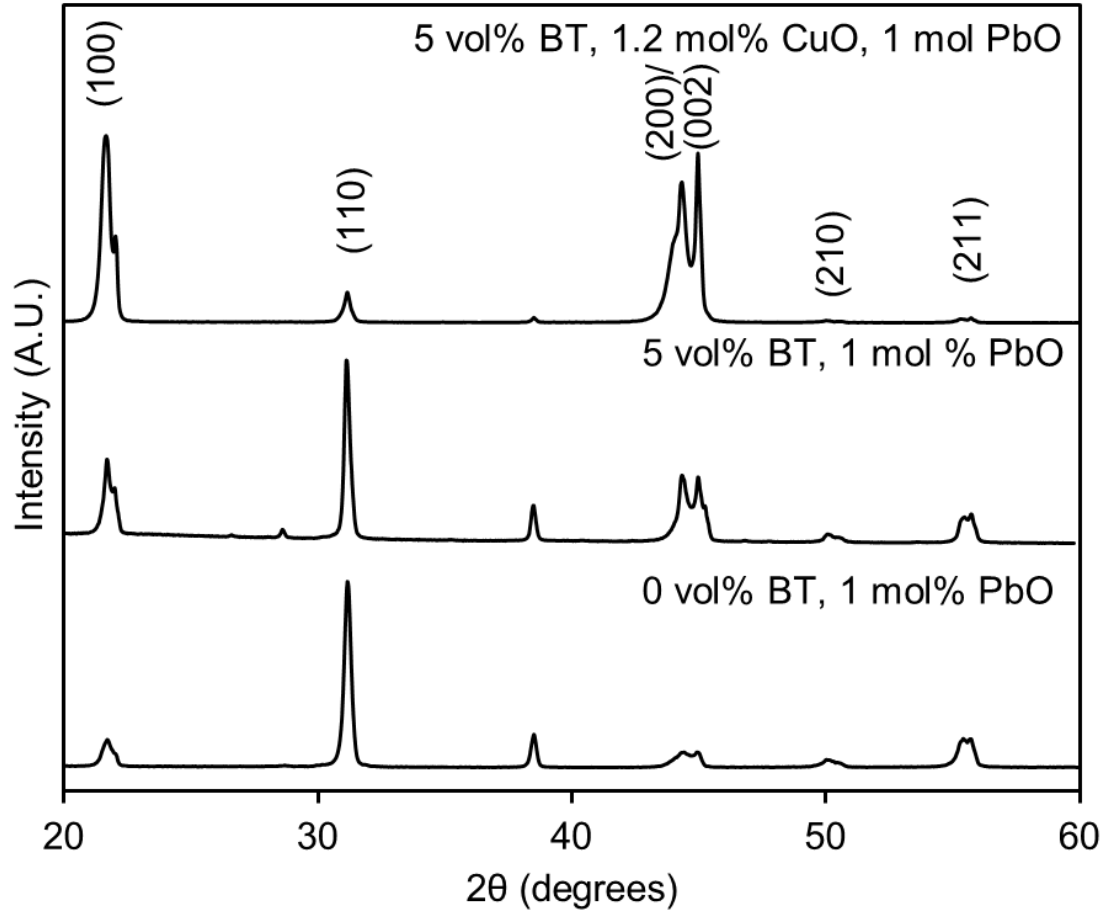


Figure 4.5. XRD of random and textured 21PYN-41PMN-38PT with and without 1.2 mol% CuO after sintering at 1050°C for 0 h. The addition of CuO substantially increased the amount of template growth which resulted in increased {001} peak intensity.

Figure 4.6 shows SEM micrographs of random and textured 21PYN-41PMN-38PT ceramics doped with 1 mol% PbO and 1.2 mol% CuO sintered at 1050°C for 10 h. Random PYN-PMN-PT had an equiaxed microstructure with an average grain size of $\sim 6 \mu\text{m}$. Texturing changed the fracture mode from intergranular to intragranular which makes it difficult to evaluate the extent of template growth. Residual barium titanate templates can be seen in the middle of large textured grains. Template growth stops when the growth fronts of adjacent grains impinge. Areas without barium titanate templates had regions of

randomly oriented grains. This result shows that liquid phase formers can be used to facilitate template growth in TGG of materials with limited grain matrix growth.

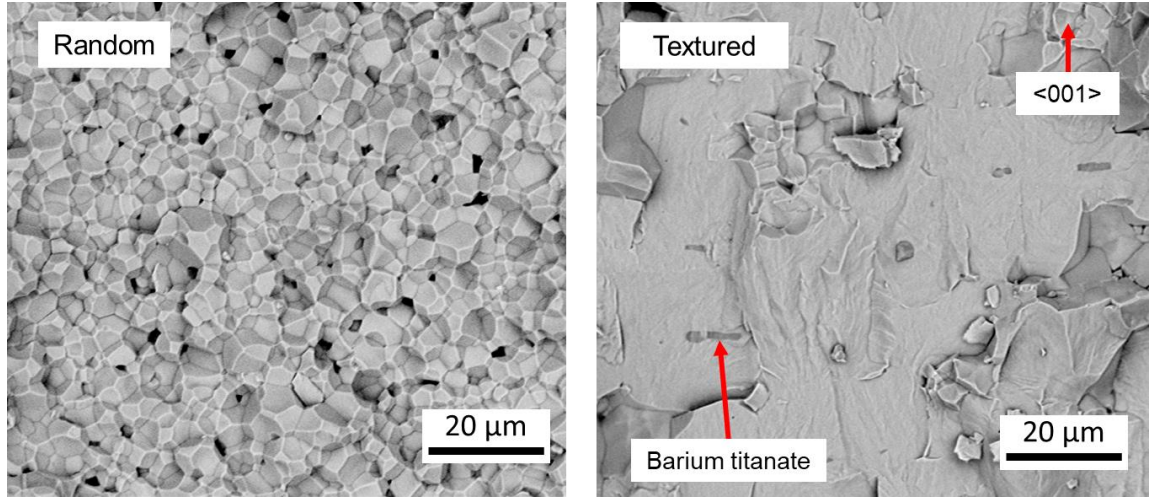


Figure 4.6. SEM micrographs of random and templated 21PYN-41PMN-38PT ceramics doped with 1.2 mol% CuO after sintering at 1050°C for 10 h.

4.3.3 Properties of textured PYN-PMN-PT

Figure 4.7 shows the unipolar strain loops of random and textured 1 mol% PbO and 1.2 mol% CuO-doped 21PYN-41PMN-38PT collected at a maximum applied field of 30 kV/cm. Texturing increased the unipolar-peak strain to 0.226 % from a peak strain of 0.125% in the random ceramic. This corresponds to a textured ceramic d_{33}^* of 754 pC/N compared to 413 pC/N for the random ceramic. This 83% increase in piezoelectricity is similar to results reported for PMN-PT ceramics textured through templated grain growth. The d_{33} measured by Berlincourt was 416 pC/N in the random ceramic compared with 409 pC/N for the textured ceramic. This very slight difference in piezoelectric charge

coefficient is because the Berlincourt meter measurement is dominated by intrinsic piezoelectric (lattice) contributions.²² The small differences in the intrinsic piezoelectricity indicates that the high strain of textured 21PYN-41PMN-38PT largely originates from extrinsic non-180° domain wall motion at higher applied fields.²³ This result is further supported by the increased strain hysteresis in textured (15.0%) versus random ceramics (11.1%) which is indicative of increased domain motion.²³ Further enhancements to the strain behavior of textured PYN-PMN-PT can likely be achieved by adjusting the composition to the rhombohedral side of the morphotropic phase boundary to facilitate 4R domain engineering.^{1,8}

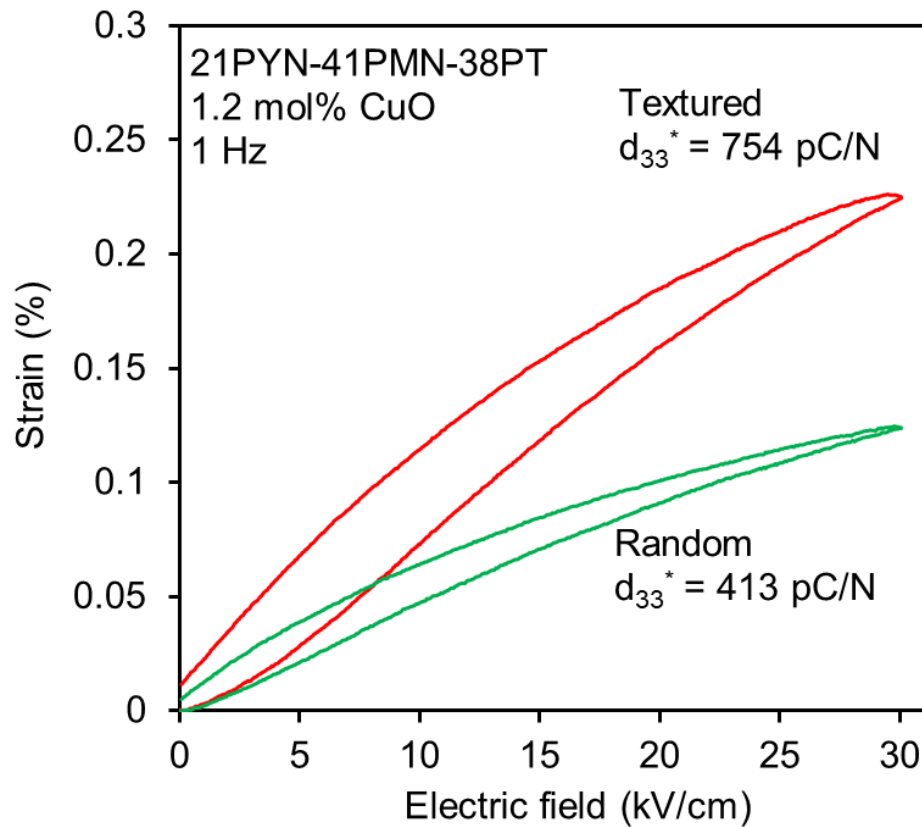


Figure 4.7. Unipolar-strain loops of random and textured 1 mol% PbO and 1.2 mol% CuO-doped 21PYN-41PMN-38PT ceramics sintered at 1050°C for 10 h. The textured ceramic exhibited a peak strain of 0.226% compared to 0.124% of the random ceramic.

Figure 4.8 shows the dielectric constant as a function of temperature for textured and random 1 mol% PbO and 1.2 mol% CuO-doped 21PYN-41PMN-38PT ceramics. Random PYN-PMN-PT ceramics had a T_C of 236°C while textured 21PY-41PMN-38PT had a T_C of 224°C. The slight reduction in T_C may be the result of the composite effect with the residual barium titanate ($T_C \sim 120^\circ\text{C}$) due to the interfacial stress and elastoelectric effect.^{10,22} It is also possible that the reduction in T_C is due to minor diffusion of Ba^{2+} into PYN-PMN-PT. However; template dissolution was not observed even after sintering at 1150°C for 10 h. The lack of dielectric dispersion in both random and textured ceramic indicates that both materials behave as normal ferroelectrics. The room temperature dielectric loss was 2.1% in the random ceramic versus 3.2% in the textured material. The increased dielectric loss in the textured ceramic may be attributed to the increased non-180° domain wall motion associated with the enhanced strain behavior.^{22,23}

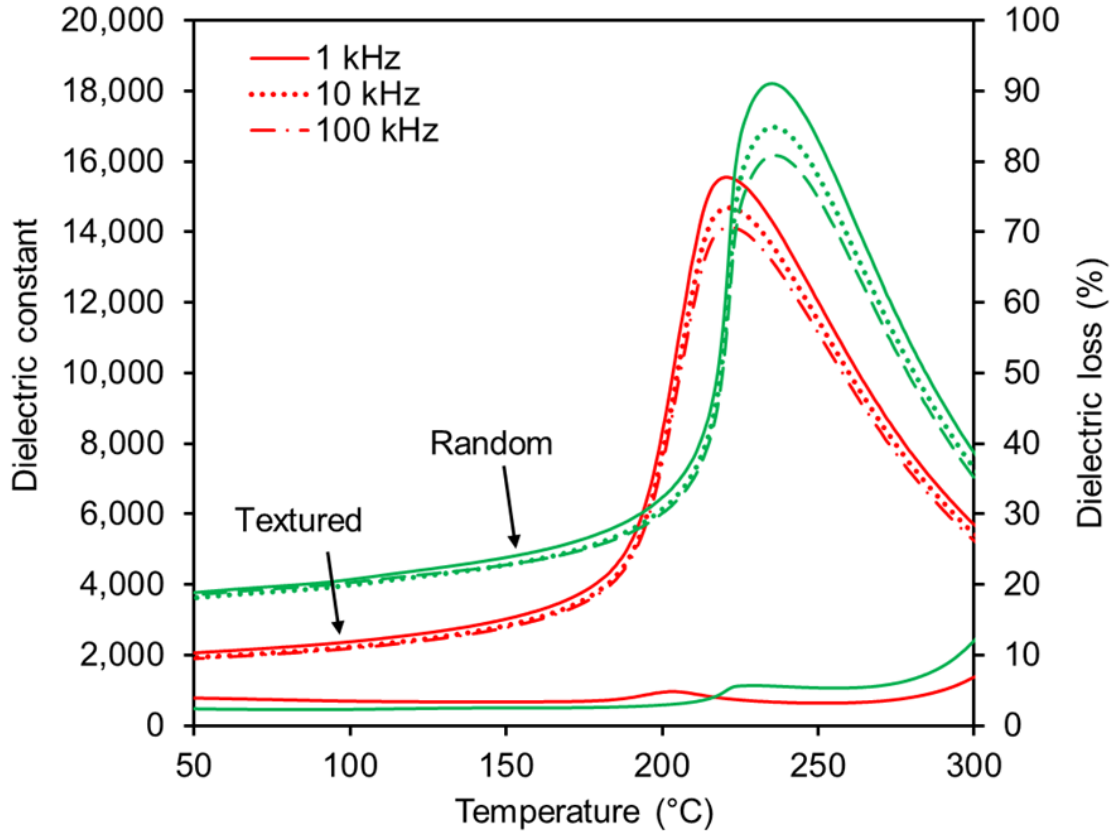


Figure 4.8. Dielectric properties of random and textured 1 mol% PbO and 1.2 mol% CuO-doped 21PYN-41PMN-38PT as a function of temperature. Texturing with 5 vol% BT reduced the Curie temperature from 236°C to 224°C.

Figure 4.9 compares the polarization-electric field (PE) loops of random and textured 1 mol% PbO and 1.2 mol% CuO-doped 21PYN-41PMN-38PT ceramics. Texturing reduced the P_r from 33.7 to 26.7 $\mu\text{C}/\text{cm}^2$ and increased the E_c from 11.5 to 13.9 kV/cm. The decrease in polarization may be due to the composite effect of residual barium titanate ($P_r \sim 12 \mu\text{C}/\text{cm}^2$) in addition to associated residual stresses. The increased coercive field may be due to impeded domain switching as a result of the residual stress associated with barium titanate platelets.¹⁰ Furthermore, the presence of BT increases the tetragonality of

textured piezoelectrics which additionally increases the coercive field.⁸ This composite effect further increases the range of electric fields at which PYN-PMN-PT can be used without depoling because of the increased coercive field.²³

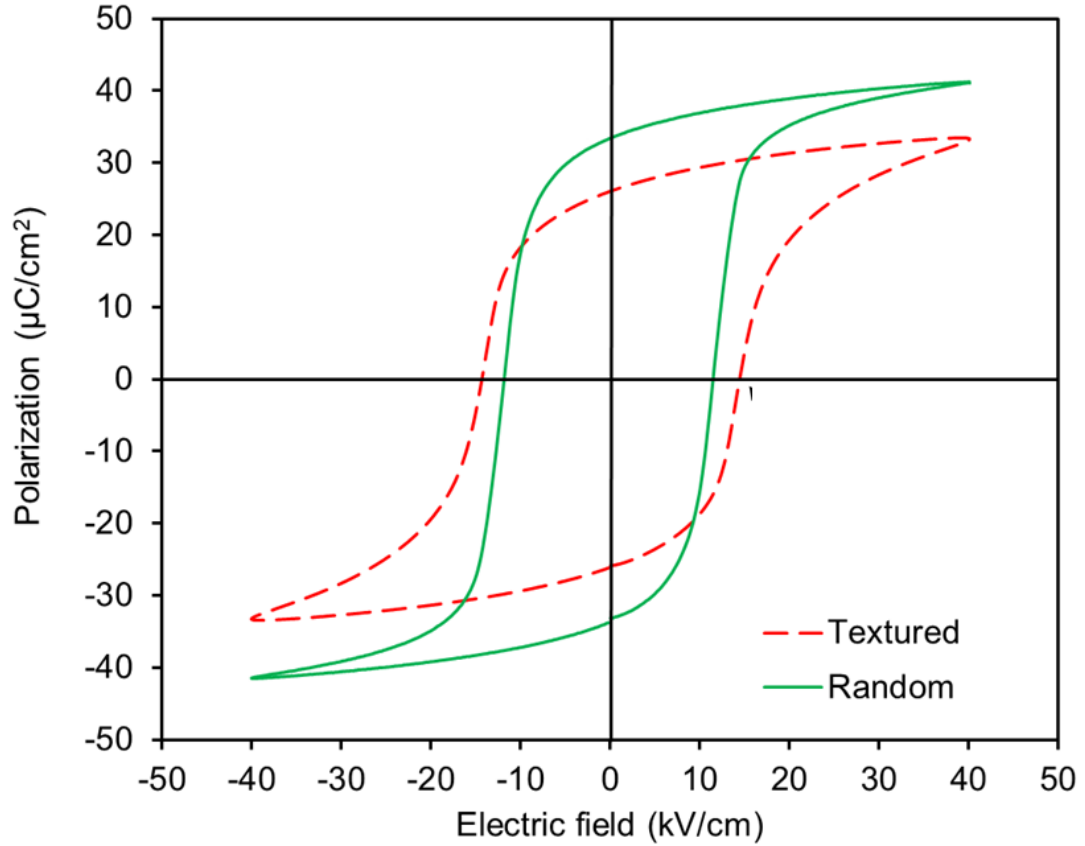


Figure 4.9. Polarization-electric field loops of random and textured 1 mol% PbO and 1.2 mol% CuO-doped 21PYN-41PMN-38PT. Texturing increased the coercive field while decreasing the polarization due to the composite effect with residual BT.

4.4 Conclusions

This study showed the role of composition and PbO-CuO doping in templated grain growth of PYN-PMN-PT on barium titanate platelet particles. Increasing the PYN content of PYN-PMN-PT to 28 mol% PYN prevented PYN-PMN-PT from nucleating and growing on barium titanate. PbO-CuO doping substantially increased the templated growth of 21PYN-41PMN-38PT. Co-doping with PbO and CuO was found to be more effective at promoting template growth than doping with either PbO or CuO. Texturing 21PYN-41PMN-38PT resulted in an 83% improvement in strain behavior compared to the random counterparts. Texturing additionally increased the coercive field (11.5 to 13.9 kV/cm), decreased the polarization (33.7 to 26.2 $\mu\text{C}/\text{cm}^2$), and decreased the Curie temperature (236 to 224°C) due to the composite effect from residual barium titanate templates. The high PYN content of textured PYN-PMN-PT ceramics resulted in a high coercive field of 13.9 kV/cm which is substantially better than textured PIN-PMN-PT and PMN-PZT ceramics.

4.5 References

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Chapter 5

Relationship between Composition and Properties of CuO-doped Textured PYN-PMN-PT Ceramics

5.1 Introduction

Lead-based single crystals and ceramics are the active component in a variety of transducers and actuators because of their excellent piezoelectric properties.^{1,2} Relaxor-based single crystals such as $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbZrO}_3\text{-PbTiO}_3$ (PMN-PZT) are the state of the art lead-based piezoelectric materials due to their exceptional piezoelectric charge coefficients ($d_{33} > 2000$ pC/N) and large electromechanical coupling factors ($k^2 > 90\%$).³⁻⁵ The large electromechanical responses of these materials are due to their the electrostriction in conjunction with 4R domain engineering of $\langle 001 \rangle_c$ poled rhombohedral crystals.³ A 4R domain engineered state allows for large piezoelectric response because the enhanced intrinsic and lattice contribution to piezoelectric contribution.⁶ In single crystal rhombohedral PMN-PT, the intrinsic contribution was is >95% of the total piezoelectric response. A large intrinsic response and small extrinsic allows for reduced electromechanical hysteresis.⁶

Although relaxor-based single crystals have excellent piezoelectric properties relative to polycrystalline ceramics, their use in high-power actuation and transducer applications has been primarily restricted by their limited available shapes, high cost, and low compositional uniformity.^{7,8} The current generation of single crystals also have prohibitively low coercive fields (E_c of 3-7 kV/cm), and low rhombohedral to tetragonal phase transition temperatures ($T_{r-t} < 100^\circ\text{C}$).^{3,5,9} A cost-effective alternative for high-performance piezoelectric applications to single crystals is textured piezoelectric ceramics achieved through templated grain growth (TGG).^{7,10,11} The TGG process allows for substantially improved compositional control relative to single crystal growth because growth maintains the chemical homogeneity of the greenbody.¹⁰ The scalability of tape casting additionally allows for high-volume production of compositionally-uniform parts of various sizes and shapes.⁷

Textured PIN-PMN-PT and PMN-PZT ceramics, templated with barium titanate platelets, show improved piezoelectric properties (600-850 pC/N) compared to their random counterparts (400-550 pC/N).¹²⁻¹⁵ While texturing improves the piezoelectric properties, current generation textured ceramics are limited by the low E_c ($\sim 7-8$ kV/cm), T_{r-t} ($100-120^\circ\text{C}$), and low T_C 's ($150-215^\circ\text{C}$) properties, like single crystal analogs, because these properties are dominated by material composition rather the final microstructure.^{13,15}

Single crystal PYN-PMN-PT have comparable piezoelectric coefficients to PIN-PMN-PT and PMN-PZT crystals but with higher T_{r-t} 's ($\sim 120-130^\circ\text{C}$) and substantially higher coercive fields (5-10 kV/cm).^{16,17} While PYN-PMN-PT crystals shows promise in terms of electromechanical properties, they are commercially challenging to produce in appreciable size due to severe compositional segregation during crystal growth.¹⁷⁻¹⁹ Duran et al

investigated templated grain growth of textured 15.5PYN-46.5PMN-38PT ceramics with barium titanate platelet (BT) particles.¹⁸ They showed that texturing increased the unipolar peak strain to 0.33 % (measured at 50 kV/cm) compared with 0.21 % in random PYN-PMN-PT ceramic.¹⁸ CuO-doped textured 21PYN-41PMN-38PT ceramics were shown to have ~70% higher E_c of 13.9 kV/cm compared to textured PIN-PMN-PT and PMN-PZT ceramics and to be much higher than that of single crystal PYN-PMN-PT.^{17,18}

Textured PYN-PMN-PT ceramics show significantly higher E_c 's and comparable peak strain to other textured lead-based ceramics, but textured PYN-PMN-PT ceramic compositions show comparably low degrees of intrinsic (low hysteresis) piezoelectricity.¹⁸ This is because current textured PYN-PMN-PT ceramic studies investigated tetragonal compositions (15.5PYN-46.5PMN-38PT and 21PYN-41PMN-38PT) which do not lead to a 4R domain engineered state.¹⁸ This is because the rhombohedral side of the morphotropic phase boundary of PYN-PMN-PT heavily deviates from a straight line between PMN-PT and PYN-PT.^{16,18} Additionally, the of residual barium titanate templates shift the resulting structure towards the tetragonal side of the MPB due to residual stresses.⁷

There is currently little understanding about how the properties of textured PYN-PMN-PT ceramics change with composition. In this paper we compare the electromechanical properties CuO-doped random and textured PYN-PMN-PT as a function of composition (20PYN-(1-x)PMN-(x)PT). The composition is additionally related to the change enhancement in intrinsic and extrinsic piezoelectricity. We also show how changing composition (20PYN-(1-x)PMN-(x)PT and (1-x)PYN-41PMN-xPT) affects the TGG of CuO-doped PYN-PMN-PT on barium titanate templates.

5.2 Experimental Procedure

All PYN-PMN-PT perovskite powders were synthesized by a two-stage Columbite precursor method to inhibit pyrochlore formation. MgO was reacted with Nb₂O₅ to form MgNb₂O₆, and Yb₂O₃ was reacted with Nb₂O₅ to form YbNbO₄. These immediate compounds prevent the direct reaction between PbO and Nb₂O₅ which forms pyrochlore.^{19,20} MgNb₂O₆ and YbNbO₄ were fabricated by milling MgO (99.9%, Mallinckrodt, Dublin, Ireland) with Nb₂O₅ (99.9%, H.C. Starck, Munich, Germany), and Yb₂O₃ (99.9%, Alfa Aesar, Massachusetts, USA) with Nb₂O₅ in 190 proof ethanol for 24 h. Zirconia milling media (3 mm diameter) was used in all ball milling processes. The milled powders were heated in air at 1000°C for 6 h and 1100°C for 4 h to form MgNb₂O₆ and YbNbO₄ powders, respectively. Mixtures of MgNb₂O₆, YbNbO₄, PbO (99.9%, Alfa Aesar Haverhill, Massachusetts, USA), and 20 nm TiO₂ (99.9%, Evonik Industries, Essen, Germany) were vibratory milled in ethanol for 24 h, and subsequently dried. All perovskite powders were batched with 1 mol% excess PbO to account for lead loss during texturing and to promote liquid phase transport. The powder mixture was then heated in air at 750°C for 2 h and phase compositions determined by x-ray diffraction (XRD, Xpert Pro MPD diffractometer, PANalytical, Inc., The Netherlands). The reacted perovskite powder was then vibratory milled for 24 h with 1.2 mol% CuO nanopowder (99.99%, Sigma Aldrich, St. Louis, Missouri, USA) and 1 mol% PbO excess.²¹

PYN-PMN-PT matrix powder with 1.2 mol% CuO dopant was ball milled for 24 h in an aqueous acrylic binder system (Polymer Innovations, Inc, California, USA). 5-10 µm barium titanate platelet particles were added to the mill bottle for the final 30 min of milling. The resulting slurry was then tape cast at a doctor blade height of 0.200 mm and a

casting speed of 100 cm/min. The dried tape was cut, stacked, and compacted. The organic binder was removed by heating at 0.1°C/min to 370°C, and the parts were subsequently isostatically pressed at 200 MPa. Random ceramic green bodies were formed through dry pressing. Untemplated and templated PYN-PMN-PT parts were embedded in powder of the same composition and cofired at 1050°C for 10h in flowing oxygen (25 mL/min). The sintered densities were measured by Archimedes' method after a light polishing to remove surface pyrochlore and residual embedding powder. The phase composition and texture degree of the sintered samples was evaluated by XRD. The Lotgering factor (LF) of the <001> fiber texture was calculated from the relative peak heights of diffraction patterns of templated and random PYN-PMN-PT ceramics using the following formula^{13,22}:

$$LF = \frac{P - P_0}{1 - P_0} \times 100\% \quad \text{Eqn. 5.1}$$

$$P_0 = \frac{\sum I_{0\{00l\}}}{\sum I_{0\{hkl\}}} \quad \text{Eqn. 5.2}$$

$$P = \frac{\sum I_{\{00l\}}}{\sum I_{\{hkl\}}} \quad \text{Eqn. 5.3}$$

where I is the XRD peak intensity.

Silver electrodes (DuPont 850, DuPont, Wilmington, DE) were fired on both faces of the samples by heating to 750°C for 30 min. Capacitance (C) and dielectric loss ($\tan \delta$) were measured as a function of temperature (30-300°C) using an LCR meter (Agilent 4284A, Agilent Technologies, CA, USA). Bipolar polarization vs electric field loops were measured at 1 Hz using a custom Sawyer-Tower circuit. Samples were poled in silicone oil at 100°C under 30 kV/cm for 15 min and cooled with the field still applied. Strain-electric field (SE) PiezoMeter System, Piezotest Ltd, Singapore) and Sawyer-Tower circuit

with a lock-in amplifier after aging for 24 h after poling. The strain hysteresis was calculated from difference between the decreasing and increasing strain curves at half the maximum applied field and dividing by the peak strain.

The intrinsic and extrinsic coefficients of the converse piezoelectric effect were determined using Rayleigh analysis by measuring the peak to peak strain of bipolar SE loops from 0.5 to 2.5 kV/cm. The intrinsic response ferroelectrics is piezoelectric is determined by lattice motion while the extrinsic response is determined by domain motion. The Rayleigh equations are:^{6,23}

$$S(E) = (d_{33int} + \alpha E_0)E \pm \alpha (E_0^2 - E^2)/2 \quad \text{Eqn. 5.4}$$

$$S(E_0) = (d_{33int} + \alpha E_0)E_0 \quad \text{Eqn. 5.5}$$

$$d(E_0) = (d_{33int} + \alpha E_0) (pC/N) \quad \text{Eqn. 5.6}$$

where $S(E)$ is the field induced strain, d_{33int} is the intrinsic piezoelectric response, E_0 is the maximum applied field, E is the applied field, α is the extrinsic piezoelectric response.

5.3 Results and Discussion

5.3.1 Effect of Composition on Texturing of PYN-PMN-PT

Figure 5.1(a) shows XRD patterns of textured (1-x)PYN-41PMN-(x)PT with increasing PYN content after heating at 1050°C for 10 h. 21 mol% PYN resulted in a Lotgering factor of 93%. Increasing the PYN content to 22 mol% PYN resulted in a Lotgering factor of 77%, and increasing the PYN content to 23 mol% reduced the

Lotgering factor to 3%. Figure 5.1(b) shows XRD patterns of textured 20PYN-(1-x)PMN-(x)PT with increasing PMN content after heating at 1050°C for 10 h. 20PYN-40PMN-40PT had <001> fiber texture with a Lotgering factor of 93%. Increasing the PMN content to 44 and 46 mol% PMN resulted in similar degrees of texture. These results show that PMN can be continuously added to PYN-PMN-PT without affecting the texturing on barium titanate templates while increasing PYN results in less epitaxial growth. While increasing the PYN content reduced the degree of fiber texture, the small enhancements in <001> intensity suggest that the material still nucleated on barium titanate.

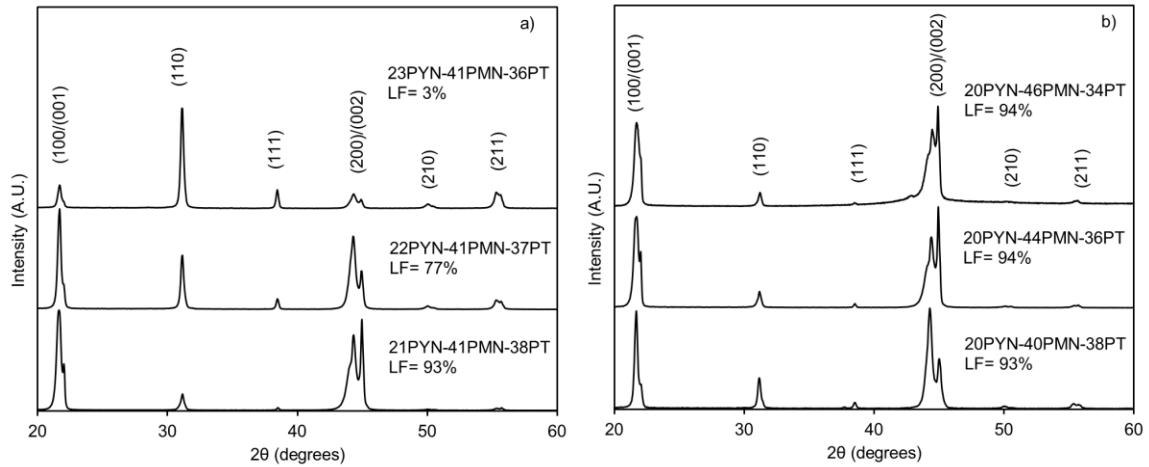


Figure 5.1(a). XRD patterns of textured (1-x)PYN-41PMN-(x)PT as function of PYN content after sintering for 1050°C for 10 h. Increasing PYN content resulted in reduced texture. Fig. 5.1(b). XRD patterns of textured 20PYN-(1-x)PMN-(x)PT as function of PMN content after sintering for 1050°C for 10 h. Texture was insensitive relative to PMN content.

Figure 5.2 shows SEM micrographs of 20PYN-46PMN-34PT and 23PYN-41PMN-36PT with and without 5 vol% barium titanate after heating at 1050°C for 10 h. Heating

untemplated 20PYN-46PMN-34PT resulted in a uniform microstructure of 4-5 μm equiaxed grains. The addition of 5 vol% barium titanate changed the mode of fracture from intergranular to intragranular, however, matrix grains can be seen in between templated grains. Heating 23PYN-41PMN-36PT without barium titanate resulted in a uniform equiaxed microstructure of 5 μm grains. The addition of 5 vol% barium titanate resulted in the formation of 1 μm epitaxial layers of 23PYN-41PMN-36PT on the barium titanate templates. Template growth was inhibited by matrix coarsening as the matrix grain size was comparable to the template size, reducing the thermodynamic driving force for TGG. Barium titanate was found to be chemically stable in PYN-PMN-PT at all investigated compositions.

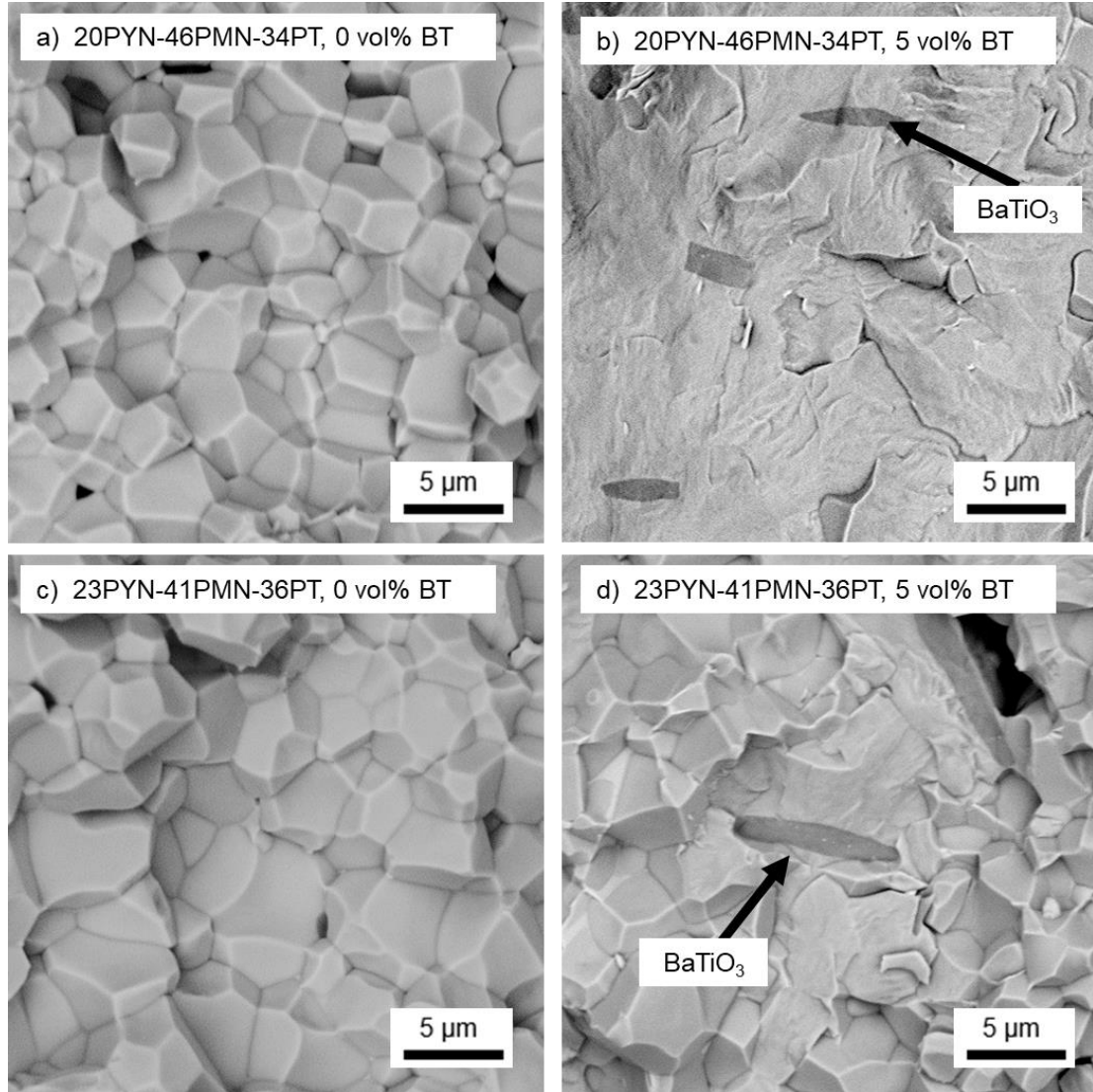


Figure 5.2. SEM micrograph of random and textured 20PYN-46PMN-34PT and 23PYN-41PMN-36PT after heating at 1050°C for 10 h. Matrix grains coarsened to the size of the barium titanate templates inhibiting TGG.

To compare the TGG of 20PYN-46PMN-34PT with 23PYN-41PMN-36PT, templated samples were heated to 1050°C for 0 min. Figure 5.3 shows SEM micrographs of the resulting microstructures. Heating templated 23PYN-41PMN-36PT at 1050°C for 0 min resulted in a $\sim 1 \mu\text{m}$ epitaxial layer of 23PYN-41PMN-36PT, and the matrix grains

coarsened to $\sim 3 \mu\text{m}$. Conversely, heating 20PYN-46PMN-34PT at the same conditions resulted in a 5-10 μm growth layer of 20PYN-46PMN-34PT and coarsening of the matrix grain size to 2-3 μm . Interestingly, this result shows that PMN can be continuously increased in PYN-PMN-PT without substantially altering the TGG behavior while increasing PYN content greatly reduces the achievable texture fraction.

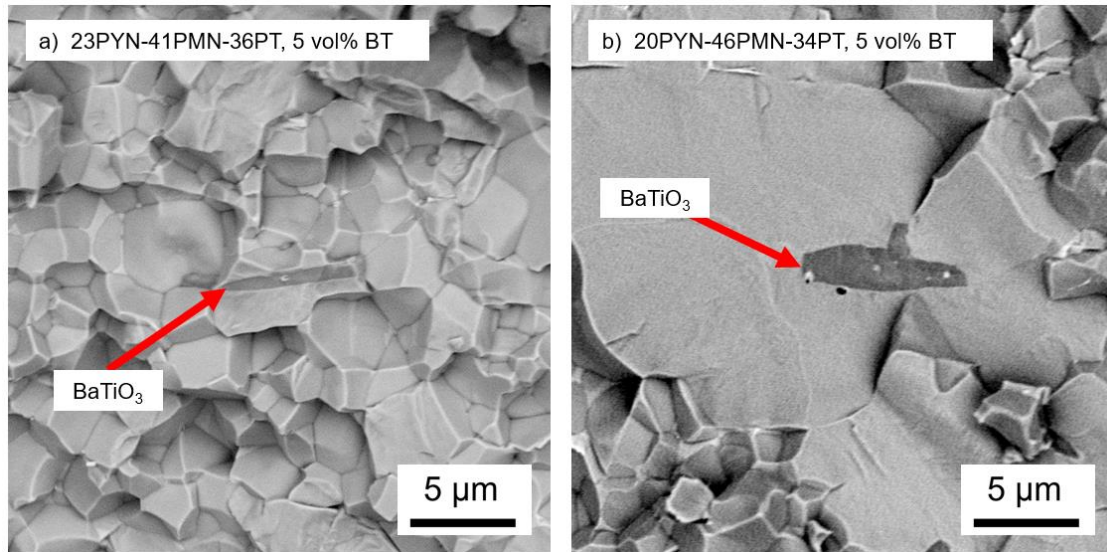


Figure 5.3. SEM micrograph of templated 23PYN-41PMN-36PT and 20PYN-46PMN-34PT after heating at 1050°C for 0 h. Heating 23PYN-41PMN-36PT resulted in little template growth while heating 20PYN-46PMN-34PT resulted in a large 6-10 μm epitaxial layer.

Figure 5.4 shows XRD patterns highlighting the (002)/(200) peaks of PYN-PMN-PT ceramics with and without barium titanate templates as a function of PMN content after heating at 1050°C for 10 h. Untemplated 20PYN-40PMN-40PT ceramics show clear tetragonal splitting of the 45° peak due to its elevated PT content. Textured 20PYN-

40PMN-40PT ceramics show similar tetragonal splitting. Increasing the PMN content to 44 mol% PMN results in a singlet peak with substantial broadening due to this composition's close proximity to the morphotropic phase boundary (MPB). The presence of templates in textured 20PYN-44PMN-36PT resulted in enhanced tetragonal splitting due to the lattice mismatch between 20PYN-44PMN-36PT and barium titanate. Untemplated 20PYN-46PMN-34PT shows a rhombohedral peak with a broad shoulder due to its proximity to the MPB. The addition of 5 vol% barium titanate in the textured 20PYN-46PMN-34PT similarly resulted in enhanced tetragonal splitting of the (002)/(200) peaks. This result shows that PYN-PMN-PT must be sufficiently rhombohedral relative to the MPB before the addition of barium titanate templates in order to maintain a rhombohedral or MPB composition after texturing. This effect is likely enhanced with increasing volume fraction of barium titanate templates. Based on the peak splitting of the (200/002) peak, 20PYN-44PMN-36PT and 20PYN-46PMN-34PT were found to exist on the morphotropic phase boundary while 20PYN-42PMN-36PT, and 20PYN-40PMN-40PT were conclusively tetragonal.

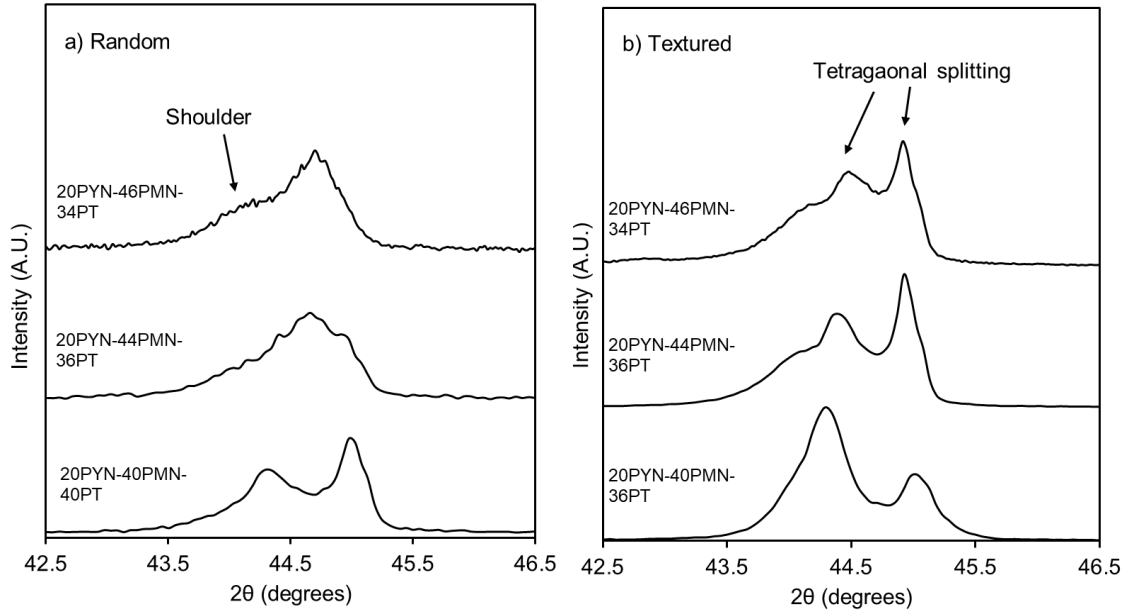


Figure 5.4. XRD of the (200)/(002) peak of random (a) and textured (b) 20PYN-(1-x)PMN-(x)PT as function of PMN content after heating at 1050°C for 10 h. The addition of 5 vol% BT resulted in increased tetragonal splitting in 20PYN-46PMN-34PT and 20PYN-44PMN-36PT.

5.3.2 Electromechanical properties of random and textured PYN-PMN-PT ceramics

Figure 5.5(a) shows the PE loop of random and textured 20PYN-40PMN-40PT ceramics measured at 30 kV/cm. Figure 5.5(b) shows the effect of PT concentration on the coercive field and remnant polarization of random and textured PYN-PMN-PT. Increasing the PT content of random and textured PYN-PMN-PT linearly increased the coercive field while textured PYN-PMN-PT coercive fields were always ~ 1 kV/cm higher than their random counterparts. Figure 5.5(c) shows the effect of PT content on the remnant polarization of random and textured PYN-PMN-PT ceramics. Texturing resulted in a decreased remnant polarization in all explored compositions compared to the random counterparts. Increasing the PT content from 34 mol% to 40 mol% of random PYN-PMN-

PT reduced the remnant polarization from $\sim 37 \mu\text{C}/\text{cm}^2$ to $\sim 30 \mu\text{C}/\text{cm}^2$. Increasing the PT content from 34 mol% to 40 mol% of textured PYN-PMN-PT reduced the remnant polarization from $\sim 30 \mu\text{C}/\text{cm}^2$ to $\sim 24 \mu\text{C}/\text{cm}^2$. The change in coercive field and polarization maybe due to a composite effect resulting from residual barium titanate templates.⁷

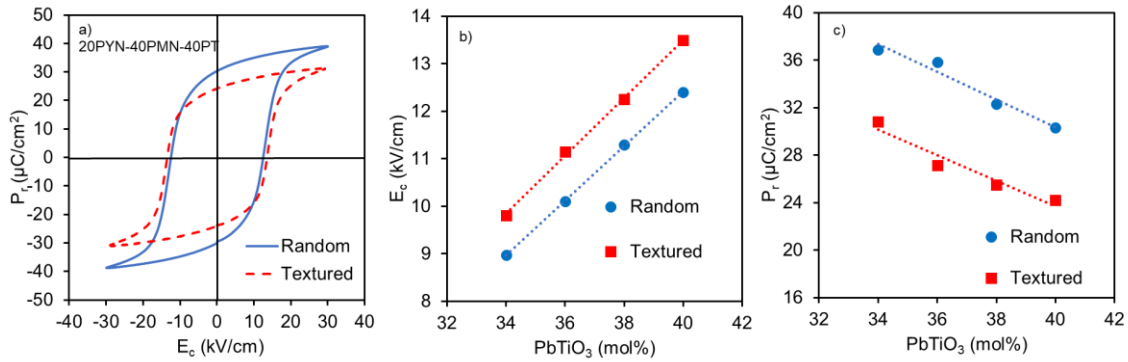


Figure 5.5(a). PE loops of random and textured 20PYN-46PMN-34PT ceramics. Effect of composition on the (b) coercive field and (c) remnant polarization of 20PYN-(1-x)PMN-(x)PT. Increasing PT content increased the coercive field and decreased the polarization.

Figure 5.6(a) shows the unipolar SE loop of 20PYN-46PMN-34PT measured at 30 kV/cm. The peak strain of random 20PYN-46PMN-34PT was $\sim 0.10\%$ while texturing resulted in a peak strain of $\sim 0.18\%$. Figure 5.6(b) shows the peak strain of random and textured PYN-PMN-PT as a function of PT content measured at 30 kV/cm. All explored random ceramic compositions showed comparable peak strain of $\sim 0.10\%$. Texturing was found to enhance the peak strain of all explored compositions. Decreasing PT content correlates with an increase in enhancement as texturing 20PYN-40PMN-40PT resulted in a 45% enhancement of peak strain while textured 20PYN-46PMN-34PT had an 81% increase in peak strain compared to its random counterpart. This enhancement may be

attributed to the increased rhombohedral character of this composition which may promote a 4R domain-engineered state.²⁴ This result suggests that PYN-PMN-PT composition determines is related to what piezoelectric contribution are enhanced by texturing. Further increases in strain values can be by increasing the texture fraction and quality through improved tape casting and firing processes. Figure 5.6(c) shows the unipolar strain hysteresis of random and textured 20PYN-(1-x)PMN-xPT as a function of PT content. While random compositions show no clear trend, increasing PT increased the strain hysteresis from ~ 8% in 20PYN-46PMN-34PT to ~ 16% in 20PYN-40PMN-40PT. This result also suppose that the increased piezoelectricity found in compositions with greater PT content may be due to an increase in extrinsic piezoelectricity contributions.²

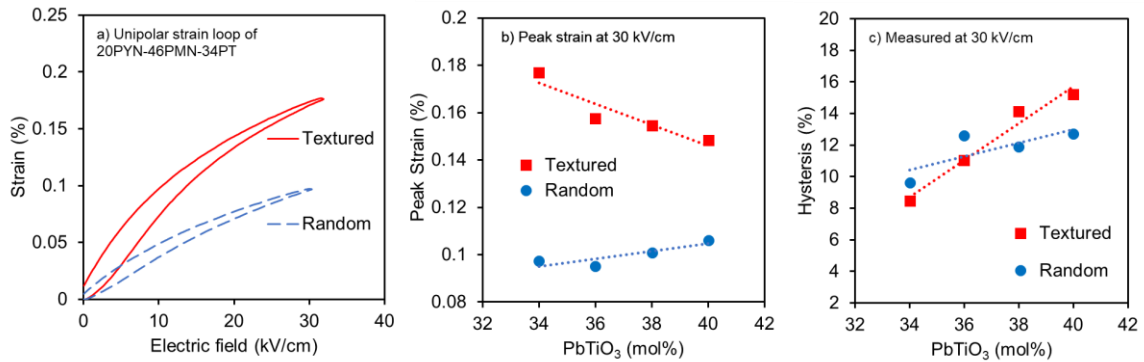


Figure 5.6(a). SE loops of random and textured 20PYN-46PMN-34PT ceramics. Effect of composition on the (b) unipolar polar peak strain of 20PYN-(1-x)PMN-(x)PT. The peak strain of random ceramics was relatively insensitive to PT content while textured PYN-PMN-PT strain increased with decreasing PT.

In order to elucidate the effect of texturing and composition in enhancing the intrinsic and extrinsic piezoelectric response of PYN-PMN-PT, Rayleigh analysis was performed

on random and textured 20PYN-40PMN-40PT and 20PYN-46PMN-34PT ceramics. Figure 5.7(a) shows d_{33}^* of random and textured PYN-PMN-PT as determined from bipolar SE loops. Random 20PYN-40PMN-40PT ceramics show an intrinsic d_{33}^* of 340 pm/V and $\alpha \times 10^{-15}$ of 43 m²/V². Texturing 20PYN-40PMN-40PT resulted in a reduced intrinsic d_{33}^* of 326 pm/V and an increased $\alpha \times 10^{-15}$ of 124 m²/V². This result shows that texturing predominantly tetragonal PYN-PMN-PT reduces the intrinsic piezoelectricity contributions while increasing the extrinsic piezoelectric contributions, which may be due to the formation of a 1T domain-engineered state. Random 20PYN-46PMN-34PT ceramics show an intrinsic d_{33}^* of 291 pm/V and $\alpha \times 10^{-15}$ of 52 m²/V². The increased extrinsic piezoelectricity of 20PYN-46PMN-34PT compared with 20PYN-40PMN-40PT may be due to the reduced coercive field of 20PYN-46PMN-34PT which allows for increased domain mobility. Texturing 20PYN-40PMN-40PT resulted in an increased intrinsic d_{33}^* of 426 pm/V and an increased $\alpha \times 10^{-15}$ of 168 m²/V². This result shows that texturing predominantly rhombohedral PYN-PMN-PT results in increased intrinsic piezoelectricity which may be attributed to mix of 4R and 1T domain-engineered state.^{6,24} Figure 5.7(b) shows an SE loop for 20PYN-40PMN-40PT calculated using data from Figure 5.7(a) compared with the measured data collected at 2.5 kV/cm. The measured and calculated bipolar SE loops show good agreement with only minor discrepancies in strain behavior likely due to hysteresis.

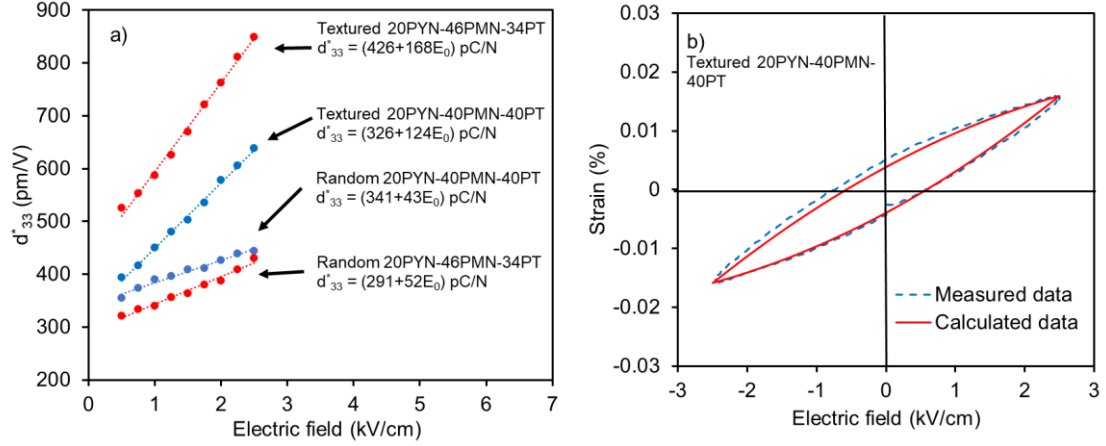


Figure 5.7(a). Electric field dependent d_{33} of random and textured 20PYN-40PMN-40PT and 20PYN-46PMN-34PT. Texturing 20PYN-46PMN-34PT resulted in increased intrinsic and extrinsic piezoelectric contributions. (b) Measured bipolar SE loop compared to calculated SE loop of 20PYN-40PMN-40PT based on data from Rayleigh analysis.

Table 5.1 shows the electromechanical properties of random and textured PYN-PMN-PT as a function of composition. There is no clear trend in regards to dielectric loss in both the textured and the random samples. This may be because the loss is dominated by vacancies produced by the incorporation of Cu^{2+} into the perovskite B-site which results in oxygen vacancies. There is significant deviation between the d_{33} as measured by Berlincourt versus unipolar strain loops. This is because Berlincourt is dominated by intrinsic piezoelectric motion. In the Rayleigh analysis it was found that texturing tetragonal 20PYN-40PMN-40PT resulted in a decrease in $d_{33\text{int}}^*$ and a similar decrease in piezoelectricity is seen using the Berlincourt measurement. Texturing resulted in small decreases in the Curie temperature, however, transition temperatures were still above 200°C exceeds that of textured PIN-PMN-PT and PMN-PZT. Texturing PYN-PMN-PT additionally reduced the dielectric constant of all explored compositions.

Table 5.1. Electromechanical properties of random and textured 20PYN-(1-x)PMN-(x)PT sintered at 1050°C for 10 h.

	Composition	d_{33} (pC/N)	d_{33}^* (pC/N)	T_c (°C)	E_c (kV/cm)	Pr ($\mu\text{C}/\text{cm}^2$)	$\tan \delta$ (%)	ϵ_r
Random	20PYN-40PMN-40PT	412	353	-	12.4	30.3	2.1	3805
	20PYN-42PMN-38PT	406	337	228	11.3	32.2	2.2	3765
	20PYN-44PMN-36PT	387	317	221	10.1	35.9	2.2	3782
	20PYN-46PMN-34PT	380	324		9.0	37.0	2.0	3802
Textured	20PYN-40PMN-40PT	406	511	-	13.5	24.2	1.8	1945
	20PYN-42PMN-38PT	403	512	214	12.3	25.5	2.3	1912
	20PYN-44PMN-36PT	410	525	209	11.2	27.2	2.3	1932
	20PYN-46PMN-34PT	460	589	-	9.8	30.8	1.9	1960

5.4 Conclusions

This study explored relationship between composition and the electromechanical properties of random and textured CuO-doped PYN-PMN-PT. Texturing improved the unipolar strain of all explored compositions. The residual barium titanate templates resulted in an increase in tetragonality of the perovskite structure which increased the coercive field. Rayleigh analysis showed that more rhombohedral compositions benefit from an increase in both extrinsic and intrinsic piezoelectric mechanisms, while more tetragonal compositions only show enhanced extrinsic piezoelectricity. These results show

that reducing strain hysteresis in textured PYN-PMN-PT requires compositional selection that is sufficiently rhombohedral to accommodate the presence of residual templates to obtain a 4R domain-engineered state.

5.5 References

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Chapter 6

Summary and Future Work

6.1 Summary

6.1.1 Phase formation of ZnO-doped PIN-PZN-PT powder

To investigate the role of ZnO doping in the phase formation of PIN-PZN-PT perovskite, powders were heated with 0.04 – 0.083 mol% ZnO dopants. At all concentrations, times, and temperatures, ZnO doping increased the rate of phase formation and improved the resulting phase fraction of perovskite. Perovskite phase fraction could not be increased by heating above 800°C. PbTiO_3 formed by a reaction between PbO and TiO_2 , and $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ formed by a reaction between PbO and InNbO_4 . PbO and ZnNb_2O_6 reacted to form cubic $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore instead of $\text{Pb}(\text{Zn}_{1/2}\text{Nb}_{1/2})\text{O}_3$ perovskite. In the case of both undoped and ZnO-doped PIN-PZN-PT, perovskite formation followed the preliminary formation of PbTiO_3 , $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$, and $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore. In undoped powder, $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore was insufficiently reactive to produce 100% perovskite powder, and in ZnO-doped powder, $\text{Pb}_2\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.565}$ pyrochlore was more reactive due to the substitution of Zn^{2+} on the pyrochlore Nb^{5+} sites. The incorporation of Zn^{2+} in the pyrochlore lattice was charge balanced by the formation of oxygen vacancies. Oxygen vacancies increased the processing sensitivity in terms of P_{O_2} , as the amount of powder in the crucible effected the

resulting phases after heating. Heating ZnO-doped PIN-PZN-PT powder at 800°C for 4 h at an intermediate P_{O_2} resulted in 100% perovskite. Increased P_{O_2} inhibited the formation of oxygen vacancies which reduced the solubility of Zn^{2+} in $Pb_2Zn_{0.29}Nb_{1.71}O_{6.565}$ pyrochlore, resulting in PIN-PZN-PT perovskite and large phase fractions of $Pb_2Zn_{0.29}Nb_{1.71}O_{6.565}$ pyrochlore. Heating in a reduced P_{O_2} was found to destabilize 50.5PIN-21PZN-28.5PT perovskite and result in the formation in a mixture of tetragonal and rhombohedral PIN-PZN-PT and pyrochlore. This study shows for the first time how to fabricate phase pure equiaxed PIN-PZN-PT perovskite powder.

6.1.2 Processing and electromechanical properties of high coercive field ZnO-doped PIN-PZN-PT

In this study, the effect of ZnO doping was related to the densification, perovskite symmetry and electromechanical properties of PIN-PZN-PT ceramics. Heating undoped PIN-PZN-PT at a variety of times and temperatures resulted in a maximum density of ~83% and the formation of zinc-based pyrochlore. ZnO doping substantially increased the rate of densification of PIN-PZN-PT at all investigated times and temperatures while also stabilizing the perovskite phase. Heating ZnO-doped PIN-PZN-PT at temperatures $\geq 1100^\circ\text{C}$ resulted in 100% perovskite phase. This was attributed to the formation of oxygen vacancies due to the substitution of Zn^{2+} on the perovskite B site. Heating 0.35 mol% ZnO doped PIN-PZN-PT at 1150°C for 0 min in either static air or flowing oxygen resulted in > 95% relative densities. Sintering ZnO-doped PIN-PZN-PT in flowing oxygen limited the solubility of Zn^{2+} into the perovskite lattice which resulted in the formation of

rhombohedral PIN-PZN-PT perovskite. Sintering ZnO-doped samples in flowing oxygen also reduced the rate of densification compared to doped samples sintered in static air.

Heating ZnO-doped PIN-PZN-PT powder in static air results in tetragonal splitting of the (200)/(002) due to the formation of oxygen vacancies. Increasing ZnO dopant in air-fired samples increases the degree of tetragonal splitting and Curie temperature but decreases T_{rt} . Samples with different ZnO-dopant concentrations sintered in flowing oxygen had similar T_{rt} 's and T_C 's. ZnO-doped PIN-PZN-PT ceramics sintered in flowing oxygen have greater electromechanical properties than those of PIN-PZN-PT ceramics sintered in static air due to the formation of a secondary phase of unknown structure. The electromechanical properties of samples with 0.35 mol% ZnO were much more sensitive to the oxygen partial pressure than samples doped with 0.1 mol% ZnO. Sintering 0.1 mol% ZnO-doped 48PIN-21PZN-31PT in oxygen resulted in a high d_{33} of 550 pC/N, high coercive field of 13 kV/cm, and high T_{rt} of 165°C. The d_{33} and E_c were reduced at ZnO concentrations > 0.1 mol% due to the presence of ZnO inclusions.

6.1.2 Templated grain growth of high coercive field CuO-doped, textured PYN-PMN-PT

The templated grain growth of high coercive field PYN-PMN-PT compositions was related to PYN-PMN-PT composition and a PbO-CuO liquid phase. Compositions with 0 – 21.5 mol% PYN were shown to form complete epitaxial layers around barium titanate templates. Increasing the PYN content to 25 mol% resulted in incomplete layers of PYN-PMN-PT around template particles. Additionally, non-wetting matrix grains were found to be in contact with the barium titanate templates, indicating local chemical heterogeneity.

28PYN-29.5PMN-42.5PT and 50PYN-50PT did not grow on barium titanate. The resulting microstructures only showed non-wetting matrix grains in contact with the template particles. 21PYN-41PMN-38PT was doped with PbO and CuO to investigate the role of the PbO-CuO liquid on templated grain growth. Heating PYN-PMN-PT doped with only 1 mol% PbO resulted in $\sim 1 \mu\text{m}$ of epitaxial growth and a Lotgering factor of 11%. Doping with only PbO did not enhance TGG, while co-doping increased the degree of epitaxial growth. Increasing the CuO doping level increased degree of templated grain growth. Heating 1.2 mol% CuO-doped and 1 mol% PbO-doped PYN-PMN-PT at 1050°C for 0 h resulted in a PbO-CuO grain boundary phase. Doping with either 1.2 mol% CuO or 3 mol% PbO only minimally increased epitaxial growth. Doping with only 3 mol% PbO substantially increased the matrix grain growth and resulted in cuboidal matrix grains which reduced the driving force for TGG. Furthermore, CuO and PbO must be localized at the grain boundary to improve TGG.

Heating 1.2 mol% CuO-doped and 1 mol% PbO codoped PYN-PMN-PT at 1050°C for 10 h resulted in a Lotgering factor of 93%. Textured 1.2 mol% CuO-doped and 1 mol% PbO-doped PYN-PMN-PT exhibited a peak strain of 0.23% compared to 0.12% for the random ceramic. The increased strain hysteresis suggested that increased piezoelectricity is due to an increase domain motion indicating texturing increased the extrinsic piezoelectric contribution. The presence of residual barium titanate templates reduced the Curie temperature slightly, to 224°C from 236°C, but improved E_c from 11.5 to 13.9 kV/cm. Texturing also reduced the dielectric constant of PYN-PMN-PT from ~ 3900 to ~ 2000 . These results show that CuO and PbO codoping can be used to facilitate templated

grain growth and thus property enhancements in PYN-PMN-PT compositions with higher coercive fields.

6.1.3 Composition and property relationships of CuO-doped, textured PYN-PMN-PT ceramics

The objective of this work was to relate PYN-PMN-PT composition and therefore structure of 20PYN-(1-x)PMN-(x)PT and (1-x)PYN-41PMN-(x)PT, to the electromechanical property enhancements achieved by templated grain growth. Increasing PYN content decreased the texture fraction due to an increase in matrix grain growth, which reduced the driving force for templated grain growth. Increasing PMN content had no affect on the texture fraction, and was evaluated for electromechanical behavior. In random PYN-PMN-PT ceramics, increasing PMN content reduced the tetragonal splitting observed in the (002)/(200) peaks. The presence of residual barium titanate templates in textured PYN-PMN-PT increased the (002)/(200) peak splitting, due to mismatched thermal expansion coefficients. Random 20PYN-46PMN-34PT ceramics had XRD patterns consistent with MPB compositions, while 20PYN-40PMN-40PT were clearly tetragonal. In both random and textured PYN-PMN-PT, increasing PbTiO_3 content linearly increased the coercive field and linearly decreased the remnant polarization. Textured PYN-PMN-PT ceramics had a 1 kV/cm higher coercive field than that of the random counterpart of the same composition for all explored compositions. Texturing increased the strain behavior of all compositions, but the magnitude of enhancement increased with increasing PMN content. Textured 20PYN-40PMN-40PT exhibited a 45% increase in peak strain to 0.155% compared to random 20PYN-40PMN-40PT, while textured 20PYN-46PMN-34PT exhibited an 81% increase in peak strain to 0.177% compared to its random

counterpart. Increasing PMN content reduced the strain hysteresis in both random and textured PYN-PMN-PT.

Rayleigh analysis was performed on both random and textured PYN-PMN-PT ceramics to further analyze the role of texturing in enhancing the extrinsic and intrinsic piezoelectric mechanisms. Texturing 20PYN-40PMN-40PT reduced the intrinsic piezoelectric coefficient from 341 to 326 pC/N, while increasing the extrinsic piezoelectric from 43 to 124 pC/N. This is likely due to the formation of a 1T domain-engineered state. Texturing the MPB composition 20PYN-46PMN-34PT increased the intrinsic piezoelectric coefficient from 291 to 426 pC/N, and increased the extrinsic contribution from 52 to 168 pC/N. The enhancements to both intrinsic and extrinsic piezoelectric contributions may be attributed to a mix of 4R and 1T domain-engineered states. These results reveal the critical relationship between PYN-PMN-PT composition, structure, texturing, and strain behavior.

6.2 Future Work

6.2.1 Pb-based platelets as a replacement for barium titanate

While this thesis presents many advances in the synthesis of high coercive field Pb-based ceramics, several challenges remain, which must be addressed to fully realize such materials for high power transduction applications. A primary limitation in templated grain growth of both PIN-PZN-PT and PYN-PMN-PT is the use of barium titanate templates. Although barium titanate is chemically stable in PIN-PZN-PT, PIN-PZN-PT fails to

nucleate on barium titanate, which disallows templated grain growth and thus, textured PIN-PZN-PT ceramics. Figure 6.1 shows the resulting microstructure after heating 0.35 mol% ZnO-doped PIN-PZN-PT with barium titanate templates at 1150°C for 1h. The result of heating is a composite microstructure where PIN-PZN-PT would densify around the template particle. PIN-PZN-PT failed to grow on barium titanate templates at all times and temperatures. This including changing the dopant concentration and the changing the dopant species from ZnO to CuO. Barium titanate appeared to be chemically stable in PIN-PZN-PT.

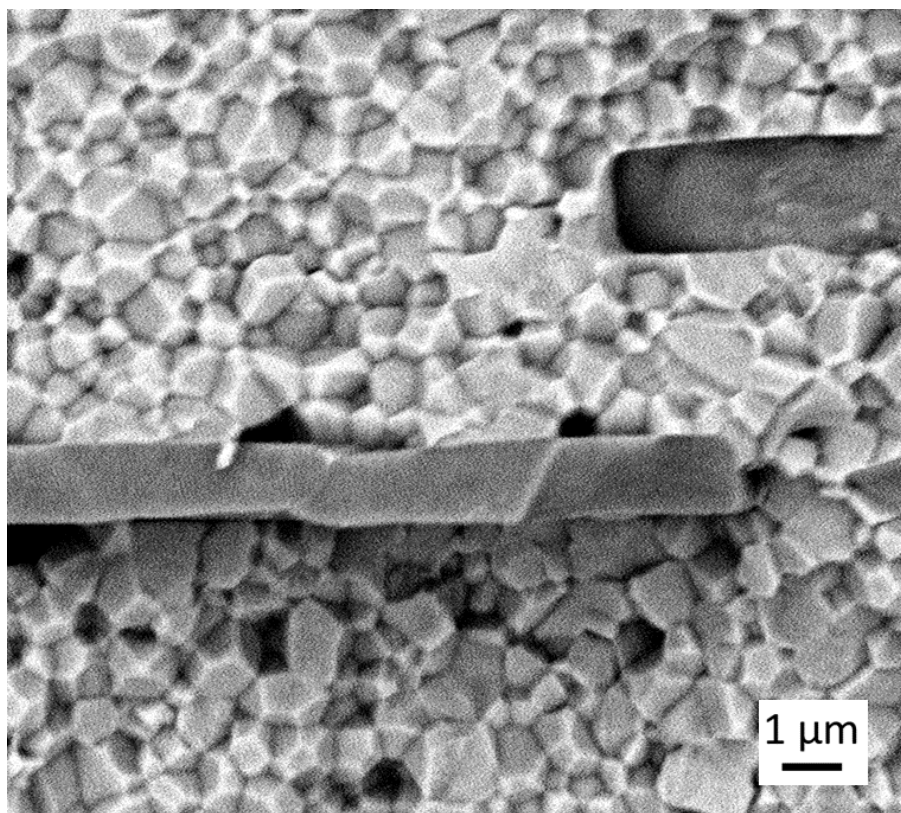


Figure 6.1. Microstructure after heating 0.35 mol% ZnO-doped PIN-PZN-PT with barium titanate templates at 1150°C for 1h.

Similarly, barium titanate is chemically stable in PYN-PMN-PT, but only compositions with < 25 mol% PYN were observed to nucleate on the template particles. Although it is unclear exactly why these materials fail to nucleate on barium titanate, replacing barium titanate with a chemically stable Pb-based template material would likely increase the range and number of compositions viable for texturing. Current Pb-based templates show insufficient chemical stability, which greatly limits the achievable texture fraction.¹ One potential candidate for a chemically stable Pb-based platelet is PZT.² It has been shown that PZT platelets can be fabricated through hydrothermal processing, however, current aspect ratios achieved in the literature are inadequate for high degrees of alignment via tape casting.^{2,3}

6.2.2 Low loss PYN-PMN-PT through MnO-doping

MnO has been used in a large number of Pb-based piezoelectrics to reduce the dielectric and mechanical loss through domain pinning.^{4,5} The use of MnO as a dopant would improve the performance of textured PYN-PMN-PT in high-power applications by substantially reducing dielectric and mechanical loss. MnO doping may be challenging to achieve in CuO-doped PYN-PMN-PT, due to reductions in templated grain growth. Preliminary data shows that the direct substitution of PYN for $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ prior to powder sintering results in substantially limited template growth. This is shown in Fig 6.2 which presents an SEM micrograph of $20\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $43\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 34PbTiO_3 - $3\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ doped with 1.2 mol% CuO and 1 mol% PbO after heating at 1050°C for 10 h. Another method of manganese doping may involve the direct addition of MnO particles to PbO and CuO doped perovskite PYN-PMN-PT powder. This may allow

for TGG of PYN-PMN-PT prior to the incorporation of manganese into the perovskite lattice.

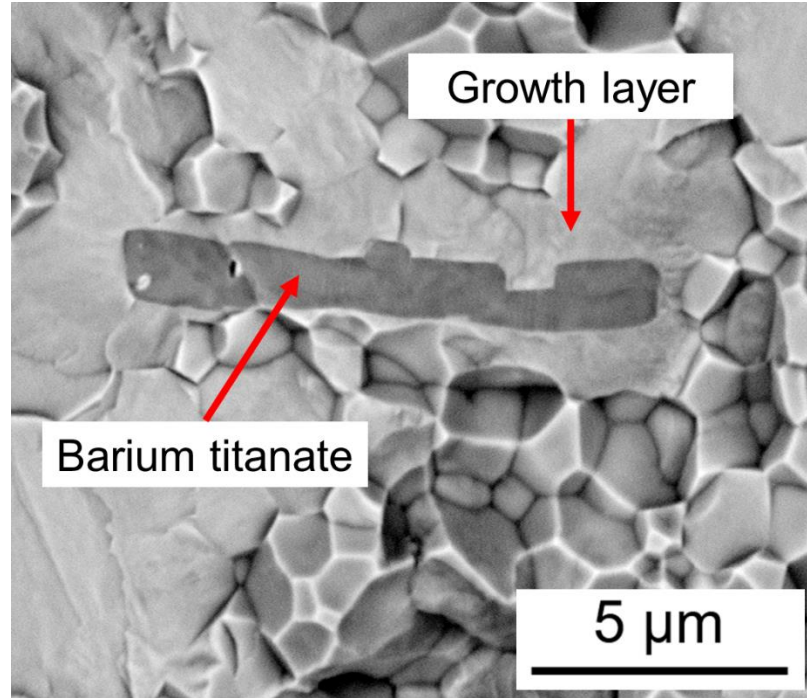


Figure 6.2. SEM micrograph of $20\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $43\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 34PbTiO_3 - $3\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ doped with 1.2 mol% CuO and 1 mol% PbO after heating at 1050°C for 10 h.

6.2.3 Low temperature texturing of PYN-PMN-PT by PbO-B₂O₃ doping

In this work, CuO was used in combination with PbO to increase the achievable texture fraction of high PYN content of PYN-PMN-PT ceramics. PbO forms a liquid phase with a large multitude of elements. Therefore, other dopant candidates, in combination with PbO, may be used to increase templated grain growth with a reduced impact on the electromechanical properties compared to CuO. One potential candidate is B₂O₃. B₂O₃ forms a eutectic with PbO at 480°C , allowing for ultra-low temperature texturing. PbO-

B₂O₃ liquid is routinely used in the growth of single crystal, Pb-based materials due to its propensity to dissolve Pb-based and negligible impact on final crystal properties.⁶⁻⁸ This may be due to the small size of boron which inhibits its incorporation into the perovskite lattice.⁹ Small concentrations of boron oxide on the grain boundary of textured PYN-PMN-PT are unlikely to effect the electromechanical properties.

6.2.4 Improve texture fraction and quality of PYN-PMN-PT

The strain behavior of textured PYN-PMN-PT would be further enhanced by increasing the texture fraction. In this work, the maximum Lotgering factor was approximately 93%. Further characterization of the texture through alternative diffraction methods such as rocking curves could reveal additional characteristics of the textured material, such platelet misorientation angle.¹ Regions of untemplated matrix grains were also observed in all textured samples. Increasing the barium titanate platelet loading would likely eliminate these untextured regions and improve the Lotgering factor and thus, piezoelectric strain. An alternative method may be increasing the PbO-CuO liquid content which may increase the template growth; however, excessive liquid phase may result in enhanced loss due to a residual grain boundary film.

6.2.5 Characterize resonance behavior of textured PYN-PMN-PT ceramics

The impact of residual barium titanate templates and large grain size of textured piezoelectrics on resonance behavior is not fully known. Most high-power transduction applications are designed to accommodate the resonance behavior of various types of PZT ceramics.¹⁰ It is likely that the stresses associated with residual templates cause additional

resonance modes which would require adaptations of current electromechanical device design. Unlike conventional PZT ceramics, where grains are 3 – 10 μm and equiaxed, textured ceramics contain 30 – 50 μm cuboidal grains.³ This difference in grain size and morphology may require adaptation of device designs, to accommodate for deviations in acoustic behavior. Analyzing the impact of texturing on the resonance behavior and mechanical quality factor would provide further insight to electromechanical behavior.

6.3 References

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