

AN ABSTRACT OF THE THESIS OF

Kyle M. Grove for the degree of Master of Science in Materials Science presented on July 1, 2019.

Title: Impact of Process Optimization and Composition on Thin Film BNKT Microstructure, Ferroelectric and Piezoelectric Response

Abstract approved: _____

Brady J. Gibbons

Recent changes in legislation restricting lead content in waste streams produced during electronics manufacturing have inspired a strong push to develop alternative lead-free materials systems for piezoelectric applications. One lead-free piezoelectric material system, $(100-X)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-XBi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BNKT), has shown promising properties in bulk research, however, difficulties have arisen in the development of marketable thin film BNKT. The first part of this study focuses on process optimization for a thin film BNKT chemical solution deposition process using a rapid thermal annealer (RTA). Various process conditions were evaluated based on their impact on key film properties including crystallinity, surface morphology, cross sectional microstructure, dielectric properties, ferroelectric response and piezoelectric response. The process conditions evaluated include: anneal temperature, anneal time, ramp rate, oxygen flow, excess cation content, and pyrolysis temperature.

The majority of BNKT research has been done near the observed MPB composition of $80\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}20\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ due to its characteristically large piezoelectric response. The second part of this study evaluates the impact of composition

on thin film BNKT properties. Three separate compositions were evaluated: 40BNT-60BKT, 60BNT-40BKT, and 80BNT-20BKT. It was found that dielectric loss is considerably lower in 40BNT-60BKT ($\tan \delta = 0.02-0.05$) than at the MPB ($\tan \delta = 0.05-0.1$). Piezoelectric response is maximized near the MPB with d_{33} ranging from 30-40 pm/V at 40BNT-60BKT, 50-60pm/V at 60BNT-40BKT, and 60-90pm/V at the MPB. Composition experiments were performed using a box furnace anneal method in addition to the optimized RTA process. This was done in order to illustrate the impact of process optimization on realized film properties. While little impact was shown on piezoelectric response between the two compositions considerable differences are observed in cross sectional microstructure, film crystallinity, and dielectric loss. Films produced using a box furnace instead of an RTA were considerably less dense, showed inconsistent dielectric loss, and for compositions off the MPB considerably lower 100 to 110 x-ray diffraction peak intensity ratios compared to those made in the RTA.

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July 1, 2019

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Impact of Process Optimization and Composition on Thin Film BNKT
Microstructure, Ferroelectric and Piezoelectric Response

by
Kyle M. Grove

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented July 1, 2019
Commencement June 2020

Master of Science thesis of Kyle M. Grove presented on July 1, 2019

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Kyle M. Grove, Author

ACKNOWLEDGEMENTS

I would like to express my immense gratitude to the many mentors, family members, and friends that have made this accomplishment possible. My parents Pam and Marty Grove have whole heartedly supported me in every stage of my life and career and I am truly grateful to them. I would also like to thank Dr. Geoff Brennecke at the Colorado School of Mines for introducing me to the field of electroceramics, giving me my first real experience in a laboratory, and recommending me to further positions at the Army Research Laboratory and OSU. I want to thank Dr. Ronald Polcawich for mentoring me for two consecutive summers at the Army research lab. Dr. Brady Gibbons, my advisor at OSU, for providing me with all the tools, advice, funding, and support necessary to complete this work. Thanks to Dr. David Cann for acting as a mentor and providing me with no small amount of insight as well as inviting me to work alongside his own research group. I also want to thank the many students and colleagues from the materials science program at OSU for supporting me. Maddie Bahmer, Dr. Joel Walenza-Slabe, Dr. Ashley Mason and Dr. Austin Fox played direct roles in making this research possible by providing me with invaluable training, advice and assistance. A sincere thanks to Nicole Barrett and Sean Davis, our undergrad lab assistants, for their time spent helping with everything from sample preparation to running characterization equipment. Finally, I would like to thank all the members of my committee Dr. David Roundy, Dr. John Conley, and Dr. David Cann for their flexibility and professionalism during the scheduling of my defense.

CONTRIBUTION OF AUTHORS

Dr. Brady Gibbons provided the funding resources and initial direction for the research. Dr. Austin Fox ran several supporting experiments and assisted with maintaining and running lab and characterization equipment. Maddie Bahmer assisted with data collection and sample processing.

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1. Introduction

Many applications in electronics design require materials with the ability to convert energy from mechanical strain to electric field and vice versa. Materials with this ability are known as piezoelectric materials. Piezoelectric materials are typically electrical insulators with the ability to transduce dielectric displacement and mechanical strain when used as dielectrics. Some of the most prominent applications for piezoelectric materials are electromechanical sensors, ultrasonic transducers, resonators and microelectromechanical actuators[1], [2].

Microelectromechanical systems or MEMS are becoming a prominent technology in electronic device design as the push for device miniaturization increases. The most successful piezoelectric material currently used for MEMs applications is lead zirconate titanate, $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, commonly referred to as PZT. PZT has shown the most favorable properties for MEMs device design boasting exceptionally high strain per applied electric field, acceptably high Curie temperature, and stable dielectric properties[3]. Despite its exceptional material properties PZT has one major drawback. It has high lead content. Lead is an exceptionally toxic element which leads to many environmental and health concerns when used in larger scale device manufacturing [1]. As a result, numerous pieces of legislation limiting lead content in electronic design and manufacturing waste streams including Restriction of Hazardous Substances (RoHS), Waste Electrical and Electronic Equipment (WEEE), and Registration Evaluation Authorization and Restriction of Chemicals (REACH) have been implemented [2], [4]. This legislation as well as concerns for environmental sustainability have led to a large push to develop lead-free alternatives to PZT for piezoelectric design applications.

To date no one lead-free material has rivaled PZT in terms of overall properties, however, some promising lead-free systems have displayed specific properties which may allow them to replace PZT for specific applications [1]. Typically, bulk ceramic research is used initially to identify the most promising materials systems. One group of lead-free piezoelectric materials which bulk research has identified to have potentially

adequate properties to replace PZT in MEMS actuator design applications are bismuth based piezoelectric materials. Bismuth based piezoelectric materials such as bismuth sodium titanate (BNT) and bismuth potassium titanate (BKT) display high piezoelectric response, however, these individual systems also have drawbacks such as high loss in the case of BNT or sintering difficulties in BKT. One way these drawbacks can be mitigated is through development of binary, ternary, and doped variations of bismuth based piezoelectric materials[1], [2].

A major concern for development of lead-free replacements for PZT in MEMs design is the development of thin film variations of lead-free materials with comparable properties to their bulk counterparts. Bulk materials generated via powder processing techniques cannot be used in MEMs fabrication. As such thin films are the most important second step after bulk materials with favorable properties have been identified. In this study thin films are defined as having thickness of approximately $2\mu\text{m}$ or less. In the case of BNT and BKT based materials, highly volatile cations amongst other concerns pose challenges to development of high-quality thin films. Chemical solution deposition is one of the most promising thin film processing methods for up-scaling to industry applications and is thus a primary focus in lead-free material research [5]. The research detailed in this thesis focuses on optimization of a chemical solution deposition process for BNT-BKT thin films as well as observing compositional trends in BNT-BKT thin film properties. Furthermore, a comparison between two processing routes, one using a rapid thermal annealing process and the other using a box furnace annealing step will be completed. Compositional trends in properties of films prepared by both processing routes will be measured and compared to ascertain their dependence on process conditions. This thesis should provide a strong starting point for future chemical solution deposition process development for BNT-BKT based thin films as well as insight into compositional trends for the BNT-BKT binary system.

2. Background

This section details the basic principles that must be understood when studying thin film piezoelectric and ferroelectric materials. Key material properties will first be defined, then underlying structures and mechanisms giving rise to these properties will be explored. Thin film material fabrication techniques will be briefly described as well. Finally, techniques used to characterize thin film properties and performance will be described.

2.1 Material Properties

This section details the key material properties of interest when designing and researching piezoelectric thin film materials. The underlying mechanisms that give rise to these properties will also be identified and described. One common visual representation of the material property relationships between mechanical stress, electric field, and temperature is known as the Heckmann diagram which is depicted in figure 2.1. This diagram defines the relationship between electric field and stress as piezoelectricity, the relationship between temperature and stress as thermoelasticity and the relationship between temperature and electric field as pyroelectricity [6].

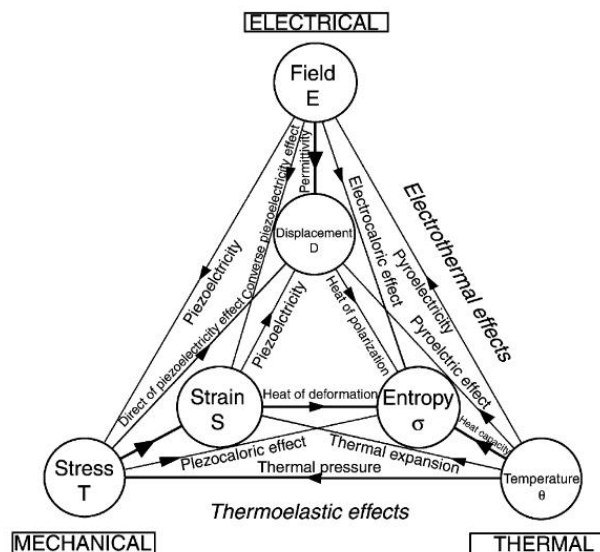


Figure 2.1 Heckmann Diagram [6]

Dependent properties including strain, entropy and dielectric displacement are shown as the inner triangle of the Heckmann diagram. For any given application, mechanical, chemical, electrical, structural, and optical properties will be evaluated with specific weight. In most MEMs applications mechanical stress and electric field relationships are of great importance as is dielectric permittivity.

2.1.1 Properties of Dielectric Materials

Dielectrics are electrically insulating materials often associated with use in capacitor devices. Dielectric materials are most useful when they are polarizable and thus store charge when exposed to an electric field. The amount of electric field that can be stored within a dielectric is known as the material's relative permittivity (ϵ_r) or dielectric constant (κ). Polarization in its most basic sense is the separation of charge within a material. When an electric field is applied to a dielectric material charge is redistributed within the dielectric to generate dipoles. These dipoles lead to a polarization within the material given by equation 2.1.

$$P = Nqd \quad (2.1)$$

Where P is polarization, N is the number of dipoles per unit volume, q is the magnitude of charge, and d is the distance separating opposite charges within each dipole [7]. There are four different mechanisms that can give rise to polarization within a material: Electronic, Ionic, Dipolar, and interfacial. Electronic polarization occurs when electrons within atoms in the material are displaced relative to the atomic nucleus. The uneven distribution of electrons generates a dipole across each individual atom. Ionic displacement occurs when ionic bonds are elastically deformed under an electric field generating a dipole. Dipolar polarization occurs when dipoles are reoriented within the material. In most dipolar materials dipoles are randomly oriented and thus show a net zero charge. With application of an electric field, dipoles reorient and become aligned with one another opposite the direction of the applied electric field. Interfacial polarization occurs when charge carriers and defects collect at interfacial barriers under an applied electric field. Total material polarization is defined by the sum of contributions from the above mechanisms. A material's dielectric constant is related to the ease with which it polarizes under an electric field. Materials with large dielectric constant polarize

easily and thus are capable of storing larger quantities of electric field. Dielectric constant is interchangeable with relative permittivity which is defined as the amount of resistance to forming an electric field within the material relative to vacuum.

In a capacitor device, the capacitance (C) is the amount of stored charge over the magnitude of applied electric field across two electrodes. The relationship between capacitance and permittivity in a parallel plate capacitor is shown in equation 2.2.

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad (2.2)$$

Where C is capacitance, ϵ_r is relative permittivity, ϵ_0 is the permittivity of free space, A is electrode area, and d is distance separating electrode plates[7].

When dielectrics are exposed to alternating electric field, dipoles realign. Dipole realignment takes time. The amount of time required for dipole realignment depends largely on the polarization mechanism. The highest frequency of electric field at which a dipole can completely realign is known as the dipole's relaxation frequency. At frequencies above the relaxation frequency, dipoles of the given type cannot realign in time and thus do not contribute to the overall polarization of the material. The frequency dependence of the contributions from each polarization mechanism are shown in figure 2.2.

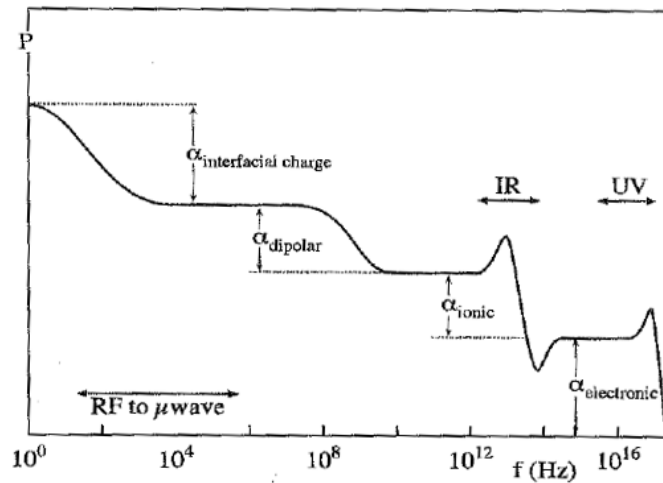


Figure 2.2 frequency dependence of polarization mechanisms [7]

When an alternating electric field is applied to a dielectric material its permittivity can be represented as a sum of real ϵ' and imaginary ϵ'' components shown by equation 2.3 [7].

$$\epsilon = \epsilon' - j\epsilon'' \quad (2.3)$$

A certain amount of loss in the form of heat is associated with dipole realignment. The amount of electric energy lost to heat per unit time is known as dielectric loss. Dielectric loss is proportional to the tangent of the delay angle δ . The loss tangent is related to a ratio of the real and imaginary portions of permittivity as shown by equation 2.4 [7].

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (2.4)$$

Since loss tangent is proportional to resistive loss in a capacitor it is often used to measure and describe the quality of dielectric materials. For piezoelectric dielectrics in MEMS design high dielectric constant and low loss tangent are desirable for optimal device efficiency and functionality.

2.1.2 Piezoelectric Materials

Piezoelectric materials are dielectric materials with non-centrosymmetric crystal structures that produce electrical energy when undergoing mechanical strain. Any dimensional change imposed upon a non-centrosymmetric material will cause an uneven distribution of charge generating a voltage. This phenomenon is known as the direct piezoelectric effect and is described by equation 2.5.

$$D_i = d_{ijk}\sigma_{jk} \quad (2.4)$$

Where D_i is dielectric displacement, d_{ijk} is the piezoelectric coefficient, and σ_j is applied stress [1]. Piezoelectricity can also be observed by the inverse piezoelectric effect or the generation of a mechanical strain within a material when it polarizes under applied electric field. This effect is described by equation 2.5.

$$S_{jk} = d_{ijk}E_i \quad (2.5)$$

Where S_i is the electric field induced strain and E_j is the applied electric field [1].

Coordinate axes are defined by the polarization direction of the material. The direction of polarization is assigned the 3 direction. If an applied electric field is in the 3-direction and induced strain is measured in the 3-direction the relevant piezoelectric coefficient is written as d_{33} . Numerous other pairs of piezoelectric strain and polarization directions are

possible within a real piezoelectric material. In addition to piezoelectric coefficients another important factor used to describe the piezoelectric response of a material is the electromechanical coupling coefficient k . k^2 is defined as the ratio of mechanical energy converted to electrical energy to the input mechanical energy as shown in equation 2.6.

$$k^2 = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}} \quad (2.6)$$

This factor is difficult to directly measure in most real material systems due to the presence of loss [7].

Many piezoelectric materials additionally display a spontaneous polarization due to the separation of charge centers. One specific structure which is both non-centrosymmetric and able to display spontaneous polarization is the perovskite structure. The perovskite structure is described by the formula ABO_3 . A perovskite unit cell is depicted in figure 2.3 [8].

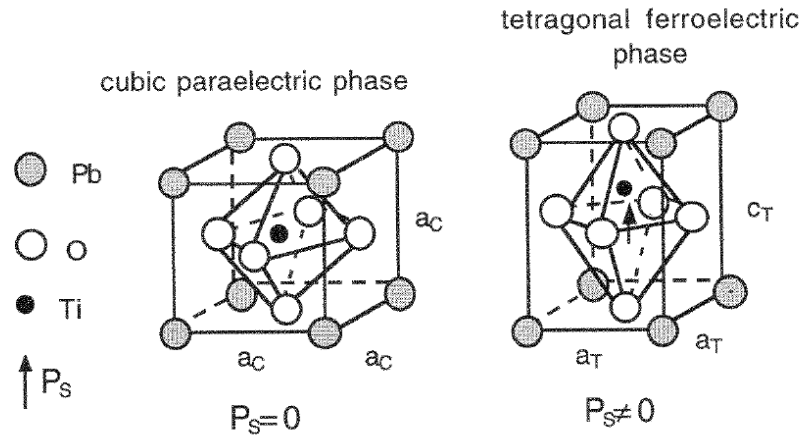


Figure 2.3 Perovskite structure and tetragonal distortion [8]

When exposed to an electric field the B-site cation and oxygen atoms undergo non-uniform displacement giving rise to a spontaneous polarization within the material causing the structure to lose its center of symmetry. Numerous directions of spontaneous polarization are possible for various perovskite materials. The change in polarization direction due to various structural distortions can often be predicted using the Goldschmidt tolerance factor shown in equation 2.7.

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (2.7)$$

Where r_A is the radius of the A-site cation, r_0 is the radius of the anion, r_B is the radius of the B-site cation. When the tolerance factor is 1 the material forms a cubic structure. When the tolerance factor is less than 1 the structure distorts to form either a rhombohedral or orthorhombic structure. When the tolerance factor is greater than one the structure is distorted to form a tetragonal or hexagonal structure [9]. Materials with perovskite structures often display inflated dielectric and piezoelectric response. Certain phase transitions and states can contribute to the degree to which spontaneous polarization and inflated properties occur and will be described in detail in the next section.

2.1.3 Phase Transitions

Properties of piezoelectric materials are strongly influenced by material structure. As such, solid state phase transitions and specific phase regions play a key role when designing piezoelectric actuator materials. The excellent piezoelectric response, electromechanical coupling coefficients, and dielectric properties of PZT can in a large part be attributed to the existence of a morphotropic phase boundary (MPB) between the rhombohedral and tetragonal phase regions. Figure 2.4 from Zhang et al. shows both a PZT phase diagram as it relates to electromechanical coupling coefficient and dielectric constant [10].

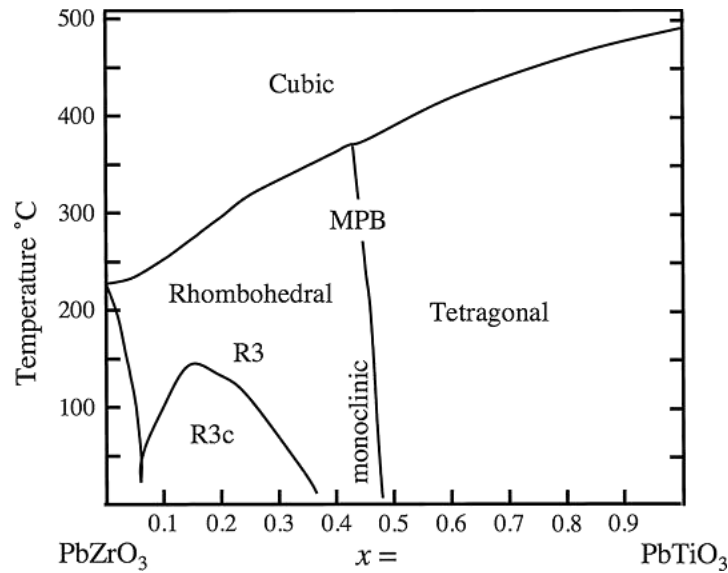


Figure 2.4 PZT phase diagram showing compositional dependence of electromechanical coupling coefficient and dielectric constant [10]

As the composition nears the MPB at 48 mole percent PbTiO_3 both electromechanical coupling coefficient and dielectric constant spike. This has been attributed to the mutual stability of the rhombohedral and tetragonal phases within this phase region, however, recent studies have also shown the presence of a stable monoclinic phase as well [11]. The inflated properties at the MPB are known to have two causes. First, the crystal lattice is softened by two phases with equivalent free energy. Second, the two phases have different crystal symmetries allowing a large number of possible polarization directions to exist improving alignment of ferroelectric domains. It can also be observed from the phase diagram in figure 2.4 that above a certain temperature threshold a cubic perovskite phase becomes stable. The temperature at which the cubic phase becomes stable for a given composition is known as a Curie temperature. This causes the material's piezoelectric response and dielectric constant to be greatly reduced. For high temperature applications, the Curie temperature of materials is a major concern when designing piezoelectric materials.

2.1.4 Ferroelectric Materials and Relaxor Ferroelectrics

Many piezoelectric materials are also ferroelectric. Ferroelectrics are materials that exhibit a spontaneous polarization which can be switched through the application of an

external electric field. Similarly, to polycrystalline materials which can have numerous grains with different crystal orientations, ferroelectric materials can have numerous regions with different polarization states. Localized regions in ferroelectric materials which share the same polarization orientation are known as ferroelectric domains. Regions separating ferroelectric domains are known as domain walls. Two types of domain walls exist: 180° and 90° . 180° domain walls are walls that separate domains with opposite polarization states while 90° domain walls separate domains with perpendicular polarization states. When no external field is present and the ferroelectric material is unpolled, these domains orient randomly leading to a net zero polarization across the bulk of the material. With the application of an external electric field these ferroelectric domains reorient with the external field as shown in figure 2.5.

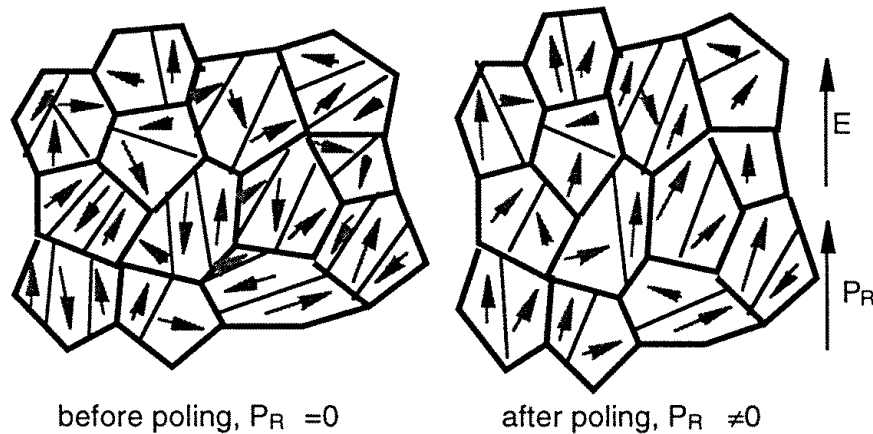


Figure 2.5 Polling of ferroelectric domains [10]

When an alternating electric field is applied to a ferroelectric material, realignment of ferroelectric domains as the field changes gives rise to a polarization hysteresis loop as shown in figure 2.6.

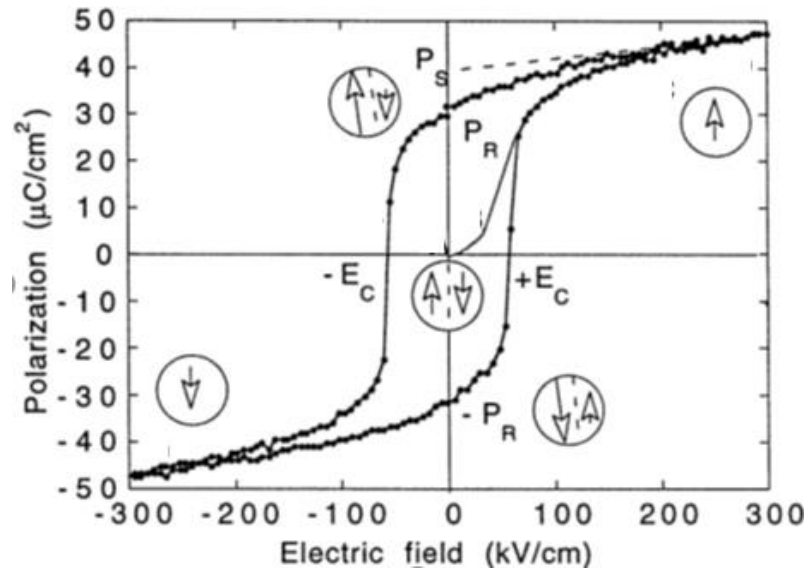


Figure 2.6 Ferroelectric polarization hysteresis [10]

When an unpoled ferroelectric material is exposed to an alternating field it begins at both 0 polarization and electric field. As the applied field is increased the polarization begins to increase as ferroelectric domains begin to align. After reaching a maximum the electric field is incrementally decreased to zero. At zero applied electric field the material still maintains some residual polarization, P_R . The polarization begins to decrease as a negative electric field is applied until reaching the coercive field, E_C , which is the field required to reach zero polarization within the material. As the field is even further decreased the polarization begins to increase in the opposite or negative orientation. Finally, after reaching a maximum the material goes through a similar set of polarization transformations as the electric field is again reversed and increased yielding a hysteresis loop. Ferroelectric materials are often designed to have specific hysteresis features. For example, in ferroelectric memory applications a high remnant polarization and coercive field are ideal while high maximum polarization and low remnant polarization is ideal for MEMS actuator applications.

Ferroelectric materials with piezoelectric properties display strain electric field hysteresis loops as well. Ferroelectric strain electric field loops are often referred to as butterfly loops due to their shape. Figure 2.7 shows a theoretical strain hysteresis loop side by side with an experimental strain loop overlaid with a polarization loop.

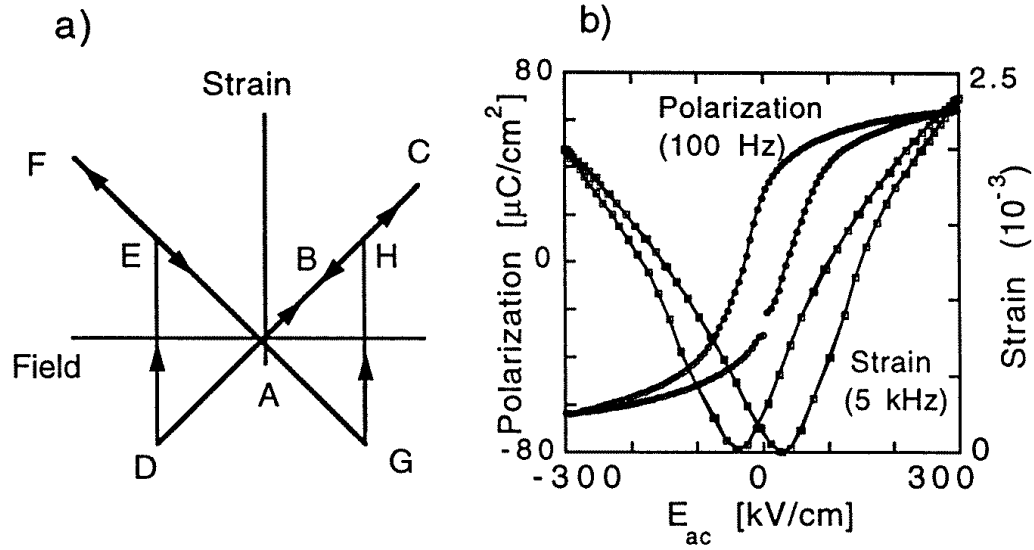


Figure 2.7 Strain vs electric field loops: a) theoretical b) experimental strain and polarization loops [10]

Point A from the theoretical hysteresis loop in figure 7 represents a ferroelectric piezoelectric material under zero field. When the field is increased through point B the material undergoes an increasing mechanical strain to its maximum at point C. At this point the field begins to decrease and the material strain decreases as well through point B back to point A at zero field. Note that real materials often have remnant strain and do not return to their original unpolled state at zero field. As the field is increased in the negative direction the material undergoes negative strain until reaching its coercive field at point D. At this field the material switches polarization states and begins to undergo increasing positive strain with increasing negative magnitude of electric field to point F. Finally, as the electric field is again reduced towards zero the material undergoes a similar strain behavior through points E, A, G, and finally back to point H. As can be observed in the measured strain and polarization loops material strain behavior is rarely perfectly theoretically ideal and numerous different extrinsic mechanisms, mechanism not originating from the crystal lattice, can contribute to variations in strain behavior.

As before mentioned above the Curie temperature perovskite materials undergo a transformation to a cubic phase. This causes the material to become paraelectric and eliminates any ferroelectric contribution to piezoelectric and dielectric response. Above

the Curie temperature the permittivity of the material can be described by the Curie-Weiss law shown by equation 2.8.

$$\varepsilon = \varepsilon_0 + \frac{C}{T-T_0} \approx \frac{C}{T-T_0} \quad (2.8)$$

Where C is the Curie constant, T_0 is the Curie-Weiss temperature, and T is temperature [8]. As shown in equation 2.8 the dielectric permittivity of a material begins to decrease with increasing temperature above the Curie-Weiss temperature. At the Curie temperature cubic paraelectric perovskite material transforms into a ferroelectric tetragonal or rhombohedral phase. This has a strong observable impact on dielectric, elastic, and thermal properties of the material as well as causing a spontaneous strain in the material.

Traditional ferroelectrics have distinct phase transitions and polarize as a result of reorientation of ferroelectric domains. Relaxor ferroelectrics or relaxors are ferroelectric materials with diffuse phase transitions rather than transitions occurring at a specific temperature or composition. These material's polarization mechanism has been attributed to the existence of polar nanoregions (PNRs) or polar regions which exist on the nanometer scale. Relaxor behavior is often associated with extreme compositional disorder. This disorder is often generated through the use of multiple different A or B site cations. The extent of disordering can have a large impact on the ferroelectric and piezoelectric properties of relaxor materials. When cooling from a cubic paraelectric phase relaxor ferroelectrics typically begin to form PNRs at a certain temperature known as the Burns temperature. The formation of these regions however is not associated with a structural phase change. Additionally, the appearance and development of PNRs occurs over a range of temperatures and as such is described as a diffuse transition [12]. Figure 2.8 shows a direct comparison of typical relaxor behavior with traditional ferroelectric behavior [13].

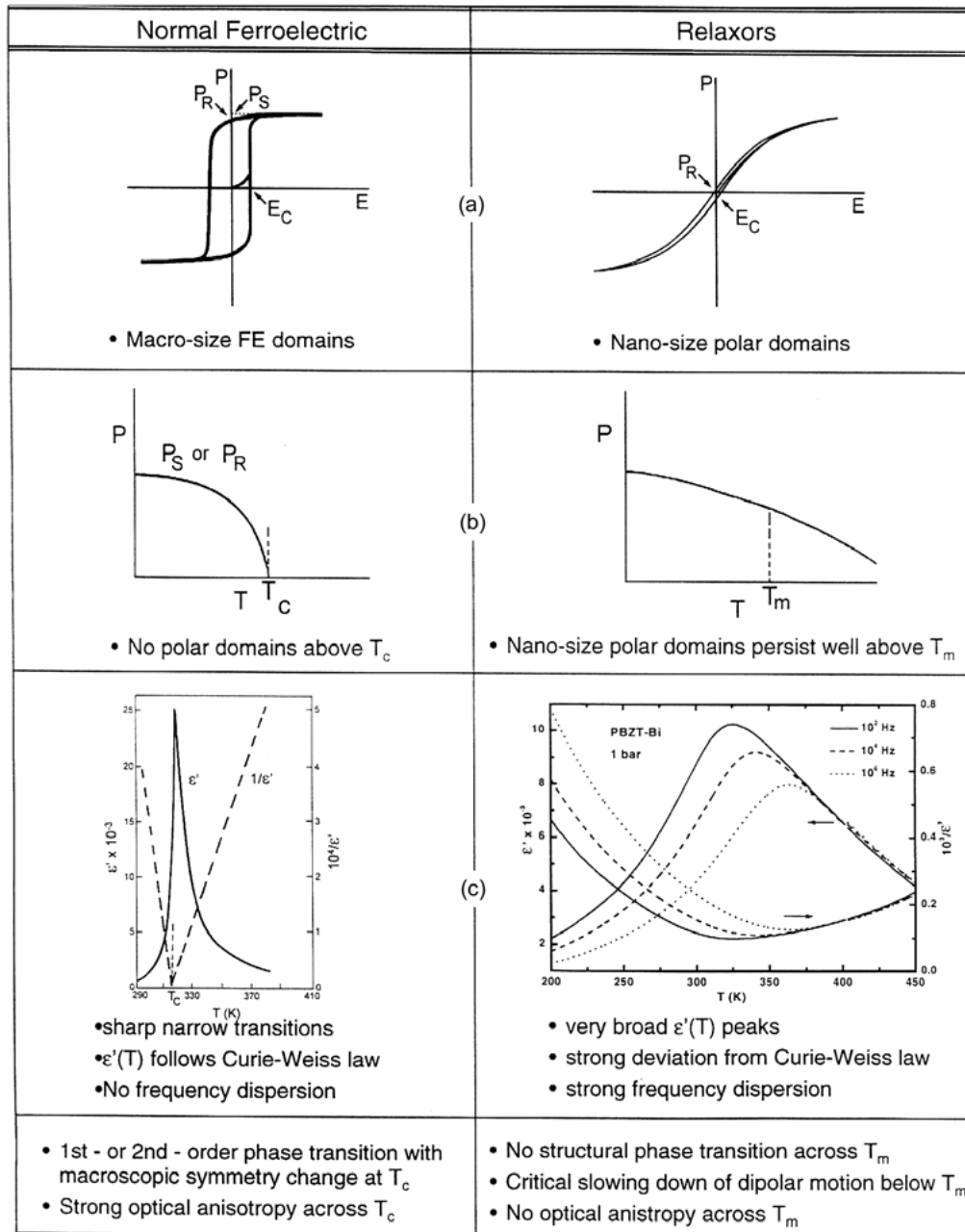


Figure 2.8 Comparison between relaxor ferroelectrics and traditional ferroelectrics [13]

When cooled from high temperatures relaxor ferroelectrics display two transformations. First at the T_B the development of mobile PNRs give rise to an ergodic relaxor. Ergodic relaxors reversibly develop ferroelectric domains under a strong applied electric field but return to their original PNR state after the removal of the external field. At even lower temperatures PNR kinetics are considerably slowed and nonergodic relaxor behavior can

be observed. Nonergodic relaxors undergo a permanent irreversible transformation into a ferroelectric state with the application of a strong electric field. Ergodic relaxors often show extremely small or nonexistent remnant polarization giving rise to a slim or pinched polarization loop. Nonergodic relaxors on the other hand display a higher remnant polarization [12]. Relaxor materials that show the transition from paraelectric to ergodic to non-ergodic behavior are described as canonical relaxors. Other relaxor materials display a direct transformation from ergodic relaxor behavior to traditional ferroelectric behavior at low temperatures and are described as non-canonical relaxors. Figure 2.9 shows the temperature dependence of relative permittivity for canonical and noncanonical relaxors in their various behavioral regions [14].

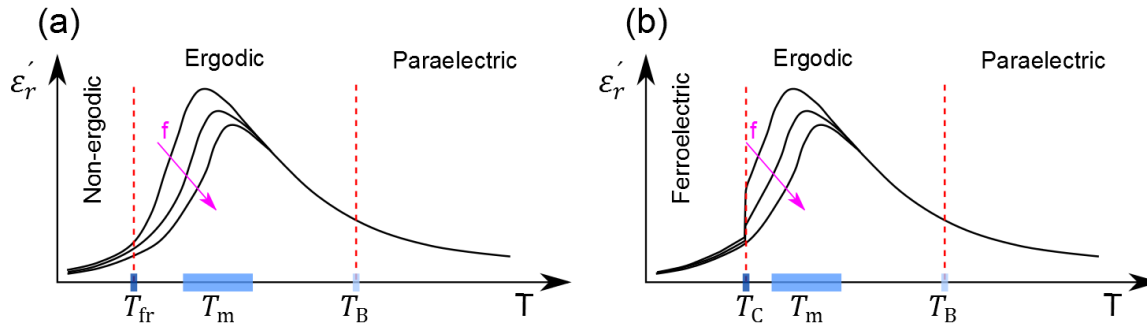


Figure 2.9 Temperature dependent behavior of ϵ_r' for (a) canonical relaxors and (b) non-canonical relaxors [14]

2.1.5 Electromechanical Strain Mechanisms

Electromechanical strain in piezoelectric materials can be a result of either intrinsic lattice contributions or extrinsic domain wall and phase wall contributions. The most common intrinsic strain mechanisms are electrostriction and the piezoelectric effect. All electrically insulating materials and dielectrics undergo some amount of deformation when exposed to an electric field. This phenomenon is described as electrostriction. In most cases contributions to electromechanical strain due to electrostriction are extremely small, however, in some relaxor ferroelectrics electrostriction contributions can be quite significant [8] [15]. In traditional ferroelectrics domain wall motion plays a major role in observed polarization and strain hysteresis. Extrinsic domain wall and phase contributions to electromechanical strain are temperature dependent mechanisms. As

such, at very low temperatures the dynamics for extrinsic contribution are significantly slowed so intrinsic strain contributions, which are relatively independent of temperature, can be isolated. Domain walls are also sensitive to the presence of defects such as oxygen vacancies in a material. Defects often have a pinning effect on domain walls increasing the energy demand for domain wall motion. Though largely insensitive to temperature change, intrinsic electromechanical strain contributions can be drastically impacted by stress. In piezoelectric thin films substrate interactions can give rise to significant levels of residual stress which can have a distinct impact on their strain behavior [16]. The next section describes thin film processing and deposition techniques which is closely related to how films interact with substrates.

2.2 Thin Film Processing

Piezoelectric and ferroelectric materials, though easily studied and fabricated in their bulk forms, are most useful in their thin film form. Almost all piezoMEMs applications from actuators to resonators require a thin film piezoelectric material to function. Thin film fabrication of complex material systems required for many of these applications pose numerous processing challenges. These challenges demand variations in techniques used in thin film fabrication. Each system requires specific optimization and tuning to develop films with useful properties. This section will provide a brief overview of the most common thin film processing techniques along with a more in-depth description of chemical solution deposition (CSD) which is the primary fabrication technique used in this research.

2.2.1 Overview of Thin Film Deposition Techniques

Numerous thin film processing methods exist each presenting its own set of benefits and challenges. This section will briefly introduce several techniques including: evaporation, pulse laser deposition (PLD), sputtering, chemical vapor deposition (CVD), and atomic layer deposition. Note that both evaporation and sputtering are classified as physical vapor deposition (PVD) processes [7] [17].

Evaporation is the most basic of the PVD thin film processing methods.

Evaporation is accomplished simply by heating a bulk liquid or solid material to a high

temperature in a low-pressure environment causing the material to evaporate or vaporize. A substrate placed at correct geometry will collect atoms from the vaporized material on its surface ultimately generating a thin film. Many different techniques can be used to heat materials for evaporation processes and each has their own advantages and disadvantages. The most common techniques include resistive, electron beam and pulse laser deposition (PLD). For many materials such as pure metals, and extremely stable compounds evaporation is a simple and effective method for thin film fabrication; however, for complex oxides decomposition and dissociation make evaporation more difficult often requiring atmospheric control and complex geometric solutions to achieve desired film stoichiometry. Electron-beam evaporation allows for sensitive control over evaporation rate from specific targets and can be an effective method for evaporating compounds and composite materials. PLD involves focusing a high-power laser pulse upon the target material. This causes ablation of the target material and ultimately generates a plasma plume. The ablated material then deposits on the surface of a heated substrate leading to the growth of a thin film. PLD is a very complex deposition method requiring involved control over deposition conditions to generate films with desired stoichiometry and properties. PLD is a difficult technique to scale up for manufacturing processes and is primarily used in low throughput lab and research settings [7] [17].

One technique that is more attractive for fabrication of complex oxide thin films is sputtering. Sputtering does not require melting and evaporation of the material but rather generates a flux of atoms via ion bombardment. Sputtering methods generally display better step coverage than evaporation techniques. Sputtering in its most basic form is the generation of a plasma in an argon rich environment through the application of a strong electric field. This causes positive argon ions to bombard a target of desired film material scattering atoms which in turn adhere to the desired substrate. Sputtering, though effective at avoiding dissociation and decomposition, has its own set of challenges. DC sputtering for example cannot be used for insulating materials so AC sputtering must be used on dielectric oxide materials. Alternatively, reactive magnetron sputtering or sputtering of cations in an oxygen or nitrogen rich controlled environment can be used to sputter insulating oxides [18]. Sputtering itself is an extremely slow deposition technique, however, the use of a magnetron to influence plasma behavior can

be effective at increasing deposition rates. Damage and modification to film properties can occur as a result of bombardment with charged particles during the sputtering process. Particle bombardment can be purposefully used to modify film properties or can be avoided using specific geometries for substrate placement and target alignment. The most common techniques for sputtering complex oxide dielectrics are reactive magnetron sputtering and AC magnetron sputtering [18].

Chemical vapor deposition or CVD is a thin film synthesis process which involves either reacting volatile compounds with gases to deposit a non-volatile film or the decomposition of a compound at high temperature to form a solid thin film. Numerous different forms of chemical vapor deposition exist including but not limited to atomic layer deposition (ALD), atmospheric pressure (AP) CVD, low pressure CVD (LPCVD), and plasma enhanced CVD (PECVD). CVD is a widely used method for deposition of complex oxide thin films and semiconductor materials, however, it requires involved control over environmental and process conditions and often involves use of highly toxic compounds and gases [7].

2.2.2 Chemical Solution Deposition

Chemical solution deposition or CSD involves the use of a solution containing desired cations to coat a substrate and synthesize a thin film material. Unlike many of the deposition methods described in section 2.2.1 chemical solution deposition does not require the use of a vacuum system or controlled gaseous environment. This makes CSD an ideal synthesis route for high throughput industrial processing as it is relatively inexpensive, has low energy requirements, and is easily upscaled from a lab to an industrial setting. There are many different CSD methods all of which share the same general processing steps: precursor solution synthesis, deposition of solution on substrate, and thermal treatment to form and densify a thin film. Solution synthesis entails the dissolution or refluxing of desired precursors in stoichiometric ratios along with any necessary stabilizers and additives. Compositional adjustments and additives can be used to account for volatilization of cations, diffusion of compounds into the substrate material, and formation of undesired phases. After solution synthesis the solution must be

deposited on a substrate. This is achieved by spin-coating, dip coating, spray coating, or ink jet printing. Solution deposition leaves a wet film on the surface of the substrate. It should be noted that this step often controls the ultimate thickness of the deposited thin film layer. In general layer thickness can be controlled in the solution synthesis step by adjusting solution viscosity and molarity. Spin speed also directly impacts layer thickness if a spin coating technique is used. After the coating step, the wet film then undergoes a drying step either at room temperature or an elevated temperature. The resulting film takes the form of a gel matrix of both organic and inorganic components. Pyrolysis is then performed to burn off any organic molecules often allowing the formation of oxides. This leaves an amorphous inorganic film which can be crystalized at high temperature to form a dense polycrystalline film. At this point the film can be characterized and/or used in a fabrication process. Figure 2.10 shows a flow chart of the steps that take place during a CSD process [19].

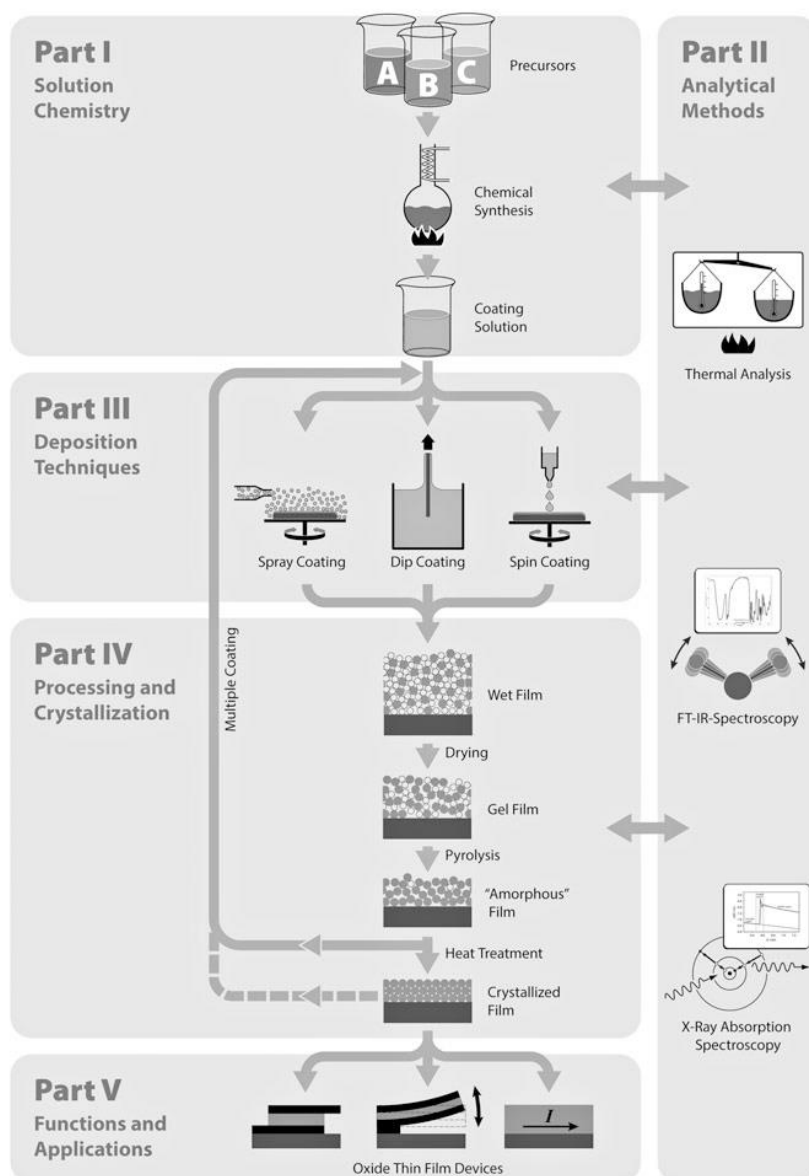


Figure 2.10 Chemical solution deposition flow chart [19]

The successful development of a CSD process must have the following assets to function properly: solubility of precursors in chosen solvent, stability of precursor solution, proper conditions and precursor selection so only oxygen and cations remain after pyrolysis, solution must wet substrate, and the solution must display chemical homogeneity [19], [7], [20].

Three of the most commonly used CSD methods used for complex oxide thin film synthesis are the sol-gel process, the chelate process, and metal organic deposition. Sol-

gel processes involve a transition from a liquid solution to a gel phase. Typical sol-gel precursors include metal organic compounds and metallic salts. The most common precursors are specifically metal alkoxides and the most common solvent for sol-gel processes for perovskites is 2-methoxyethanol. The gel forms after the hydrolysis of the alkoxides or metal organics. This method, though effective, is extremely sensitive to atmospheric interactions due to sensitive hydrolysis reactions and as a result requires refluxing and distilling techniques within a controlled environment. The chelate process is similar to the sol gel process but relies on use of chelating agents to molecularly modify the metal alkoxides making them less sensitive to hydrolysis. In this method acids such as citric or acetic acid are used to chelate metal ions making them less sensitive to hydrolysis. Upon heating and drying a polymeric glass is formed and finally at a higher temperature the desired amorphous oxide film is formed. This method is advantageous because it allows for simplification of solution preparation not requiring reflux or distillation and the generation of solutions that are water insensitive. Metal organic deposition or (MOD), unlike the sol-gel method, does not require the hydrolysis of metal cations. In MOD metal organic compounds are suspended in a solvent, usually xylene, then combined to achieve desired stoichiometry. The solutions can be classified as simple mixtures as no oligomerization of precursors occur and precursors in solution remain chemically similar to the starting precursors used. Upon heating the organics decompose and the desired metal oxides are formed. This process is ideal for rapid compositional mapping due to the simplicity of solution preparation, however, nonreactive starting precursors make the solutions more difficult to modify using reactions during preparation [19], [20].

2.2.3 Nucleation Growth and Crystallization of Thin Films

As deposited films derived from chemical solution deposition methods are amorphous. As such, the thermodynamics of crystallization are dictated by a phase transition from an amorphous glass to a crystalline perovskite phase by a nucleation and growth process [20], [19]. Figure 2.11 shows the free energies with respect to temperature for equilibrium liquid, amorphous film, and finally the crystalline perovskite phase. This figure is useful

for the visualization of the driving forces in play during the crystallization of a CSD derived thin film [20].

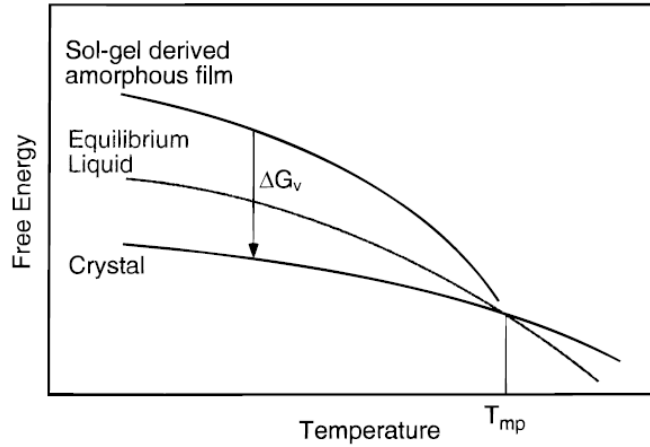


Figure 2.11 Free energy diagram of equilibrium liquid, amorphous, and crystalline films derived from a CSD process. ΔG_v represents the driving force for Crystallization and T_{mp} is melting temperature [20].

It is important to note that the final crystalline phase produced after an anneal step in a CSD process is not a perfectly equilibrium phase. Given enough energy and time to overcome kinetic restrictions further reductions in free energy are possible. In nucleation and growth theory energy barriers for homogenous and heterogenous nucleation are defined by equations 2.9 and 2.10 respectively [20].

$$\Delta G_{homo}^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \quad (2.9)$$

$$\Delta G_{hetero}^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} f(\theta) \quad (2.10)$$

Where γ is interfacial energy, ΔG_v is the free energy difference per unit volume of the amorphous to crystalline film transition, and $f(\theta)$ is related to the contact angle with the nucleation surface. Equation 2.11 gives $f(\theta)$ for a hemispherical nucleus [20].

$$f(\theta) = \frac{(2-3\cos(\theta)+\cos^3(\theta))}{4} \quad (2.11)$$

Where θ is the contact angle. During crystallization processes it is likely that the energy barriers for both homogenous and heterogenous nucleation will be overcome. The dominant type of nucleation behavior during film crystallization can have a drastic impact on film microstructure. In a case where heterogenous nucleation is dominant film

microstructures form elongated columnar grains. Often times, films with columnar microstructures are only one grain thick. If homogenous nucleation occurs in tandem with heterogenous nucleation films typically display a polycrystalline microstructure through the thickness of the film. Other factors such as the formation of metastable phases can, however, cause a preference towards one type of nucleation event or another. In the case of PZT an intermediate metastable fluorite phase reduces the driving force for crystallization causing only heterogenous nucleation to occur. PZT films often display columnar microstructures while other compositions which do not develop an intermediate phase display a polycrystalline microstructure. Nucleation events affect not only grain type by grain size as well. Films processed at lower temperatures will typically have a lower nucleation rate (see equation 2.12) and thus display a finer grained microstructure [19], [20]. Rapid thermal annealing is useful because it allows for control over the temperature at which crystallization occurs. If a film is heated at a fast-enough rate, the majority of crystallization events can be pushed to higher temperatures. This lowers the overall driving force for the nucleation of a crystalline phase. This in turn can cause a reduction or complete elimination of homogenous nucleation during film development. Rapid thermal annealing techniques are often used when trying to promote the development of films with columnar microstructures or with preferred crystalline orientation [20].

2.2.4 Thin Film Chemical Solution Deposition Processing Challenges

Two major factors that are not present in bulk processing but are major concerns in thin film processing are substrate interactions and high surface to volume ratio. Substrates impact the films grown on them in numerous ways and thus it is extremely important to find a substrate compatible not only with the desired application but with the piezoelectric material itself. If a substrate has a substantially different thermal expansion coefficient than the film deposited on it large residual stresses can develop during high temperature processing. Additionally, certain substrates can be reactive with solution chemicals and thin film materials making it imperative that compatible substrates and solution chemistries are selected. Often times, thin film stoichiometries can change during processing. This is due to the loss of cations through volatilization and diffusion

into the substrate. The high surface to volume ratio characteristic of thin films exacerbates both substrate interactions and impact of cation volatility on film stoichiometry. In most cases substrates are many times thicker than the films deposited on them often stressing films or causing them to crack during high temperature processing. Extremely thin films also provide a large surface area for volatilization and diffusion of cations. As a result, measures must be taken to compensate for substrate interactions and cation loss in any CSD thin film synthesis process.

Cation volatility refers to the loss of cations through vaporization. Materials with high vapor pressures vaporize to a larger degree and at lower temperatures. For example in PZT thin film processes PbO is highly volatile at temperatures greater than 500°C [19]. Figure 2.12 shows vapor pressures for several common elements. Three elements commonly used in lead-free piezoelectric materials are highlighted: sodium, potassium, and bismuth [21].

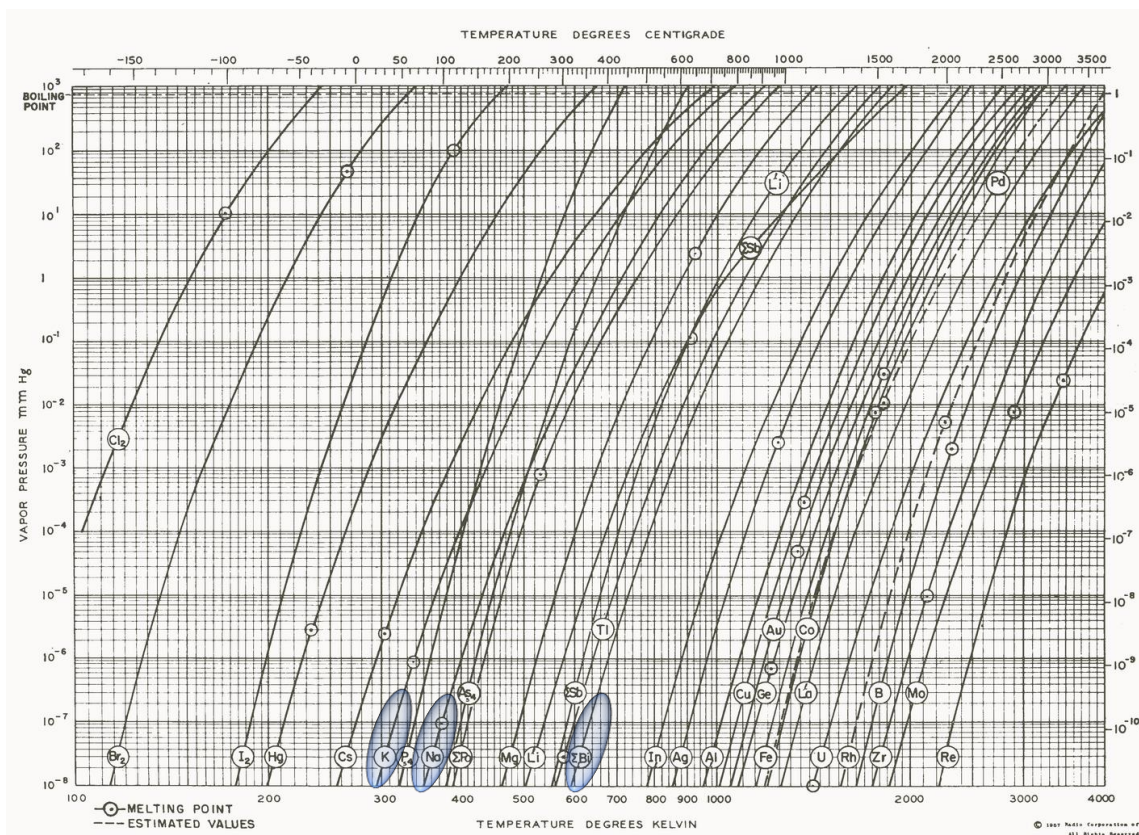


Figure 2.12 Vapor pressures of common elements [21]

As can be seen in figure 2.12 all three elements are highly volatile at common sintering temperatures for BNT/BKT based thin films (600°C to 800°C). Sodium and potassium are particularly volatile. Volatilization of cations and compounds during annealing of thin films, if not properly controlled, can lead to the alteration of material stoichiometry and the generation of defects such as pores and vacancies. Several methods can be implemented to control cation volatility. The simplest of these methods is increasing the concentration of the volatile species within the precursor solution. Adding excess precursors allows for a certain amount to volatilize without adversely affecting film stoichiometry. Another common method is the use of a buffer surface layer of volatile substance. In PZT, for example, it has been shown that a surface PbO layer can help to control Pb volatilization [19]. Lastly, control of gas partial pressures in the annealing environment can help suppress volatilization of certain compounds. For example, the driving force for volatilization of oxides can be reduced by annealing in an atmosphere

with a high oxygen partial pressure. It should be noted that increased cation excess and surface layers can also assist with alteration of stoichiometry via substrate diffusion.

Though control of cation volatility can be very complex, particularly for systems with multiple highly volatile species, substrate interactions in many ways pose the greatest challenge to thin film process design. For many applications the list of economically, and technically viable substrate materials is short. Platinized silicon for example is an extremely well-understood and established substrate material for MEMs device design. Use of new substrate materials can lead to numerous new design and fabrication challenges. As such, for new thin film materials to be competitive it is important they can be processed in such a way that they are compatible with certain substrate materials. The biggest qualifications for substrate compatibility are chemical stability, diffusivity of film elements in the substrate, and low thermal expansion coefficient mismatch. Solution additives and process control can help to increase substrate film compatibility; however, these techniques can only go so far and often times require expensive modifications to fabrication techniques. High mismatch between thermal expansion coefficients can lead to the development of high residual stresses in films which in turn impact piezoelectric, dielectric and ferroelectric response as well as potentially resulting in mechanical failure and cracking.

2.3 Thin Film Characterization

Once films are synthesized it is important to be able to measure and compare key film properties and evaluate their suitability for intended applications. Various characterization techniques allow the acquisition of both qualitative and quantitative information on film properties which can in turn be used to compare different types of thin films and evaluate their usefulness. In general, the most important properties to measure and observe in piezoelectric thin films are crystallinity, phase purity, surface morphology, microstructure, dielectric properties, mechanical properties, and finally piezoelectric response.

2.3.1 X-ray Diffraction

X-ray diffraction (XRD) is the most prominent technique used in measurement and identification of the internal structure of crystalline materials. This technique can be used to determine the crystal structure of a material as well as the presence of multiple crystalline phases. At its most basic, XRD involves the use of an x-ray source to direct a beam of x-rays over a specific range of angles and the use of a detector to measure the intensity of scattered x-rays. The relationship between the inner atomic spacing of the material and the XRD measurement parameters is known as Bragg's law as shown in equation 2.12 [22].

$$n\lambda = 2d\sin(\theta) \quad (2.12)$$

Where n is the order of diffraction, d is atomic spacing, λ is the wavelength of the source x-rays, and θ is the angle of incidence. Figure 2.13 is a diagram of the behavior of x-rays scattered by a crystalline material [22].

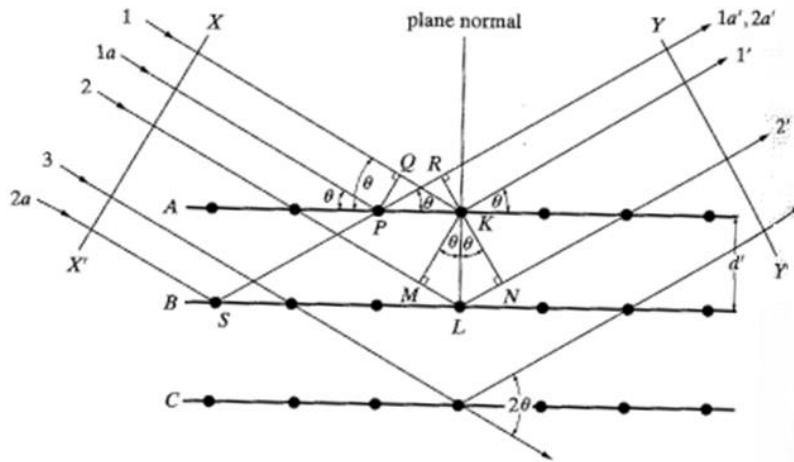


Figure 2.13 X-ray diffraction behavior in a crystalline material [22]

X-rays diffracted by all the atoms in all the atomic planes are in phase and constructively interfere with one another while in all other directions of space scattered beams are out of phase and destructively interfere with one another. As a result, during an XRD sweep intensities measured over a range of detector angles generate peaks of intensity corresponding to spacing of atomic planes. Atomic plane spacing is dependent only on the dimensions of the unit cell of the crystalline material. Patterns of peaks can then be

indexed and used to determine material structure and phase. X-ray diffraction can also be used to determine whether a polycrystalline material is textured or randomly oriented. This is achieved by observing intensity ratios of peaks associated with specific atomic orientations or in the case of perfect texturing the complete lack of specific orientation peaks. In this research the two primary uses for x-ray diffraction are detection of unwanted secondary phases and determination of the degree of film texturing [22].

2.3.2 Atomic Force Microscopy

Atomic force microscopy or AFM is a surface imaging method which employs a sharp tipped cantilever to measure atomic forces from the surface atoms of a sample. AFM allows for high resolution imaging of both conducting and insulating materials. In thin film research, AFM is used to measure surface morphology including grain size, surface roughness, and surface uniformity. AFM involves the use of a cantilever with an extremely soft spring coefficient to maximize the amount of deflection attained from atomic force. This is made more complicated, however, from the presence of noise generated from external vibrational sources. The best method for reduction of noise in AFM method is the use of a cantilever spring which is sufficiently stiff to display high resonance frequency. Equation 2.13 shows the resonant frequency of the spring system [23].

$$f_0 = (1/2\pi)(k/m_0)^{1/2} \quad (2.13)$$

Where f_0 is the resonance frequency, k is the spring constant and m_0 is the effect mass loading the spring. In order to use a sufficiently soft spring to maximize deflection the effective mass said spring is loaded with must also be decreased in order to maintain a sufficiently high resonance frequency for the elimination of noise from external vibration sources [23].

All AFM systems must have the following features to function: a sharp tip mounted on a cantilever with known spring constant, a method for measuring cantilever deflection, a feedback system to control deflection, a system to move the sample or tip in a raster pattern with respect to one another, and finally a program for conversion of measured data to an image[24]. In this research an Asylum MFP-3D AFM model is used

for surface imaging. Figure 2.14 is a general schematic for the Asylum AFM measurement configuration [25].

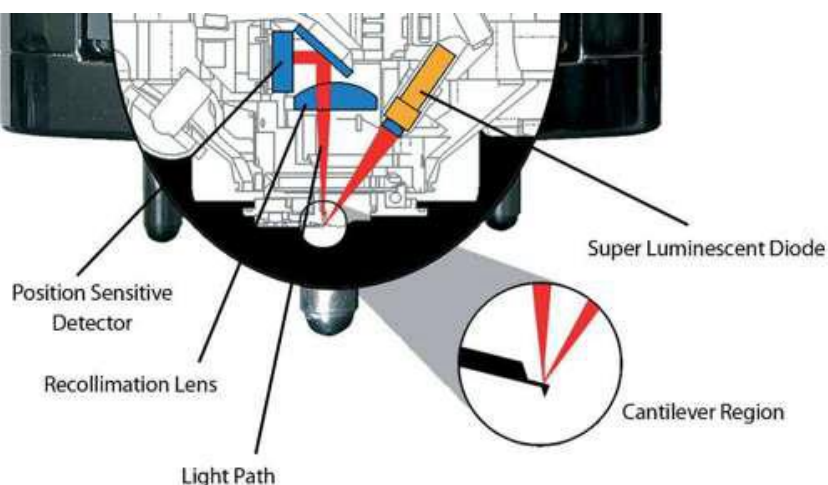


Figure 2.14 Asylum MFP-3D optical cantilever detection schematic [25]

In this case a super luminescent diode is reflected off the cantilever tip through a recollimation lens and into a position sensitive detector. As the tip's deflection changes the position sensor monitors sensitive changes in beam position thus generating an atomic surface image. Figure 2.15 shows a simple graphic of how various states of cantilever deflection correspond to beam positions on the photodiode [25].

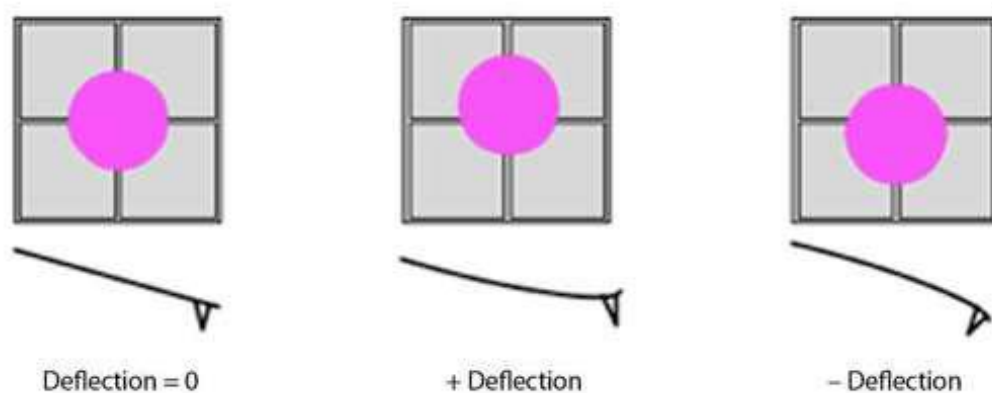


Figure 2.15 Cantilever deflection states corresponding to beam positions on photodiode [25]

2.3.3 Scanning Electron Microscopy

Scanning electron microscopes are useful for observing features smaller than those discernable by optical microscopy. Optical microscopy is limited by the wavelength of light with the most optimal optical microscopes attaining resolutions of approximately 200nm. Electron microscopy overcomes the limitations of optical microscopy by using an electron beam rather than a beam of light. Electrons have wavelengths many times smaller than light beams and the typical resolution limit of SEMs ranges from 1nm to 10nm though some specialized SEMs have attained resolutions as low as 0.4nm [26]. SEMs function by measuring signals from electron specimen interactions. These interactions can be classified as elastic or inelastic. Elastic interactions result in deflection off of an atom in the sample either by an atomic nucleus or shell of electrons of similar energy. These electrons lose little energy but experience a wide-angle change in direction. Elastically scattered electrons with a deflection angle greater than 90° are known as back scattered electrons or BSEs. Inelastic interactions involve the transfer of substantial energy to the specimen atom from the electron resulting in the ionization of the specimen atom which in turn generates electrons. Electrons generated from ionization of specimen atoms are known as secondary electrons or SEs and possess energies less than 50 eV [26]. Both BSEs and SEs provide useful data for sample imaging. BSEs are higher energy than SEs typically burrow deeper within the specimen before scattering and are sensitive to average atomic number and sample density making them ideal for realizing contrast between materials with differing atomic/molecular masses. SEs are lower energy and as such do not burrow as far into the sample making them ideal for imaging surface features with great detail [7]. Additional sample-electron beam interactions such as the production of characteristic x-rays occur during SEM measurements and can be useful for obtaining additional information about the specimen such as chemical or compositional analysis. Figure 2.16 shows a schematic of a basic SEM [26].

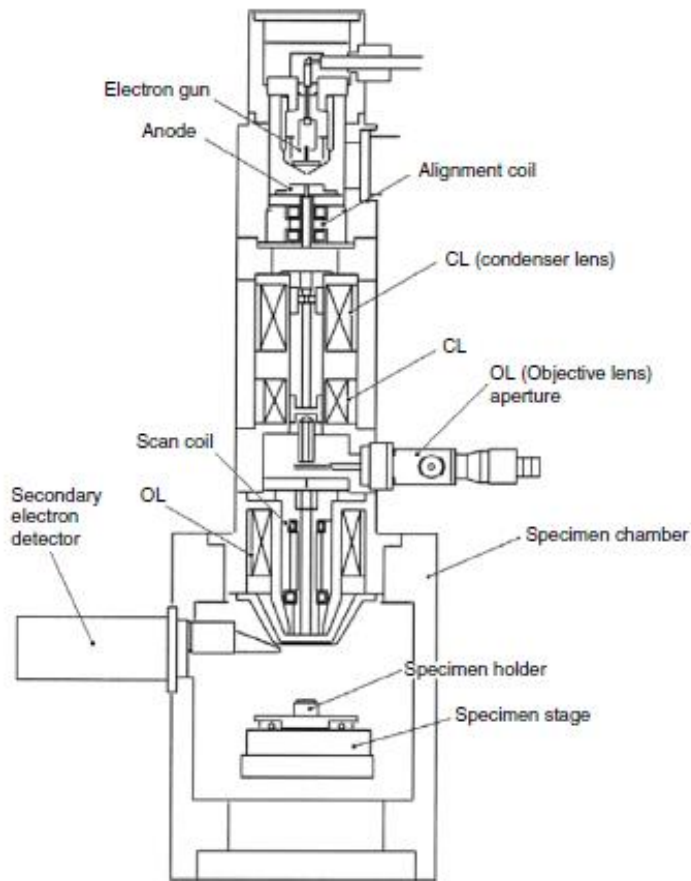


Figure 2.16 Schematic of a basic scanning electron microscope [26]

The most important components of an SEM can be broken down into an electron source or gun, lenses for the focusing of the electron beam, a specimen chamber which is held under vacuum, and finally detectors for the various generated signals of interest. In this work SEMs are primarily used for imaging the surface and cross-sectional microstructure of films.

2.3.4 Dual Beam Laser Interferometry

Dual beam laser interferometry is a technique for measuring strain response in piezoelectric thin film materials. When an electric field is applied in the same direction as the polarization direction the amount of strain per unit field in the out of plane direction is known as d_{33} . In thin film materials substrate interactions play a major role in the strain behavior of a material. The measured strain of a thin film material per applied field with

substrate interactions is known as the effective piezoelectric coefficient or $d_{33,f}$ in the case where the field is applied in the direction of polarization. Equation 2.14 shows the relationship between the fundamental d_{33} and the effective $d_{33,f}$ [27].

$$d_{33,f} = d_{33} - 2d_{31} \frac{s_{11}^E}{s_{11}^E + s_{12}^E} \quad (2.14)$$

Where d_{31} and d_{33} are fundamental piezoelectric constants and s_{11} and s_{12} are elastic compliance coefficients. Dual beam laser interferometers measure effective piezoelectric coefficients by splitting a single intensity laser into two perfectly in phase beams. One beam acts as a reference and is pointed at the back of a polished substrate while the measurement beam is placed on an electrode on the film surface. Figure 2.17 shows the optical beam path for the aixACT DBLI system used in this research.

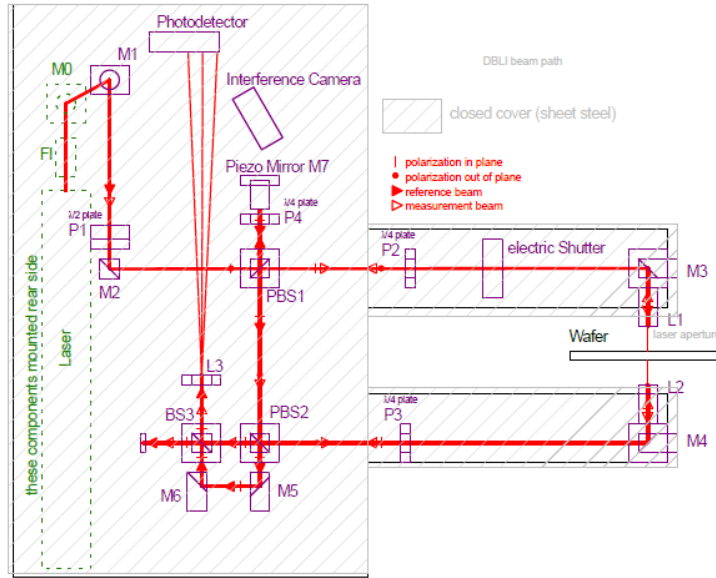


Figure 2.17 Optical laser path for aixACT DBLI system [27].

Once the beam is split and the reference and measurement beams are properly placed on the sample an electric field is applied to the sample. Strain in the material manifests as a change in film thickness thus changing the optical path length which in turn leads to a change in the interference pattern between the reference beam and measurement beam. A photodetector realizes the change in the interference pattern as a change in output voltage which is in turn translated as a specific change in sample thickness [27].

3. Literature Review

Numerous lead-free piezoelectric systems have been studied in an effort to replace PZT for various applications. Of these, the most thoroughly researched systems are barium titanate, alkaline niobates (KNbO_3), and bismuth sodium titanate (BNT) based systems [1]–[3]. At present none of these systems have matched PZT in terms of overall properties, however some materials rival PZT in specific circumstances. Figure 3.1 shows the behavior of the most common lead free material systems as compared to PZT in terms of electromechanical coupling coefficients k_p and k_{33} [28].

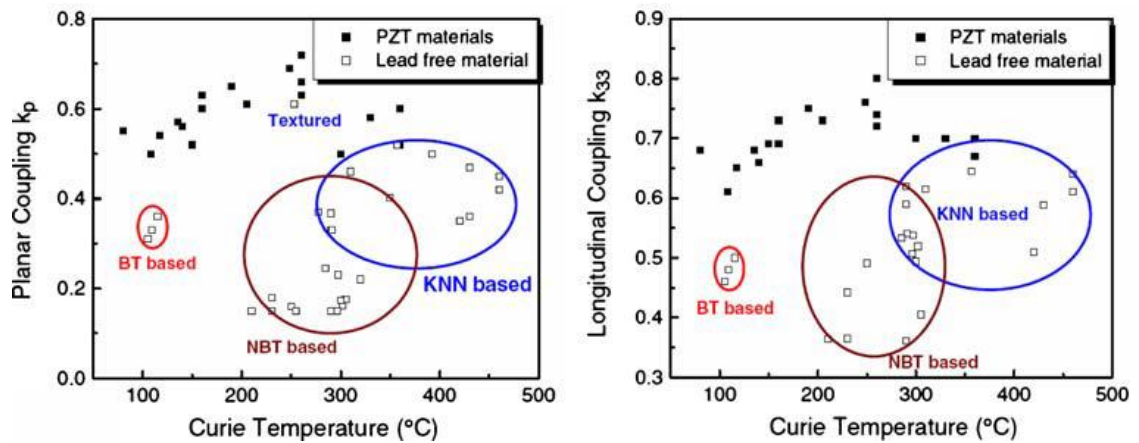


Figure 3.1 Planar and longitudinal coefficients as a function of temperature for PZT and common lead-free piezoelectric systems [10].

The research completed in this work is focused on BNT based systems. As a result, the remainder of this review section will be focused on reporting developments in single component, binary, and ternary compositions of BNT in both their bulk and thin film forms.

3.1 Bulk BNT Based Lead Free Piezoelectric Materials

In 1961 Smolenskii *et al.* reported that BNT shows a near-rectangular hysteresis loop at high fields. Smolenskii also reported BNT's temperature dependence of permittivity and coefficients of thermal expansion leading to its classification as a ferroelectric material with a Curie temperature of 320°C [29]. BNT as a single component system, however, has an extremely high coercive field (greater than 70 kV/cm) as well as presenting issues

with high conductivity which is realized as dielectric loss. These features make poling single component BNT difficult which in turn drastically impacts the piezoelectric performance of the material [12]. Additionally, more recent research has shown that BNT does not display traditional ferroelectric behavior. Rather it displays relaxor like behavior displaying a lack of long range order when cooling from high temperatures and the development of polar nanoregions [30]. As a result of the difficulties presented with poling single component BNT numerous binary compositions have been evaluated in an effort to generate a material with the same promising properties of BNT but with more manageable coercive field, loss and poling behavior [31].

Binary systems with BNT were researched in hopes of finding an MPB region with inflated piezoelectric response similar to that observed between lead zirconate and lead titanate in PZT. The two most heavily researched BNT binary systems are BNT with barium titanate (BNT-BT) and BNT with bismuth potassium titanate (BNT-BKT) [3], [4]. Takenaka et al. reported a MPB in the $(1-x)\text{BNT}-x\text{BT}$ binary system with x being between 0.06 and 0.07 with a Curie temperature of 288°C [32]. Sasaki et al. reported a MPB in the $(1-x)\text{BNT}-x\text{BKT}$ system with x lying between 0.16 and 0.2 [33].

It should be noted that the P-E loop behavior in both BNT-BT and BNT-BKT is heavily temperature dependent. T_d or the depolarization temperature is the temperature at which non-ergodic relaxor ferroelectrics stop displaying traditional polarization behavior and develop polar nanoregions PNRs. For temperatures below T_d classical ferroelectric polarization and strain behavior is observed. Above T_d pinched P-E loops with very low or nonexistent remnant polarization are observed. At temperatures much higher than T_d the pinched loops are replaced by extremely slim loops [34]. Both BNT-BKT and BNT-BT display relatively high T_d [32], [34]. Another binary system, BNT with bismuth zinc titanate (BNT-BZnT), has also been evaluated. Although BZnT is not ferroelectric by itself under standard conditions, it has been found that it can form solid solutions with other ferroelectric end materials generating materials with improved permittivity and piezoelectric response [35]. Like BNT-BKT and BNT-BT, BNT-BZT shows temperature and composition dependent ferroelectric and piezoelectric response. Figure 3.2 shows the change in ferroelectric response in BNT-BZnT with temperature and composition [35].

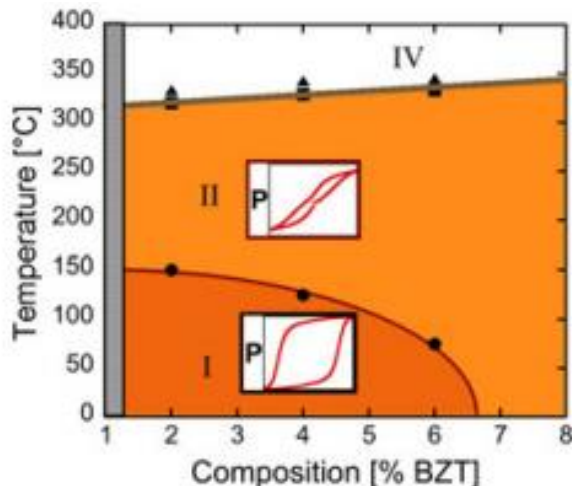


Figure 3.2 Ferroelectric response of BNT-BZT as related to a phase diagram with respect to temperature [34].

Though binary compositions in many cases have improved both the ferroelectric response and sinterability of BNT based ferroelectric ceramics, more improvements are required to generate a truly competitive material.

In an effort to further optimize properties and increase piezoelectric response, even more complex BNT based ternary systems have also been explored. Some of the most prominently researched compositions include BNT-BKT with potassium sodium niobate (BNT-BKT-KNN), BNT-BKT-BT, BNT-BT-KNN and BNT-BKT with bismuth zinc titanate (BNT-BKT-BZnT). BNT-BT-KNN was first researched by Zhang et al. whose work inspired Seifert et al. to research BNT-BKT-KNN ternary compositions as well [36]–[38]. Zhang et al. found that BNT-BT can achieve extremely high temperature independent strain response (0.45%) when a small amount of BNT is replaced by KNN. This corresponds to a large field d_{33} of 500pm/V or greater making the material appear attractive for actuator applications [36], [37]. Seifert et al. reported that BNT-BKT can also be improved with the addition of KNN reporting unipolar large field strains of approximately 0.48%. It was also found that the addition of KNN in BNT-BKT causes a phase change leading to the development of a nonpolar phase. The generation of this nonpolar phase causes pinching in P-E loops and the elimination of negative strain in bipolar strain loops. Figure 3.3 shows the change in behavior of BNT-BKT-KNN with respect to composition as reported by Seifert et al. [38].

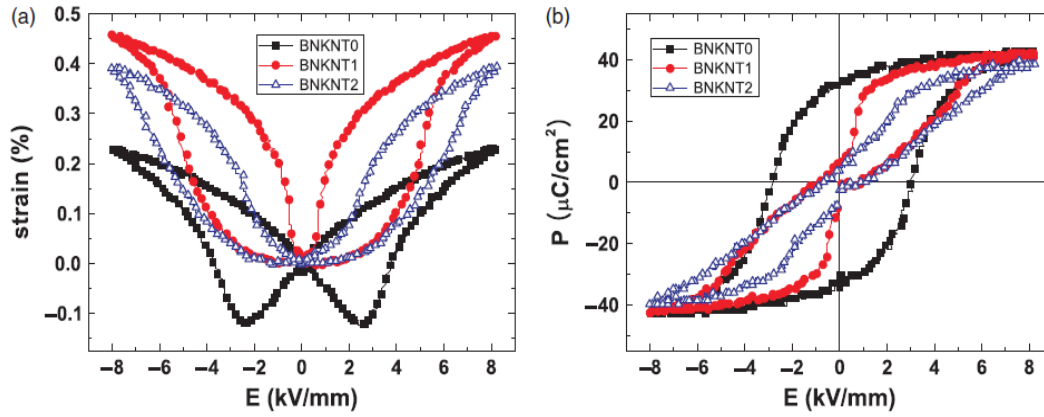


Figure 3.3 (a) strain and (b) polarization behavior of $(1-x)(0.8\text{BNT}-0.2\text{BKT})-x(0.97\text{KNN}-0.03\text{BKT})$ for $x=0, 0.01, 0.02$ denoted by BNTNT0, BNTKNT1, and BNKNT2 respectively [37]

BNT-BKT-BZnT has also received attention in lead free piezoelectric research. Dittmer et al. and Patterson et al. evaluated BZnT modified BNT-BKT in 2011 and 2012 respectively [39], [40]. It was found similarly to the BNT-BZnT binary system that a temperature and composition dependent transition in P-E and strain behavior exists. Large maximum strain values ($d_{33}^*=537\text{pm/V}$) were also realized for the ternary compositions near the transition in P-E and strain behavior (5BZT-40BNT-55BKT). Figure 3.4 shows the temperature and compositional dependence of strain and P-E behavior in BNT-BKT-BZnT [40].

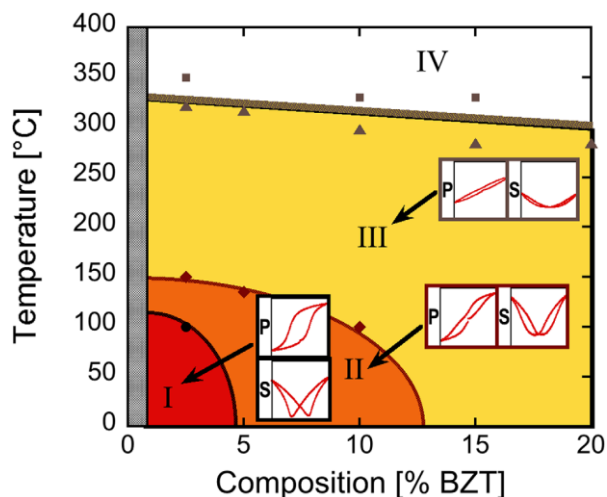


Figure 3.4 Compositional and temperature dependency of P-E and strain behavior with respect to BZnT content in BNT-BKT-BZnT [39].

In summary, during the search for lead free alternatives to PZT numerous materials systems of increasing complexity have been considered and evaluated. Promising single component lead free piezoelectric materials such as barium titanate and BNT were evaluated. Binary systems were researched in hopes of discovering MPBs with enhanced piezoelectric response similar to that found in PZT and other traditional ferroelectric piezoelectric materials. It was found that MPBs or regions with improved properties exist in both BNT-BT and BNT-BKT materials systems. In a continuing recent effort, more complex ternary compositions and modifications on binary compositions have been evaluated. It was found that the piezoelectric response and PE behavior can change drastically based on composition and temperature in many systems. It should be noted that the differences in strain and polarization mechanisms in relaxor materials when compared to traditional ferroelectrics such as PZT may not have the same requirements for optimization of piezoelectric and ferroelectric properties. As evaluated in BNT-BKT-BZnT and BNT-BT-BZnT, transitions in P-E and strain behavior can occur and high strain values can be realized even in compositions nowhere near the MPB observed in the binary compositions. As it stands research into new compositions as well as research on processing and characterization conditions in already discovered systems are still a very active area in lead free piezoelectric research. In addition to bulk compositional research some effort has also been extended to the development of BNT in its thin film form.

3.2 BNT Based Thin Film Materials

With continued research into promising lead-free piezoelectric compositions in bulk research, effort has also been allocated towards the development of thin film versions of the most promising compositions. The primary deposition techniques that have been used in the development of BNT based thin films are pulsed laser deposition (PLD), and chemical solution deposition (CSD). Some studies, though significantly fewer, reported use of RF magnetron sputtering.

Table 3-1 shows data on remnant polarization (P_r), and coercive field (E_c) taken from numerous BNT based thin film studies. As can be seen there is a large variation in the shape and P-E loop behavior even within the same material system and deposition technique. As such processing and measurement conditions as well as specific composition likely play a large role in P-E loop behavior. Some difficulty in drawing trends from reported P_r and E_c can arise due to variations in saturation of P-E loops, however, in general E_c can be lowered with the addition of binary and ternary compositions to BNT [41],[42],[43].

Studies on thin film BNT based materials use a wide range of techniques to realize optimal properties. These processing techniques include use of varying excess amounts, heat treatments, dopants and substrates. Though most studies made use of Pt/buffer/Si substrates there are examples of studies which utilized other materials in their substrate stacks and electrodes. Certain substrate materials and bottom electrodes can be used to promote epitaxy or to grow single crystals. Studies that made use of substrates other than Pt/buffer/Si are denoted by ** in table 3.1. These differences in processing techniques lead to a wide distribution of properties realized in thin film studies.

Table 3.1 Polarization-Electric field data from BNT based thin film studies

System	Deposition Method	P_r [$\mu\text{C}/\text{cm}^2$]	E_C [kV/cm]	Reference
BNT	CSD	10	130	[41]
BNT	RF Sputtering	11.9	37.9	[44]
BNT	CSD	20.9	112	[45]
BNT(Fe)**	CSD	20	100*	[46]
BNT(Mn)**	CSD	38	250	[47]
BNT	PLD	7-14	68-85	[48]
BNT**	PLD	15.9	126	[49]
BNT**	CSD(Ink-Jet)	24.7	263	[50]
BNT	CSD	9	90	[51]
BNT	CSD	15	84	[52]
BNT-BKT	CSD	13.6	104.8	[53]
BNT-BKT	CSD	13.2	100*	[54]
BNT-BKT	CSD	38	150*	[55]
BNT-BKT	CSD	60	100*	[56]
BNT-BKT(Mn)	CSD	19.2	106	[57]
BNT-BKT**	CSD	12.1	50*	[58]
BNT-BKT	CSD	7	150*	[59]
BNT-BKT	CSD	18.3	116	[60]
BNT-BKT	CSD	20*	60*	[42]
BNT-BKT-BT	CSD	27	120	[61]
BNT-BKT-BT	CSD	6	40*	[62]
BNT-BKT-BT**	PLD	30	85-100	[63]
BNT-BT	CSD	12	150*	[64]
BNT-BT(Rb)	CSD	28.9	200	[65]
BNT-BT(Li)	CSD	23.9	124	[66]
BNT-BT	PLD	0.5	5	[67]
BNT-BT**	PLD	29.5	74	[68]
BNT-BT	CSD	12	87	[69]
BNT-BT(Mn)	PLD	25	150	[70]
BNT-BT(Mn)**	PLD	25	150	[71]
BNT-BT**	CSD	10*	100*	[72]
BNT-BT	CSD	20	55*	[73]
BNT-BT	CSD	9*	70*	[74]
BNT-BT-ST**	CSD	10.5	100	[75]
BNT-BT-ST**	CSD	10	70*	[76]
BNT-BT-ST	CSD	5	100*	[77]
BNT-BKT-BMgT	CSD	12	57	[43]
BNT-BKT-BZnT	CSD	5	50*	[78]
BNTZr, BNTZr-BNTFe**	CSD	20	150*	[79]
BNT-Al	CSD	19.5	250*	[80]

*Values approximated from provided data

**indicates substrates other than Pt/buffer/Si were utilized

(X) indicates material is doped with X

Table 3.2 shows values for d_{33} taken from studies where piezoelectric properties of films were measured. Similar to the E_c data from table 3-1 a wide range of d_{33} values are observed even within similar material compositions. The highest reported d_{33} values (120-210pm/V) are reported in studies where epitaxy is promoted within the films through use of a highly textured or single crystal substrate [81],[75], [76]. In studies making use of Pt/buffer/Si substrates the reported BNT d_{33} value is slightly lower (47 pm/V) than the binary and ternary compositions where the majority of reported d_{33} values lie between 50 and 100pm/V.

Table 3.2 Reported values of d_{33} from BNT based thin film studies

System	Deposition Method	Measurement Technique	d_{33} [pm/V]	Reference
BNT	CSD	Contact AFM	47	[59]
BNT-BKT	CSD	Contact AFM	56	[53]
BNT-BKT	CSD	Contact AFM	98	[54]
BNT-BKT	CSD	PFM	75	[56]
BNT-BKT(Mn)	CSD	Contact AFM	67	[57]
BNT-BKT	CSD	PFM	76	[59]
BNT-BKT	CSD	Contact AFM	64	[60]
BNT-BKT-BT	CSD	PFM	79	[61]
BNT-BT(Rb)	CSD	PFM	86	[65]
BNT-BT(Li)	CSD	PFM	57.3	[66]
BNT-BT	CSD	Contact AFM	83	[69]
BNT-BT	CSD	Contact AFM	97.7	[73]
BNT-BT(Mn)**	PLD	PFM	124	[71]
BNT-BT-ST**	CSD	PFM	210	[75]
BNT-BT-ST**	CSD	PFM	200	[76]
BNT-BT-ST	CSD	PFM	120	[77]
BNT-BT-ST**	CSD	PFM	140	[82]
BNT-BKT-BMgT	CSD	DBLI	75	[43]
BNT-BKT-BZnT	CSD	PFM	40	[78]
BNT-Bal	CSD	Laser Vibrometer	57	[80]

****indicates substrates other than Pt/buffer/Si were utilized
(X) indicates material is doped with X**

Two major complicating factors must be taken into consideration when synthesizing a thin film version of a material with known bulk properties: substrate interactions and high surface to volume ratio.

Unlike bulk materials thin films must be deposited on a substrate that is often many times thicker than the film itself. As such substrate interactions play a dominant role in the properties realized from thin film materials. One of the more obvious substrate interactions is the generation of residual stress within the thin film due to mismatch in thermal expansion coefficients. As such many lead based thin film studies have investigated the impact of stress and film thickness on film properties [16], [83], [84]. Considerably fewer studies exist on residual stress impact on BNT based lead free thin films. Li et al. studied the impact of substrate interactions and residual stress in BNT-BT-ST ceramics on various substrate types (MgO, STO, and LaAlO₃) [76]. It was found that substrate material and residual stress can cause considerable change in the functional properties in BNT-BT-ST thin films. Figure 3.5 shows the P-E loop behavior of films on the three substrate materials. By $\sin^2\psi$ residual stress measurement it was found that MgO imparted the lowest residual stress while LaAlO₃ imparted the highest residual stress [76].

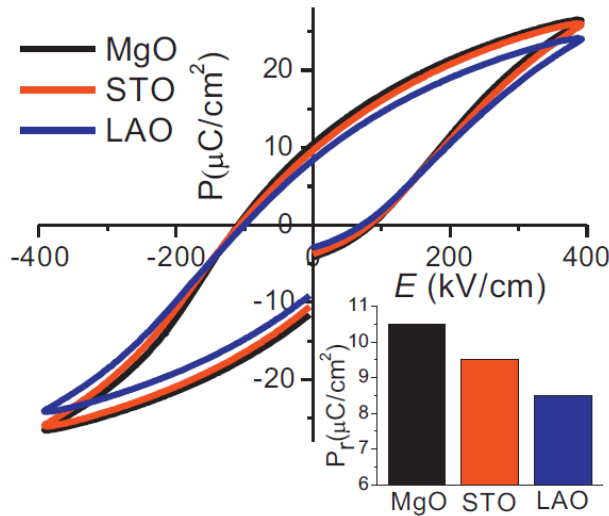


Figure 3.5 Polarization vs electric field loops from BNT-BT-ST thin films on three different substrate materials [75].

Another consideration that must be considered when processing thin film materials is the high surface to volume ratio. This can lead to a higher density of defects resulting from volatilization during high temperature processing. In most studies the use of excess amounts of volatile cations during synthesis is used to compensate for volatilization. Wu et al. evaluated the impact of changing Na and K excess in BNT-BKT

thin films [53]. As shown in figure 3.6 excess amount can have a considerable effect on the polarization behavior. This impact is likely due to modification of post anneal film stoichiometry and a change in the density of defects present in post anneal films.

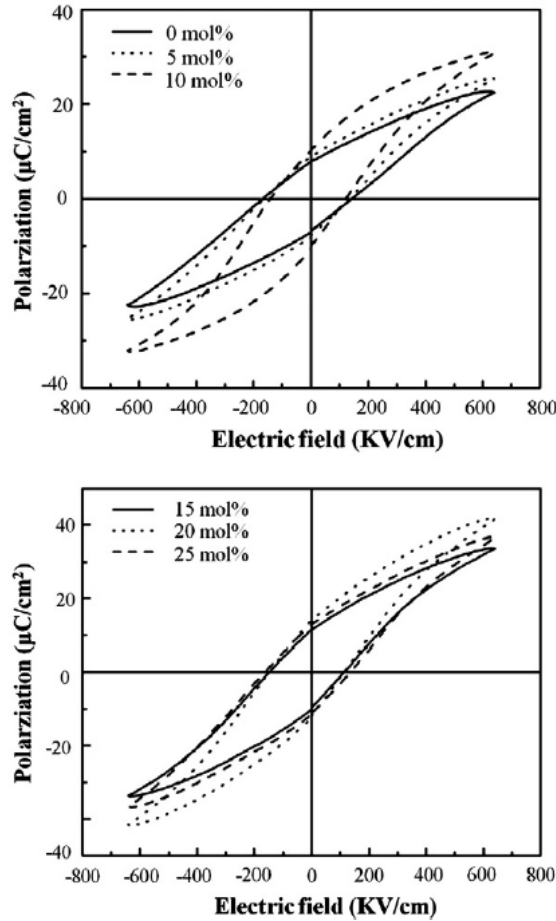


Figure 3.6 Impact of Na/K excess on BNT-BKT polarization vs electric field loops from Wu et al. [52].

In summary, piezoelectric lead-free thin film studies are considerably rarer than their bulk counterparts and cover a wide range of processing techniques, compositions, and methods for controlling properties. Due to the wide range of properties observed in BNT based thin film materials it is clear that processing conditions, synthesis routes, substrate choice and other factors have a drastic effect on film properties. As such, much more research must be completed to develop a more complete understanding of the numerous factors which influence lead-free thin film properties. The next section will describe the techniques and parameters used to process films for the research detailed in this thesis.

4. Experimental Methods

This section details the experimental methods used during the synthesis and characterization of thin film samples. In this study films were fabricated using chemical solution deposition CSD. Solutions were spin cast, pyrolyzed, and annealed in a rapid thermal annealing (RTA) system. This section will include details on solution synthesis, heat treatments, sample metallization, and specifics on characterization methods.

4.1 Solution Synthesis

Solutions were synthesized an inverse mixing order (IMO) solution processing route [20], [43], [62]. The precursors used in the process were bismuth (III) acetate (99.9999%, Alfa Aesar), sodium acetate trihydrate (99%, Macron), potassium acetate (99%, Macron), and titanium (IV) isopropoxide (97%, TCI). Precursors and solvents are weighed in amounts to generate a 0.5 M solution. Bismuth acetate is first dissolved in propionic acid at room temperature by stirring on a hotplate for approximately 1 hour. Sodium acetate trihydrate and potassium acetate are weighed in a dry nitrogen atmosphere and dissolved in methanol by stirring at room temperature for approximately 1 hour. The titanium isopropoxide is weighed and chelated in a dry nitrogen atmosphere using a mixture of acetic acid and a small amount of propionic acid. After each solution has been allowed to stir for approximately 1 hour an appropriate amount of the bismuth precursor solution is weighed into the chelated titanium solution. This solution is allowed to mix for approximately 1 hour before the sodium and potassium precursor solution is weighed into the titanium/bismuth solution mixture. After the final addition of the sodium and potassium precursor solution the final solution is allowed to mix for approximately 10 to 15 hours to ensure complete homogeneity before being used for deposition. Solution compositions and excess amounts are controlled by adjusting measured amounts of precursors during the solution synthesis process. Figure 4.1 shows a flowchart for the solution synthesis process.

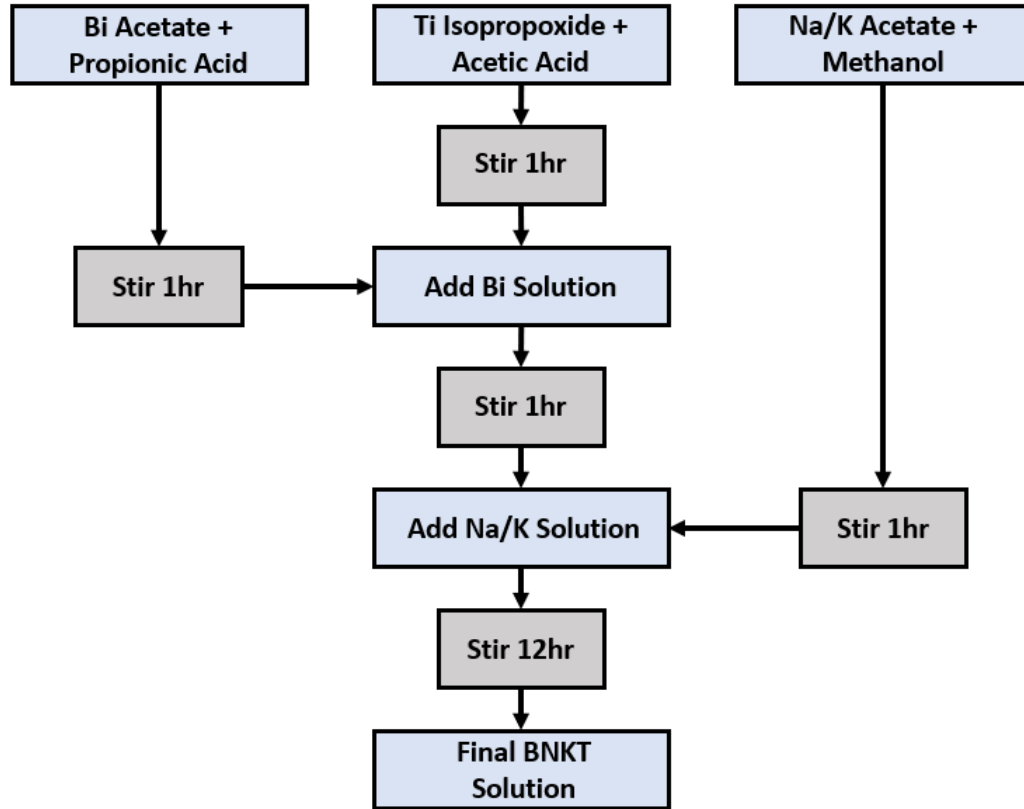


Figure 4.1 Solution synthesis flowchart

4.2 Thin Film Fabrication and Sample Metallization

The films were deposited on platinized silicon substrate stacks (Pt (110nm)/TiO_x(30nm)/SiO₂(500nm)/Si). The substrates were first cleaned through a 3-step sonication process in acetone, methanol, and isopropyl alcohol for 5 minutes each. Afterwards, the substrates are dried with a dry nitrogen gun and heated to 350°C for 2 minutes on ab hotplate to burn off any residual organic contaminants. The films were then wetted with the precursor solution and spin cast at 3000 rpm for 30 seconds. The pre-anneal heat treatment process includes a 1-minute dry at 100°C and a 4-minute pyrolysis at 350°C on a hotplate. Finally, an RTA anneal is performed at 700°C for 5 minutes with 100°C/s ramp rate and 2 slpm of UHP oxygen flow. Note that values listed in this section describe the general synthesis process. For samples prepared using modifications to the standard process the differences will be clearly stated in later sections. For a 0.5 M solution deposited using the above standard conditions the typical

per layer thickness achieved is approximately 70nm. Figure 4.2 shows a flowchart for the film deposition process.

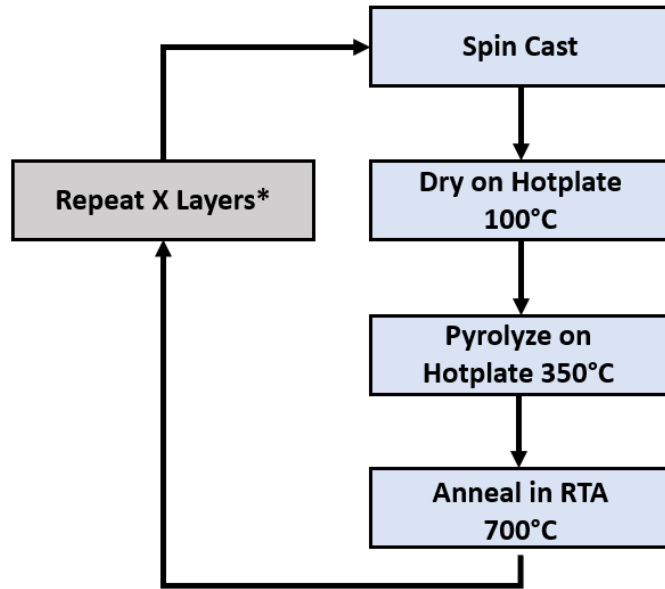


Figure 4.2 Thin film fabrication flowchart

For samples measured on the DBLI a polishing process was done on the back of the substrate to create a smooth reflective surface. The polishing process used 15 μ m, 5 μ m, 1 μ m and 0.3 μ m lapping paper. Films were protected using a layer of Kapton tape. Before deposition of electrodes a 15-minute 400°C heat cleaning was performed to remove any residue remaining from the tape layer. To prepare samples for electrical characterization, Pt top electrodes were sputtered through a shadow mask. The diameter of the electrodes on the shadow mask was 0.675mm with a space left for AFM characterization and a corner left clean for etching. To expose the bottom electrode, etching was done by applying 10% hydrofluoric acid to the corner of the film on a cotton tipped applicator.

4.3 Materials Characterization

After fabrication several standard characterization techniques were used to analyze the quality and properties of the resulting films. Crystallinity and phase purity were verified using a Bruker D8 Discover with CuK α radiation. An Asylum 3D atomic force microscope (AFM) was used to analyze surface morphology and roughness. 1 μ m by 1 μ m

as well as $5\mu\text{m}$ by $5\mu\text{m}$ AFM scans were taken on all samples. An HP 4192A impedance analyzer was used to measure dielectric constant and $\tan(\delta)$ over a frequency range of 0.1 to 10kHz. P-E and strain loops were taken concurrently using an aixACCT DBLI system. Strain and P-E loops were taken at 1kHz with fields up to 800kV/cm. To prepare for cross sectional SEM, samples were cleaved using a scribe and an iridium conduction layer was deposited using a Denton sputter coater. SEM scans were taken using a FEI Helios 650 Dual Beam SEM/FIB.

5. Process Optimization for BNKT Thin Films

Developing a specifically tailored deposition and annealing process for thin film materials is extremely important for the synthesis of films with optimal properties. CSD thin film materials synthesis is an extremely delicate and sensitive process and small differences in processing conditions can lead to drastic differences in film properties. Lead-free material systems in particular are sensitive to process conditions due to their complex chemistries, mechanical properties and highly volatile cations [3]. As such it is imperative that proper methodology is used to determine optimal processing conditions to achieve acceptable film quality. More control over environmental factors and conditions over the course of thin film material synthesis allows for more specific tuning and understanding of film properties. This section will cover process optimization experiments for cation excess, film pyrolysis, annealing temperature and time, ramp rate, and annealing atmosphere.

5.1 Excess Cation Optimization

One primary challenge that arises during process optimization for CSD BNKT is the high cation volatility. As seen in section 2.2.4 bismuth, sodium and potassium are all considerably volatile elements. During high temperature processing cation volatilization can lead to both the generation of defects and a change in the composition of the final film. One simple but effective method used to counter cation volatility is the inclusion of excess cations within the precursor solution. This section details an experimental approach to the optimization of excess amounts based upon phase purity and electrical characterization of the resulting films. Note that sodium and potassium are significantly more volatile than bismuth and, as such, the combinations of excess cations all include more percent excess sodium and potassium than bismuth.

An initial series of excess experiments were completed evaluating the effects of excess cation amounts on film phase and crystallinity, dielectric properties, polarization, and strain behavior. All films were three layers thick, pyrolyzed at 300°C for four minutes, and annealed in an RTA for 5 minutes at 700°C. The initial excess amounts

evaluated included 6% Bi excess with 8%, 10%, 12% and 14% Na/K as well as 8% Bi excess with 8% and 12% Na/K excess as shown in the list below.

- 6-8-8 Bi-Na-K
- 6-10-10 Bi-Na-K
- 6-12-12 Bi-Na-K
- 6-14-14 Bi-Na-K
- 8-8-8 Bi-Na-K
- 8-12-12 Bi-Na-K

Figures 5.1 and 5.2 show dielectric properties and polarization/strain curves for 6-8-8, 8-8-8, 6-12-12 and 8-12-12 Bi-Na-K excess amounts respectively.

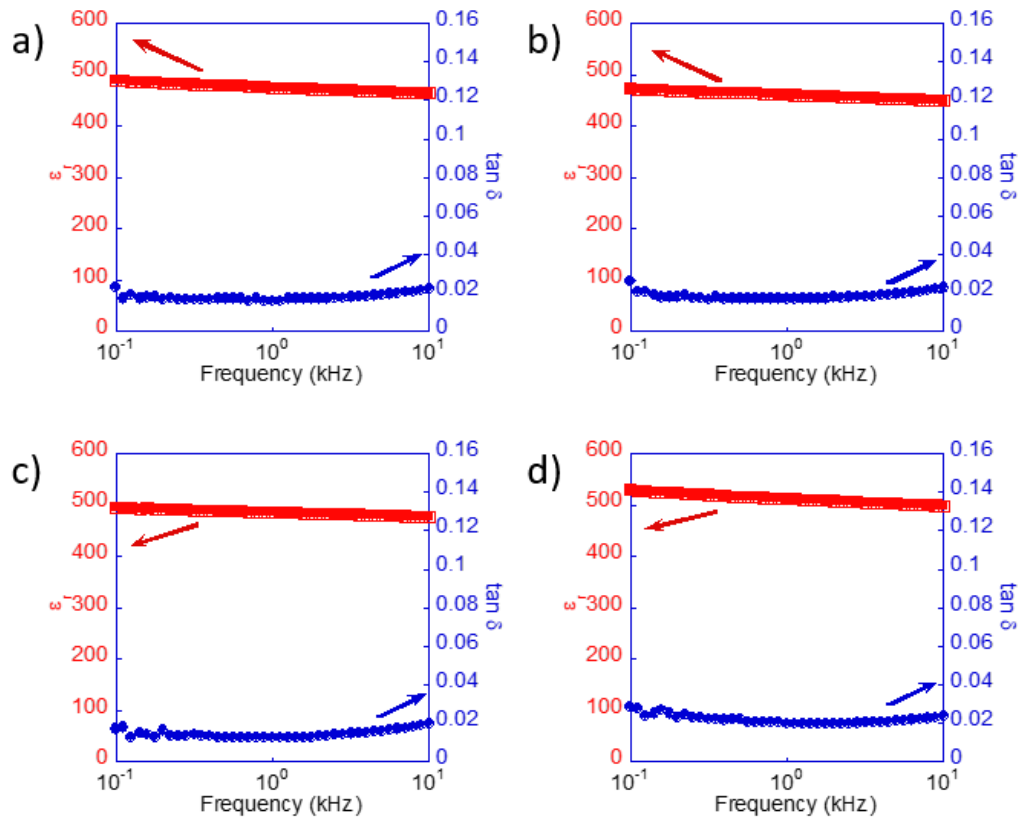


Figure 5.1 Dielectric constant and $\tan \delta$ as a function of frequency for a) 6-8-8 b) 8-8-8 c) 6-12-12 d) 8-12-12 Bi-Na-K excess in 80BNT-20BKT

From figure 5.1 it can be observed that dielectric loss remains relatively constant across all excess amounts. Dielectric constant remains constant between 6-8-8 and 6-12-12,

however, with the introduction of 8% Bi excess a reduction in dielectric constant occurs in 8-8-8 and an increase in dielectric constant occurs in 8-12-12. Since all excess values are the same in the 8-8-8 sample it is likely that the Bi to Na/K ratio is modified during the high temperature annealing phase due to Na/K being significantly more volatile. This likely leads to a slight change in composition causing the decrease in dielectric constant. Note that all samples were phase pure perovskites based on XRD scans.

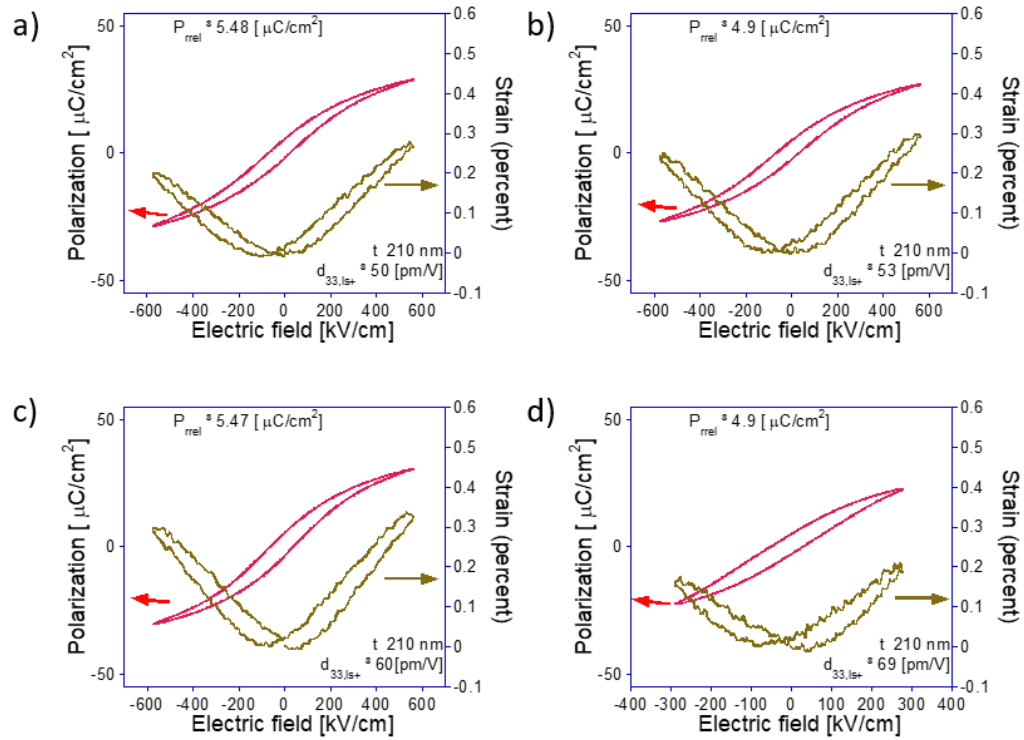


Figure 5.2 Polarization and strain response for a) 6-8-8 b) 8-8-8 c) 6-12-12 d) 8-12-12 Bi-Na-K excess in 80BNT-20BKT (P_{rel} represents relaxed remnant polarization)

From figure 5.2 note should be taken that the 8-12-12 scans only reach 300kV/cm rather than 600kV/cm due to a significant decrease in breakdown field. This decrease in breakdown field occurs due to an excess of cations present within the material.

Polarization behavior remains constant for all samples (With the exception of the 8-12-12 sample.). A distinct increase of about 10pm/V in d_{33} is observed between the 8% Na/K and 12% Na/K excess amounts while no trend is observed with increasing bismuth excess. Due to the distinct increase in piezoelectric response between the 8% and 12%

Na/K it was found that Na/K excess has a greater impact on functional properties than bismuth excess. As such a broader study on the effects of Na/K excess was performed. Figure 5.3 shows dielectric and polarization/strain properties for 6-10-10, 6-12-12, and 6-14-14 Bi-Na-K excess.

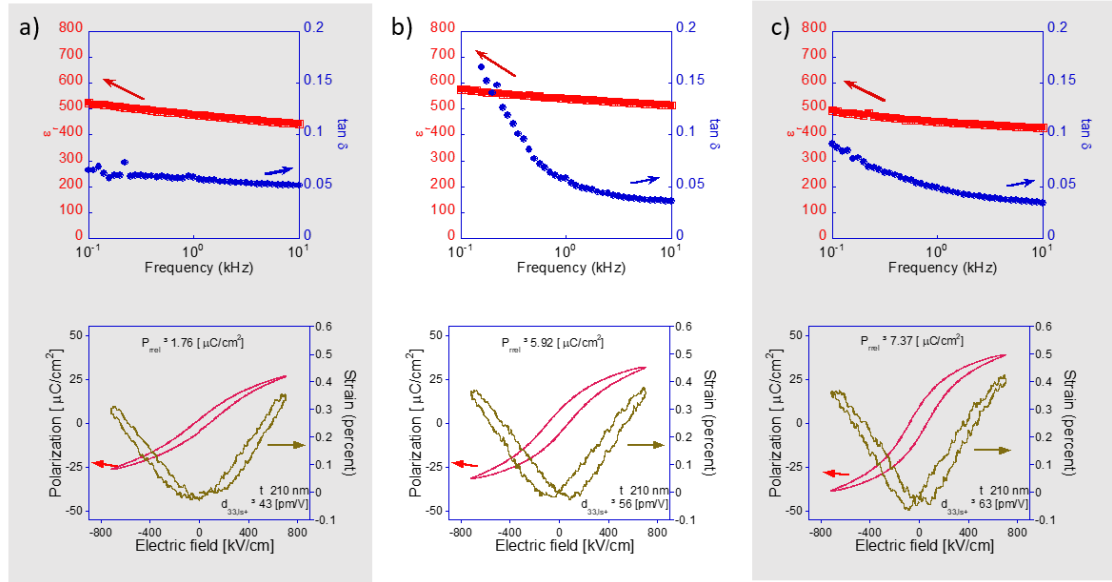


Figure 5.3 Dielectric constant, loss, polarization, and strain behavior for a) 6-10-10, b) 6-12-12 and c) 6-14-14 Bi-Na-K excess in 80BNT-20BKT (P_{rel} represents relaxed remnant polarization)

The 6-10-10 sample displays a softer and more linear polarization hysteresis than the other two samples. This is indicative of a change in cation ratios and film stoichiometry pushing the material further from the MPB observed at 80BNT-20BKT. This is supported further by an observed decrease in piezo response. The 6-12-12 excess sample displays a significantly higher dielectric constant (540 at 1 kHz) than the 6-10-10 or 6-14-14 samples (approximately 450 at 1 kHz). The highest d_{33} value (63 pm/V) was observed in the 6-14-14 sample. From figure 5.3 the optimal excess would appear to be 6-14-14, however, a large percentage of electrodes for samples made at this excess amount were shorted and unmeasurable while very few were shorted in 6-12-12 excess samples. As such, 6-12-12 was selected as the ideal excess for initial processing conditions. One important consideration to make is the increase in $\tan \delta$ between the initial set of samples and the second set of samples. This is indicative of factors which are not controlled such as ambient temperature and humidity impacting film properties. Additionally, these

experiments were performed in a relatively new and almost completely clean RTA system.

After approximately 1 year of operation excess experiments were repeated as a second phase was observed in XRD scans of 80BNT-20BKT samples using 6-12-12 Bi-Na-K excess. Figure 5.4 shows XRD scans for 6-8-8, 6-10-10, and 6-12-12 excess amounts from the repeated excess experiments.

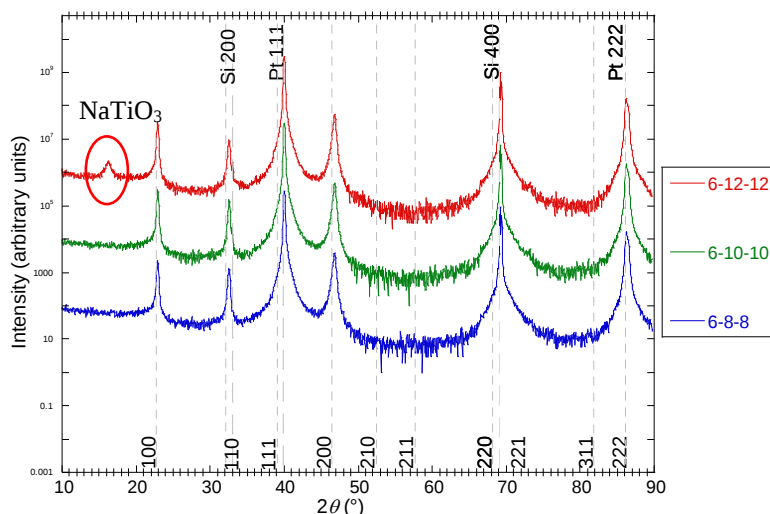


Figure 5.4 XRD scans for repeated 6-8-8, 6-10-10, and 6-12-12 Bi-Na-K excess experiments

From figure 5.4, the 6-12-12 excess amount (previously selected as the optimal excess for this synthesis process) now shows an unwanted NaTiO_3 second phase in the X-ray scan. The cause for this is due to the buildup of oxide in the RTA chamber causing an increased base oxide partial pressure in the annealing environment. This in turn inhibits some cation volatilization thus reducing the amount of required film excess to maintain the desired stoichiometry in the final film material.

In summary, excess is an extremely important factor to control when attempting to synthesize high quality BNKT films of specific composition. It is important to include more excess Na/K than Bi since Na/K are significantly more volatile. Optimal excess amounts are sensitive to process conditions and must be adjusted as conditions change. For our process 6-12-12 percent Bi-Na-K excess was ideal and as the RTA chamber became more contaminated with oxides over the course of months of processing the optimal required excess decreased to 6-10-10 percent excess Bi-Na-K.

5.2 Optimization of Pyrolysis Temperature

The first heat treatment after deposition and drying is pyrolysis. At this stage of processing organic material from the solution is vaporized ideally leaving behind a layer cations and oxygen. The specific conditions during the pyrolysis step can have drastic effects on film microstructure and electrical performance. For example, temperatures that are too high can cause crystallization to begin to occur impacting film properties. Pyrolysis temperatures and times that are too low can lead to residual organics which remain within the film after the pyrolysis step. These unwanted residual organics then violently decompose during the high temperature annealing step again imparting porosity and defects to the film. Pyrolysis temperatures evaluated included 300°C, 350°C, and 400°C for 4 minutes. All films were phase pure and displayed stable ferroelectric hysteresis loops. The only trend observed with pyrolysis temperature was an increase in both loss and dielectric constant with increasing temperature. Figure 5.5 shows dielectric and loss data for all three pyrolysis temperatures.

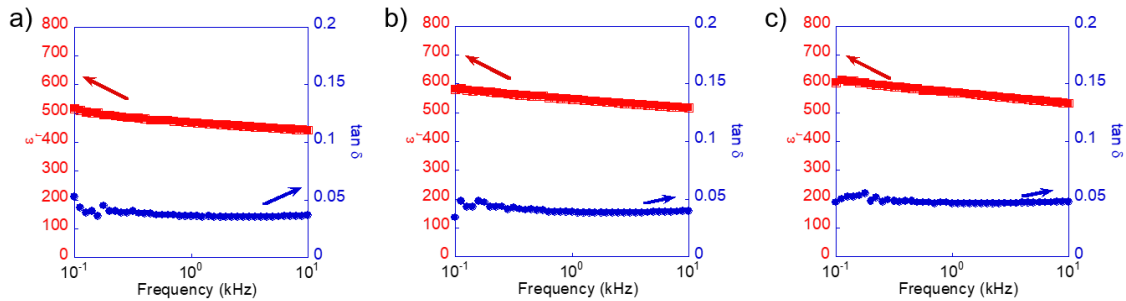


Figure 5.5 Dielectric constant and $\tan \delta$ of BNKT thin films pyrolyzed at a) 300°C, b) 350°C, and c) 400°C

Dielectric constant at 1kHz was 468 at 300°C, 546 at 350°C, and 570 at 400°C. $\tan \delta$ at 1kHz stays relatively steady between 300°C and 350°C only increasing from 0.036 to 0.039. A more considerable increase occurs at 400°C with a $\tan \delta$ at 1 kHz of 0.046. 350°C was chosen as the optimal condition due to only achieving a modest increase in dielectric constant with a more considerable increase in loss between 350°C and 400°C.

5.3 Optimization of Anneal Conditions

Annealing was done using an Allwin21 rapid thermal processing system RTP. The following sections describe optimization of various RTA conditions and their impact on

film properties. A general set of goals for the anneal step is to form a pure crystalline perovskite phase, minimize the generation of defects such as pores, and to mitigate any change in stoichiometry due to loss of volatile cations. Many of the annealing condition experiments were done as a collaboration with Dr. Austin J. Fox whose PhD thesis is referenced here and on some experimental data plots in this section [85].

5.3.1 Optimization of Ramp Rate

For the ramp rate experiments all films were annealed at 700°C for 5 minutes. Ramp rates from 200°C to 700°C of 75°C/s, 100°C/s, 125°C/s, 150°C/s were evaluated. No trend in crystallinity and phase purity was observed in the BNKT binary system. Increased ramp rate lead to a decrease in dielectric loss ($\tan \delta$) and also showed some impact on dielectric constant which was maximized in the 75°C/s and 150°C/s samples. Figure 5.6 shows dielectric constant and loss measurements as well as piezoelectric and ferroelectric loops for all four ramp rates.

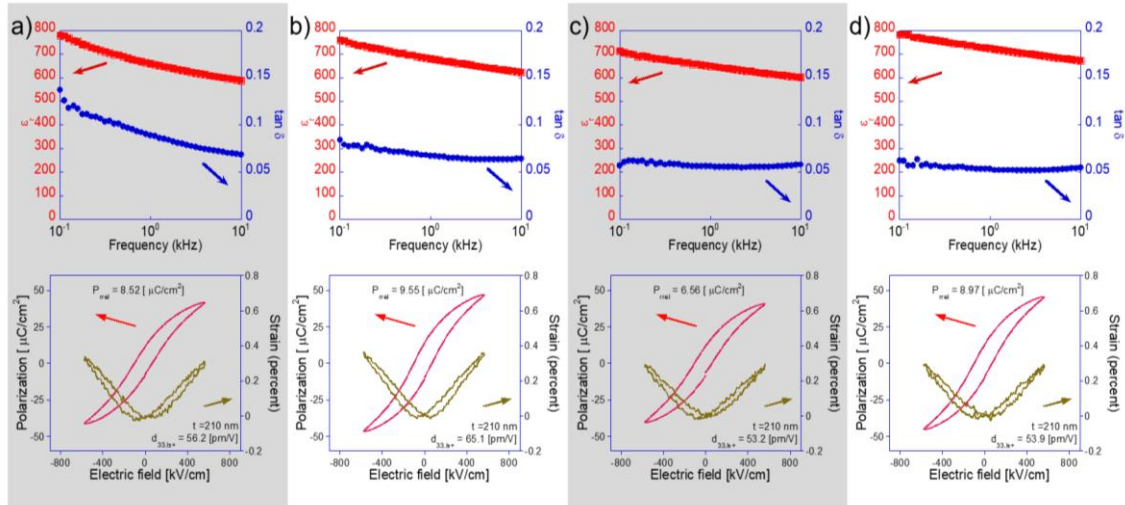


Figure 5.6 Dielectric constant, $\tan \delta$, polarization loops, and strain loops for a) 75°C/s, b) 100°C/s, c) 125°C/s, and d) 150°C/s (P_{rel} represents relaxed remnant polarization)

No major trends with composition were observed in polarization behavior. Piezoelectric constant was maximized at 100°C/s (65pm/V) with a range from 53pm/V to 65pm/V. Similar experiments were completed by Dr. Fox with a range of ramp rates from 25°C/s

to 100°C/s. It was similarly observed that 100°C/s displayed the highest piezoelectric constant (64pm/V) with a wide range from 16-64pm/V for the data set [85].

5.3.2 Optimization of Anneal Temperature

RTA anneal temperature experiments were performed using a 100°C/s ramp rate and 5-minute hold time. All films were 210nm thick. Anneal temperatures ranging from 650°C-800°C were evaluated. It was found that at temperatures above 700°C a bismuth titanate second phase was formed and for temperatures below 700°C XRD peak intensities were considerably lower than those at 700°C indicating reduced crystallinity. As the 700°C anneal temperature produced films which were both phase pure and displayed high XRD peak intensities it was selected as the optimal anneal temperature [85].

5.3.3 Optimization of Annealing Atmosphere

Oxygen flow experiments were performed to evaluate the impact of annealing atmosphere on film properties. All films were 210nm thick annealed at 700°C for 5minutes with a ramp rate of 100°C/s. Four separate O₂ flow rates were evaluated: 0.5 SLPM, 2SLPM, 6SLPM, and 10SLPM. For all samples excluding the 2 SLPM O₂ flow sample a sodium titanate second phase was detected by X-ray diffraction. Figure 5.7 shows XRD scans for the oxygen flow rate experiments.

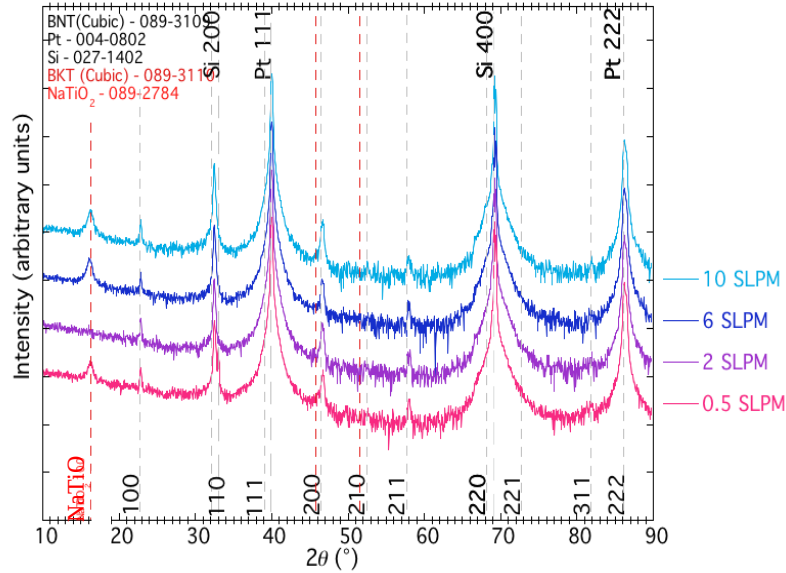


Figure 5.7 XRD patterns for films annealed with 0.5, 2, 6, and 10 SLPM O₂ flow [85]

Additionally, oxygen flow rate impacted the dielectric and piezoelectric properties of the films. The highest dielectric constant was observed in the 2SLPM and 6SLPM samples, however, this was accompanied by increased loss the highest of which was observed in the 2 SLPM sample ($\tan \delta = 0.1$ at 1kHz). Dielectric constant and loss data are shown in figure 5.8. As can be seen no clear trend in dielectric constant and loss was observed with increasing O₂ flow. Piezoelectric constant values ranged from 56pm/V to 96pm/V, however, again no clear trend was observed with increasing O₂ flow. The largest piezoelectric response was observed in the 2SLPM and 6SLPM samples with d_{33} values of 96pm/V and 69pm/V respectively. 2SLPM of O₂ flow was chosen as an optimal condition due to the inhibited formation of a NaTiO₂ second phase from the XRD scans [85].

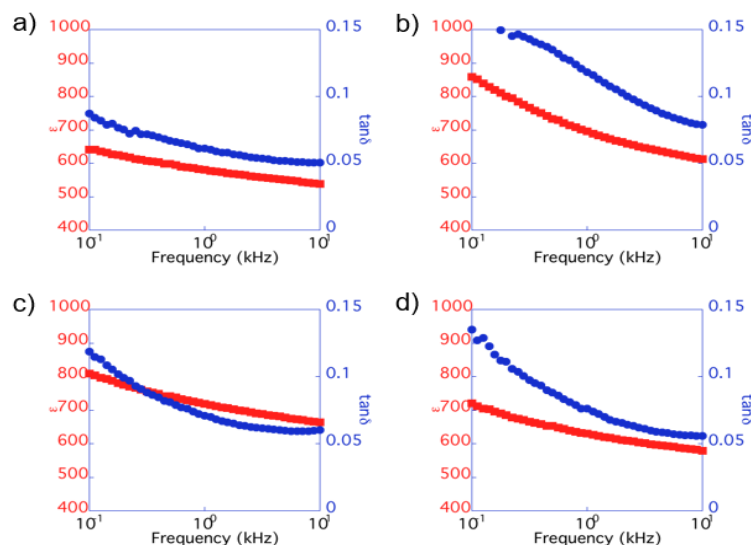


Figure 5.8 Dielectric constant and $\tan(\delta)$ vs frequency for BNT-BKT film annealed with a) 0.5 SLPM, b) 2 SLPM, c) 6 SLPM, d) 10 SLPM [85]

5.4 Summary

The primary goals for process optimization are to maximize film crystallinity, maintain phase purity, achieve desired stoichiometry and minimize defects. Optimal conditions for cation excess, pyrolysis temperature, ramp rate, annealing temperature, and oxygen flow were identified. The optimal values for CSD process conditions follow: pyrolysis 350°C for 4 minutes, anneal ramp rate 100°C/s, anneal temperature 700°C, anneal time 5 minutes, O₂ flow 2SLPM.

Due to high surface to volume ratio and the use of highly volatile cations, steps must be taken to control film stoichiometry during high temperature processing. Excess optimization is one method for control of film stoichiometry during the high temperature anneal step. The optimal excess amount is highly sensitive to changes in annealing conditions and must be adjusted accordingly. For example, as excess oxide contaminants built up in the RTA chamber the optimal excess amount had to be reduced to realize phase pure perovskite films.

The results found in this study can provide a starting point and methodology for the development of future processes for lead-free CSD thin films. Additionally, the

optimization of process conditions allows for experimentation with minimized variation in film properties due to process conditions.

6. Compositional Dependence of BNKT Thin Film Properties

This chapter details the impact bismuth sodium titanate to bismuth potassium titanate (BNT to BKT) ratio has on thin film properties. Dielectric constant and loss, ferroelectric response, piezoelectric performance, and film microstructure will be compared for three separate compositions: 40BNT-60BKT, 60BNT-40BKT, and the morphotropic phase boundary composition 80BNT-20BKT. Additionally, films of the above compositions will be prepared using two different optimized annealing procedures. The first is the rapid thermal annealing process route. Optimization for this process route is described in chapter 5. The second is a box furnace anneal process route optimized previously by Dr. Yu Hong Jeon, Dr. Ashley Mason, Dr. Joel Walenza-Slabe, and Dr. Austin Fox [85]–[88]. A comparison of film properties realized from each process route will both provide insight into the pros and cons of each and the impact that processing conditions have on compositional trends in BNKT thin film properties.

6.1 Compositional Dependence of BNKT Films Processed via Rapid Thermal Annealing

This section details the compositional dependence of crystallinity, microstructure, and surface morphology for BNT-BKT films prepared via a rapid thermal annealing route. For details on process optimization procedures refer to chapter 5. All films were prepared from 0.5 molar solutions spun at 3000 rpm for 30 seconds, dried at 100°C for 1 minute, pyrolyzed at 350°C for 4 minutes, and annealed each layer for 5 minutes at 700° with 2 SLPM O₂ flow and 100°C/s ramp rate. Excess ranged from 6% Bi, 10% Na, and 10% K to 6% Bi, 12% Na, and 12%K. For details on selections of excess amounts refer to section 5.1.

6.1.1 Compositional Dependence of Film Microstructure and Crystallinity

This section provides data on film crystallinity and microstructure as a function of composition. All three compositions show similar properties in terms of crystallinity. Figure 6.1 shows XRD scans for all three compositions.

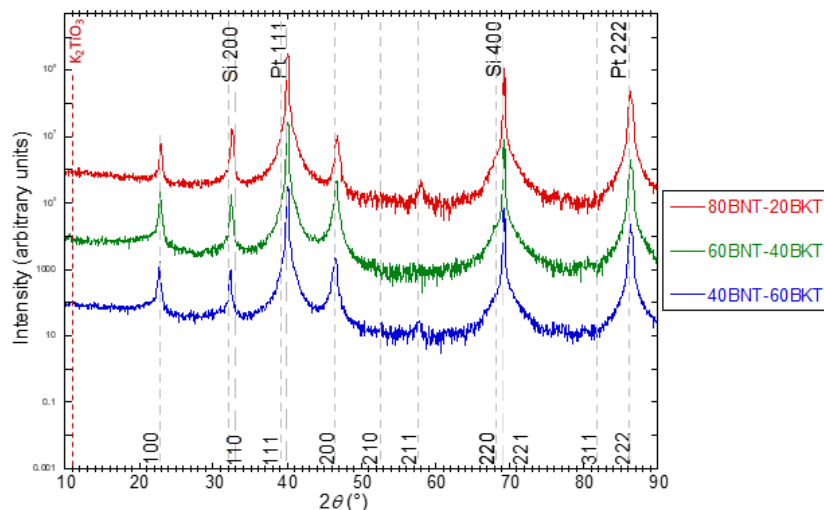


Figure 6.1 XRD patterns for 40BNT-69BKT, 60BNT-40BKT, and 80BNT-20BKT thin films

Based on the XRD scans the 60BNT-40BKT and 80BNT-20BKT films displayed a phase pure randomly oriented perovskite structure while a low intensity potassium titanate second phase peak was observed in the 40BNT-60BKT film. Additionally, AFM scans were taken on films of all three compositions in order to compare surface morphology and surface roughness. Figure 6.2 shows AFM scans and surface roughness values for all three compositions.

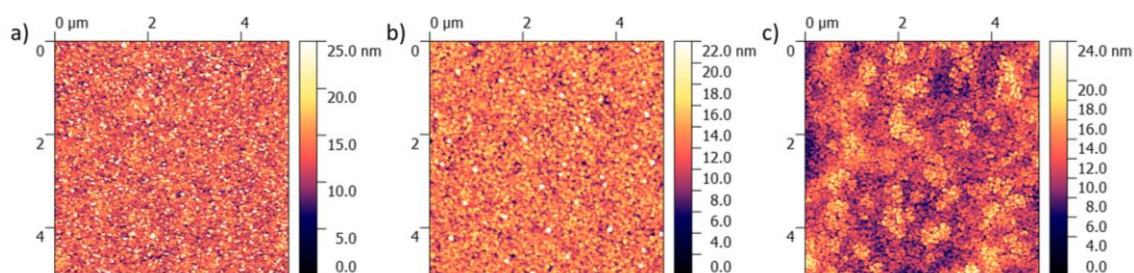


Figure 6.2 AFM scans for a) 40BNT-60BKT, b) 60BNT-40BKT, and c) 80BNT-20BKT thin films. RMS Surface roughness values were a) 4.00nm, b) 2.92nm, and c) 2.90nm.

No distinct trend in surface roughness with composition was observed. RMS surface roughness values fell between 2.9nm and 4nm indicating that the films are relatively smooth which is ideal for electrical characterization of the films. Small surface precipitates were observed in the 40BNT-60BKT film and in the 60BNT-40BKT film. The 60BNT-40BKT film had a significantly lower density of surface precipitates. Based

on the XRD scans and film compositions these surface precipitates likely consist of a potassium titanate phase. These surface precipitates are also responsible for the increased roughness observed in the 40BNT-60BKT film (RMS roughness = 4nm) over 60BNT-40BKT and 80BNT-20BKT films (RMS roughness = 2.90nm and 2.92nm respectively). The formation of the surface precipitates could likely be eliminated through the adjustment of potassium excess for compositions with higher BKT content, however, due to the low concentration and small size they are unlikely to have any drastic impact on morphological and electrical characterization.

The cross-sectional microstructure of the films was observed by SEM. The films were first cleaved using a diamond scribe, then mounted and coated in an iridium conduction layer. A distinct trend in film microstructure was observed with composition. For reference, the ideal microstructure associated with optimal ferroelectric, dielectric and piezoelectric performance in PZT is a dense columnar microstructure such as that shown in figure 6.3 from Kazushi et al. [89] Figure 6.4 shows cross sectional SEM scans for all three BNT-BKT compositions. Finally, figure 6.5 shows a higher magnification image of an 80BNT-20BKT film with labels for each unique layer of the substrate/film stack.

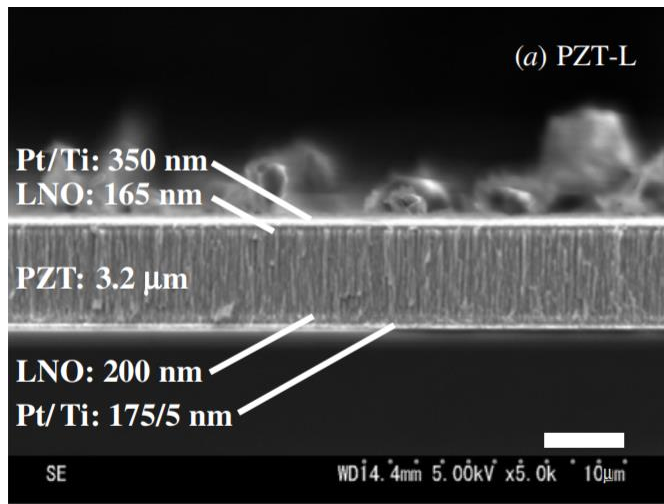


Figure 6.3 Cross sectional SEM image of a dense columnar PZT microstructure from Kobayashi et al. [90]

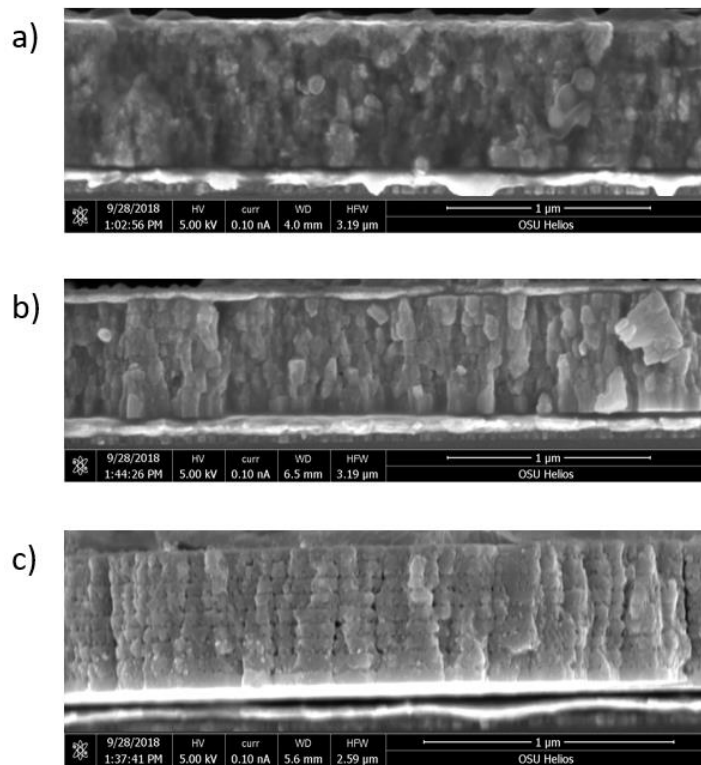


Figure 6.4 Cross sectional SEM scans of a) 630nm thick 40BNT-60BKT, b) 560nm thick 60BNT-40BKT, and c) 630nm thick 80BNT-20BKT films.

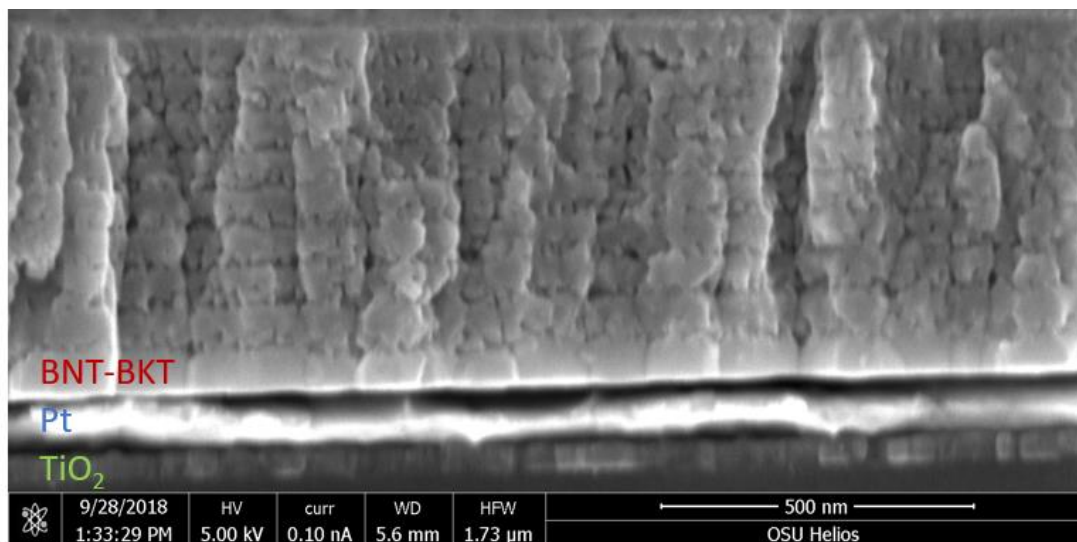


Figure 6.5 Increased magnification SEM image of the 630nm 80BNT-20BKT thin film with TiO₂ buffer layer and Pt layer labeled.

Porosity in dielectrics can lead to a number of negative impacts on piezoelectric actuator material performance. Porosity can both cause a decrease in dielectric constant as well causing dielectric breakdown to occur at lower fields. As such, it is desirable that porosity be minimized or eliminated. As can be seen in figures 6.4 and 6.5 a considerable amount of porosity forms between layers in the 80BNT-20BKT film. It should also be noted that no porosity occurs at the bottom of the first layer deposited directly on platinum. A dense columnar microstructure exists only through the bottom layer. Very little porosity is observed in the bulk of each layer. Interestingly, a considerably lower density of interlayer porosity is observed in the 60BNT-40BKT film. The dense columnar microstructure can be observed continuously through the first two layers for a considerable portion of the 60BNT-40BKT film. The 40BNT-60BKT film displays no porosity between layers, however, the microstructure of the film is drastically altered from the 80BNT-20BKT and 60BNT-40BKT films. No evidence of a columnar microstructure is observed even in the first layer of the 40BNT-60BKT film.

6.1.2 Compositional Dependence of Dielectric Properties, Polarization Response, and Piezoelectric Response

This section details the compositional dependence of dielectric, piezoelectric and ferroelectric properties in BNT-BKT thin films prepared via a rapid thermal annealing process. The ideal properties for a piezoelectric actuator material are as follows: maximized dielectric constant, minimized dielectric loss, and maximized piezoelectric response. Figure 6.6 shows dielectric constant and loss as a function of frequency for all three BNT-BKT compositions.

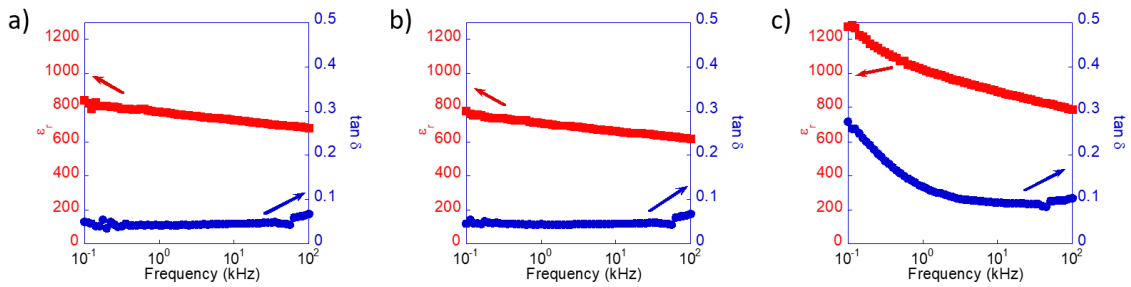


Figure 6.6 Dielectric constant and dielectric loss as a function of frequency for a) 40BNT-60BKT, b) 60BNT-40BKT, and c) 80BNT-20BKT thin films

The 40BNT-60BKT and 60BNT-40BKT compositions showed very similar dielectric properties to one another while the 80BNT-20BKT shows considerably different behavior. In terms of dielectric loss the 40BNT-60BKT and 60BNT-40BKT both showed considerably lower loss ($\tan \delta = 0.04$ at 1 kHz) than the 80BNT-20BKT MPB composition ($\tan \delta = 0.13$ at 1 kHz). Dielectric constant was also considerably higher in the 80BNT-20BKT film ($\epsilon_r = 1024$ at 1 kHz) than the 40BNT-60BKT ($\epsilon_r = 795$ at 1 kHz) and 60BNT-40BKT ($\epsilon_r = 708$ at 1 kHz) compositions. The slight dip in dielectric constant between the 40BNT-60BKT and the 60BNT-40BKT compositions could be explained by the increase in interlayer porosity in the 60BNT-40BKT films. The more considerable increase in dielectric constant observed in the 80BNT-20BKT composition occurs due to the characteristic increased disorder at the MPB composition. Figure 6.7 shows ferroelectric and piezoelectric loops for all BNT-BKT compositions.

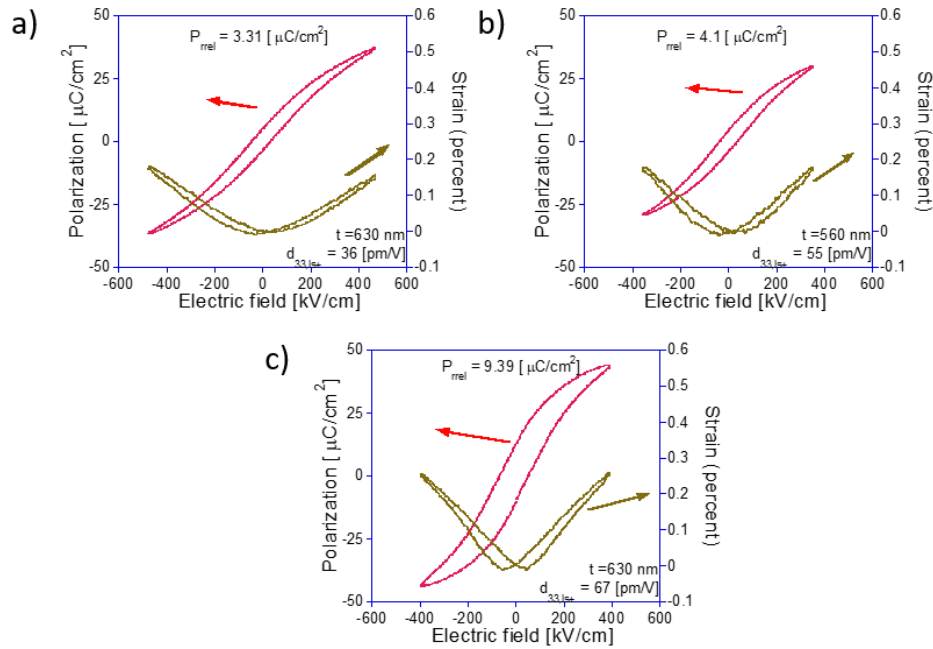


Figure 6.7 Ferroelectric and piezoelectric loops for a) 40BNT-60BKT b) 60BNT-40BKT and c) 80BNT-20BKT (P_{rel} represents relaxed remnant polarization)

Distinct trends were observed in ferroelectric behavior with composition. Compositions further from the MPB show more relaxorlike behavior while compositions near the MPB show more traditional ferroelectric behavior. As the composition nears the MPB at 80BNT-20BKT remnant polarization also increases. The 40BNT-60BKT composition shows the lowest remnant polarization ($P_{rel} = 3.31 \mu\text{C}/\text{cm}^2$) while the 60BNT-40BKT composition shows a slightly higher remnant polarization ($P_{rel} = 4.1 \mu\text{C}/\text{cm}^2$) and the 80BNT-20BKT composition shows the highest remnant polarization ($P_{rel} = 9.39 \mu\text{C}/\text{cm}^2$). High remnant polarizations are associated with traditional ferroelectrics where ferroelectric domains dominate while low remnant polarizations are associated with relaxor ferroelectrics dominated by polar nanoregions (see section 2.1.4). No clear trend in coercive field was observed between the 40BNT-60BKT and 60BNT-40BKT films, however, it was found that the 80BNT-20BKT film displayed significantly higher coercive field. Additionally, all films showed higher negative coercive field than positive coercive field. The negative/positive coercive fields for the 40BNT-60BKT, 60BNT-40BKT, and 80BNT-20BKT films were $-42.7/34.2 \mu\text{C}/\text{cm}^2$, $-36.3/35.7 \mu\text{C}/\text{cm}^2$, and $-67.7/51 \mu\text{C}/\text{cm}^2$ respectively. Compositional trends were also observed in piezoelectric response. Piezoelectric constant increases as compositions near the MPB. The 40BNT-60

BKT film had a d_{33} of 36 pm/V, the 60BNT-40BKT had a d_{33} of 55 pm/V and the 80BNT-20BKT film displayed a d_{33} of 67 pm/V.

6.2 Compositional Dependence of Box Furnace Annealed BNKT Thin Films

In this chapter compositional trends are evaluated for films annealed in a box furnace rather than an RTA. The purpose for this section is to compare the effectiveness of each process route as well as show the importance of process control when evaluating compositional trends.

Films were annealed for 10 minutes at 700°C in a box furnace. This technique is significantly less controlled than the optimized RTA process as ramp rate cannot be adjusted and cooling rate is significantly faster when films are removed from the furnace rather than cooling in the RTA chamber. Additionally, no oxygen flow or atmospheric control was used during the box furnace anneal. Drying and pyrolysis steps were kept identical to the RTA process (1 minute at 100°C drying step, 4 minute 350°C pyrolysis). Due to the longer anneal step and the lack of atmospheric control a larger amount of excess cations are included in solutions for box furnace processing. The excess amount used was 8% excess bismuth and 16% excess sodium and potassium. All films are 5 layers and are approximately 350nm thick.

6.2.1 Thin-film Microstructure and Crystallinity

This section shows data on microstructure, surface morphology and crystallinity as a function of composition for box furnace films (see section 6.1.1 for similar data on RTA annealed films). Figure 6.8 shows x-ray scans for 40BNT-60BKT, 60BNT-40BKT, and 80BNT-20BKT films.

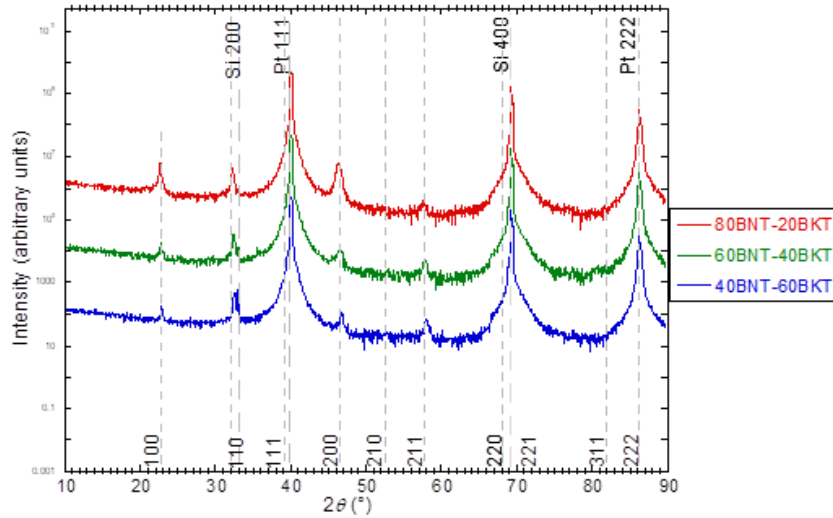


Figure 6.8 XRD scans for BB films of various composition annealed using a box furnace method.

All films are phase pure, however, compared to RTA annealed films (see figure 6.1) the 100 peak intensities are significantly lower. Additionally, the 80BNT-20BKT film shows higher 100 peak intensity than the 60BNT-40BKT and 40BNT-60BKT films which was not observed in the RTA annealed films. Based on this data the optimized RTA annealing process was superior to the box furnace method for crystallizing BNT-BKT films particularly for compositions containing higher proportions of BKT (40BNT-60BKT and 60BNT-40BKT). 100 to 110 peak intensity ratios for the 40BNT-60BKT and 60BNT-40BKT films made in the box furnace were 0.37, 0.51 respectively while those made in the RTA were 0.41 and 1.56 respectively.

Figure 6.9 shows AFM surface scans for box furnace films of all three compositions.

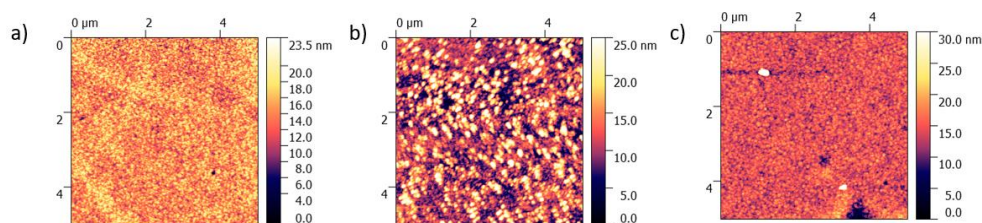


Figure 6.9 AFM scans for box furnace films a) 40BNT-60BKT, b) 60BNT-40BKT, c) 80BNT-20BKT. RMS roughness values for a), b) and c) were 2.3nm, 5.3nm, and 2.5nm respectively.

Surface roughness for the three compositions were similar in magnitude to those measured in films processed via RTA (see figure 6.2). The roughness of the 60BNT-40BKT film is significantly higher than the 40BNT-60BKT and 80BNT-20BKT films. In the case of the RTA annealed films the 40BNT-60BKT films showed the highest surface roughness. It can be concluded based on these two sets of data that process conditions as well as uncontrolled factors such as ambient conditions (humidity, room temperature) have a more dominant impact on surface morphology than film composition. In terms of surface morphology, no major difference in film quality is apparent between the box furnace and RTA processing routes.

Figure 6.10 shows cross sectional SEM scans of all three box furnace films.

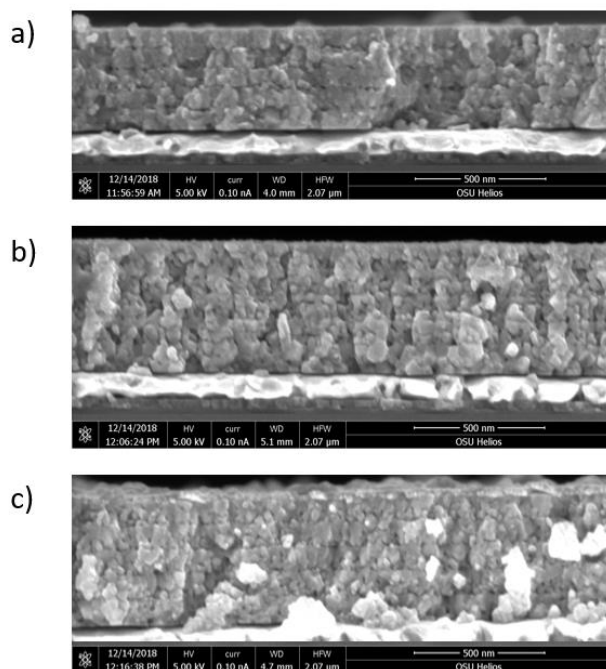


Figure 6.10 Cross sectional SEM scans of box furnace films with the following compositions: a) 40BNT-60BKT, b) 60BNT-40BKT, and 80BNT-20BKT.

The films processed in the box furnace displayed significantly less dense microstructures than those processed in the RTA (see figure 6.4). The box furnace 40BNT-60-BKT film has a significantly less porosity than the 60BNT-40BKT or the 80BNT-20BKT films however displays significantly increased porosity compared to the 40BNT-60BKT film processed in the RTA. No clear difference in porosity is observed between the box furnace 60BNT-40BKT and the box furnace 80BNT-20BKT films. In the RTA annealed films, a clear trend of increasing porosity with increasing BNT to BKT ratio was observed. Based on these observations the RTA is significantly more effective for synthesizing films with dense microstructures. Film density is compositionally dependent based on SEM scans of films synthesized using the optimized RTA process, however, this trend could not be fully observed in the box furnace films due to the considerable increase in porosity compared to the RTA annealed films.

6.2.2 Thin-film Dielectric Properties, Ferroelectric Response, and Piezoelectric Response

This section details the dielectric, ferroelectric, and piezoelectric properties of films annealed in the box furnace with a range of compositions. These properties will also be compared to films processed using the optimized RTA process. Figure 6.11 shows dielectric constant and loss over a range of frequencies for the box furnace films.

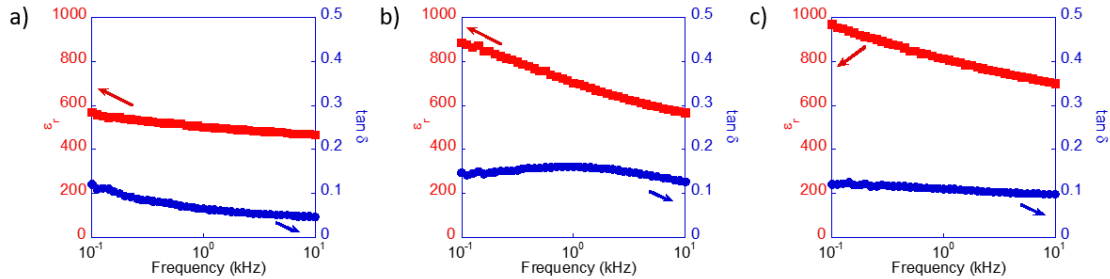


Figure 6.11 Dielectric constant and loss from 1 to 10 kHz for box furnace films of compositions: a) 40BNT-60BKT, b) 60BNT-40BKT, and c) 80BNT-20BKT.

A clear trend in dielectric constant with composition was observed in the box furnace films. Dielectric constant is lowest in the 40BNT-60BKT film (502 at 1kHz), higher in the 60BNT-40BKT film (704 at 1kHz) and maximized in the 80BNT-20BKT film (812 at 1kHz). Dielectric constants are significantly lower than the RTA annealed films for the 40BNT-60BKT (795 at 1kHz for the RTA film) and 80BNT-20BKT (1024 at 1kHz for the RTA film) compositions. Dielectric constant is approximately equivalent for the 60BNT-40BKT film (708 at 1kHz for RTA film), however, the box furnace 60BNT-40BKT film displays significantly higher loss ($\tan \delta = 0.16$ at 1kHz) than the 60BNT-40BKT film made in the RTA ($\tan \delta = 0.04$ at 1kHz). The large difference in loss for the 60BNT-40BKT films makes any comparison of the dielectric constants for these two films less reliable. The 40BNT-60BKT films made in the box furnace showed similar loss to those made in the RTA ($\tan \delta = 0.06$ for the box furnace film and 0.04 for the RTA film at 1kHz). The 80BNT-20BKT films also showed similar loss for the two annealing techniques ($\tan \delta = 0.11$ for the box furnace film and 0.13 for the RTA film at 1kHz).

Figure 6.12 shows ferroelectric and piezoelectric hysteresis loops for the box furnace annealed films.

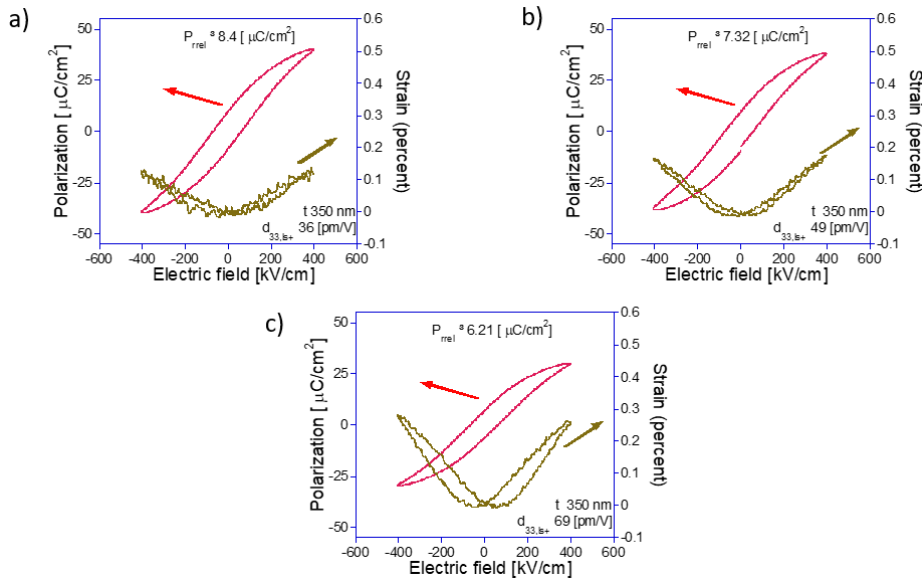


Figure 6.12 Ferroelectric and piezoelectric hysteresis loops for box furnace films with compositions a) 40BNT-60BKT, b) 60BNT-40BKT, and c) 80BNT-20BKT.

Of all the measured thin film properties piezoelectric response shows the least dependency on anneal method. The box furnace annealed films show nearly identical compositional trends in piezoelectric coefficient to those observed in the RTA annealed samples (see figure 6.7). 40BNT-60BKT displays the lowest coefficient, 60BNT-40BKT shows a higher piezoelectric coefficient, and 80BNT-20BKT shows the highest piezoelectric coefficient. No notable change in piezoelectric coefficient values for films with equivalent composition but different annealing step were observed.

The polarization loop for the box furnace 60BNT-40BKT film is discontinuous due to high loss. This along with the high loss from the dielectric data indicates the box furnace anneal method has more variability in realized dielectric and ferroelectric properties than the RTA anneal.

6.3 Summary

Several compositional trends were observed from the films annealed in the RTA. Dielectric constant increases with increasing BNT content up to the MPB at 80BNT-20BKT. Dielectric loss is considerably lower for compositions containing a larger ratio of BKT than the MPB composition. Interlayer porosity increases as compositions near the

MPB composition. Piezoelectric coefficient increases as composition nears the MPB with 40BNT-60BKT displaying the lowest coefficient, 60BNT-40BKT displaying a higher coefficient and the 80BNT-20BKT composition displaying the highest coefficient. No clear compositional trend in crystallinity or surface morphology was observed indicating that other factors such as process conditions, solution chemistry, and ambient conditions likely have more impact on these properties.

Box furnace films displayed considerably more unstable dielectric properties compared to the RTA annealed films. 100 peak intensities were significantly lower in box furnace films compared to the RTA annealed films indicating that the RTA process is the more optimal process for film crystallization. A large increase in interlayer porosity and decrease in film density was observed in the box furnace films compared to the RTA annealed films. Additionally, the 60BNT-40BKT films showed uncharacteristically high loss indicating that box furnace annealing conditions may be less repeatable and more dependent on uncontrolled factors than RTA process.

7. Conclusions and Recommended Future Work

This section focuses on presenting the primary conclusions from the studies performed and how these conclusions can apply to future research and optimization of BNT-BKT based piezoelectric materials. For specific more detailed conclusions please refer to the summary sections (see section 5.4 and section 6.3).

The BNT-BKT process optimization experiments (see chapter 5) provided data on the impact of various process conditions used on film properties and presented the optimal conditions for a specific CSD synthesis route. This information can be used as a starting point when developing synthesis processes for other CSD synthesis routes, chemistries and compositions. Excess amount in particular is important to optimize as it can have a large impact on film properties and the optimal amount can change based on process conditions, solution chemistry, and even states of RTA chamber contamination. Optimal conditions for pyrolysis temperature, ramp rate, annealing temperature, and oxygen flow were identified. The optimal values for CSD process conditions follow: pyrolysis 350°C for 4 minutes, anneal ramp rate 100°C/s, anneal temperature 700°C, anneal time 5 minutes, O₂ flow 2SLPM. Cation excess was optimized at 6%Bi, 12% Na/K in the clean RTA chamber and was decreased to 6%Bi and 10% Na/K after the RTA chamber became more contaminated via volatilized cations.

Many compositional trends were identified in BB during the experiments presented in chapter 6. Additionally, a comparison of properties realized from two different annealing methods, box furnace and RTA, was made for all three evaluated compositions. This data is useful when selecting a composition for a specific application and for reference when making more complex designs for piezoelectric applications such as multilayer composites. Additionally, this data can be used to help identify whether composition change is to blame for unexpected differences in film properties during future process optimization experiments. It was found that dielectric constant and piezoelectric coefficient increases as compositions near the MPB between 40BNT-60BKT and the MPB composition 80BNT-20BKT. It was also found that the MPB composition displays higher dielectric loss than compositions closer to 40BNT-60BKT. Additionally, cross sectional microstructure images revealed that porosity also increases

as compositions neared the MPB. The comparison between the box furnace anneal method and the RTA annealing methods showed that film crystallinity and film microstructure are the most dependent properties on annealing method. A considerable decrease in film density was observed for all compositions annealed in the box furnace compared to those annealed in the RTA. 100 peak intensity was considerably higher in the X-ray scans of the RTA films compared to the box furnace films. Additionally, it was found that dielectric constant and piezoelectric coefficient were considerably less dependent on annealing conditions and more dependent on film composition.

While an increased understanding of the impact of process conditions and composition of BNT-BKT binary thin films was achieved with the presented experiments much more effort must be put forth to develop thin films of acceptable quality for use in a manufacturing or application design setting. In order to further increase the realized quality of BNT-BKT based piezoelectric thin films the following future work is recommended. Using knowledge of process optimization to develop thin film versions of more complex chemistries such as BNT-BKT based ternary compositions with enhanced properties. Additional process design such as a multistep RTA process or more specific atmospheric control during annealing. Composite designs, for example, layering different compositions of BB or BB based ternary compositions to design a piezoelectric with favorable properties for specific applications. Analysis of compositional and processing trends for additional important film properties such as residual stress. Finally, performing process optimization and compositional experiments on BB based materials used in released structures to identify effects on piezoelectric response with reduced substrate contribution.

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