

AN ABSTRACT OF THE DISSERTATION OF

Yu Hong Jeon for the degree of Doctor of Philosophy in Materials Science
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Title: Development of Bi-based Lead-free Piezoelectric Materials: Thin Film
Piezoelectric Materials via PVD and CSD Routes

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Brady J. Gibbons

Piezoelectric materials have been widely used in electromechanical actuators, sensors, and ultrasonic transducers. Among these materials, lead zirconate titanate $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) has been primarily investigated due to its excellent piezoelectric properties. However, environmental concerns due to the toxicity of PbO have led to investigations into alternative materials systems. Bismuth-based perovskite piezoelectric materials such as $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (BNT - BKT), $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ - BaTiO_3 (BNT - BKT - BT), $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ - $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BKT - BZT), and $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ - $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BNT - BKT - BMgT) have been explored as potential alternatives to PZT. These materials systems have been extensively studied in bulk ceramic form, however many of the ultimate applications will be

in thin film embodiments (*i.e.*, microelectromechanical systems). For this reason, in this thesis these lead-free piezoelectrics are synthesized in thin film form to understand the structure-property-processing relationships and their impact on the ultimate device response.

Fabrication of high quality of 0.95BKT – 0.05BZT thin films on platinized silicon substrates was attempted by pulsed laser deposition. Due to cation volatility, deposition parameters such as substrate temperature, deposition pressure, and target-substrate distance, as well as target overdoping were explored to achieve phase pure materials. This route led to high dielectric loss, indicative of poor ferroelectric behavior. This was likely a result of the poor thin film morphology observed in films deposited via this method. Subsequently, 0.8BNT – 0.2BKT, 85BNT – 10BKT - 5BT, and 72.5BNT – 22.5BKT – 5BMgT (near morphotropic phase boundary composition) were synthesized via chemical solution deposition. To compensate the loss of A-site cations, overdoped precursor solutions were prepared. Crystallization after each spin cast layer were required to produce phase pure material. Good permittivities and low dielectric loss over the frequency range of 100 Hz to 1 MHz were obtained. Dependent upon annealing conditions, various film morphologies and compositional distributions were observed via electron microscopy and composition measurements. As opposed to previously reported work, good ferroelectric response at low frequency (200 Hz) were found. For BNT – BKT – BMgT, the maximum polarization was over 50 $\mu\text{C}/\text{cm}^2$ with high d_{33f} of 75 pm/V were

obtained. Additionally, the extrinsic and intrinsic contributions to the dielectric response for solution-derived BNT – BKT and BNT – BKT – BMgT films were studied via Rayleigh analysis. For sub-switching fields a good agreement between predicted polarization behavior from Rayleigh analysis and experimentally measured polarization indicated the validity of this approach for BNT-based thin films.

Results of this thesis proved that high quality bismuth-based piezoelectric thin films with good electrical response can be fabricated with suppression of cation volatility for various processing conditions. Furthermore, these thin films can be considered as alternatives to PZT thin films as potential candidates for piezoelectric-based microelectromechanical systems (MEMS).

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Development of Bi-based Lead-free Piezoelectric Materials: Thin Film

Piezoelectric Materials via PVD and CSD Routes

by

Yu Hong Jeon

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APPROVED:

Major Professor, representing Materials Science

Director of the Materials Science Program

Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Yu Hong Jeon, Author

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Chapter 1. Introduction

Piezoelectric materials, which convert electrical energy into mechanical energy or vice versa, have been developed for many years for applications such as electromechanical actuators, sensors, and ultrasonic transducers.[1]

Researchers in the field of microelectromechanical systems (MEMS) have paid strong attention to the incorporation of piezoelectric thin films into MEMS due to the need for devices with better actuation at lower applied voltages.[2-4] Among the best candidate piezoelectric materials is lead zirconate titanate, $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT), a solid solution of ferroelectric PbTiO_3 and antiferroelectric PbZrO_3 . PZT has been utilized into MEMS applications due to its superior piezoelectric properties resulting from the existence of structural instabilities that enhance the piezo-response.[5, 6] This is due to the electronic structure of Pb^{2+} with a lone pair of $6s^2$ electrons, as well as the formation of a morphotropic phase boundary (MPB).[7, 8] However, the environmental concerns due to the toxicity of lead and the disposal of lead-based electronics are a major concern. Recent worldwide environmental regulations such as Waste from Electrical and Electronic Equipment (WEEE), Restriction of Hazardous Substances (RoHS), and End-of-Life Vehicles have become a driving force requiring lead to be replaced with more environmentally benign materials.[9] In light of this, there have been numerous efforts to develop new materials that have comparable or higher

piezoelectric properties as that of PZT, only without including lead as a major component.

Perovskite type materials such as BaTiO_3 (BT), $(\text{Bi}_{1/2}, \text{Na}_{1/2})\text{TiO}_3$ (BNT), $(\text{Bi}_{1/2}, \text{K}_{1/2})\text{TiO}_3$, and KNbO_3 (KN) and their solid solutions have been investigated as potential candidates for lead-free piezoelectric systems.[10, 11] Bi^{3+} has a similar electronic structure to Pb^{2+} , with a lone pair of $6s^2$ electrons. When these Bi-based materials are prepared as solid solutions with other tetragonal perovskites such as PbTiO_3 (PT), BKT, and BT, a similar structural instability as in PZT can be found.[12] Therefore, Bi-based perovskites have been extensively researched as a potential alternative for PZT.

There are many previous works on bismuth-based materials including binary and ternary solid solutions such as BNT – BKT, BNT – BT, BKT – BZT, BNT – BKT – BT, BNT – BKT – BLT, BNT – BKT – BMgT. (BZT = $\text{Bi}(\text{Zn}_{1/2}, \text{Ti}_{1/2})\text{O}_3$, BLT = $(\text{Bi}_{1/2}, \text{Li}_{1/2})\text{TiO}_3$, BMgT = $\text{Bi}(\text{Mg}_{1/2}, \text{Ti}_{1/2})\text{O}_3$)[12-17] Relatively good remanent and saturation polarizations were observed in these systems, as well as large dielectric constants and low loss tangents over a wide frequency range. However, there is still a lack of progress in synthesizing these materials in thin film embodiments. Due to the anisometric nature of thin films, it is even more difficult to control volatile elements like Bi, Na, and K during deposition and processing, thus it has been a significant challenge to understand if these promising properties can be reproduced in thin film form.[18]

The goal of this thesis is to develop high quality bismuth-based perovskite thin films via pulsed laser deposition (PLD), a physical vapor deposition (PVD) method, and chemical solution deposition (CSD) techniques. The specific objectives are as follows:

1. Develop $(\text{Bi}_{1/2}, \text{K}_{1/2})\text{TiO}_3 - \text{Bi}(\text{Zn}_{1/2}, \text{Ti}_{1/2})\text{TiO}_3$ (BKT – BZT) thin films via pulsed laser deposition.

- Polycrystalline thin film are deposited on platinized silicon. To control the cation volatility, overdoped targets (those with excess amounts of cations) were prepared via conventional solid state processing. Deposition parameters such as substrate temperature, deposition pressure (O_2), target – substrate distance, and laser power were investigated to produce high quality thin films.

2. Develop $(\text{Bi}_{1/2}, \text{Na}_{1/2})\text{TiO}_3 - (\text{Bi}_{1/2}, \text{K}_{1/2})\text{TiO}_3$ (BNT – BKT) thin film near MPB compositional regions.

- Chemical solution deposition was utilized to produce polycrystalline BNT – BKT thin films. To compensate the volatility of cations, overdoped precursor solutions were utilized. To achieve enhanced electrical properties annealing conditions were varied and compositional studies were performed to confirm the final composition of crystallized BNT – BKT thin films.

3. Develop $(\text{Bi}_{1/2}, \text{Na}_{1/2})\text{TiO}_3 - (\text{Bi}_{1/2}, \text{K}_{1/2})\text{TiO}_3 - \text{BaTiO}_3$ (BNT – BKT – BT) thin film near MPB compositional regions.

- Similar approaches of overdoping and annealing condition studies were used as above to optimize properties of these films. Polarization hysteresis loops as a function of temperature was observed, as well as dielectric behavior.

4. Develop $(\text{Bi}_{1/2}, \text{Na}_{1/2})\text{TiO}_3 - (\text{Bi}_{1/2}, \text{K}_{1/2})\text{TiO}_3 - \text{Bi}(\text{Mg}_{1/2}, \text{Ti}_{1/2})\text{O}_3$ (BNT – BKT – BMgT) thin film.

- Similar approaches to the previous two approaches were used to achieve high quality BNT – BKT – BMgT thin films. Dielectric and ferroelectric properties as a function of annealing temperature were investigated. Piezoresponse of BNT – BKT – BMgT films was obtained via double beam laser interferometer.

Elemental distribution and quantitative composition of the films were observed.

5. Characterize the dielectric nonlinearity in BNT – BKT and BNT – BKT – BMgT thin films.

- The intrinsic and extrinsic contributions to the dielectric properties were investigated by Rayleigh analysis. The sub-switching ac field dependence of the dielectric permittivity at different frequencies was obtained. The measured hysteresis loop and calculated hysteresis loop from Rayleigh analysis were compared, which verified the applicability of the Rayleigh law.

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Chapter 2. Background and literature review

This chapter reviews the relevant literature for this dissertation. A general background of ferroelectric and piezoelectric materials is provided. The ferroelectric domain structures will be discussed along with intrinsic and extrinsic effects. Finally, the current state-of-the-art for lead-free piezoelectric materials will be reviewed and an overview of thin film deposition methods such as pulsed laser deposition and chemical solution deposition will be described.

2.1. Dielectrics

A dielectric material is an electrical insulator resulting from its large energy band gap. When an external electric field is introduced to a dielectric, the material undergoes polarization through the finite rearrangement of charge.[1] The polarization induces a dielectric displacement forming dipoles in the material. When a dielectric material is inserted between parallel conductive plates, the dipoles are aligned according to the direction of an applied electric field and additional charge is stored on the plates. As illustrated in Figure 2.1, the charge on the capacitor plates increases from Q_0 to Q and this increase in capacitance or the charge storage ability of the dielectric material is defined as permittivity ϵ_r (or dielectric constant).

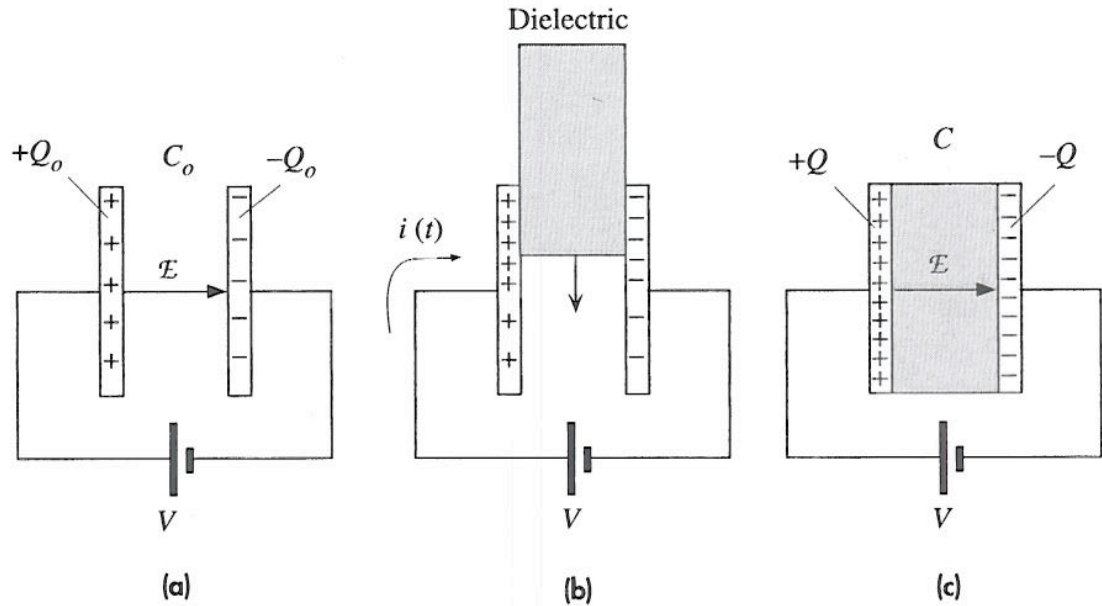


Figure 2.1 Illustrations of the charge storage ability by a dielectric (a) free space between the plate capacitors (b) dielectric material is inserted between the plates (c) the increase in the capacitance after inserting a dielectric material.[2]

An important concept in a dielectric is the dipole moment. The dipole consists of the same value but opposite sign of charges separated by a distance d . The dipole moment as a vector from the center of negative charge to the center of positive charge is given by:

$$\vec{p} = q\vec{d} \quad (2.1)$$

where q is the charge and d is the distance. Polarization is the total dipole moment in a unit volume and defined by:

$$\vec{P} = N\vec{p} \quad (2.2)$$

where N is the number of dipoles per unit volume.

The induced dipole moment is dependent on the applied electric field and the coefficient called polarizability α :

$$\vec{p} = \alpha\vec{E} \quad (2.3)$$

To express the dependence of the polarization on the electric field, electric susceptibility is introduced and is defined by

$$\vec{P} = \chi_e \epsilon_o \vec{E} = (\epsilon_r - 1) \epsilon_o \vec{E} \quad (2.4)$$

where χ_e is the electric susceptibility defined as $\frac{1}{\epsilon_o} N\alpha = \epsilon_r - 1$, ϵ_o is the

permittivity of vacuum and ϵ_r is the relative permittivity.

The electric field between parallel plates after the dielectric is inserted is given by:

$$E = \frac{V}{d} = \frac{Q}{Cd} = \frac{Q}{\epsilon_o \epsilon_r A} \quad (2.5)$$

where Q is the charge, C is capacitance, and A is the area of electrode.

If the distance between two plate electrodes is thought of as the dielectric thickness t , Equation (2.5) can be rewritten in terms of dielectric constant as:

$$\varepsilon_r = \frac{Ct}{\varepsilon_0 A} \quad (2.6)$$

The polarization is generated via the alignment of permanent or induced dipoles under the applied electric field. There are 4 different contribution mechanisms to the polarization on the microscopic scale including electronic, ionic, orientation, and space charge.[3] Electronic polarization arises from the displacement of the negatively charged electron cloud surrounding the positive nucleus of an atom. Secondly, ionic polarization is created when cations and anions react in opposite directions to an applied field. Thirdly, dipolar or orientation polarization results from reorientation of the permanent dipoles in the direction of the applied field. Finally, space charge (interfacial) polarization arises from the build-up of charge at the interface of two regions in a material through migration or hopping of charge carriers. Figure 2.2 schematically illustrates the different polarization mechanisms and the relative permittivity of a dielectric material is the sum of these contributions.

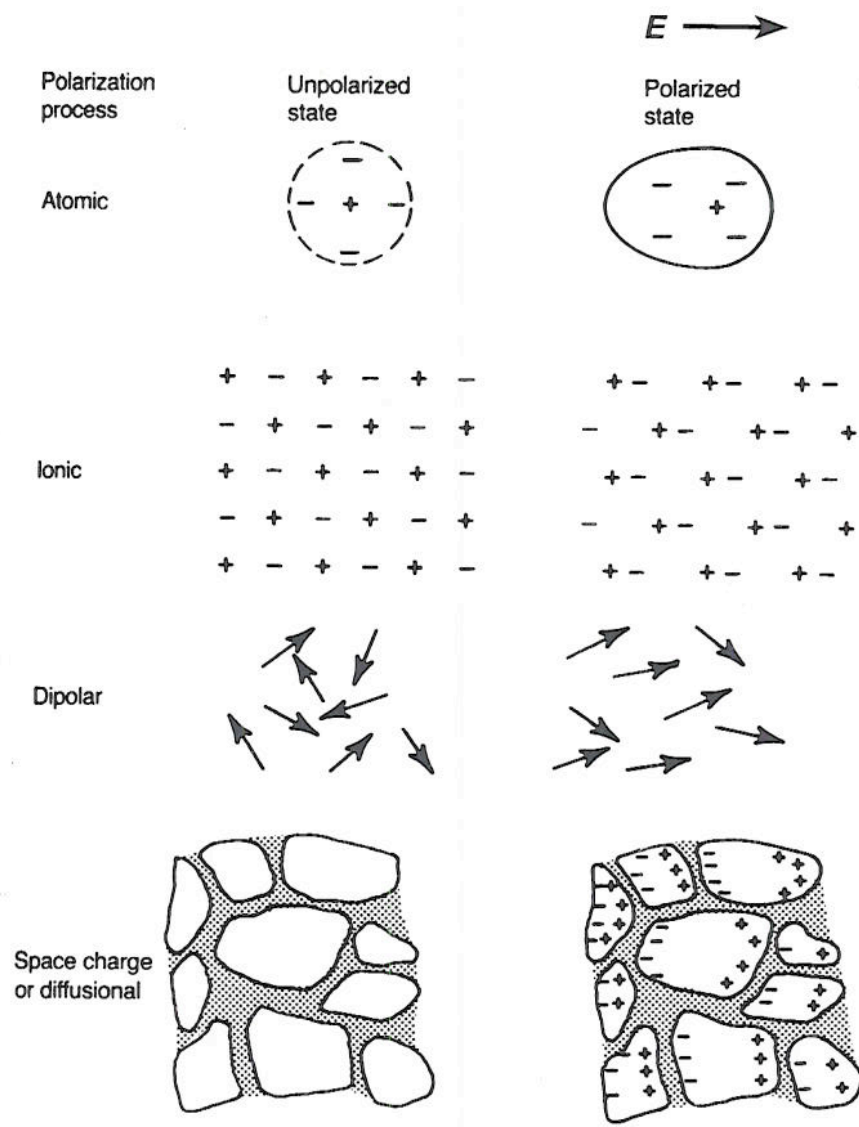


Figure 2.2 The 4 polarization mechanisms. [1]

When a dielectric material is under dc field, it shows static dielectric behavior. However, when an alternating field is applied, the polarization of the material leads to an ac dielectric constant that could be different from the static

dielectric constant. In this case, the permittivity is recognized as a complex quantity and is expressed by:

$$\varepsilon^* = \varepsilon'_r - j\varepsilon''_r \quad (2.7)$$

where ε'_r and ε''_r are the real and imaginary parts of the permittivity respectively.

The loss tangent is defined as:

$$\tan \delta = \frac{\varepsilon''_r}{\varepsilon'_r} \quad (2.8)$$

and describes the dissipation of electromagnetic energy in a reactance.

Since different polarization mechanisms have different rates of dielectric response, the permittivity of a dielectric material is also frequency dependent. Figure 2.3 shows the real and imaginary parts of the permittivity as a function of the frequency. As frequency increases, some polarization mechanisms are no longer active because the reorientation of dipoles cannot follow the electric field. In light of this, the real part of the permittivity drops and a corresponding peak in loss tangent is also observed. This phenomenon is related to the relaxation or resonance of the different polarization modes in the material.[2]

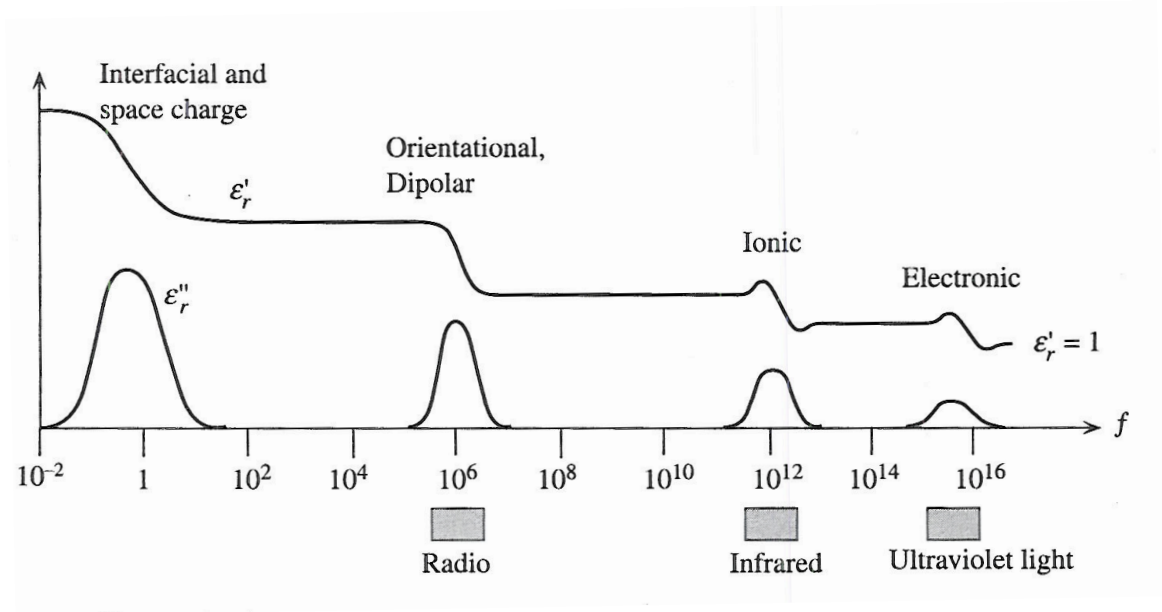


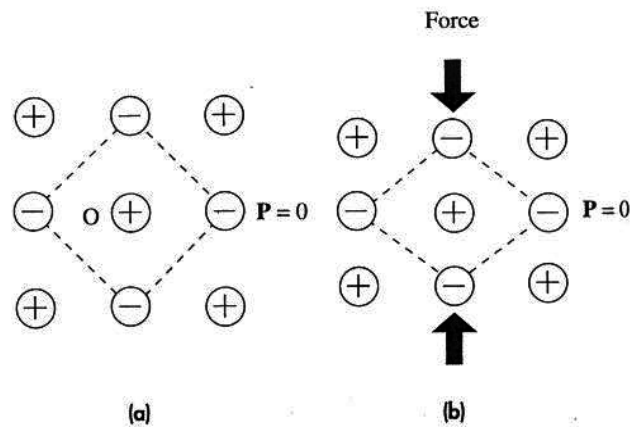
Figure 2.3 The frequency dependence of the real and imaginary parts of the permittivity. [2]

2.2 Piezoelectricity

Piezoelectricity was first discovered by Jacques and Pierre Curie who found that pressure produced an electrical charge in several crystals such as quartz, zinc-blende, and tourmaline.[4] Piezoelectricity is classically defined by Cady as an electric polarization created by an applied mechanical stress in certain crystal classes. The amount and sign of the generated polarization are dependent on the magnitude and direction of the applied stress. [5]

Crystals are divided into 32 different point groups characterized by different symmetry elements such as centers of symmetry, axes of rotation, mirror planes, and combinations of these. Furthermore, these 32 point groups

can be categorized into the 7 basic crystal systems: cubic, hexagonal, tetragonal, rhombohedral (trigonal), orthorhombic, monoclinic and triclinic. Piezoelectricity requires non-centrosymmetric crystals. Of the 32 total point groups, 21 are non-centrosymmetric and, except for one class, 20 of these exhibit piezoelectricity.[6] Figure 2.4 describes the state of polarization with and without an applied force on a rock-salt crystal that has an inversion center. Under stress, the positions of the positive and negative charges change but the centers of these charges do not shift. The net polarization is still zero, equal to the unstressed crystal. This shows that a center of symmetry destroys piezoelectricity.



*Figure 2.4 The state of the net polarization of NaCl type crystal
(a) in the absence of an applied stress and (b) under force [7]*

Piezoelectricity has both a direct and indirect or converse effect. The direct effect is mentioned above where polarization occurs under mechanical stress. The indirect or converse effect is where an applied electric field generates

mechanical strain or distortion depending on the polarity. These two effects are represented in Equations 2.9 and 2.10 respectively:

$$P_i = d_{ij} X_j \quad (2.9)$$

$$x_j = d_{ji} E_i \quad (2.10)$$

where P_i is an induced polarization, d_{ij} is a piezoelectric coefficient, X_i is the stress, x_j is the induced strain, and E_i is the applied electric field.

Electric field and polarization are first rank tensors or vectors, but stress and strain are second rank tensors and the piezoelectric coefficient is a third rank tensor. Reduced notations with 2-subscript notation for a 3rd rank tensor and 1-subscript notation for a 2nd rank tensor are used in Equation 2.2 and 2.3. In general, second and third rank tensors have 9 and 27 components respectively, but by consideration of crystal symmetry and appropriate choice of reference axes the number of independent components in tensor may be reduced.[8] Figure 2.5 shows the most common reference axes used in piezoelectric materials. Directions 1 ~ 3 define the poling axes while 4 ~ 6 define the shear planes which are normal to the 1 ~ 3 directions. This simplifies the tensor notation allowing only 18 and 6 components for the 3rd and 2nd rank tensors respectively.

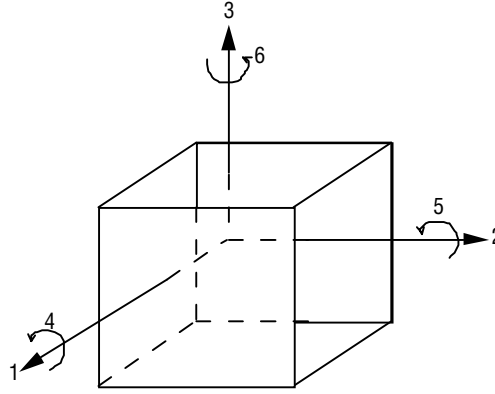


Figure 2.5 The most common reference axes in piezoelectric materials [8]

When considering piezoelectric materials, the most important parameters are usually piezoelectric coefficients and electromechanical coupling factors.

From 2.9 and 2.10, the piezoelectric coefficients are the proportionality constant between polarization and stress or strain and electric field. For example, in the piezoelectric coefficient d_{ij} , the first subscript i represents the direction of the applied field or dielectric displacement and the second subscript j indicates the direction in which mechanical strain occurs. Crystal symmetry determines how many components the piezoelectric matrix has. As seen in Equation 2.11, materials with symmetry ∞mm have only 5 components in the matrix, three of which are independent, the piezoelectric coefficients d_{31} , d_{33} , and d_{15} . [9, 10]

$$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (2.11)$$

The electromechanical coupling factor describes how well the electrical energy is converted into mechanical energy or vice versa. This relationship is defined in terms of k^2 .

$$k^2 = \frac{\text{electrical energy converted to mechanical energy}}{\text{Input of electrical energy}} \quad (2.12)$$

or

$$k^2 = \frac{\text{mechanical energy converted to electrical energy}}{\text{Input of mechanical energy}} \quad (2.13)$$

2.3 Ferroelectricity

Ferroelectric materials have a spontaneous polarization, due to a permanent dipole, which exists even in the absence of an electric field. The orientation of the spontaneous polarization is switchable by the direction of an applied electric field.

The aforementioned 20 piezoelectric point groups can be further classified into pyroelectrics which have a polar axis. Only 10 point groups have a permanent dipole or polar axis and their polarization is dependent on the temperature. Some of them exhibit ferroelectricity. Since dipoles may not be able reorientable or since the required field to switch the direction of the polarization

can be higher than the breakdown field of the sample, all ferroelectrics are pyroelectric but not vice versa. [11]

There are two different origins of spontaneous polarization. The first type of ferroelectrics are characterized by a spontaneous polarization that results from the displacement of atoms below the Curie temperature (T_c) where the ferroelectric phase transition occurs. These are called the displacive ferroelectrics. The other type develops ferroelectricity from an order-disorder transition.[6, 10] Below the Curie temperature, there is an ordering of dipoles in the materials and it generates a spontaneous polarization but above Curie temperature, random orientations of dipoles cancel any net polarization.

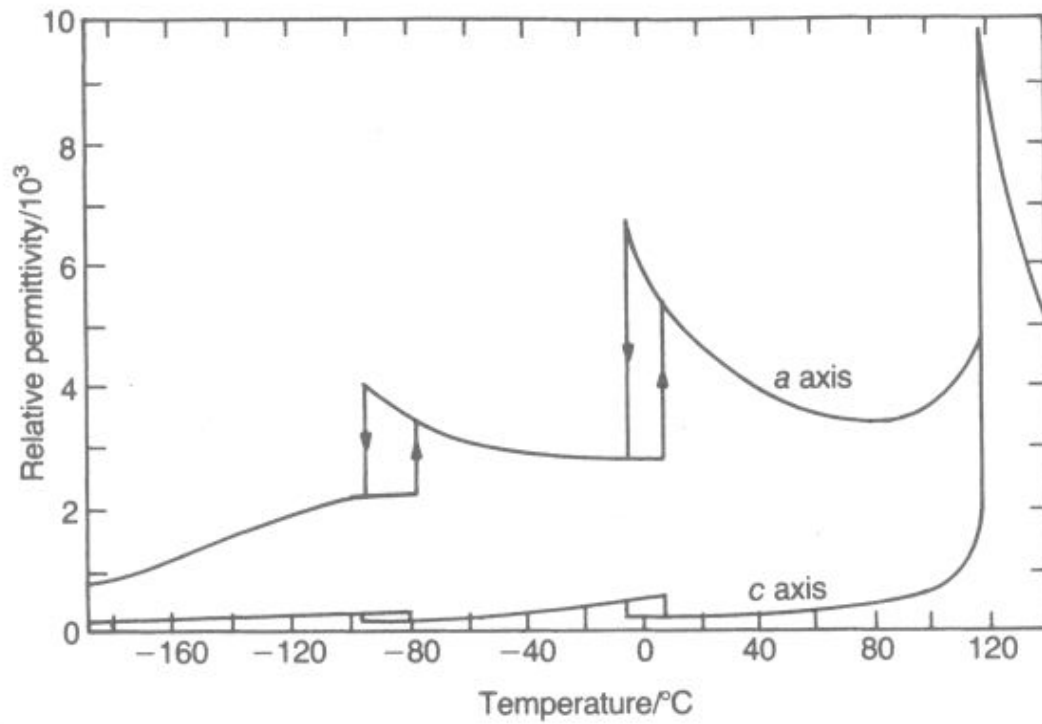
As temperature increases, ferroelectric materials undergo a phase transition from ferroelectric to non-ferroelectric (paraelectric). This phase transition is accompanied by the disappearance of the spontaneous polarization. Above the transition temperature, the dielectric constant in ferroelectric materials follows Curie-Weiss law:

$$\epsilon_r = \epsilon_0 + \frac{C}{T - \theta} \approx \frac{C}{T - \theta} \quad (2.14)$$

where ϵ_r is the relative permittivity, ϵ_0 is the permittivity of vacuum, C is the Curie constant and θ is the Curie-Weiss temperature. The Curie temperature T_c is equal to θ for a second order ferroelectric material but for a first order ferroelectric material, T_c is higher than θ . [12] Two different transitions describe

how the spontaneous polarization behaves at the Curie temperature. A first order transition shows a discontinuity in the spontaneous polarization, falling to zero at the transition temperature. In contrast, the spontaneous polarization in a second order transition decreases continuously to zero. A plot of inverse of permittivity versus temperature is used to determine the Curie-Weiss temperature. There is a gap between θ and T_c for the first order transition but no gap for the second order transition. The differences in behavior at transition temperatures are related to volume change and latent heat. [13]

One of the most well studied ferroelectric materials is barium titanate (BaTiO_3) whose spontaneous polarization is derived from the displacement of the Ti^{+4} ion inside the octahedral site formed by the oxygen sublattice when its crystal structure distorts tetragonally. Some ferroelectric materials, like BaTiO_3 , undergo several phase transitions; each transition being accompanied by a structural change and anomalies in dielectric constant. The Curie temperature is only the first phase transition from the paraelectric to ferroelectric state.[14] The phase transitions of BaTiO_3 are observed in the temperature dependence of the relative permittivity as shown in Figure 2.6. At 130 °C, the crystal structure transforms from cubic to tetragonal and displays ferroelectric behavior. Between 0 and 130 °C the tetragonal structure is stable, from 0 to -90 °C an orthorhombic structure exists and then below -90 °C BaTiO_3 has the rhombohedral structure.



1)

Figure 2.6 Temperature dependence of the relative permittivity for BaTiO₃

2.3.1 Ferroelectric domains and domain walls

Ferroelectric materials create a domain structure to minimize their electrostatic energy from the generation of a depolarizing field and their elastic energy associated with mechanical stress generated from the paraelectric/ferroelectric transition as they are cooled below the Curie temperature. A domain can be defined as a region in the crystal where the spontaneous polarization is oriented in same direction. [14]

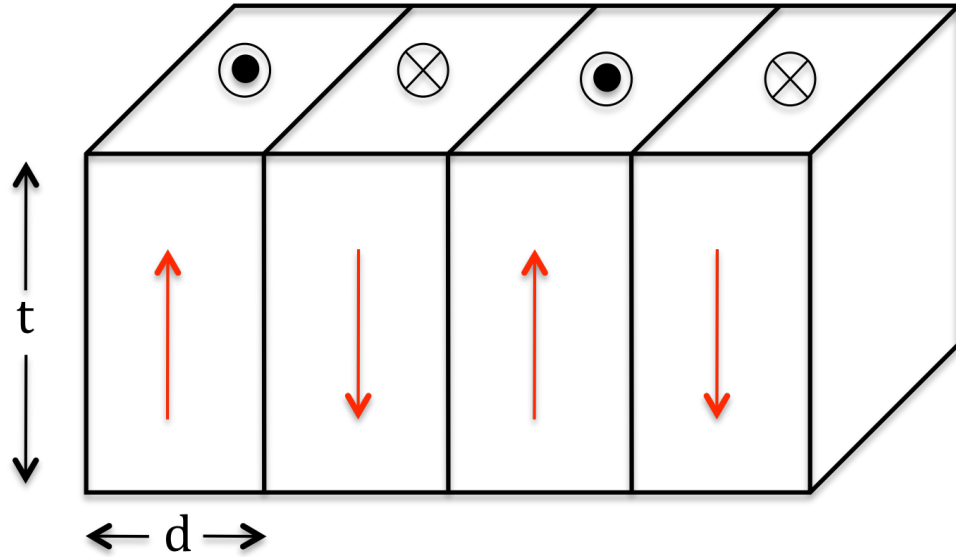


Figure 2.7 Schematic of domain structure consisting of 180° domain walls in a ferroelectric crystal (after reference[15])

Due to the presence of surfaces, the spontaneous polarization that occurs below the Curie temperature induces the formation of a surface charge. The electric field generated by the surface charge is called the depolarizing field E_d . The electrostatic energy associated with this depolarizing field is given by:

$$W_D = \frac{1}{2} \int E_d \cdot D dV \quad (2.15)$$

where D is the dielectric displacement, E_d is the depolarizing electric field and V is the volume of crystal. To minimize W_D , antiparallel regions in the ferroelectric material could be created or the depolarizing field could be compensated by electrical conduction or external charge surrounding the material. Considering

the simplified antiparallel domain structure in Figure 2.7, the electrostatic energy is given by:

$$W_D = \frac{A_\epsilon P_s^2 V d}{t} \quad (2.16)$$

where A_ϵ is a constant dependent on the dielectric constant, P_s is the spontaneous polarization, V is the volume of the crystal, d is the domain width and t is the thickness of the ferroelectric. The depolarizing field might be strong enough to make a single domain system energetically unfavorable but it is noted that smaller domain widths reduce the electrostatic energy. Therefore, the crystal forms multiple domains to lower electrostatic energy.[6, 16] Creation of multiple domains implies that a domain wall between two different domains is also created. The energy associated with a domain wall W_w is defined by:

$$W_w = \frac{\sigma}{d} V \quad (2.17)$$

where σ is the energy per unit area of domain wall. When $W_D + W_w = 0$ the domain structure is stable. The low energy configuration expressed in terms of domain width is obtained by combining Equation (2.16) and (2.17):

$$d = \sqrt{\frac{\sigma t}{A_\epsilon P_s^2}} \quad (2.18)$$

The domain width, then, is proportional to the square root of the crystal size. This implies that there is a domain size limitation depending on the crystal size.

Depending on the crystal structure, different types of domain walls are possible. Domain walls are characterized by the angle between spontaneous polarization vectors in adjacent domains. In the tetragonal structure, the available domain walls are 180° or 90° . For a rhombohedral crystal, the direction of polarizations in two adjacent domains gives rise to 180° , 109° or 71° domain walls. As mentioned earlier, cooling below Curie temperature induces electrostatic energy and elastic energy resulting from the structural change. In a tetragonal crystal, 180° domains, which are anti-parallel to each other, can form to reduce the depolarizing field as shown in Figure 2.8. 90° domain walls is also reduce the depolarizing field. However, only 90° domain walls can contribute to minimization of the elastic energy associated with mechanical stress from the deformation of the crystal structure. Thus, 180° domain walls are ferroelectric but non- 180° domains are both ferroelectric and ferroelastic. [15]

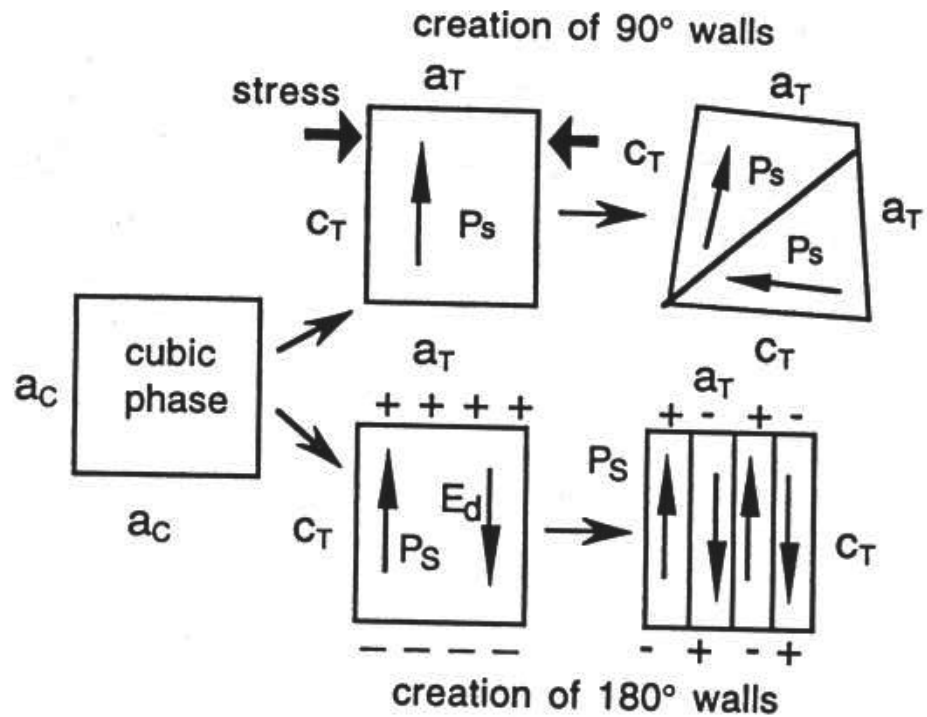


Figure 2.8 The domain structure with 90° and 180° oriented domain walls in a tetragonal perovskite ferroelectric [14]

2.3.2 Polarization hysteresis

The ability to switch direction of the polarization by an external electric field is the most important characteristic of a ferroelectric material. Figure 2.9 shows a typical hysteresis loop for a ferroelectric and the corresponding change in domain structure. Even if a ferroelectric material has a spontaneous polarization it displays zero polarization without the presence of an applied electric field (Point A) due to the random domain orientation. At lower electric fields, the polarization increases linearly with electric field but is insufficient to

change the orientation of the domains; only field-induced polarization exists. At higher electric field, the polarization shows nonlinear behavior because the orientations of the domains start to switch in the direction of the electric field. Once all domains are aligned in the direction of the field (Point B), polarization shows linear behavior again and reaches saturation. If the field is reduced to zero, the polarization decreases but retains some non-zero value (Point C) which is called the remanent polarization P_r . The field at point D required to bring the polarization back to zero is called the coercive field E_c . When ferroelectric materials have high or low apparent E_c , they are called as hard or soft ferroelectrics, respectively. In piezoelectric applications, the magnitude of E_c is important. For a polycrystalline material to be piezoelectric-active, it must be poled. By applying an appropriate electric field higher than E_c , the domains in the material are aligned (point B). This process is called poling and depending on the magnitude of E_c , the ease of the poling process is determined. Typically this process is carried out at relatively high temperature (100 – 150 °C) in order to facilitate domain reorientation.

In hysteresis loops, there are linear and non-linear regions of polarization and electric field. Equation (2.4) introduced earlier does not include the non-linear response and must be modified as follows:

$$\Delta P = \epsilon_o (\epsilon_r - 1) \Delta E \quad (2.19)$$

The derivative $\partial P / \partial E$ indicates the slope at any point in the hysteresis loop and gives the permittivity.

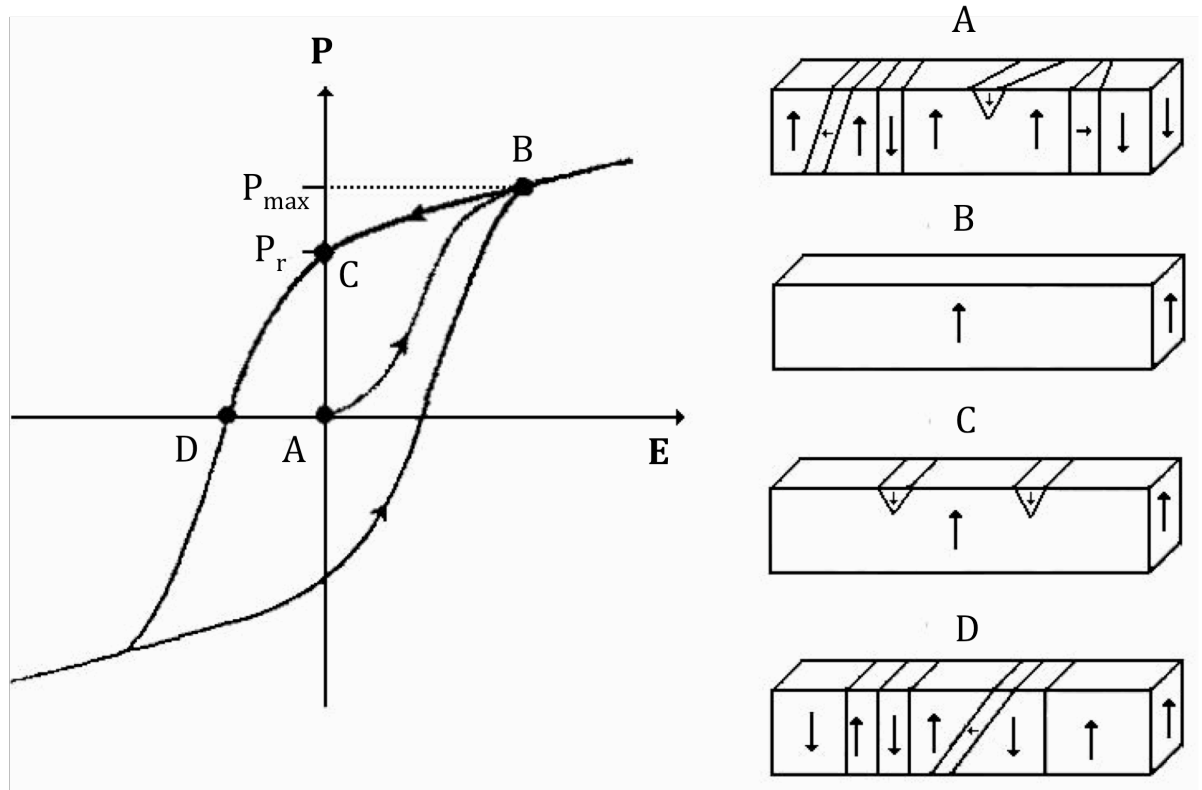


Figure 2.9. Typical ferroelectric polarization hysteresis loop and schematics of the corresponding domain structures. [15]

2.3.3 Intrinsic and extrinsic contributions

There are both intrinsic and extrinsic contributions to the dielectric and piezoelectric response in ferroelectric materials. The intrinsic mechanism is due

to the ionic response from the deformation of the unit cell. The extrinsic contribution is related to domain motion and phase boundaries. [17-19]

The intrinsic and extrinsic parts contribute to the real components of the dielectric and piezoelectric response but only the extrinsic mechanisms affect the imaginary component. [17] The dielectric and piezoelectric coefficients are expressed by:

$$\varepsilon' = \varepsilon'_{in} + \varepsilon'_{ex} \quad \text{and} \quad \varepsilon'' = \varepsilon''_{ex} \quad (2.20)$$

$$d' = d'_{in} + d'_{ex} \quad \text{and} \quad d'' = d''_{ex} \quad (2.21)$$

Different experimentally controlled parameters have been used to separate the intrinsic and extrinsic response. The effects of frequency on the measuring field, temperature and aging times have all been investigated. [18-23]

The dielectric properties of ferroelectric materials show frequency dependence and a relaxation in the GHz range. Figure 2.10 shows the frequency dependence of dielectric properties of barium titanate ceramics and the relaxation step; widely considered to be associated with domain wall vibration.[22] If the domain wall contribution is no longer active above this frequency, the remaining permittivity at higher frequency is from the intrinsic ionic response.

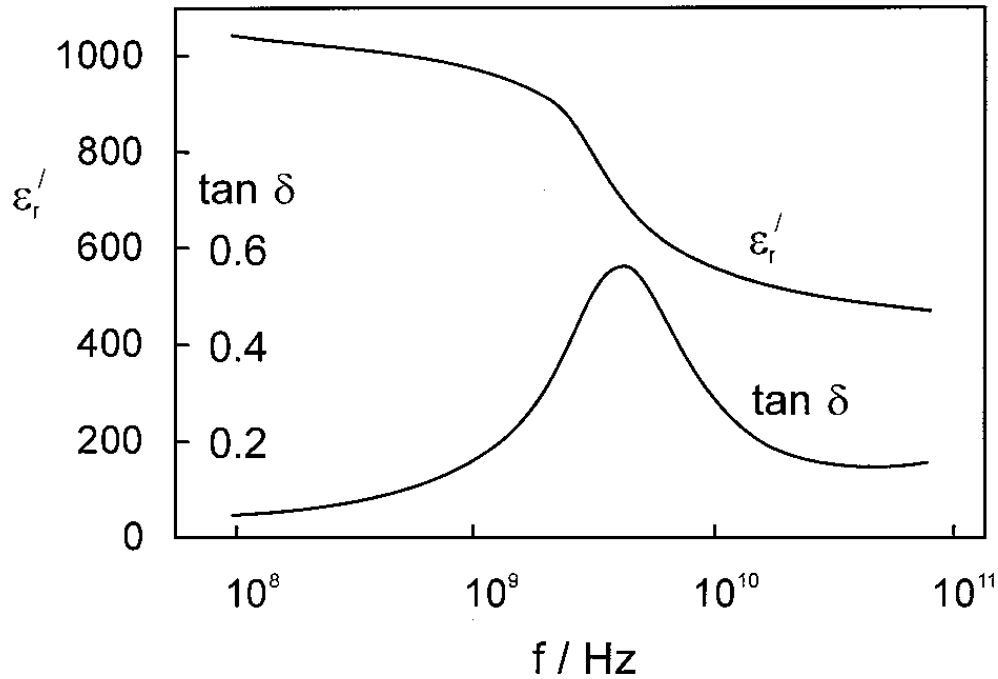


Figure 2.10 Frequency dependence of the dielectric properties of barium titanate ceramics.[22]

Another approach to separate the two different mechanisms is to investigate the temperature dependence of the dielectric and piezoelectric properties. [18, 23] Reducing the temperature close to absolute zero excludes the extrinsic contribution by freezing out domain motion. If an approximation of the temperature dependence of the intrinsic mechanism is obtained, the extrinsic contribution at any other temperature can also be determined. Figure 2.11 displays the intrinsic and extrinsic contributions for the dielectric, piezoelectric and elastic coefficients of unpoled PZT ceramics as a function of temperature.

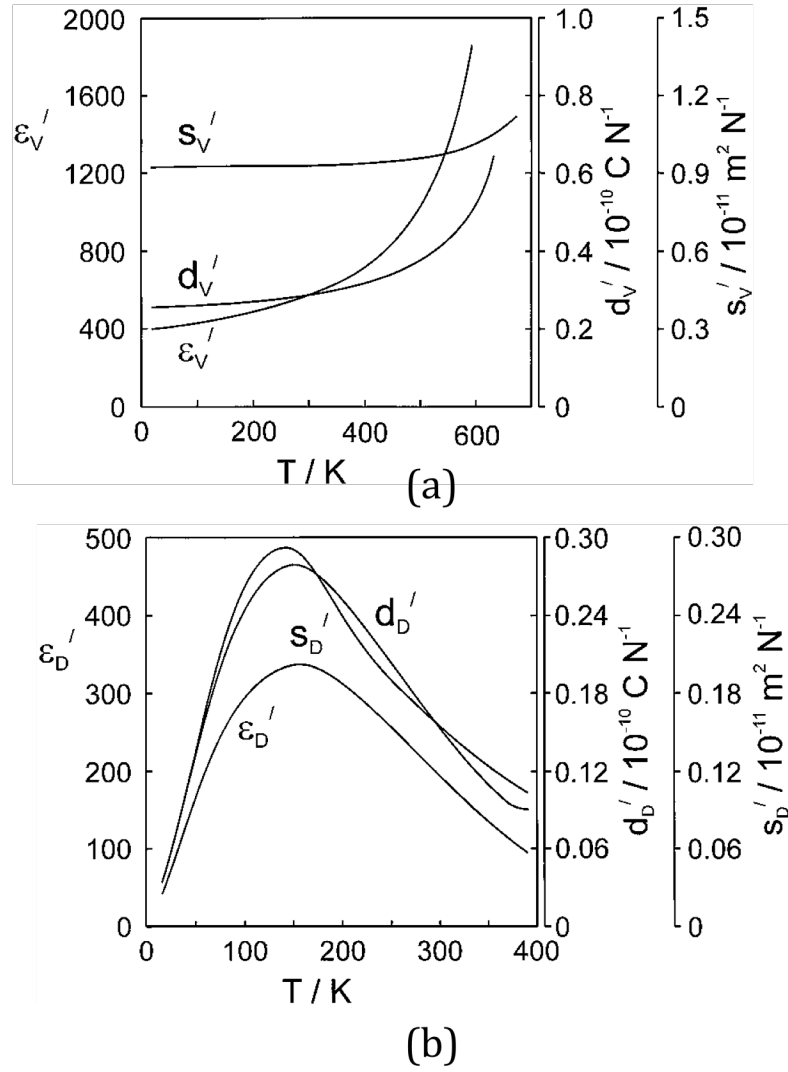


Figure 2.11 The (a) intrinsic and (b) extrinsic contribution to the dielectric, piezoelectric and elastic coefficients of PZT ceramics as a function of temperature.[18]

Zhang and co-workers separated the intrinsic and extrinsic contributions in lead zirconate titanate.[19] They assumed that the hydrostatic piezoelectric coefficient is zero because domain wall motion does not produce a volume

change. Figure 2.12 shows the difference between the intrinsic and extrinsic contributions to the piezoelectric coefficients d_{33} and d_{31} as a function of temperature.

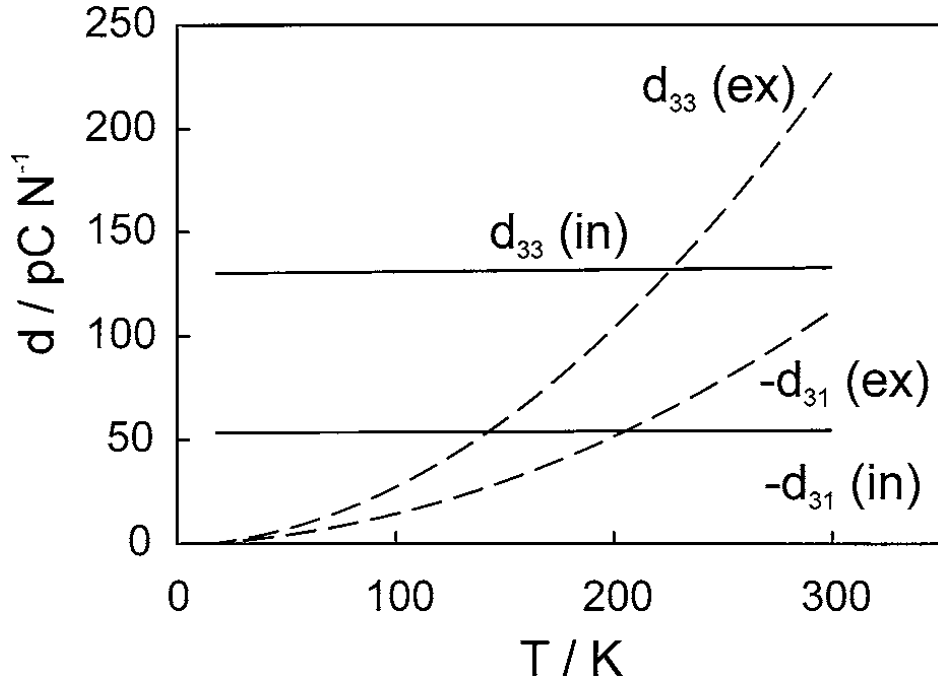


Figure 2.12 The intrinsic and extrinsic contributions to the d_{33} and d_{31} coefficients in PZT ceramics [19]

The ac field dependence of dielectric and piezoelectric responses can be used to distinguish the intrinsic and extrinsic contributions. At lower field and stress, the dielectric and piezoelectric response show non-linear behavior with the applied electric field. Both the intrinsic and extrinsic contributions are involved in this non-linear response, but below the coercive field the extrinsic contribution is dominant. [17] The Rayleigh Law has been used to describe the

non-linear behavior of the dielectric and piezoelectric properties for ac field amplitudes between the threshold and coercive field. The threshold field is the ac field amplitude below which the dielectric permittivity and piezoelectric coefficient are independent. Above the threshold field the dielectric permittivity and piezoelectric coefficient increase rapidly due to domain wall movement. [21, 24, 25]

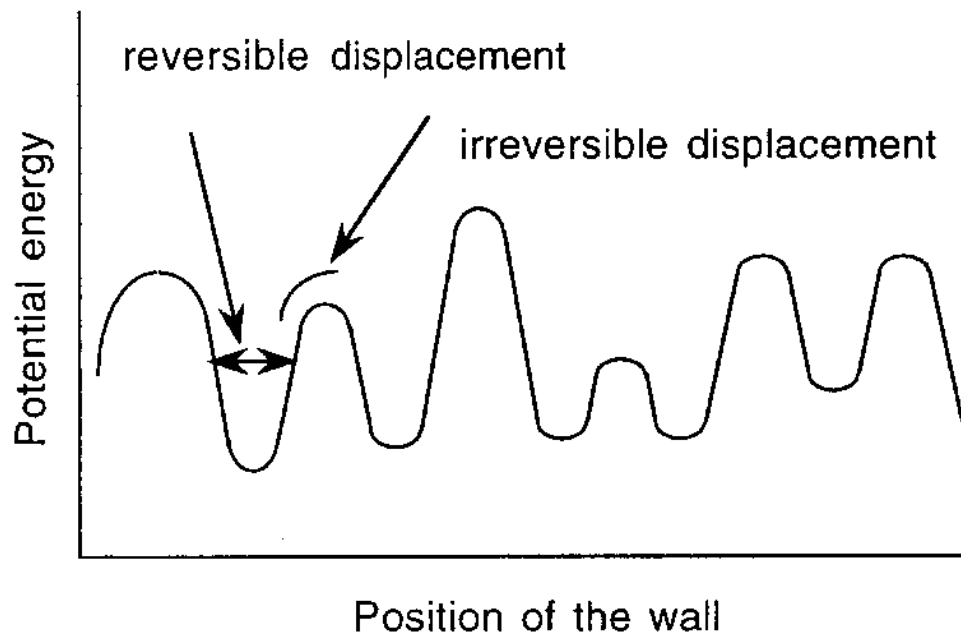


Figure 2.13 A schematic of the domain wall motion between potential energy wells.[26]

The Rayleigh law was developed to study ferromagnetic materials under weak field conditions.[27] Later it was applied to ferroelectric materials to describe the dielectric and piezoelectric non-linearities in bulk ceramics and thin

films.[26, 28-32] Rayleigh behavior involves the movement of domain walls between two potential wells as shown in Figure 2.13. Reversible motion describes domain wall movement within the potential energy well. In contrast, irreversible domain wall motion occurs when the electric field is enough to overcome the potential barrier. The motion of domain walls is associated with randomly distributed defects which act as pinning centers. [33] The Rayleigh law for the ac field dependence of the dielectric and piezoelectric response in ferroelectric materials is given by:

$$\varepsilon' = \varepsilon'_{init} + \alpha'E_0 \quad (2.22)$$

$$\varepsilon'' = \alpha''E_0 = \frac{4}{3\pi} \alpha'E_0 \quad (2.23)$$

$$P(E) = (\varepsilon'_{init} + \alpha'E_0)E \pm \frac{\alpha'}{2}(E^2 - E_0^2) \quad (2.24)$$

$$d' = d'_{init} + \alpha'E_0 \quad (2.25)$$

$$d'' = \alpha''E_0 = \frac{4}{3\pi} \alpha'E_0 \quad (2.26)$$

where ε' , ε'_{init} , d'_{init} , α' , α'' , E_0 , E and P are the real dielectric permittivities, the reversible (intrinsic) component of permittivity, reversible (intrinsic) component of the piezoelectric coefficient, the irreversible Rayleigh coefficient, the imaginary irreversible Rayleigh coefficient, the amplitude of the electric field, the electric

field and the dielectric polarization respectively. The ϵ'_{init} and d'_{init} represent intrinsic contributions but $\alpha'E_0$ describes the extrinsic irreversible domain wall motion contribution in ferroelectric materials.

2.4 The perovskite structure

The most widely used piezoelectric and ferroelectric materials have the perovskite structure. Its general chemical formula is ABX_3 where A and B represent two types of cations and X represents an anion, usually oxygen in ceramics. Figure 2.14 shows a cubic unit cell with the ABO_3 perovskite crystal structure. As seen in Figure 2.14, both cations are coordinated with oxygen anions, but the larger A cation sits in the twelve-fold coordination site and the smaller B cation is located inside the six-fold coordinated oxygen octahedron.

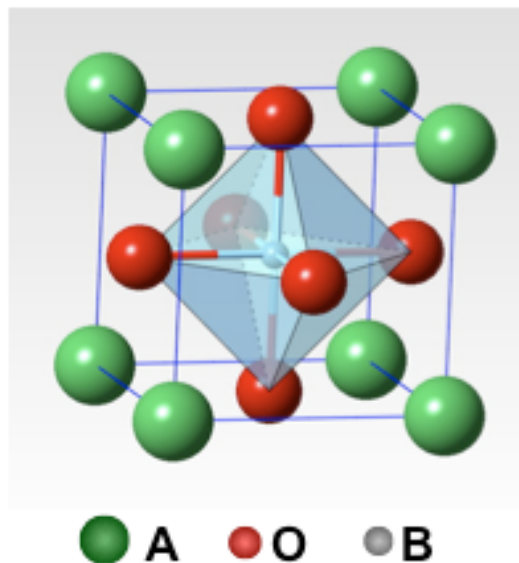


Figure 2.14 The unit cell of perovskite ABO_3

Tolerance factor is a very useful and simple tool for predicting crystallographic distortions of the perovskite structure. Using ionic radii, it determines the geometric stability of a perovskite by how well the B cation fits in the octahedral site. The Goldschmidt tolerance factor is described in equation (2.27):

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)} \quad (2.27)$$

Where R_A , R_B , and R_O are the ionic radii of the larger and smaller cations and oxygen respectively.

The tolerance factor of an ideal cubic perovskite is equal to 1. SrTiO_3 is a perfect example of this because its tolerance factor is 1 and its structure is cubic.[34] When the tolerance factor is smaller than 1, rhombohedral or orthorhombic crystal structures are common. For example, PbZrO_3 has the rhombohedral structure with a tolerance factor of 0.96.[35] When the tolerance factor is larger than 1, a perovskite will have a tetragonal structure; BaTiO_3 is good example with a tetragonal structure and tolerance factor of 1.06.[6]

Depending upon the charges and sizes of elements, a complex perovskite may have formula $(A'A'')\text{BO}_3$, $A(\text{B}'\text{B}'')\text{O}_3$ or even $(A'A'')(\text{B}'\text{B}'')\text{O}_3$. Where A' and A'' represent different cations both sitting on the A site. Many different possible elements are capable of fitting in these crystal structures resulting in a variety of

different properties including catalysts, giant-magneto-resistors, capacitors, piezoelectrics or oxide conductors.[4]

2.5 The lead zirconate titanate solid solution

$\text{Pb}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ is a solid solution of two different perovskites, PbZrO_3 and PbTiO_3 . The phase diagram for the $\text{Pb}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ solid solution is presented in Figure 2.15. As seen in Figure 2.18, PbTiO_3 has a ferroelectric tetragonal phase while PbZrO_3 has an anti-ferroelectric orthorhombic phase. When substituting Zr^{4+} for Ti^{4+} in PbTiO_3 , a phase transition from ferroelectric tetragonal to ferroelectric rhombohedral occurs around 53 mol% PbZrO_3 . Further addition of Zr^{4+} causes an anti-ferroelectric orthorhombic phase transition at around 95 mol% PbZrO_3 . The compositional boundary that separates the two ferroelectric phases is almost temperature independent and is called a morphotropic phase boundary or MPB. Recent investigations of the PZT phase diagram indicated the existence of a monoclinic phase between the rhombohedral and tetragonal phases. [36-38] The modified phase diagram is shown in Figure 2.15(b).

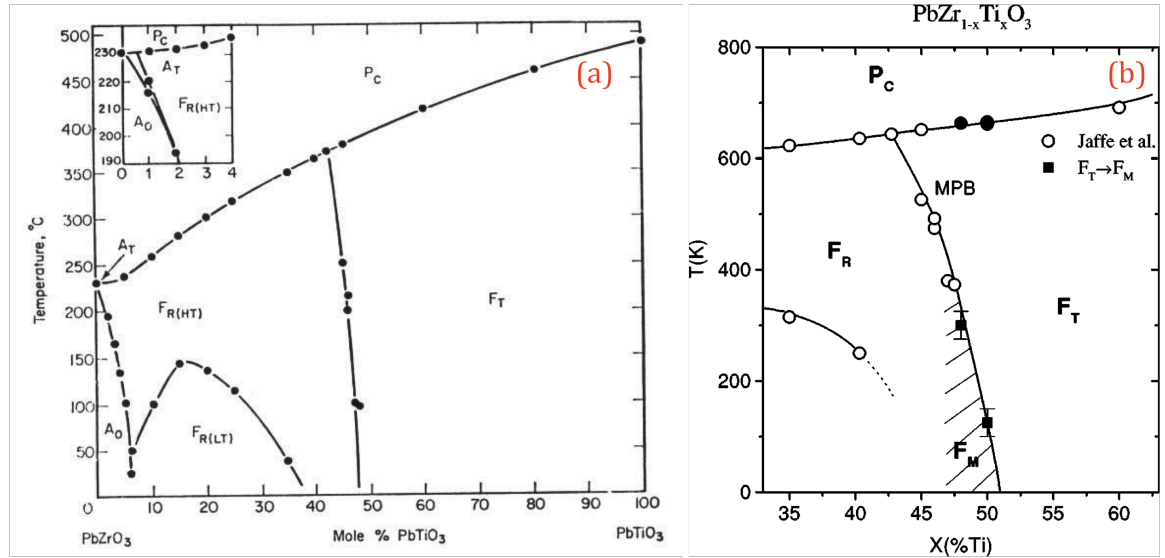


Figure 2.15 The phase diagram of PbZrO_3 - PbTiO_3 solid solution system (a) proposed by Jaffe et al. and (b) modified by Noheda et al.[9, 38]

Tetragonal crystal symmetry allows the polar axis along the $\langle 001 \rangle$ directions with 6 equivalent orientations while the polar axis in rhombohedral crystals exists along the $\langle 111 \rangle$ family with 8 equivalent directions. [9] At the MPB composition, it is energetically equivalent for PZT to have either of these two phases. When an external force is applied to MPB PZT there are 14 different directions in which the domains may be oriented to minimize electric field or mechanical stress. This feature of PZT allows for exceptional dielectric and piezoelectric properties. For example, 52/48 PZT has a $d_{33} = 130 \text{ pm/V}$, $e_{31} = -12 \text{ C/m}^2$. AlN, another popular piezoelectric (non-ferroelectric) has a $d_{33} = 3.9 \text{ pm/V}$, $e_{31} = -1.05 \text{ C/cm}^2$. [1,9]

It is well known that the ability of domains to reorient or move influences electrical properties like permittivity and coercive field. Additives like donor or acceptor dopants on the A and B sites can affect domain reorientation and subsequently the properties of PZT. Table 2.1 shows the common aliovalent dopants for PZT. Donors like La^{3+} or Sb^{5+} are used to obtain soft PZT while hard PZT can be achieved by doping with acceptors like K^+ and Fe^{3+} . Donor ions are compensated with A site vacancies which enhance domain reorientation and increase permittivity and piezoelectric coupling factor while decreasing coercive field. On the other hand, acceptor ions are compensated with oxygen vacancies that produce the opposite effect.

A site donors	$\text{La}^{3+}, \text{Bi}^{3+}, \text{Nd}^{3+}$
B site donors	$\text{Nb}^{5+}, \text{Ta}^{5+}, \text{Sb}^{5+}$
A site acceptors	K^+, Rb^+
B site acceptors	$\text{Co}^{3+}, \text{Fe}^{3+}, \text{Sc}^{3+}, \text{Ga}^{3+}, \text{Cr}^{3+}, \text{Mn}^{3+}, \text{Mn}^{2+}, \text{Mg}^{2+}, \text{Cu}^{2+}$

Table 2.1 Common aliovalent dopants for PZT. [1]

2.6 Bismuth based perovskite and solid solutions

To date, lead zirconate titanate (PZT) and its solid solutions are the most widely used piezoelectric materials because they show excellent dielectric and piezoelectric properties. PZT has been used in various applications such as micro-piezoelectric sensors and actuators in micro-electromechanical systems

(MEMS). [39, 40] The origin of the superior piezoelectric response in PZT is attributed to the existence of a morphotropic phase boundary (MPB) as described in the previous section and lone pair electrons of Pb^{2+} . [41] However, recent environmental legislation such as Waste from Electrical and Electronic Equipment (WEEE), Restriction of Hazardous Substances (RoHS) and End-of-Life Vehicles (ELV) have prompted the development of lead-free piezoelectric materials to replace PZT. [42] Since Bi^{3+} has a similar electronic configuration to Pb^{2+} and is a non-toxic material, Bi-based lead-free perovskite compounds have been widely investigated as a potential substitute for PZT systems. [42-45]

2.6.1 Bismuth based perovskite ceramics

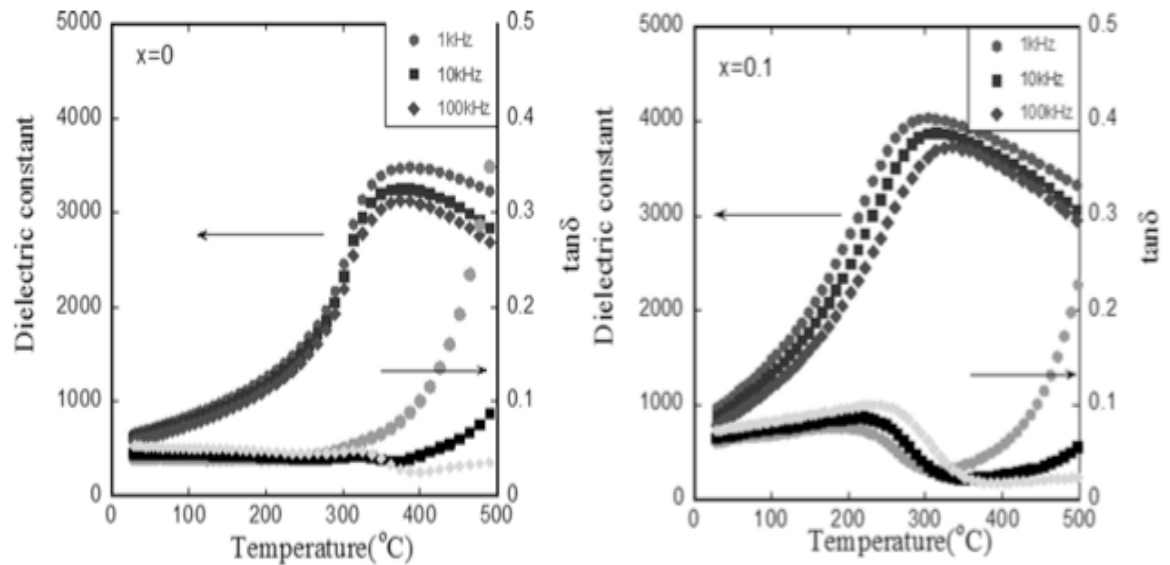


Figure 2.16 Dielectric properties of BKT (left) and 0.9 BKT – 0.1 BZT (right).[46]

Smolenskii *et al.* first reported the promising new lead-free piezoelectric materials $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) and $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (BKT). [47] Bismuth potassium titanate, BKT is a well-known non-lead ferroelectric with the perovskite structure. It has tetragonal symmetry with $a=0.391$ nm and $c=0.399$ nm at room temperature and shows a relatively high Curie temperature of 380 °C. [48] However, it is reported that BKT has poor sinterability so dense ceramic bodies are hard to achieve by conventional ceramic fabrication processes. [49] Huang *et al.* reported improvements in density as well as dielectric and piezoelectric properties by combining BKT with $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BZT). [46] X-ray diffraction patterns of BKT – BZT compounds show single-phase material with tetragonal symmetry when the BZT content was below 20-mol%. [46] Figure 2.16 displays the dielectric properties of pure BKT and 0.9 BKT – 0.1 BZT as a function of the temperature. The maximum dielectric constant increases from 630 to 900 and the dielectric spectra shifts to the left with added BZT. Figure 2.17 compares PE loops and strain data for pure BKT and 0.9 BKT – 0.1 BZT. PE loops for both compositions are not saturated even at 80 kV/cm but remanent polarization P_r increases significantly from 6.1 $\mu\text{C}/\text{cm}^2$ to 11.8 $\mu\text{C}/\text{cm}^2$ with 10% added BZT. The strain behavior at room temperature is also shown in Figure 2.20. Typical butterfly shape strain loops are observed for both compounds and maximum strain is improved for compositions with 10-mol% of BZT content.

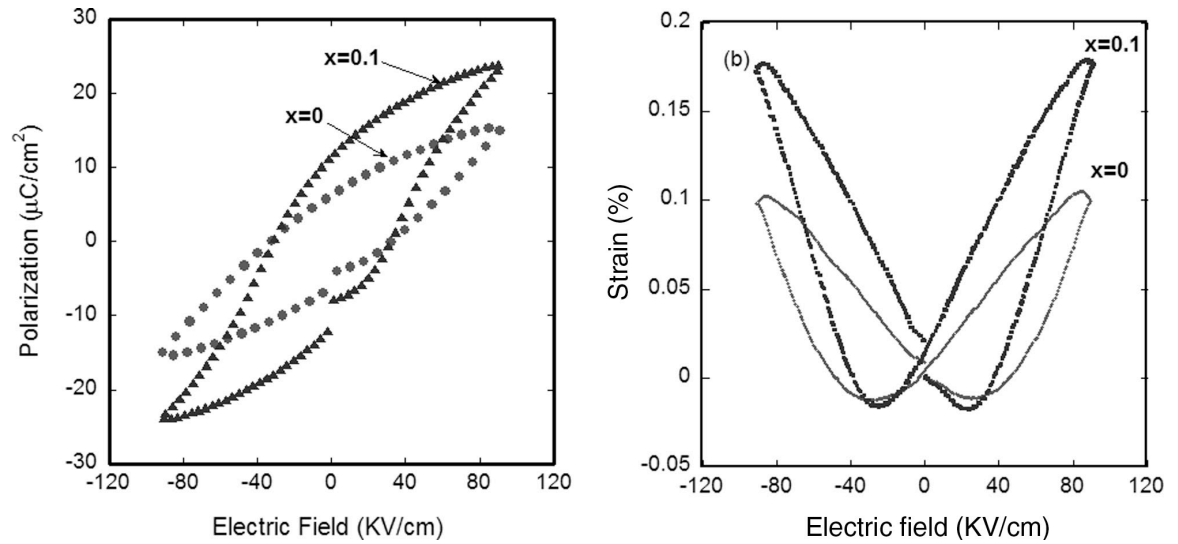


Figure 2.17 PE loops (left) and strain data (right) of pure BKT
and 0.9 BKT – 0.1 BZT [46]

Bismuth sodium titanate BNT is also considered an excellent candidate to replace Pb-based materials. BNT has the rhombohedral structure at room temperature and a transition from rhombohedral to tetragonal occurs at 300 °C. The Curie temperature for BNT is 540 °C.[48] Recent work by Aksel *et al.* found that BNT also has a monoclinic crystal structure at RT.[50] The material shows a relatively high remanent polarization ($P_r=38 \mu\text{C}/\text{cm}$) but has a large coercive field at room temperature ($E_c = 73 \text{ kV}/\text{cm}$) making BNT ceramics difficult to pole. [47, 51] A major advantage of BNT is that a morphotropic phase boundary (MPB) is observed when combined with solid solutions of other perovskite materials with tetragonal symmetry such as $\text{PbTiO}_3(\text{PT})$, $\text{BaTiO}_3(\text{BT})$ and BKT. Figure 2.18 shows the phase diagram for BNT solid solutions with BKT and BT. A

morphotropic phase boundary exists for BNT – BKT solid solutions at about 20 mol% BKT. The same can be expected for BNT – BT solid solutions at about 6 mol% BT.[52, 53]

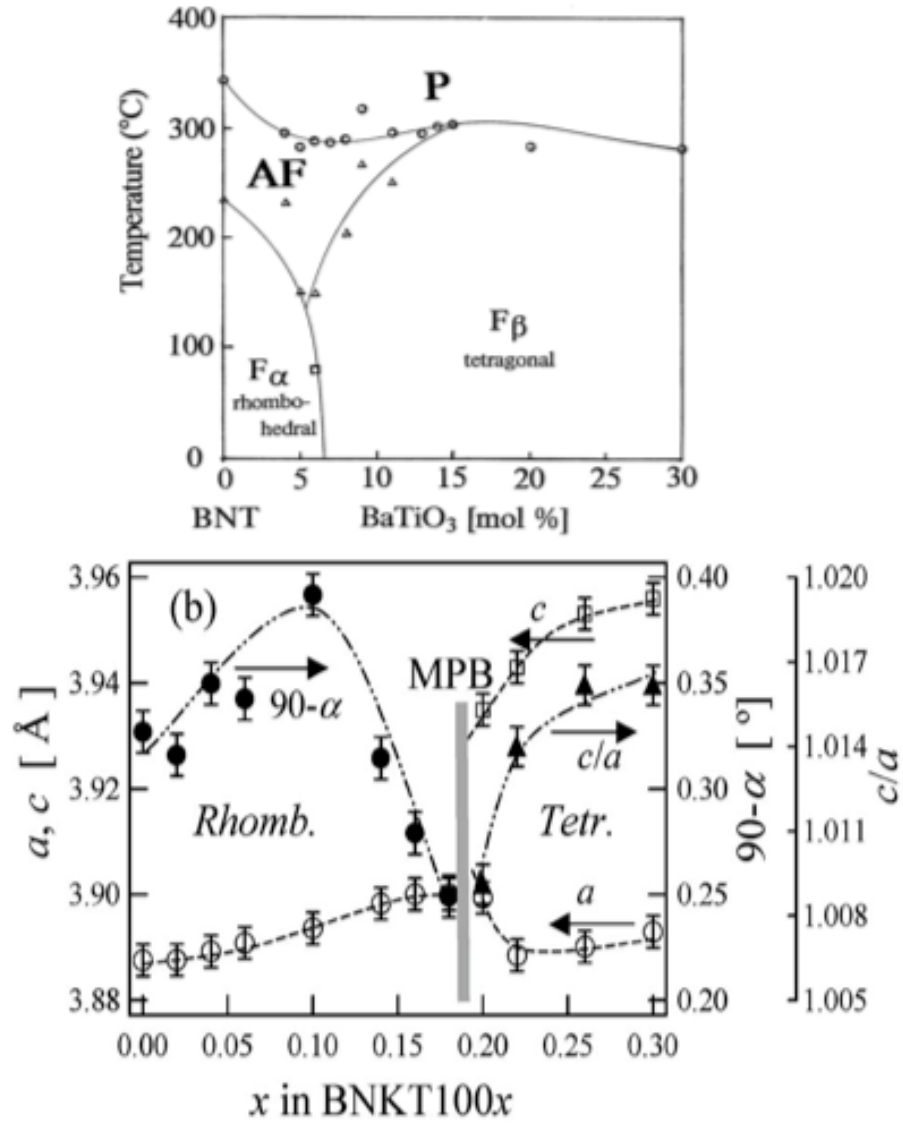


Figure 2.18 Binary phase diagrams of BNT – BT (top) and BKT – BNT (bottom) [52, 53]

As mentioned in the previous section a MPB allows materials to have large piezoelectric properties due to more available polarization directions. Thus many binary or even ternary systems have been developed and studied based on these MPB compositions.

Takenaka *et al.* reported that BNT – BT systems near the MPB composition (6 mol% BT) showed larger piezoelectric properties.[53, 54] Its dielectric constant was about 580 at 10 kHz with a d_{33} piezoelectric coefficient of 125 pC/N. However, the 94BNT-6BT composition had a Curie temperature of 288 °C and a low depolarization temperature (T_d) of 130 °C where the material loses its ferroelectric properties.

BNT-BKT solid solutions are one of the most intensively studied lead-free materials.[52, 55-58] Figure 2.19 presents PE loops of BNT-BKT for the tetragonal, rhombohedral and morphotropic compositions.[56] The highest remanent polarization was 38 $\mu\text{C}/\text{cm}^2$ at the 20 mol% BKT MPB composition. Tetragonal compositions have lower coercive fields compared with the rhombohedral side of the phase diagram. The largest coupling coefficients (k_{33}) and piezoelectric coefficients (d_{33}) of 0.56 and 167 pC/N respectively were obtained for morphotropic 0.8 BNT – 0.2 BKT. [52]

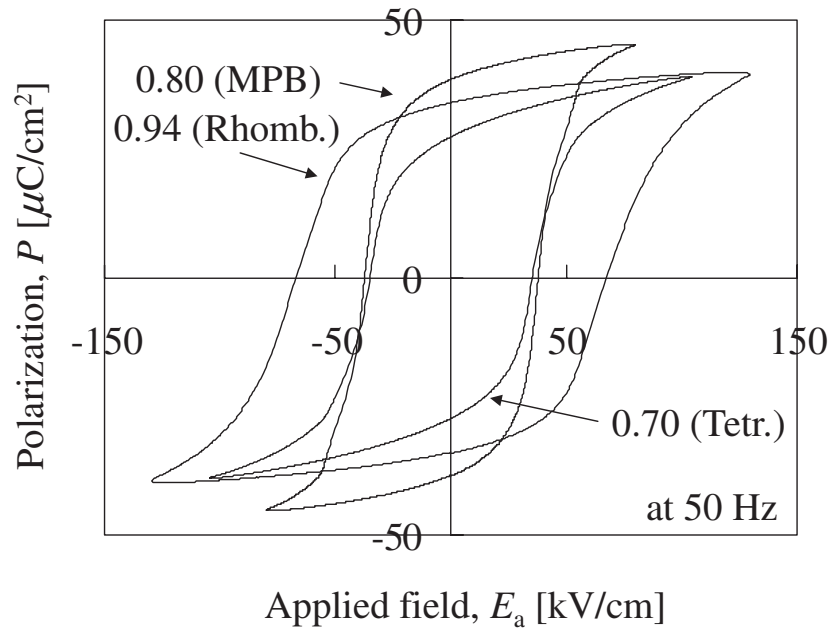


Figure 2.19 Hysteresis loops of (0.94, 0.8, 0.7) BNT – (0.06, 0.2, 0.3) BKT at room temperature. [56]

The ternary lead-free piezoelectric ceramic $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 - (\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3 - (\text{Bi}_{0.5}\text{Li}_{0.5})\text{TiO}_3$ (BNT-BKT-BLT) has also been investigated. [59-63] The partial substitution of Na with K and Li causes a reduction in the coercive field and good ferroelectric behavior was maintained. Enhanced piezoelectric properties with d_{33} and k_p of 230 pC/N and 0.41 respectively were observed for 70BNT – 20BKT – 10BLT. [63] The depolarization temperature (T_d) of BNT – BKT – BLT ceramics changes depending on the composition and the structural distortion. Adding a small amount of Li to the BNT system increases the maximum dielectric temperature (T_m) and Li-substitution in BNT-BKT system also increases the depolarization temperature. [59, 60]

Another potential lead-free piezoelectric ternary system is BNT – BKT – BT. Nagata *et al.* investigated the dielectric and piezoelectric properties of BNT – BKT – BT by exploring the mixture of two binary systems, BNT – BT and BNT – BKT near MPB compositions.[64] They found that an MPB exists between (94BNT - 6BT) – (84BNT - 16BKT) and (93BNT - 7BT) – (80BNT – 20BKT). The 85.2BNT – 12BKT – 2.8BT composition displays the maximum piezoelectric constant with d_{33} of 191 pC/N. Figure 2.20 shows the PE loops for 79BNT – 14BKT – 7BT and 88BNT – 8BKT – 4BT at room temperature. The first composition has the tetragonal phase but the latter one represents a MPB composition. As seen in Figure 2.20, the P_r and E_c for tetragonal phase were 29 $\mu\text{C}/\text{cm}^2$ and 37 kV/cm respectively at 80 kV/cm applied field. In contrast, the 88BNT – 8BKT – 4BT MPB composition showed higher P_r (40 $\mu\text{C}/\text{cm}^2$) but lower E_c (29 kV/cm). Although the dielectric and piezoelectric properties were optimum for the MPB composition it has a lower depolarization temperature.

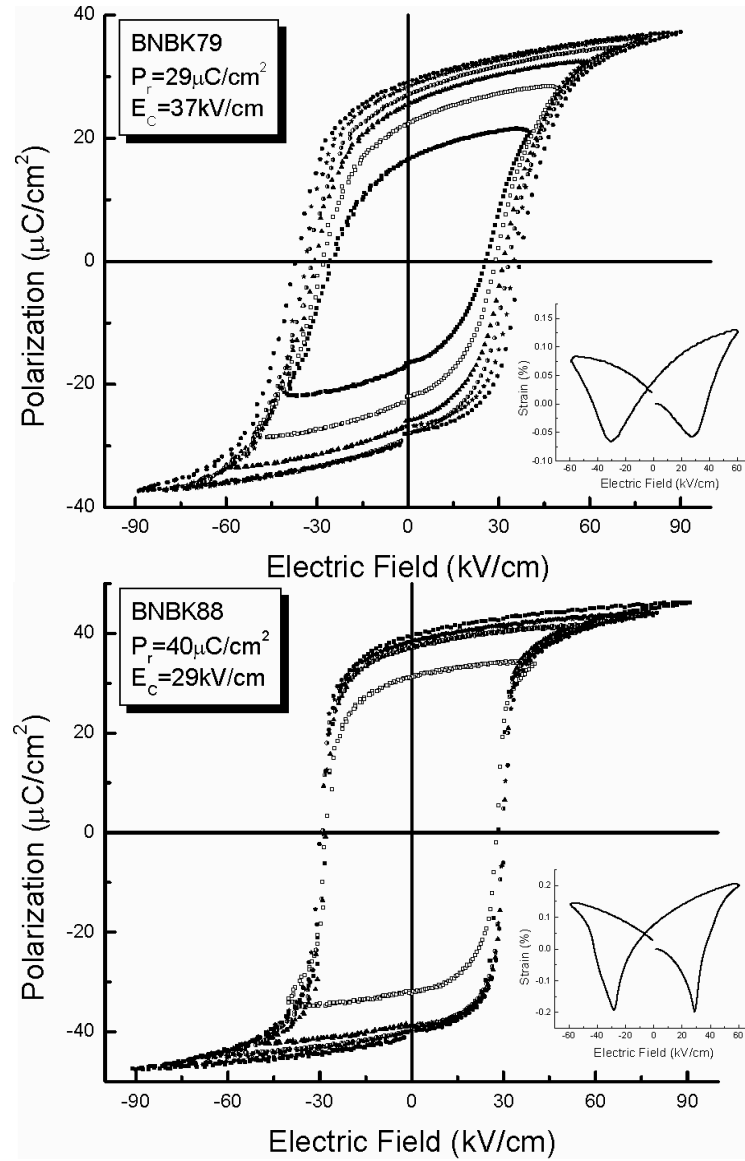


Figure 2.20 Hysteresis loops of 79BNT – 14BKT – 7BT (top) and 88BNT – 8BKT – 4BT (bottom) at room temperature [65]

Recently, Jarupoom *et al.* developed new lead-free ternary perovskite compounds based on $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 - (\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3 - \text{Bi}(\text{X}_{0.5}\text{Ti}_{0.5})\text{O}_3$ where X = Ni or Mg. [66] Interestingly, these systems exhibited large electromechanical

strains as high as 0.3% at 60 kV/cm as shown in Figure 2.21. The effective d_{33}^* derived from the strain data was 570 pm/V and 520 pm/V for the 72.5BNT – 22.5BKT – 5BMgT and 75BNT – 20BNT – 5BNiT compositions respectively. The mechanism for the large effective piezoelectric coefficient is not clearly understood. It is suggested that the addition of BMgT and BNiT to BNT – BKT system may affect the stability of the structural distortion and produce a field-induced phase transition from a non-polar to polar state. A similar feature of phase transition is found in other ternary systems such as BNT – BKT – BZT, BNT – BKT – KNN, BNT – BT – KNN. (KNN = $(K_{0.5}Na_{0.5})NbO_3$).[67-69]

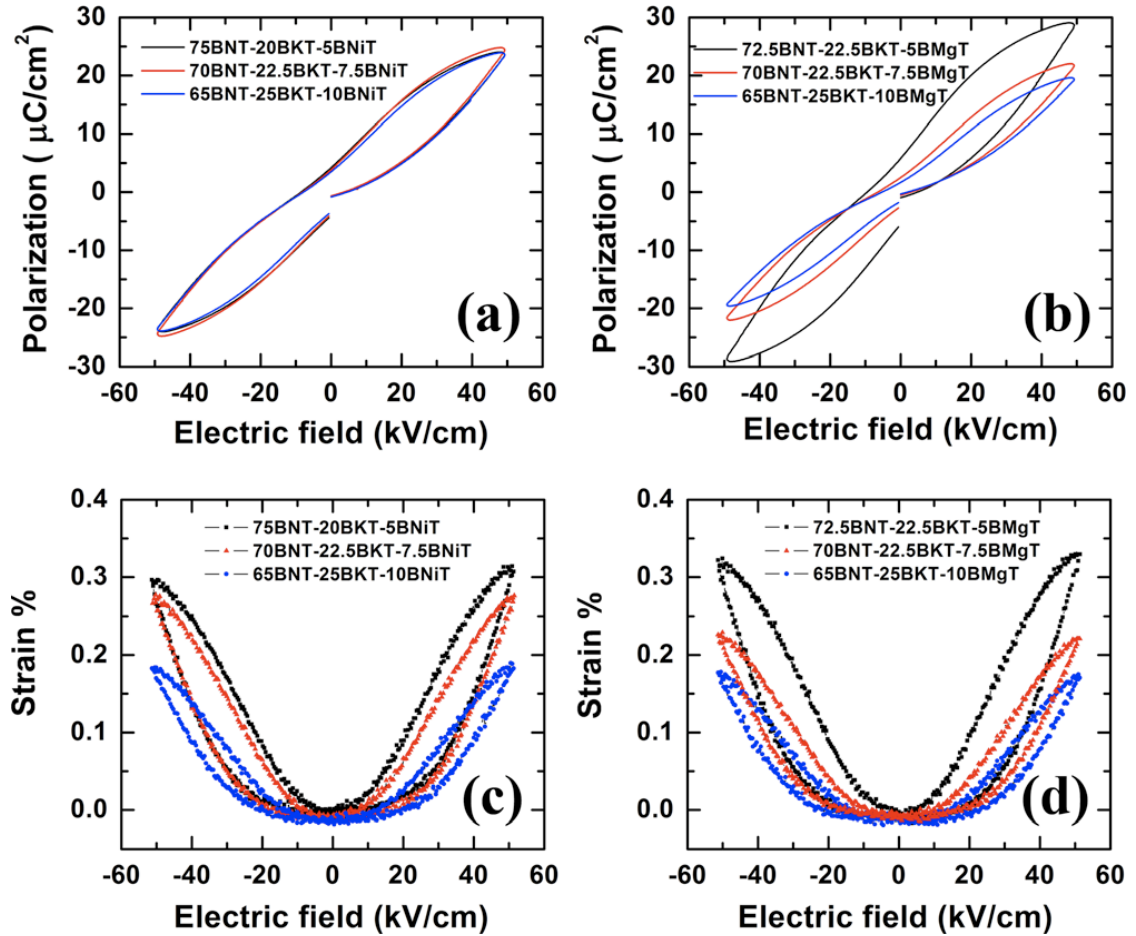


Figure 2.21 Hysteresis loops and corresponding strain data at 0.1Hz; (a) & (c) BNT – BKT – BNiT; (b)&(d) BNT – BKT – BMgT ceramics.[70]

Since BNT or BNT – BKT based thin films include highly volatile species like Bi, Na and K, preparation of high quality thin films will be challenging.[71] For light elements (Na and K) the thermalization is an additional problem. In light of this, much less work on lead-free piezoelectric thin films has been reported compared with lead-free piezoelectric ceramics.

2.6.2 Bismuth based perovskite thin films

Various techniques have been used for the fabrication of thin films such as RF sputtering, pulsed laser deposition and chemical solution deposition.[72-92] Zhou *et al.* reported BNT thin films on Pt/Ti/SiO₂/Si substrates via RF sputtering. [72] This BNT thin film was single phase as determined by XRD but exhibited a lossy hysteresis loop as shown in Figure 2.22. At room temperature, remanent polarization and coercive field were 11.9 $\mu\text{C}/\text{cm}^2$ and 37.9 kV/cm respectively. Polarization hysteresis measurements were only sustained up about 150 kV/cm because of large leakage currents (measurement frequency not reported). The inset in Figure 2.24 displays dielectric properties for these films and it was found that dielectric loss increases rapidly below 1 kHz.

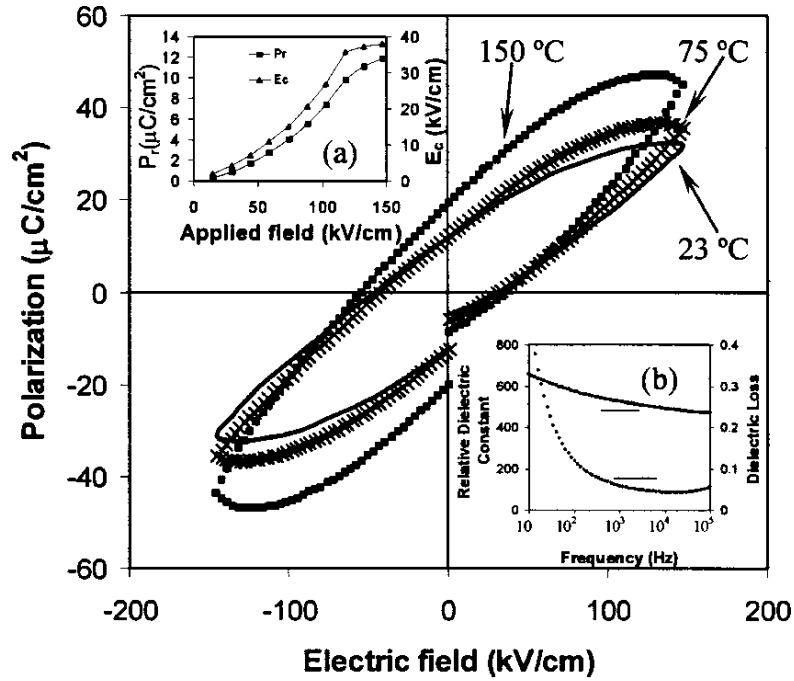


Figure 2.22 Polarization hysteresis loops for BNT thin films annealed at 700 °C and measured at different temperatures. The inset shows P_r and E_c as a function of the electric field and dielectric properties.[72]

Duclere *et al.* reported BNT thin films deposited by PLD.[76] These films were epitaxially grown on c-sapphire substrates and showed a second phase which could explain the large (126 kV/cm) coercive field. Frequency for hysteresis measurement was not reported. Another epitaxial lead-free BNT thin film on Pt/(100) MgO by pulsed laser deposition was reported by Bousquet *et al.* [78] (100) orientation was maintained until the thickness of the film exceeded 610 nm after which the film became (110) oriented. Figure 2.23 shows hysteresis loops of 610 nm BNT thin films. Remanent polarization and coercive field of these films were reported as $12.6 \mu\text{C}/\text{cm}^2$ and 94 kV/cm respectively. The vertical shift

of the PE loops with increased electric field was attributed to an asymmetry between the top and bottom Pt/BNT interfaces.

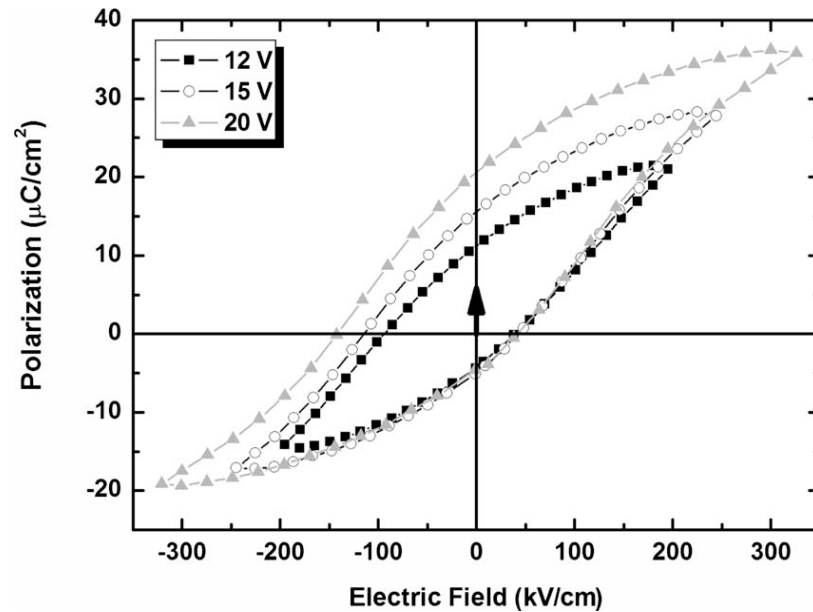


Figure 2.23 Hysteresis loops for 610 nm thick BNT thin film.[78]

BNT-BT thin film have also been synthesized by pulsed laser deposition. Cheng prepared BNT – BT thin films in a combinatorial methodology with changing BT content but most of the samples had low dielectric constants below 200 with a high value of 327 in the 9 mol% BT composition. [73] Scarisoreanu *et al.* also reported BNT – BT thin films on platinized silicon substrates by PLD.[74] However these films exhibited high dielectric loss above 10% between 0.1 - 10 kHz. PLD fabricated BNT – BT thin films doped with 0.5 mol% CeO₂ and La₂O₃ and 0.5 mol% of MnO₂ on single crystal (LaAlO₃)_{0.3}(SrAlTaO₆)_{0.35} substrates were

reported by Wang *et al.*[79] It was found that La+Ce and Mn doped films showed enhanced ferroelectric properties compared with pure BNT – BT thin films. Mn doping especially was helpful in reducing the leakage current.

Wang *et al.* fabricated polycrystalline lead-free BNT – BKT – BLT thin films on Pt/Ti/SiO₂/Si substrates using PLD.[80] The film had $d_{33,f}$ of ~ 64 pm/V and displayed a typical butterfly-shaped piezoresponse loop in Piezoresponse Force Microscopy (PFM). However, the film exhibited a lossy PE loop and the measuring frequency was not reported. Lu *et al.* studied BNT – BKT – BLT thin films on Pt/Ti/SiO₂/Si substrate by PLD. [77] It was found that dielectric properties and microstructures varied with the oxygen pressure. Dielectric constants, however, were below 200 and lossy hysteresis loops at unreported frequencies with P_r of less than $3 \mu\text{C}/\text{cm}^2$ was observed. Abazari *et al.* reported the electrical properties of BNT – BKT – BT thin films.[81] Pulsed laser deposition was used to achieve epitaxial growth of (0.88) BNT – (0.08) BKT – (0.04) BT on SrRuO₃/SrTiO₃ single crystals. Figure 2.24 shows the dielectric properties and hysteresis loop of these BNT – BKT – BT thin films. At low frequencies, high dielectric loss above 20% caused by a space charge contribution was observed. Relatively well-saturated PE loops at 1 kHz with P_r of $30 \mu\text{C}/\text{cm}^2$ were reported. The coercive field was about 95 kV/cm. A small shift to the negative field direction was observed likely the result of defects and mechanical stress during film growth.

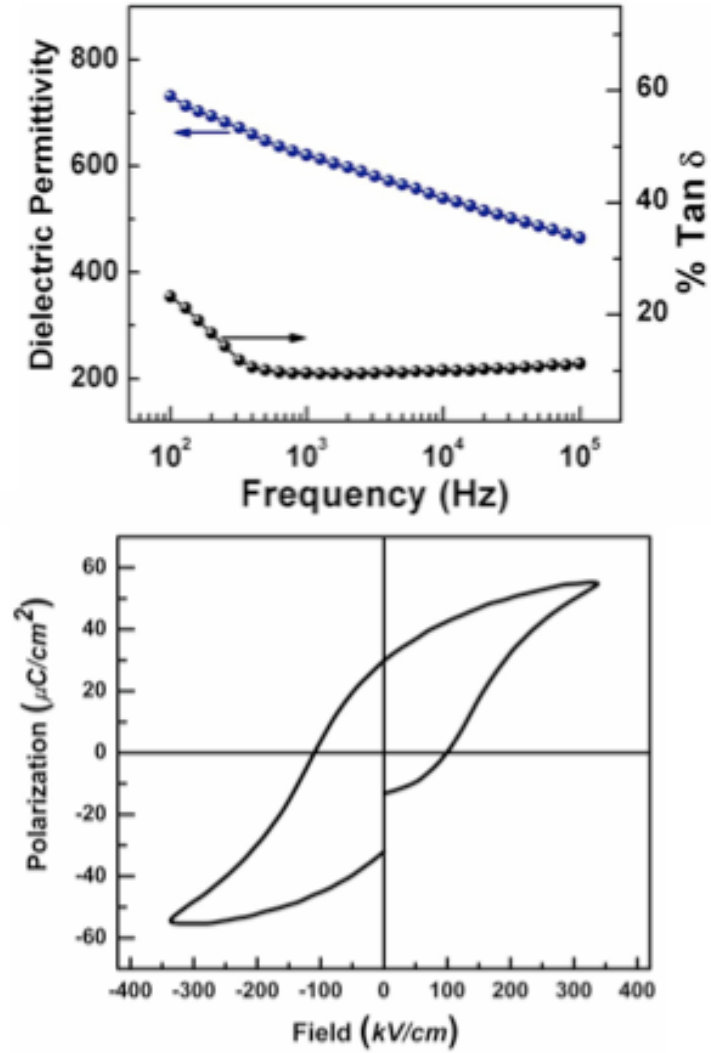


Figure 2.24 Dielectric properties (top) and hysteresis loop (bottom) for BNT – BKT – BT thin films[81]

In addition to PLD, chemical solution deposition has been widely used to fabricate lead-free BNT-based thin films and offers good stoichiometry control, chemical homogeneity and film uniformity. Yu *et al.* reported sol-gel derived BNT thin films on Pt/Ti/SiO₂/Si substrates.[88] TGA/DSC analysis indicates the BNT

precursor powder started to crystallize around 500 °C. It was noted that conventional processing where the film underwent post-annealing after multiple coatings did not produce perovskite material. When the film was annealed at 650 °C after each layer of spincoating, single phase perovskite was observed. The dielectric constant was about 300 at 1 kHz with around 4% loss. Figure 2.25 shows PE loop of BNT films with remanent polarization and coercive field of 8.3 $\mu\text{C}/\text{cm}^2$ and 200 kV/cm respectively. However, the frequency for PE loops was not included in the work.

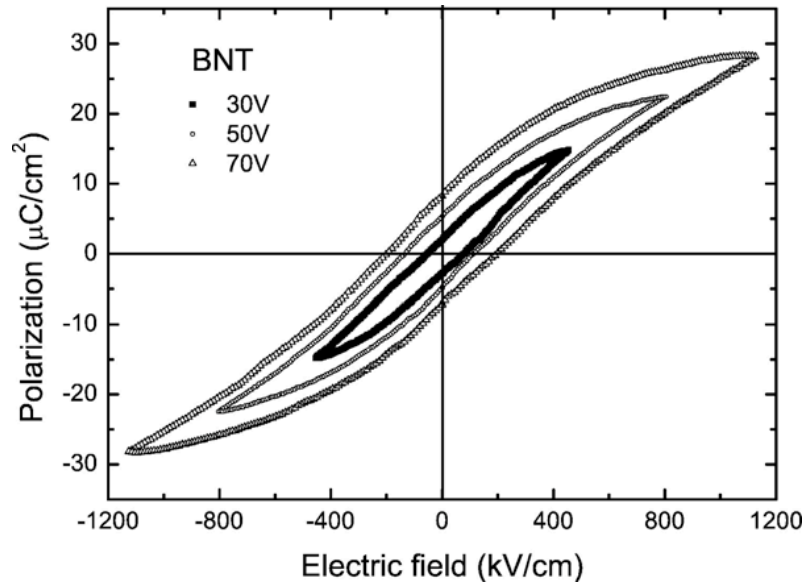


Figure 2.25 Hysteresis loops of the BNT thin films annealed at 650 °C in a RTP[88]

Guo *et al.* studied dielectric and ferroelectric properties of 94BNT – 6BT grown on $\text{LaNiO}_3/\gamma\text{-Al}_2\text{O}_3/\text{Si}$ substrates using a chemical solution deposition.[86] The dielectric loss of the (100) oriented films was between 5 ~ 10% for

frequencies of 100 - 1000 Hz but as the frequency further increased dielectric loss also increased to over 20% at 10 kHz. Ferroelectric hysteresis loops were obtained at 1 kHz but did not show saturation. Cernea *et al.* reported two separate works on BNT – BT thin films with slightly different compositions.[84, 85] First, 89BNT – 11BT thin films grown on Pt/TiO₂/SiO₂/Si had a dielectric constant below 170 at 50 kHz and the corresponding loss tangent was about 10%.[84] This film showed PE loops at 10 kHz but saturation was not observed and P_r was only 1.06 $\mu\text{C}/\text{cm}^2$. The other near MPB composition of 95BNT – 5BT was fabricated on Pt/TiO₂/SiO₂/Si substrates as well. [85] The film was not phase pure perovskite and showed a pyrochlore phase in the XRD pattern. Hysteresis loops were measured at different frequencies. No loops showed saturation and the one recorded at 100 Hz exhibited lossy behavior. Recently Bretos *et al.* investigated dielectric and ferroelectric of BNT_{1-x} – BT_x thin films on Pt/TiO₂/SiO₂/Si substrates where $x=0.055, 0.01$ and 0.015 .[90] Figure 2.26 shows the hysteresis loops of the three different BNT – BT thin films and all loops were well-defined. While the 90BNT – 10BNT film had a remanent polarization of 13 $\mu\text{C}/\text{cm}^2$, (95,85)BNT – (5, 15)BT films showed lower values of 6.4 $\mu\text{C}/\text{cm}^2$ and 3.8 $\mu\text{C}/\text{cm}^2$ respectively. Considering the dielectric and ferroelectric properties 90BNT – 10BT thin films might be situated to close to the MPB composition.

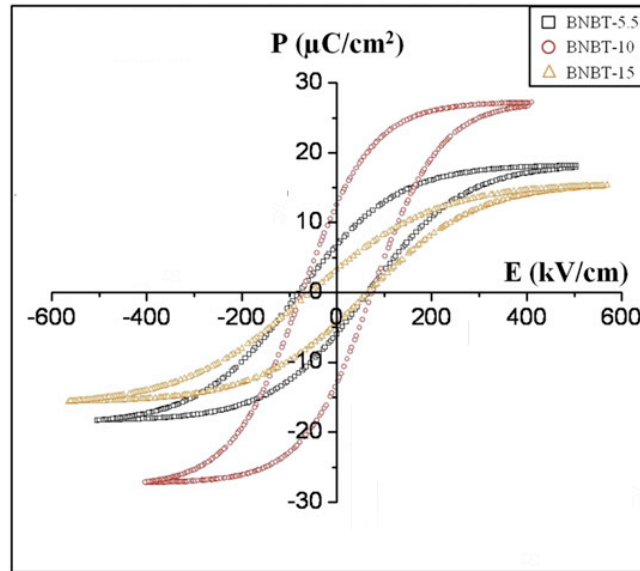


Figure 2.26 Compensated ferroelectric hysteresis loops of $BNT_{1-x} - BT_x$ thin films where $x = 0.055, 0.1$ and 0.15 . [90]

BNT – BKT thin films were also fabricated via CSD by several research groups. Yang *et al.* deposited 80BNT – 20BKT thin film on Pt/TiO₂/SiO₂/Si substrate. [83] The dielectric constant and loss at 1 MHz were about 300 and 0.045 respectively but no dielectric data below 10 kHz was included. The film exhibited lossy hysteresis loops measured at 250 kHz with Pr of about 2.3 $\mu\text{C}/\text{cm}^2$. Yu *et al.* reported sol-gel derived $BNT_{1-x} - BT_x$ thin films ($x=0, 0.1, 0.15, 0.18$, and 0.2) on Pt/Ti/SiO₂/Si substrates. [87, 88] At $x=0.15$, the film showed the best dielectric and ferroelectric properties corresponding with better crystallinity and microstructure. Even still, dielectric constant at 100 kHz was about 350 and some of hysteresis loops showed lossy behavior. Another BNT – BKT thin film was fabricated by Dong *et al.* by changing the content of BKT. [91]

The dielectric constant at 10 kHz and the piezoelectric coefficient $d_{33,f}$ measured by SPM displayed the highest values of 579 and 98 pm/V when BKT content was 18%. However, PE loops of all films did not saturate and XRD indicated there was pyrochlore present, likely resulting from the evaporation of Na, K and Bi. Wu *et al.* obtained 85BNT – 15BKT thin films on Pt/Ti/SiO₂/Si substrates with various amount of excess Na/K. [89] They found that when Na/K excess content is below 20 mol% a second phase was observed in XRD patterns. As seen in Figure 2.27, 85BNT – 15BKT films deposited with 20 mol% of Na/K excess exhibited the best ferroelectric properties with P_r of 13.6 $\mu\text{C}/\text{m}^2$. The frequency for those loops was not reported. Crystallinity and microstructure explain the difference in electrical response. Below 20 mol% of Na/K excess a second phase forms due to insufficient Na/K to compensate for loss during thermal processing. Above 20 mol%, a decrease in the grain size and crystallinity was observed also resulting in a degradation of the ferroelectric properties.

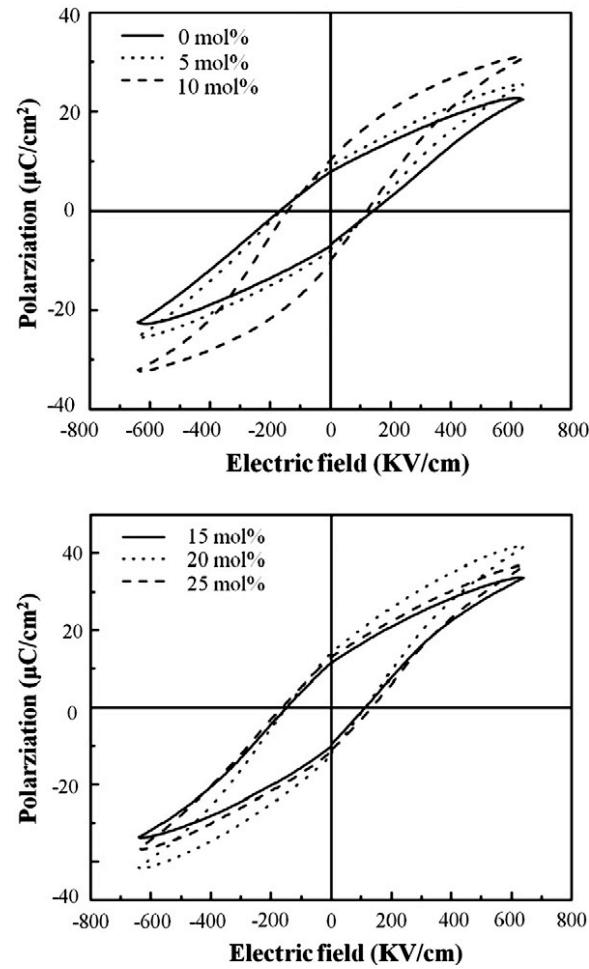


Figure 2.27 Hysteresis loops for 85BNT – 15BKT thin films deposited with different amounts of Na/K excess content[88]

2.7 Thin film related issues

A demand for miniaturized mechanical or electronic devices has spurred the development of thin film fabrication. There are several issues related to thin films different from bulk materials. The following sections will review these issues.

2.7.1 Substrate Effect

One of the biggest differences between thin film and bulk materials is that thin films are fabricated as a composite structure on top of a substrate that dominates the total elastic properties. The most widely used material for the substrate is silicon. Along the in-plane directions (indices 1 and 2), the piezoelectric thin film and the substrate will have identical strains. In contrast, perpendicular to the substrate, the thin film is free to move, meaning that there is no stress. When an electric field is applied, in-plane stress and out-of-plane strain develops. Considering this anisotropic interaction with the substrate, the equations for the strain state of the thin film could be re-written using the compliance tensor (s_{xx}^E) and piezoelectric coefficients:

$$x_1 = x_2 = (s_{11}^E + s_{12}^E)\sigma_1 + d_{31}E_3 = 0 \quad (2.28)$$

$$x_3 = 2s_{13}^E\sigma_1 + d_{33}E_3 \quad (2.29)$$

When Equation (2.28) is solved in terms of $\frac{\sigma_1}{E_3}$, an effective in-plane stress is

derived and given by:

$$e_{31,f} = -\frac{\sigma_1}{E_3} = \frac{d_{31}}{s_{11}^E + s_{12}^E} \quad (2.30)$$

Rearranging Equation (2.29) an effective out-of-plane strain is defined:

$$d_{33,f} = \frac{x_3}{E_3} = d_{33} - \frac{2s_{13}^E}{s_{11}^E + s_{12}^E} d_{31} = d_{33} - 2s_{13}^E e_{31,f} \quad (2.31)$$

The effective longitudinal $d_{33,f}$ piezoelectric coefficient represents the thickness change as a function of the electric field. The effective transverse $e_{31,f}$ piezoelectric coefficient describes in-plane stress as a function of the applied field or the charges developed by bending the substrate.[93, 94]

2.7.2 Stress-Strain Effects

The presence of the stress in a ferroelectric thin film can affect the mechanical, dielectric, piezoelectric and optical properties of the thin films or even the nature of the phase transitions.[95, 96] The thin films are constrained by large biaxial stresses associated with the interaction between the film and substrate and these stresses can be classified as intrinsic, extrinsic and thermal stresses. The intrinsic stress results from the where atoms or ions are located relative to their low energy equilibrium position. Intrinsic stress is related to processing conditions such as temperature, pressure, reactant concentration and impurities. The extrinsic stress is caused by structural changes in materials undergoing crystallization or densification. The thermal stress is induced by the differences between the coefficient of thermal expansion (CTE) of the thin film and substrate. The generated thermal stress in the film can be expressed by:

$$\sigma_{th} = \frac{E_f}{1 - \nu_f} (\alpha_f - \alpha_s)(T_d - T) \quad (2.32)$$

where E_f is the Young's modulus of the film, ν_f is the Poisson's ratio of the film, α_f is the coefficient of thermal expansion for the film, α_s is the coefficient of thermal expansion for the substrate, T_d is the film deposition temperature and T is the temperature of interest. The sign of the thermal stress will be determined by $(\alpha_f - \alpha_s)$ which indicates whether the film is under compressive or tensile stress. Utilizing the thermal stress allows domain engineering in the film. Tuttle *et al.* demonstrated controlled domain orientation of PZT thin films by using the differences of CTE between PZT and substrates. [97] Sol-gel derived PZT thin film on MgO substrates, which have higher CTE than PZT, experienced about 100 MPa compressive stress during cooling through the Curie temperature and this stress oriented the domains normal to the plane of the film (c-domains). On the other hand, PZT thin films on platinized silicon substrates, which have lower CTE than PZT, had in-plane oriented domains (a-domains) induced by about 150 MPa tensile stress. Depending on the orientation of the thin film, dielectric and ferroelectric properties vary due to anisotropy in the dielectric constant.[9] PZT thin films with "c-domains" show lower dielectric constants but larger polarization and piezoelectric coefficients. In contrast, PZT thin films with "a-domains" have larger dielectric constants. PZT thin films grown on Al_2O_3

substrate had mixed orientation and showed intermediate dielectric constant and polarization values compared to PZT grown on MgO and Si substrates. [98]

2.7.3 Size Effects

Dielectric properties are also affected by the grain size of the ferroelectric material. Figure 2.28 shows the permittivity change of BaTiO₃ as function of grain size. As grain size falls, the dielectric constant at room temperature increases. When the grain size in the ceramic is about 0.8 μm a maximum is observed. Further decreases in grain size induce lower permittivity. In general, thin films have smaller grain size than that of bulk ceramics and the size effect is more pronounced. In ferroelectric materials, dielectric properties result from intrinsic and extrinsic contributions, both of which are affected by size. Intrinsic size effects influence the ferroelectric transition and decrease the peak permittivity value as the dielectric spectrum broadens.[99, 100] The extrinsic contribution is related to the density of domains and the mobility of domain walls. Cao *et al.* demonstrated the relationship between domain size and grain size while Arlt *et al.* reported that the domain wall mobility was reduced as the number of domains increased. [101, 102] These findings demonstrate that the extrinsic contribution is affected by grain size. The homogeneous spontaneous polarization in ferroelectrics is a long-range cooperative phenomenon which comes from the interactions between the neighboring dipole moments.[6, 103] The correlation lengths that represent the interactions between dipoles are parallel and

perpendicular to the polarization vector and their values are 10~50 nm for parallel and 1~2 nm for perpendicular. When grain size is close to these ranges, phase stabilization may be affected. The decrease of the relative dielectric constant for ferroelectric materials whose grain size is less than 500 nm can be well described by the brick-wall model. [1, 104] Grain boundary regions whose permittivity is very low separate the ferroelectric grains. These grain boundary regions dilute the permittivity and lower the dielectric constant dramatically.

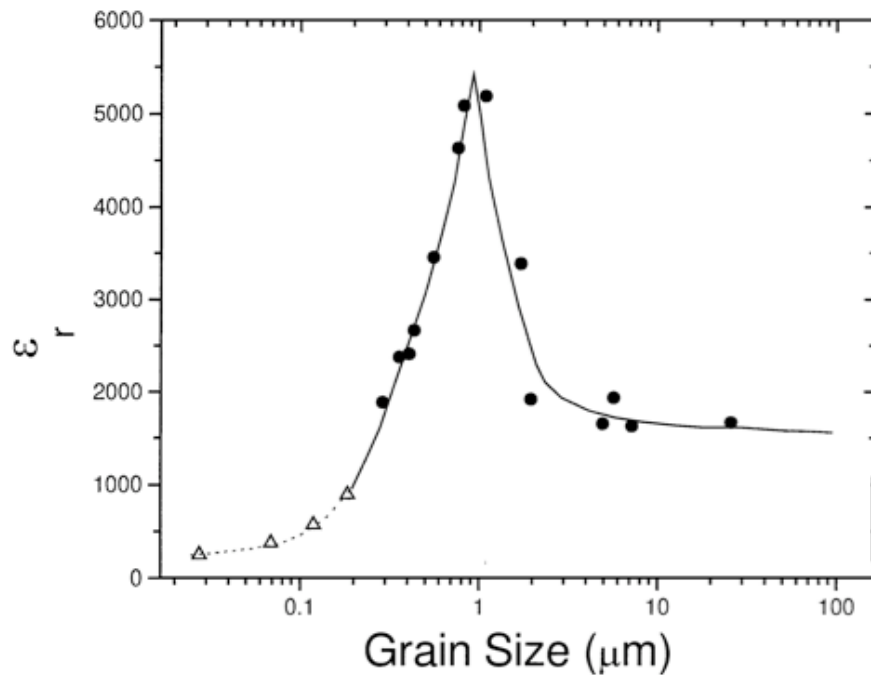


Figure 2.28 Permittivity of BaTiO₃ as a function of grain size. Dark circles represent grain size in bulk and triangles indicate grain size in thin films. [99]

2.8 Processing of thin films

The thin films have been fabricated by various deposition methods including radio frequency (RF) sputtering, chemical solution deposition (CSD), pulsed laser deposition (PLD) and metal-organic chemical vapor deposition (MOCVD). In this thesis, two deposition techniques, PLD and CSD were used and will be described briefly.

2.8.1 Pulsed laser deposition (PLD)

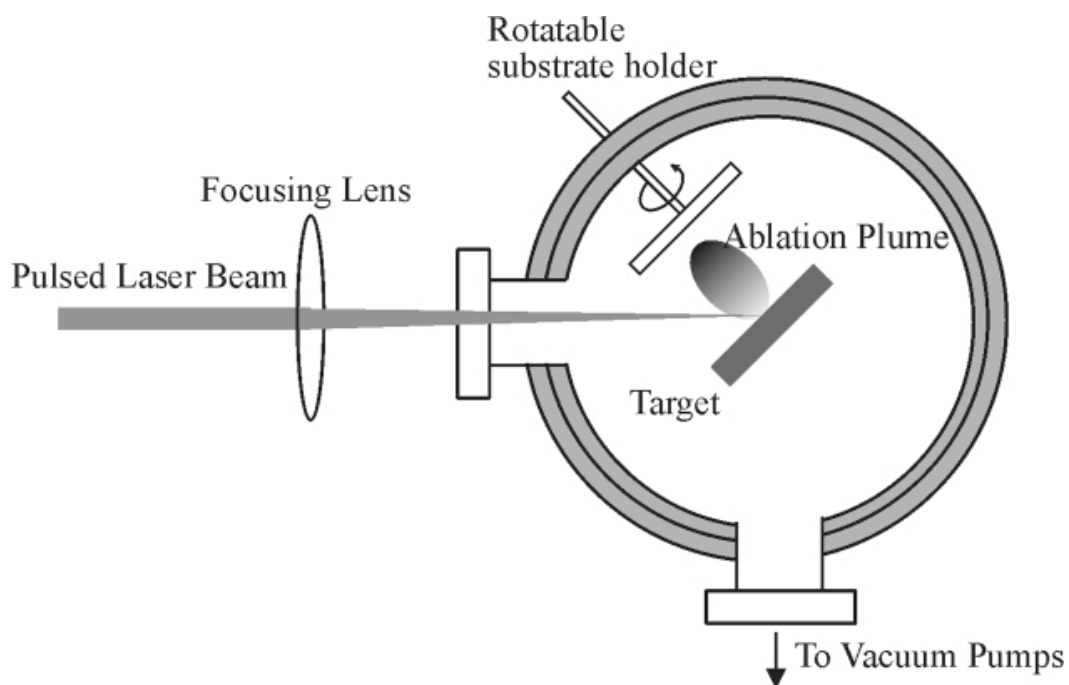


Figure 2.29 Schematic diagram of a pulsed laser deposition system.[105]

Physical vapor deposition (PVD) is a technique that uses heat or an energetic beam of electrons, laser ablation, or positive ions (sputtering) to vaporize the solid materials and deposit it on the substrate. PVD thin film techniques have some benefits compared with liquid phase based techniques; (1) They can be applied to any material, (2) a wide range of substrate temperature can be controlled, (3) during processing, access to the surface is possible.[106] Evaporation, sputtering, and laser ablation are common PVD methods and have been widely used for deposition of many different thin films.[107] Pulsed laser deposition is a PVD technique where laser radiation is utilized to ablate materials from a target. Compared to other deposition methods, pulsed laser deposition has the advantage of allowing congruent transfer from target to substrate, so thin films of complex material systems can be deposited.[108] In general, PLD happens in three stages: (1) vaporization of target materials, (2) transport of the vapor plume to the substrate and (3) growth of film on the substrate. A schematic diagram of a typical PLD system is shown in Figure 2.29.

When the high-powered laser beam, which is focused by an external lens outside of the vacuum chamber, strikes the solid target the laser radiation is absorbed by the target surface and electromagnetic energy is converted into electronic excitation followed by thermal, chemical and mechanical energy causing evaporation and ablation. [109] Evaporants create a plume, which consists of a mixture of energetic species such as atoms, molecules, ions,

electrons, particulates, and molten droplets and a plume is directed toward to the substrate. Typically, ArF (193 nm), KrF (248 nm), and XeCl (308 nm) are used as gases for excimer lasers. Figure 2.30 illustrates the thermal cycle induced by a laser pulse. The absorbed incident laser pulse causes rapid heating of the target surface and results in the phase transition through melting and vaporization. The plume is generated and accompanied by continued vaporization. After the laser pulse, the target cools down and melting is attenuated. The target re-solidifies and the surface topography is also changed.

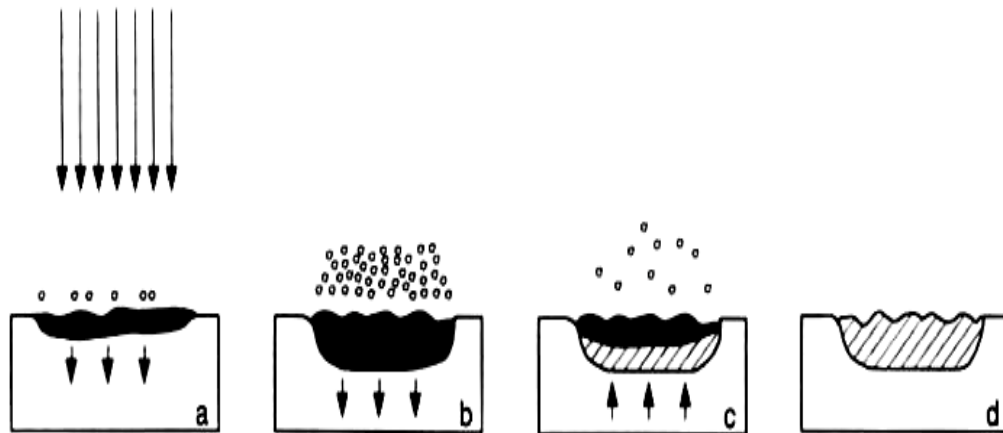


Figure 2.30 Schematic of the thermal cycle by a laser pulse. (a) Absorption of laser pulse, (b) Propagation of melt, (c) Recession of melting, (d) Re-solidification of target surface. [110]

There are two major drawbacks in the fabrication of thin films by PLD. Since the plume is highly directional with a narrow angular distribution, it is difficult to achieve good uniformity over large scale of substrates. The other

problem is the splashing effect. Three mechanisms including subsurface boiling, expulsion of the liquid layer and exfoliation create particulates.[110] If the surface of a low melting point target requires more time for vaporization than the pulse length, the subsurface can be superheated before vaporization occurs at the surface. This could cause micron-sized molten globules that are deposited on the substrate. Expulsion of the liquid layer by the shockwave also produces micron-sized globules but in a different manner than subsurface boiling. Recoil pressure from the shockwave of the plume induces some forces that expel molten globules from the liquid layer. Exfoliation results from continued laser ablation that creates a needle-shaped microstructure on the target surface. These microstructures can be sheared by the laser radiation and particulates are generated.

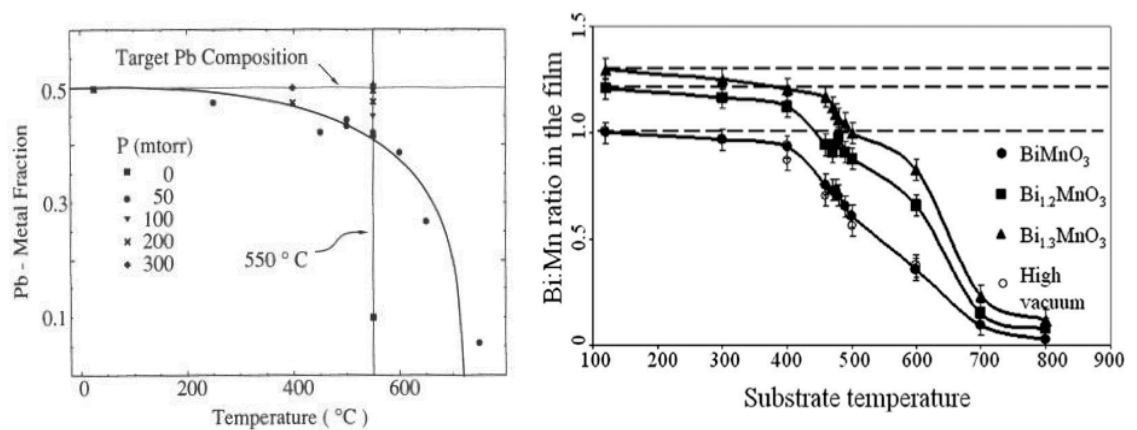


Figure 2.31 Pb content of PZT film (Left) and Bi content of BMO film (Right) at different processing temperature.[111, 112]

For optimum deposition conditions, substrate temperature, distance between substrate and target, processing pressure, laser power and repetition frequency need to be adjusted. Substrate temperature affects the crystallinity of thin film by controlling the diffusion of incoming atoms on the substrate. [105] Higher temperatures aid crystallization, but above a certain temperature films may become deficient of volatile elements like Pb, Bi, Li or K. Volatility is not only related to the temperature but also depends on laser power and repetition frequency.[110] Figure 2.31 shows the loss of the volatile Pb and Bi atoms versus temperature in thin films deposited by PLD. Laser energy is an important factor in determining the deposition rate and quality of the films. Higher energy increases the number of atoms transferred from target to substrate but increased splashing can be expected. Splashing causes particulates a few microns in size and it results in a film with a rougher surface. Increasing frequency produces higher deposition rates but at the same time may not allow enough time for the ablated atoms to diffuse to surface positions before atoms ablated by next pulse arrive. Poor crystallinity may result. Distance between substrate and target also affects the deposition rate and energy transfer. Use of an oxidizing background gas plays an important role in the incorporation of ablated atoms. Incorporating an ambient gas may prevent oxygen deficiency and affect the particle size. [110]

2.8.2 Chemical solution deposition (CSD)

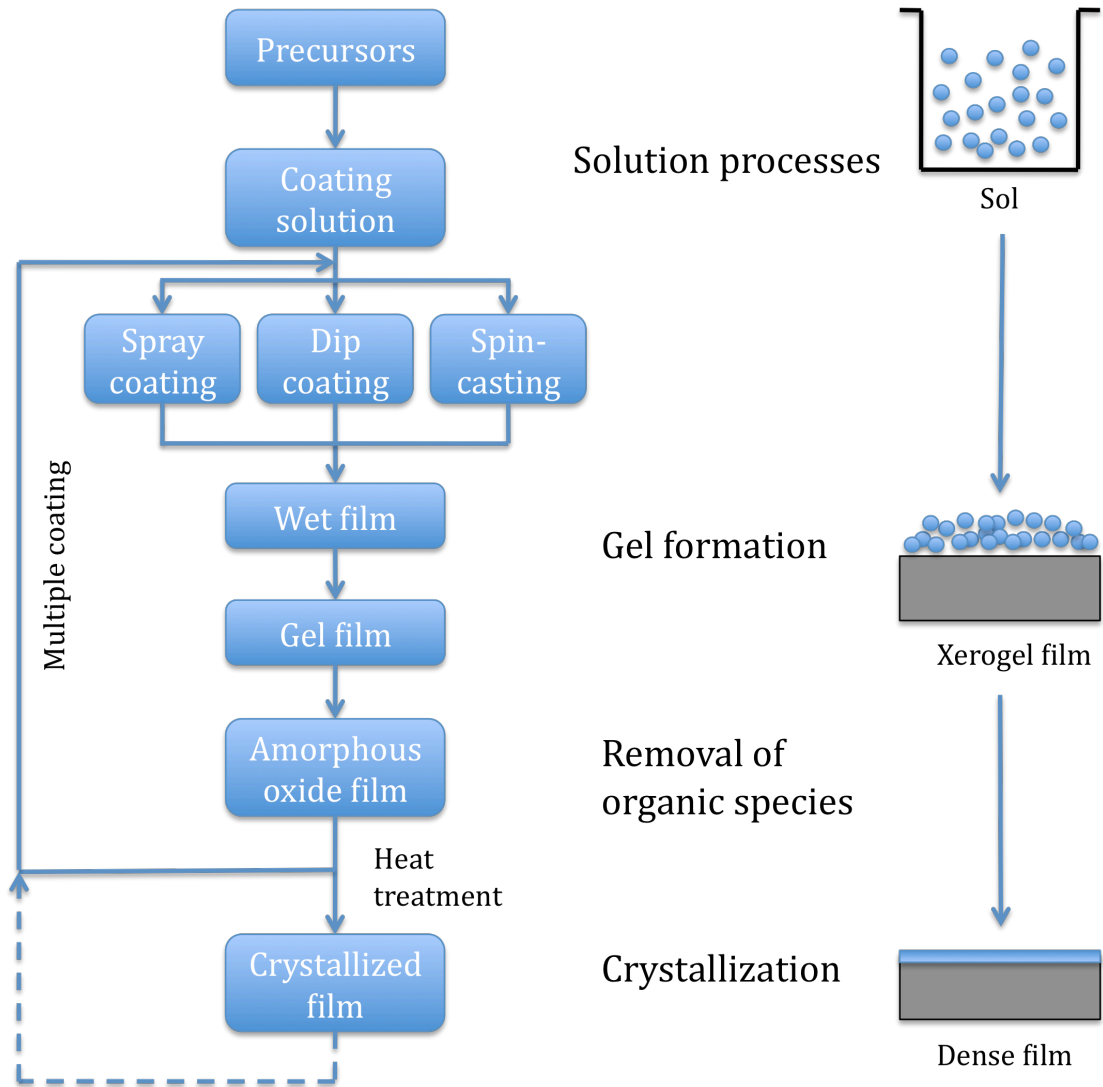


Figure 2.32 Chemical solution deposition process (After reference[113, 114])

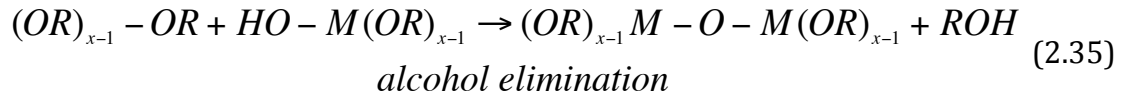
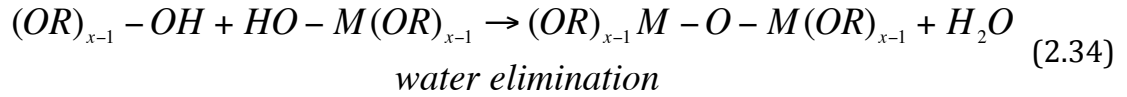
Since chemical solution deposition techniques offer advantages like low cost, high compositional uniformity and simple preparation routes, they are widely used to synthesize ferroelectric thin films.[115] Figure 2.32 shows a schematic of solution processing and it requires typically four basic steps:(1) synthesis of the precursor solution, (2) solution deposition by spin-casting using a rotating substrate, spray coating or dip coating in a solution bath, (3) low-temperature heat treatment which is drying or pyrolyzation of organic species to form amorphous film, (4) crystallization at high temperature where an amorphous film is transformed into the desired perovskite phase. [114]

Approaches for solution preparation can be grouped into three categories; sol-gel processes, metallo-organic decomposition processes and hybrid (or chelate) processes. Common sol-gel processes for perovskite thin films are based on 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$). When metal-oxygen-metal (M-O-M) bonds are formed, two key reactions called hydrolysis and condensation of the alkoxide reagents occurs. The process of hydrolysis is shown in equation (2.33):



where M represents a metal cation and R is an alkyl group. During hydrolysis, a hydroxyl ion OH^- attaches to the metal cation. Two partially hydrolyzed molecules can undergo a condensation reaction by eliminating water or alcohol

to form an M-O-M bond. Equation (2.34) and (2.35) shows these condensation reactions:



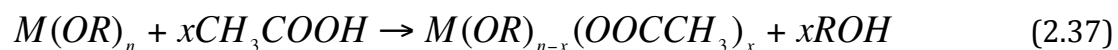
Condensation reaction can build or form larger molecules by the process called polymerization or oligomerization depending on the size.[113] There is another key reaction when 2-methoxyethanol (2-MOE) is used as a solvent. Metal alkoxides are highly reactive to water and the hydrolysis sensitivity of a metal alkoxide can be reduced by the alcohol-exchange reaction:



where OR is a reactive alkoxy group and OR' is the less reactive methoxyethoxy group. 2-MOE has advantages in the dissolution of carboxylate precursors so this solvent was traditionally used to fabricate sol-gel PZT and BaTiO₃. [116, 117] However, sol-gel processes involving refluxing, distillation and dilution to achieve the desired molarity can be complicated to the non-chemist and the use of 2-MOE is prohibited in most manufacturing facilities due to environmental concerns. [114]

The second class of solution synthesis approaches is metalloorganic decomposition (MOD), which uses large carboxylate or β -diketonate compounds as precursors. Solution preparation is straightforward. Metallo-organic compounds are dissolved in a solvent and the desired stoichiometry is achieved by mixing the solutions. Precursors used in MOD are more stable against water so the oligomerization found in sol-gel is not expected and, even after dissolution, the precursor species remain as the starting molecules. Although the MOD process is simple, there are drawbacks. Since the MOD process uses large organic ligands, large weight loss and shrinkage during thin film processing might induce cracking. Additionally, process flexibility can be limited because precursors have low reactivity.

The third synthesis approach is hybrid or chelate process. A short-chain carboxylate is used for the A-site precursor and is dissolved in carboxylic acid while a metal alkoxide compound for the perovskite B-site is reacted with chelating agents like acetic acid, acetylacetone or amine compounds. Through chelation of the B-site alkoxides, the hydrolysis sensitivity of the alkoxide compounds decreases and the solution can be handled in ambient air. The chelation with acetic acid is described in equation (2.37):



The hybrid process is relatively simple and rapid because it does not require refluxing or distillation steps and has been applied to synthesize ferroelectric

thin films like BaTiO_3 , SrTiO_3 , $(\text{Ba,Sr})\text{TiO}_3$ and PZT.[98, 115, 118-121] However, the continued reactivity of solution after synthesis alters the characteristics of the precursors and degrades the properties of ferroelectric film. [122]

2.8.3 Nucleation and growth process

The nucleation and growth process plays an important role in the resultant microstructure of thin films derived by chemical solution deposition. When only interface nucleation occurs, films frequently show columnar growth. On the other hand, when nucleation takes place throughout the film, polycrystalline microstructures with equiaxed grains are observed.

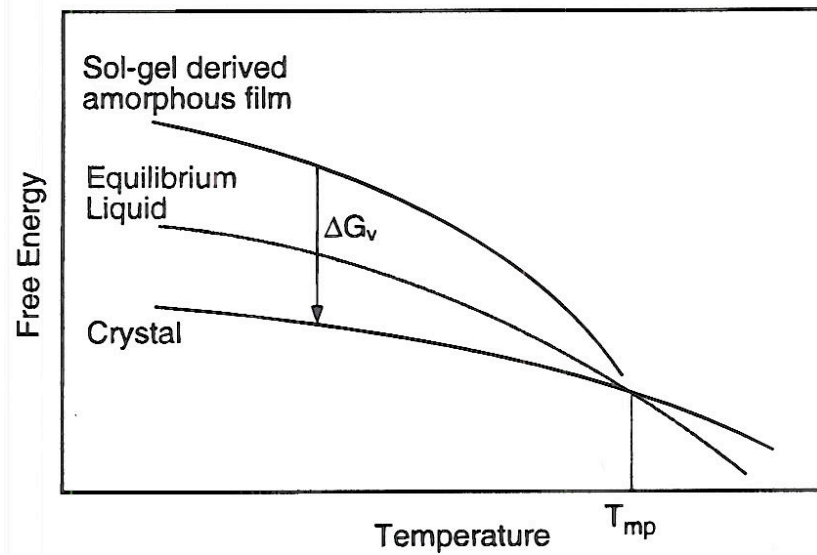


Figure 2.33 Schematic diagram of the free energy difference among amorphous films, the ideal supercooled liquid, and the crystalline film.[114]

In thermodynamics, crystallization from the amorphous film after pyrolysis into a dense thin film is determined by the driving force, which controls the active nucleation events. Figure 2.33 represents the driving force ΔG_v which indicates the free energy difference per unit volume between the amorphous film and crystallite film. The driving force is considered a barrier for nucleation at the substrate or bulk (within film). Annealing at high temperature gives enough thermal energy to surmount energy barrier and nucleation events will occur. The energy barriers for homogenous and heterogeneous nucleation are described by:

$$\Delta G_{homo}^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \quad (2.38)$$

$$\Delta G_{hetero}^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} f(\theta) \quad (2.39)$$

where γ is the interfacial energy, ΔG_v is the driving force for crystallization and $f(\theta)$ is a function related to the contact angle θ , which lowers the energy barrier and is given by:

$$f(\theta) = \frac{(2 - 3\cos\theta + \cos^3\theta)}{4} \quad (2.40)$$

These equations and Figure 2.33 introduce a few concepts to aid understanding of film crystallization behavior. When the driving force is large at low temperatures, bulk (=homogenous) nucleation is probable as well as interface (=heterogeneous) nucleation because ΔG_v is dominate. In contrast, higher crystallization temperatures lower the driving force so heterogeneous nucleation is favored. For high heating rates, heterogeneous nucleation events are more favored because delayed crystallization induces nucleation at a higher temperature decreasing the driving force. The transformation pathway also affects the structural evolution.

PZT and BT show different nucleation and growth behavior. In general, CSD derived PZT film has a columnar microstructure indicating heterogeneous nucleation events take place at the substrate interface. Grain growth from the surface develops by consuming the intermediate fluorite or pyrochlore phase. On the other hand, BT generally does not show columnar microstructures. This indicates homogeneous nucleation in the film occurs as well as heterogeneous nucleation at the interface. Similar effects are observed in BST.[119] Figure 2.34 illustrates the start of crystallization for BST and PZT thin film. As described above, when the driving force for crystallization is lowered by increased annealing temperature or by introducing an intermediate phase, heterogeneous nucleation is favored over homogeneous nucleation. The fluorite/pyrochlore grains in PZT do not lead to nucleation of the perovskite phase so heterogeneous nucleation at the interface dominates. For BST, however, the oxo-carbonate grains act as nucleation sites for the perovskite phase. Therefore, two nucleation events at the interface and at the grains compete and BST exhibits a different microstructure compared to that of PZT. Changing the deposition conditions like solution concentration, annealing conditions or using conductive oxides as a seed layer can tailor the morphology of BST, BT, and SrTiO₃ (ST).[119, 121, 123]

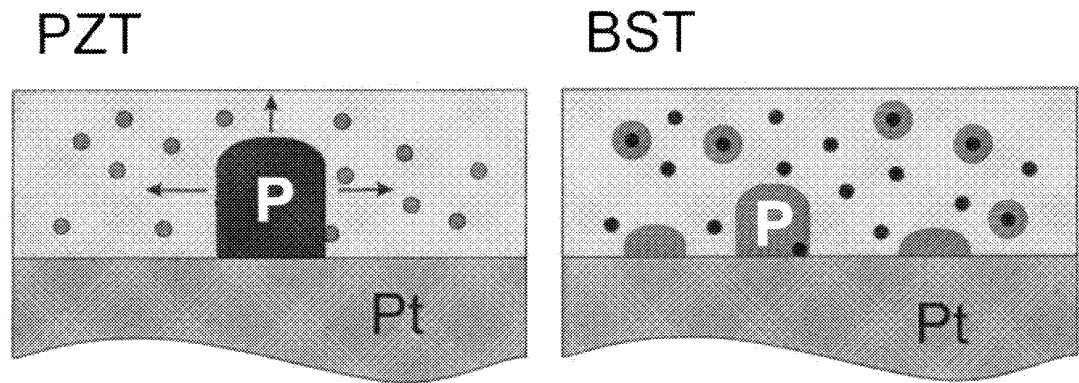


Figure 2.34 Nucleation and growth behavior of PZT and BST thin films. (P = perovskite phase, circles = intermediate phases of PZT and BST)[119]

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Chapter 3. Experimental procedure

This chapter describes the experimental procedure including target preparation, the deposition of thin film by PLD and CSD, and characterization methods of deposited films. Each process for PLD and CSD will be discussed again in following chapters.

3.1. Target preparation

Bulk ceramic targets for pulsed laser deposition (PLD) were synthesized via conventional solid state processing. An illustration of the flow chart of powder processing and the sealed alumina crucible for sintering is given in Figure 3.1. For composition 0.95BKT – 0.05 BZT, reagent grade oxide powders of Bi_2O_3 ($\geq 99.9\%$), K_2CO_3 ($\geq 99.5\%$), ZnO ($\geq 99\%$), and TiO_2 ($\geq 99.9\%$) were used as starting materials and the mixture of the powders was milled for 6h, using a vibratory milling machine with yttrium-stabilized zirconia media and ethanol. The dried powders were calcined at 920 °C for 6 hours in an alumina crucible with a cover followed by milling and drying again. These powders were then mixed with 3 wt% polyvinyl butyral (PVB) binder in ethanol and biaxially pressed into pellets with a 12.7 mm diameter. After burning out the PVB binder at 400°C, the pellets were sintered in an alumina crucible with a cover at 1045°C for 10 hours. Due to the volatility of Bi and K during processing at temperature, targets with 10 % and 20 % excess Bi and K were synthesized in addition to stoichiometric targets. Both targets had densities over 90%.

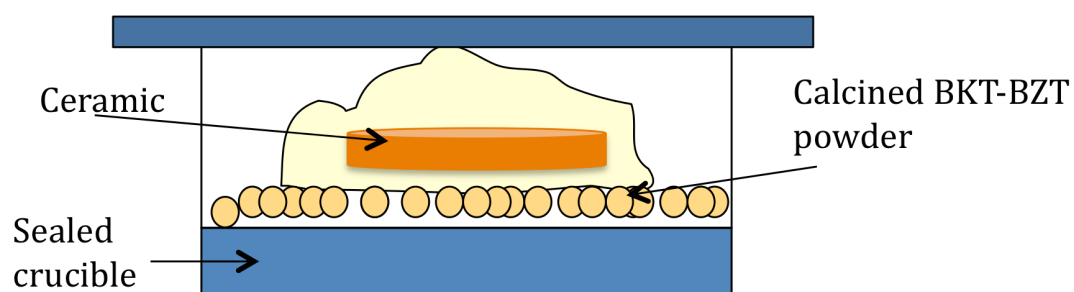
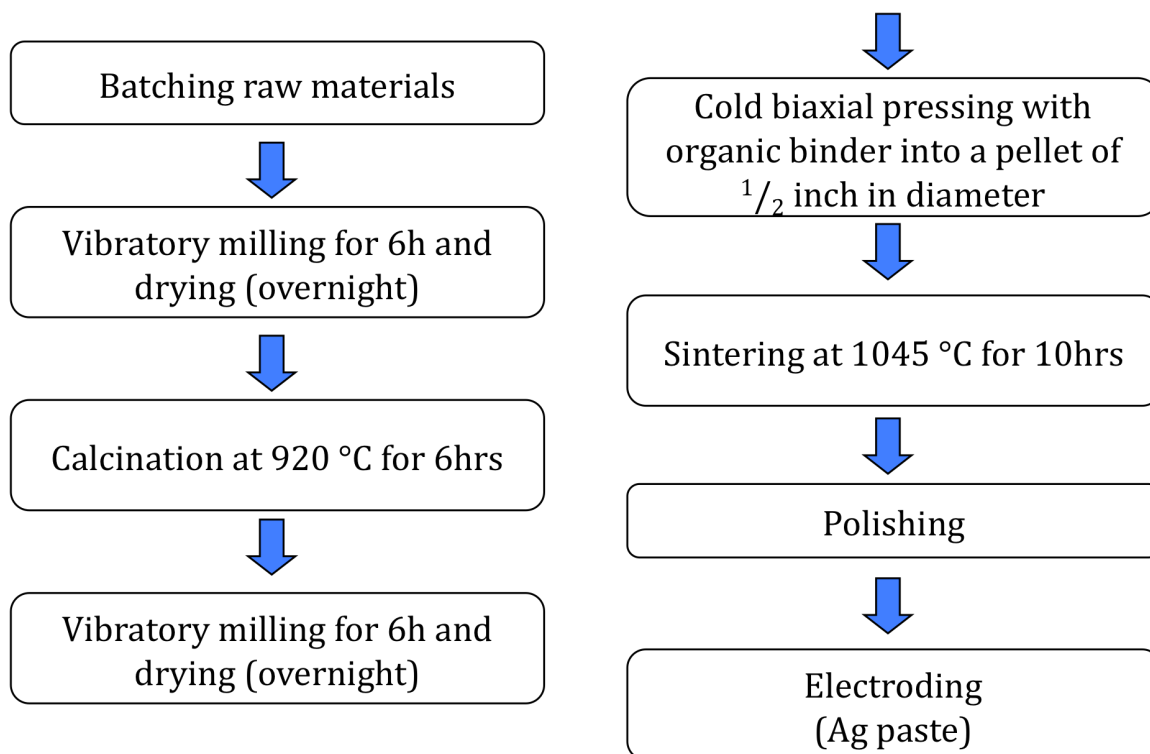


Figure 3.1 Flow chart for Powder processing (Top) and illustration of sealed crucible for sintering (bottom)

3.2. PLD processing

0.95BKT – 0.05BZT thin film was deposited using pulsed laser deposition. 1-inch targets for PLD were prepared as described above. The laser (Lambda Physik EMG 201) generated with XeCl ($\lambda=308$ nm) was utilized to produce 200 mJ/pulse $\sim$ 300 mJ/pulse. To calculate an energy density, the laser spot size was approximately measured and with power of laser, the energy density calculated to be about $1.5 \text{ J/cm}^2 \sim 3 \text{ J/cm}^2$. Platinized silicon, provided by Army Research Labs, was used for the substrate and it was adhered to a holder using silver paint (Ted Pella). To cure the silver paint a substrate holder was heated up to 100°C and kept for couple of minutes. When target and substrate were placed inside of PLD chamber, the system was first pumped down to the order of 10^{-6} Torr. Once the chamber reached to the desired pressure, the substrate holder was heated up to the processing temperatures varying from RT to 800°C and then oxygen gas was introduced to set up the processing pressure in the range of 100 mTorr $\sim$ 400 mTorr. To achieve uniform thickness, the substrate was rotated during deposition at a constant speed. After deposition, the sample was cooled to room temperature under oxygen rich atmosphere. When the processing temperature was below 400°C , the film was treated with an *ex situ* post-annealing step after deposition. A controlled atmosphere tube furnace was used to crystallize the films deposited at low temperature. Table 3.1 summarizes the processing parameters for the synthesis of 0.95BKT – 0.05BZT thin films via PLD.

Pulsed laser deposition	
Target	0.95BKT – 0.05BZT with various amount of excess cations
Substrate	Platinized silicon Pt/TiO _x /SiO ₂ /Si
Processing temperature	RT ~ 800 °C
Target to substrate distance	5 cm ~ 7 cm
Processing pressure (Oxygen)	100 mTorr ~ 400 mTorr
Laser power	200 mJ ~ 300 mJ
Repetition rate	2 Hz ~ 10 Hz
Deposition hours	10 min ~ 30 min
Post annealing	Only when processing temperature is below 400 °C

Table 3.1 Deposition parameters for the fabrication of films via PLD

3.3. CSD processing

The solutions for all BNT-based thin films were prepared using a chelate solution process. Bismuth acetate Bi(OOC₂H₃)₃, sodium acetate trihydrate Na(OOC₂H₃)•3H₂O, potassium acetate K(OOC₂H₃), magnesium acetate tetrahydrate Mg(OOC₂H₃)₂•4H₂O, barium acetate Ba(OOC₂H₃)₂, and titanium

isopropoxide $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ were chosen as precursors. Depending on the end member attached to BNT – BKT system, Mg or Ba were added to the solution. This will be described well in following chapters.

For BNT – BKT and BNT – BKT – BMgT, titanium isopropoxide was chelated with acetic acid in a 1:4 molar ratio in a dry box to prevent the reaction of the titanium precursor with H_2O . Bismuth acetate was dissolved in propionic acid and other acetates such as sodium, potassium, and magnesium were dissolved in methanol in separate bottle. An appropriate weight of the Bi, Na, K, and Mg solutions was added dropwise into the Ti solution. The molarity of the final solution was 0.3M.

For BNT – BKT – BT solution, titanium isopropoxide was stabilized with acetylacetone in a molar ratio of 1:2 in a dry box. Bismuth acetate was also dissolved in propionic acid but separately from the other cations. Potassium, sodium, and barium acetates were dissolved separately in acetic acid at 70 °C. The 0.3M final solution was achieved by dropping acetate solution into the Ti solution. It should be noted that the purity of bismuth acetate used in the researches was 99.999%. When lower purity was used, bismuth acetate could not be dissolved clearly and slightly cloudy solution was made.

The prepared solution was dispensed onto the substrate using syringes with 0.2 μm PTFE filter and then spin-coated at 3000 rpm at 3000 rpm for 30 seconds by the spin-coater (Laurel Technologies). After each spin, the film was pyrolyzed at 300°C for 5 min on a hot-plate and then annealed in air for 700°C in

a preheated furnace. These steps were repeated until the desired thickness was obtained. Figure 3.2 illustrates the flow chart of the solution process for different composition of thin films.

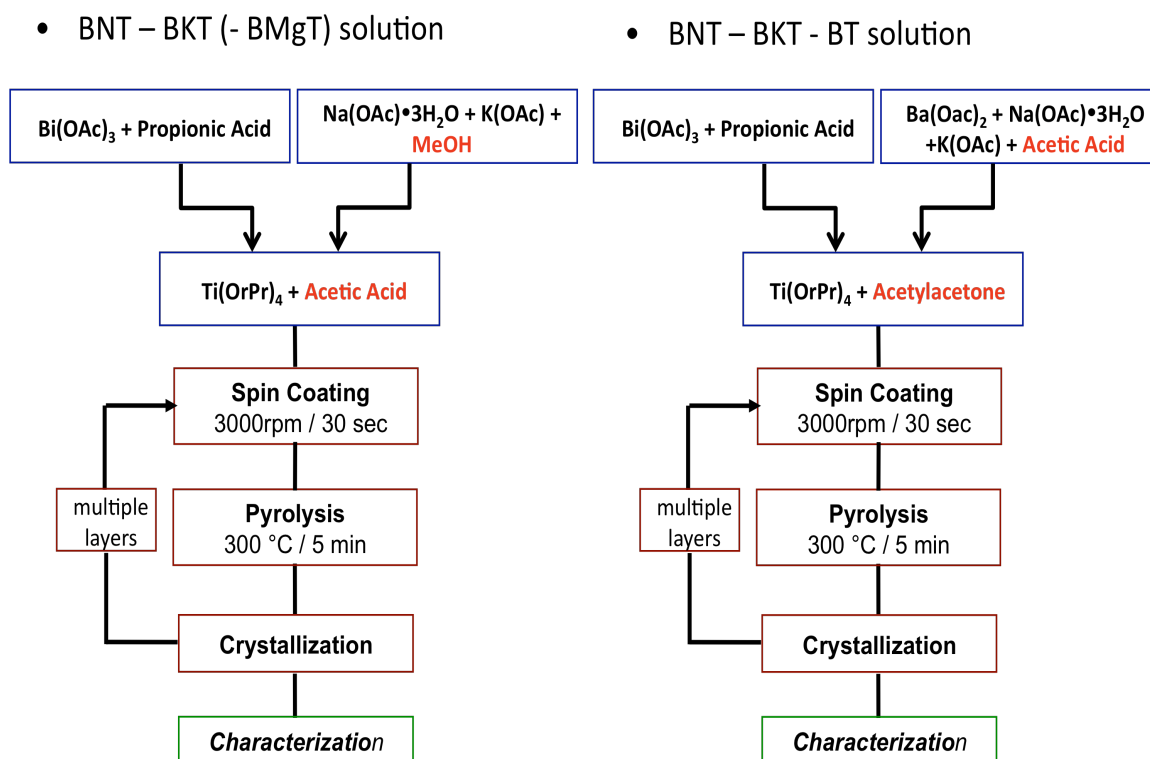


Figure 3.2 CSD process for the fabrication of BNT-based thin film

3.4. Film characterization

The phase of thin films was characterized using X-ray diffraction (XRD, Bruker AXS D8 Discover) with Cu K α radiation. The microstructures of crystallized films were confirmed via three different methods: atomic force microscopy (AFM, Asylum MFP-3D), scanning electron microscopy (SEM, FEI

Quanta 600F and FEI XL30S-2), and transmission electron microscopy (TEM, JEOL 2500 SE).

To measure an electrical response of film, top electrodes of Ag and Ir were prepared using thermal evaporator and sputter coater, respectively. The dielectric properties were characterized using an LCR meter (HP 4192a) in the range of 100 Hz ~ 1 MHz. A ferroelectric tester (Radiant RT66B, Premier II, and aixACCT TF analyzer) was utilized to take polarization versus electric field hysteresis loops at room temperature and as a function of temperature. Unipolar or bipolar strain behaviors of the films were taken using dual beam laser interferometer (aixACCT DBLI TF Analyzer systems). Small-scale piezoresponse was characterized was performed via piezo force microscopy (PFM, MFP-3D) with a conductive tip.

For the investigation on composition of thin films, X-ray photoelectron spectroscopy (XPS, PHI Quantera Scanning ESCA) and electron probe microanalysis (EPMA, Cameca SX50) were used to obtain the depth profile of each elements of the films and quantitative composition of the films, respectively.

Chapter 4. The structural development and electrical properties of polycrystalline BKT – BZT thin film via PLD

4.1. Introduction

Since Pb is a well-known toxic element and the high volatility of PbO is an environmental concern, many researchers are investigating lead-free piezoelectric materials as a replacement for lead zirconate titanate (PZT), $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ and its related solid solutions. [1-4] Among the candidates are Bismuth based perovskites such as $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT), $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (BKT) - $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BZT), $(\text{Bi}_{0.5}\text{Li}_{0.5})\text{TiO}_3$ (BLT) as well as their solid solutions. [5-13]

Bismuth potassium titanate, $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (BKT) is a ferroelectric material with tetragonal symmetry. It displays relatively high Curie temperatures ($T_c=380\text{ C}$) and a large coercive field of about 52.5 kV/cm [7] Previously Huang *et. al* reported that a solid solution of BKT and the unstable perovskite $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BZT) resulted in enhancement of density as well as dielectric and piezoelectric properties. [9] There are reports of Bi-based perovskite thin films by various methods including chemical solution deposition (CSD), RF sputtering, and pulsed laser deposition (PLD) but the fabrication of BKT – BZT thin films has not yet been reported. [14-20]

In this research, the structural development of polycrystalline 0.95BKT – 0.05BZT thin films via PLD are explored as a function of deposition parameters

like target-substrate distance, deposition temperature and oxygen pressure.

Dielectric and ferroelectric properties of the films are characterized along with microstructural analysis for films deposited at various conditions.

4.2. Experiment Procedure

0.95BKT – 5BZT targets were prepared via conventional solid state processing. For batching, reagent grade oxide powders of Bi_2O_3 ($\geq 99.9\%$), K_2CO_3 ($\geq 99.5\%$), ZnO ($\geq 99\%$), and TiO_2 ($\geq 99.9\%$) were used as starting materials. The powders were milled for 6 hours in a vibratory milling machine with yttrium-stabilized zirconia (YSZ) media and ethanol. The dried powders were calcined at 920°C for 6 hours in an alumina crucible followed by a second milling and drying step. These powders were then mixed with 3 wt% polyvinyl butyral (PVB) binder and uniaxially pressed into 12.7 mm diameter pellets. After burning out the PVB binder at 400°C , the pellets were sintered at 1045°C for 10 hours. Due to the volatility of Bi and K during heat-treatment 20% excess Bi and 10% excess K were added to the stoichiometric target composition. The BKT – BZT thin films were then deposited on Pt/Ti/ SiO_2 /Si substrates from the synthesized targets by PLD. Deposition conditions such as laser energy, repetition rate, substrate temperature, process pressure and target-substrate distance were varied systematically to explore the processing space and are summarized in the results section. After deposition, the films were cooled inside the oxygen rich atmosphere of the PLD chamber. The crystal structures of as-grown films were

determined by X-ray diffraction (Bruker, AXS D8). Film thicknesses were obtained via variable angle spectroscopic ellipsometry (J. A. Woollam, VASE). For dielectric and ferroelectric properties of films, Ag top electrodes with 0.2 mm diameter were deposited. Dielectric permittivity and polarization hysteresis measurements were performed using an impedance analyzer (HP 4192A) and ferroelectric tester (Radiant Technology Premier II) respectively. Atomic force microscopy (Asylum, MFP-3D) was used to obtain the surface morphology of the films. Microstructures of the crystallized films were observed via scanning electron microscopy (SEM FEI Quanta 600 F) and transmission electron microscopy (TEM, JEOL 2500SE). Finally, compositional analysis of thin films was performed with electron probe microanalysis (EPMA, Cameca SX50)

4.3. Results and discussion

Figure 4.1 shows the logarithmic plot of θ - 2θ XRD patterns for 0.95BKT – 0.05BZT thin films deposited from the same stoichiometric target but at different substrate temperatures. For these depositions, the repetition rate and the distance from target to substrate were fixed at 5 Hz and 6.5 cm respectively. During ablation, the PLD chamber pressure was kept at 200 mTorr pure of O₂. XRD patterns show a very small trace of the perovskite phase at around 23° and 33° 2θ (marked “P”), but this series of films showed a number of secondary phases tentatively indexed as Bi₄Ti₃O₁₂ and Bi₂O₃. The small amount of perovskite phase under the given conditions may be the result of compositional

gradients in the target due to laser ablation or possibly from the loss of the volatile elements Bi and K by evaporation during the deposition. Previous work by Havelia *et al.* illustrated the difficulty in maintaining stoichiometry in Bi-based thin films because of the volatility of cations. [21]

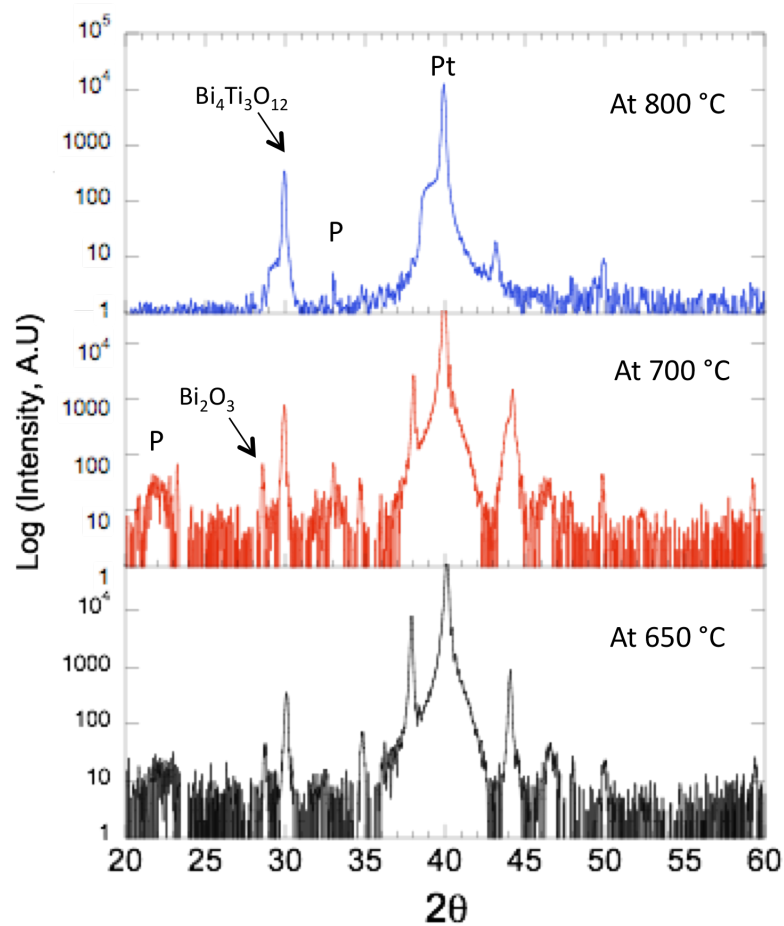


Figure 4.1. The XRD patterns of 0.95BKT – 0.05BZT deposited from 650 °C to 800 °C

To better understand compositional changes at processing temperatures several 0.95BKT – 0.05BZT films were prepared at substrate temperatures ranging from 650-800 °C. All films were deposited under the same processing

conditions as described above. EPMA was collected from five different spots on each sample using 4 tunable wavelength-dispersive spectrometers at 3 different beam energies (12 keV, 16 keV and 22 keV). Table 4.1 summarizes the results of the EPMA showing the average weight percentage of each element along with the ideal composition. The amount of Bi decreases gradually as the temperature increases with a sharp reduction above 800 °C. Above 700 °C a loss of K is also noted while for Zn a reduction in weight percentage was observed at 800 °C. Figure 4.2 displays the variation of cation concentration (Bi, K and Zn) as a function of the substrate temperature; this clearly demonstrates that films deposited from stoichiometric targets are cation deficient. The two most volatile elements, Bi and K, are sub-stoichiometric at all deposition temperatures. This suggests that more Bi and K are likely required to crystallize the perovskite phase. In contrast, the weight percentage of Ti gradually increases with the temperature. The higher weight percentage of Ti at above 700 °C may be related to Ti diffusion from the adhesion layer, which limits the usage of platinized silicon substrates at temperatures > 700 °C.[22]

		Bi (wt %)	K (wt %)	Zn (wt %)	Ti (wt %)	O (wt %)
Ideal		47.25	8.00	0.70	20.11	23.94
EPMA	650 °C	43.59	7.53	0.78	23.98	24.12
	700 °C	41.14	7.51	0.78	25.39	25.19
	750 °C	42.38	5.04	0.76	27.66	24.18
	800 °C	35.99	6.30	0.49	31.56	25.66

Table 4.1. The average weight percentage of 0.95BKT – 0.05BZT thin films deposited at different substrate temperatures.

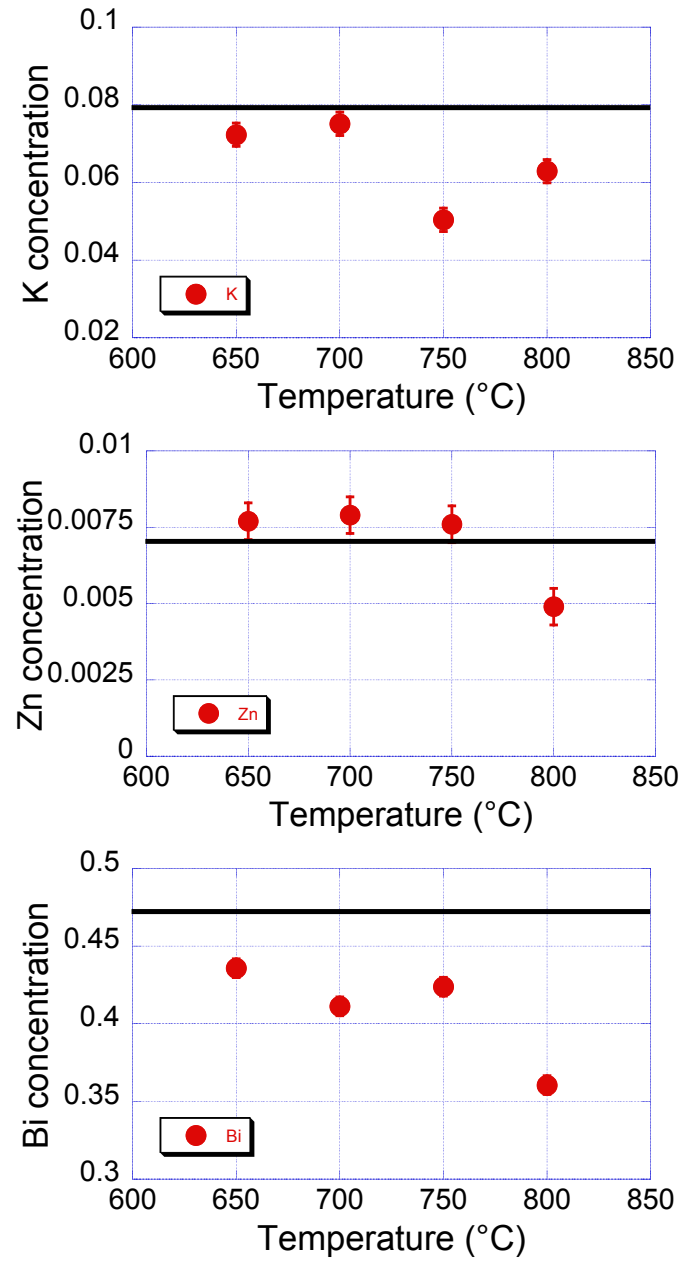


Figure 4.2. The concentrations of cations (Bi, K, and Zn) as a function of the substrate temperature when deposited from a stoichiometric target. Solid lines represent the ideal stoichiometric concentration of each element for 0.95BKT – 0.05BZT

To compensate for the loss of Bi and K during deposition, the distance between target and substrate was reduced to 5 cm and +20% Bi and +10% K were added during target preparation. Figure 4.3 shows X-ray diffraction patterns for 0.95BKT – 0.05BZT thin films with excess Bi and K. Repetition rate, pressure and laser energy for these depositions was 5 Hz, 100 mTorr of O₂ and about 200 mJ respectively. Perovskite material was observed in all the films, but a small amount of secondary phase around 30° 2θ was noted for substrate temperatures of 675 °C. At 550 °C the films have random orientation but begin to show strong (100) texture above 600 °C. In all cases, however, the perovskite peaks were broad possibly indicating poor crystallinity.

The equilibrium constant, Q^{eqm} , for the phase equilibria can be described as:

$$Q^{eqm} = P_M^2 P_{O_2}^{1/2} / a_M \quad (4.1)$$

where P and a_m are the partial pressure and the activity respectively.

Additionally, the temperature dependence of Q^{eqm} can be represented by Equation (4.2):

$$Q^{eqm} = \exp\{-\Delta G^\circ / RT\} \quad (4.2)$$

Combining (4.1) and (4.2) with the ideal gas law, the number of moles at equilibrium can be expressed by Equation (4.3):

$$n_M = V(\sqrt{a_m} / RT)(1/P_{O_2}^{1/4})\exp\{-\Delta G^\circ / RT\} \quad (4.3)$$

where n , a , V , G° are the number of moles, the activity, the volume of the system, and the standard free energy respectively[14]. Equation (4.3) suggests volatile A-site cation concentration is inversely related to oxygen pressure and temperature. Previous studies have shown a change in X-ray diffraction data resulting from lattice expansion as the oxygen process pressure changed[14]. To confirm this, 0.95BKT – 0.05BZT thin films were deposited at higher processing pressures and a fixed lower substrate temperature to produce better stoichiometry. Unfortunately, the XRD spectra of the two films shown in Figure 4.4 did not change with oxygen pressure, indicating that higher pO_2 has little impact on this system.

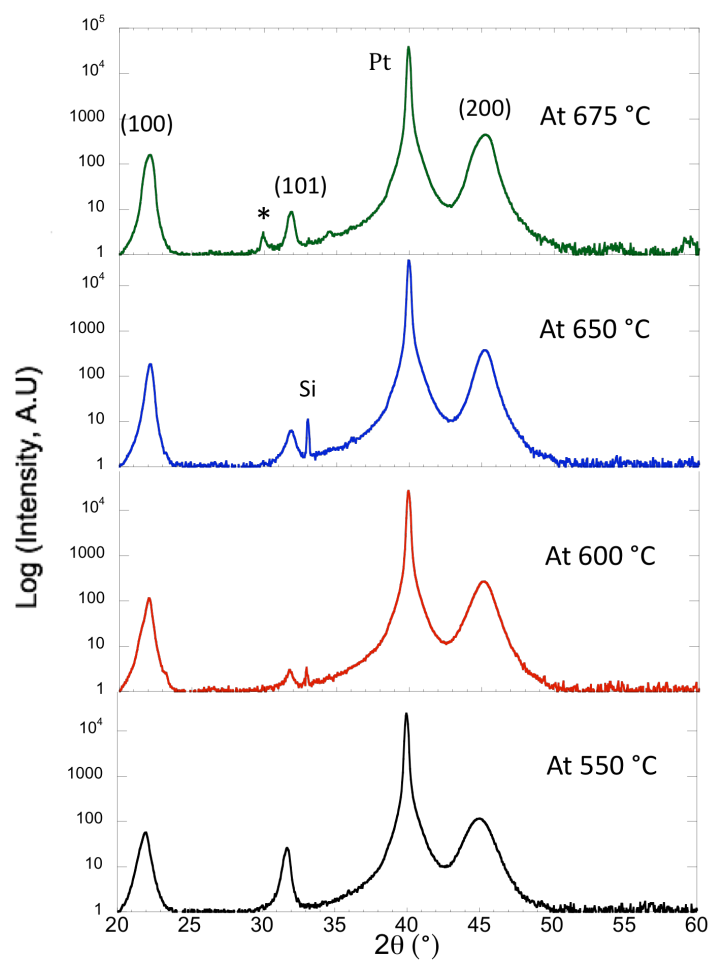


Figure 4.3. The XRD patterns of $0.95\text{BKT} - 0.05\text{BZT}$ deposited from 550 °C to 675 °C

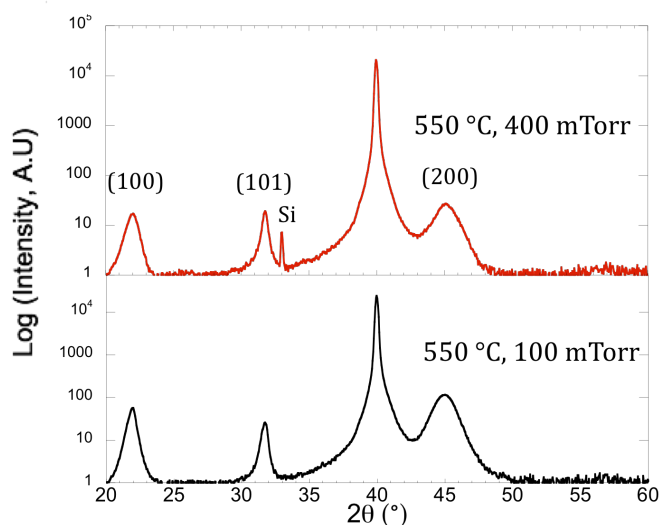


Figure 4.4. The XRD patterns of 0.95BKT – 0.05BZT thin films deposited at different oxygen pressures.

Dielectric constants and loss as a function of frequency for films deposited at various pressures and substrate temperature laser energy are plotted in Figure 4.5. The films fabricated at 100 mTorr and 650 °C have large dielectric constants over the frequency range as seen in Figure 4.5 (a). This could be related to unwanted space charge defects generated during processing. As noted previously, when 0.95BKT – 0.05BZT films were grown at 675 °C, a second phase developed with the perovskite phase. Even though this secondary phase was not observed in XRD for films deposited at 650 °C, the temperature might be high enough to induce some cation deficiency. Additionally, the dielectric loss increases at high frequency possibly indicating ionic conduction from A-site vacancies. As processing temperature is lowered, this phenomenon is no longer

observed and the dielectric constant is significantly suppressed. As seen in Figure 4.5 (b) and (c), the 1 kHz dielectric constant increased from 250 to 420 when the substrate temperature was decreased from 600 °C to 550 °C while dielectric loss remained the same (~17%). Oxygen pressure affects the dielectric constant as seen in Figure 4.5 (c) and (d) although the frequency dispersion for these two films is similar. The dielectric constant of the film deposited at 100 mTorr gradually decreases from 540 to 300 between 100 Hz and 1 MHz while the film deposited at 400 mTorr showed lower dielectric constants from 430 to 260 over the same frequency range. The dielectric losses at 1 kHz for 100 and 400 mTorr conditions were about 17% and 10% respectively. For comparison, bulk 0.95BKT – 0.05BZT has a dielectric constant of 840 and loss of 0.06 at 10 kHz.[9] Generally films of this composition show lower dielectric values compared to bulk ceramics, likely related to film crystallinity and stoichiometry as well as density during *in-situ* deposition.

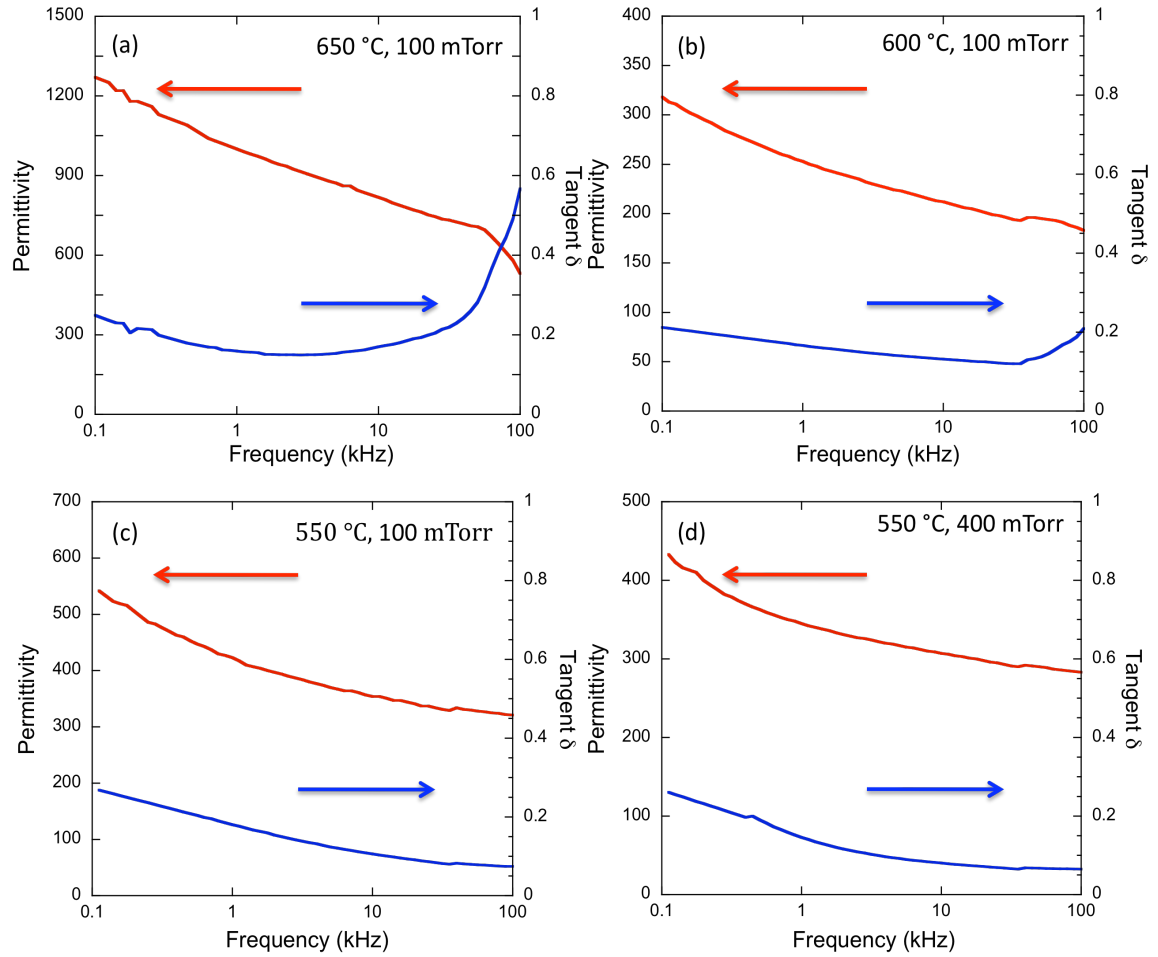


Figure 4.5 The dielectric properties as a function of frequency for the films fabricated under various conditions: (a) 650 °C and 100 mTorr; (b) 600 °C and 100 mTorr; (c) 550 °C and 100 mTorr; (d) 550 °C and 400 mTorr.

Figure 4.6 shows polarization – electric field hysteresis loops of 0.95BKT – 0.05BZT thin films at 1 kHz. PE loops of the films deposited at 600 °C and 650 °C (not shown) indicated that the films became conductive under the applied electric field. Bulk ceramic 0.95BKT – 0.05BZT PE loops start to show some saturation at 80 kV/cm but are not fully saturated due to their hard ferroelectric

nature. Maximum and remnant polarization for the bulk ceramic are $25.7 \mu\text{C}/\text{cm}^2$ and $11.2 \mu\text{C}/\text{cm}^2$ respectively[9]. In comparison, BKT-BZT thin films show nearly linear dielectric PE loops at maximum applied fields of 210 to 270 kV/cm. Maximum polarization for both films is $8.5 \mu\text{C}/\text{cm}^2$. It is likely that the higher dielectric loss and, as expected from XRD patterns, poorer crystallinity result in lower polarization values compared to that of bulk 0.95BKT – 0.05BZT ceramics.

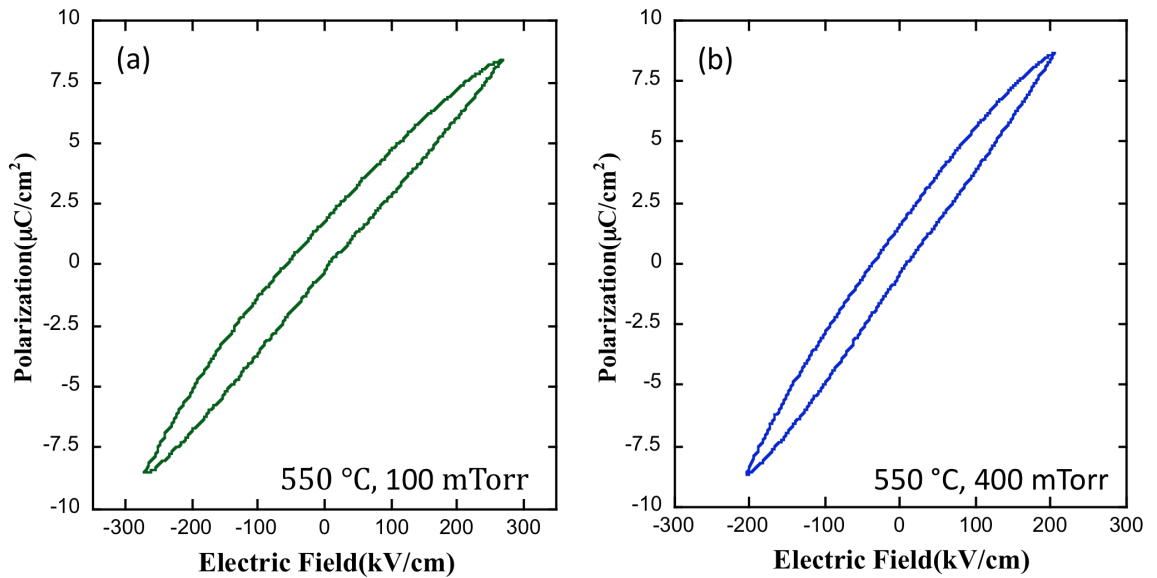


Figure 4.6 The polarization-electric field hysteresis loops for 0.95BKT – 0.05BZT thin films deposited at: (a) 550 °C and 100 mTorr; (b) 550 °C and 400 mTorr

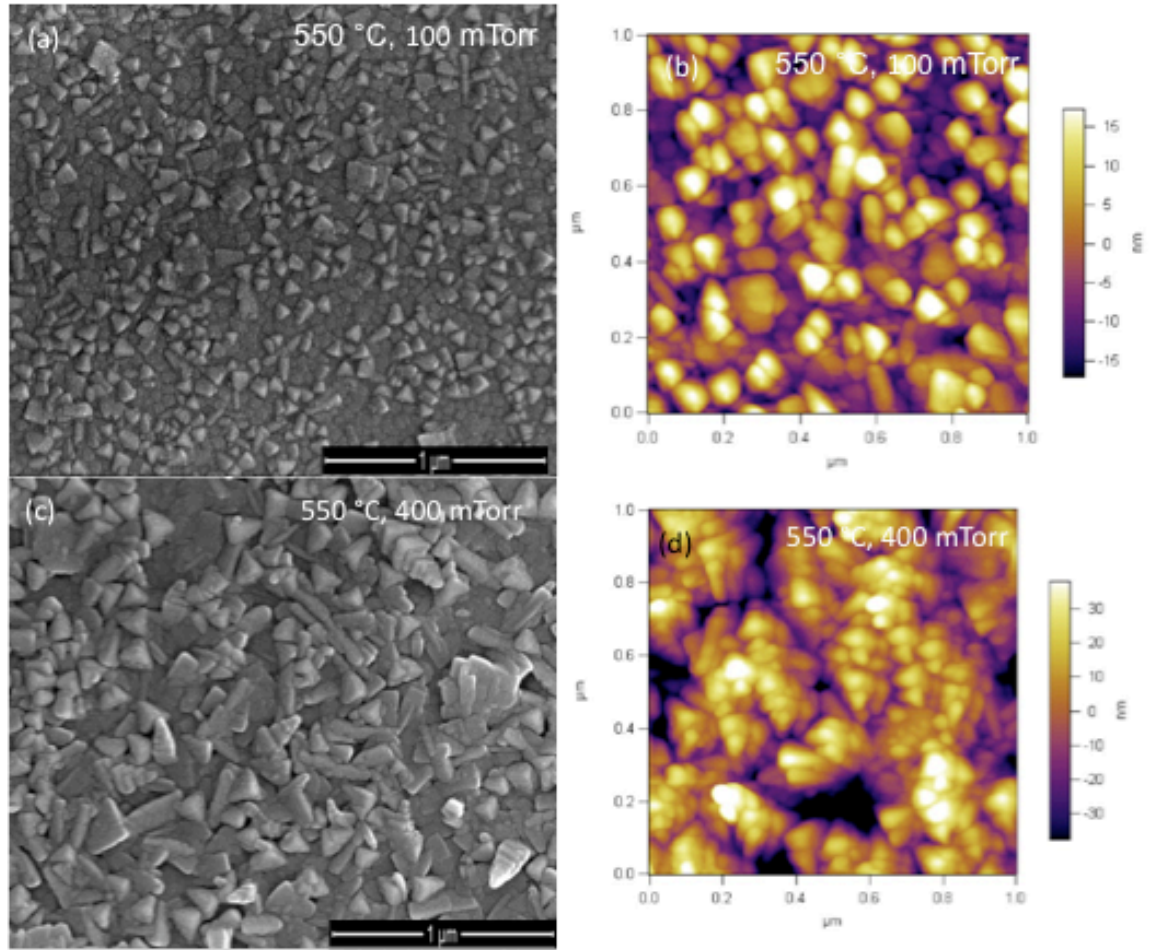


Figure 4.7 Microstructures of 0.95BKT – 0.05BZT thin films by SEM and AFM:

(a)&(b) 550 °C and 100 mTorr; (c)&(d) 550 °C and 400 mTorr

Figure 4.7 displays the microstructure of two BKT-BZT thin films prepared at different oxygen pressures. As seen in Figure (a) and (c), both films have similar faceted surface features but the film deposited at 100 mTorr has smoother morphology. This was confirmed by AFM measurements as shown in Figure (b) and (d). Roughness (RMS) for the films deposited at 100 mTorr is 8.5 nm but films deposited at 400 mTorr are much rougher with RMS = 18.7 nm.

From equation (4.3), higher material transfer rates are expected at higher oxygen pressures. Spectroscopic ellipsometry reveals that the thickness of the film deposited at 400 mTorr is about 440 nm, twice as thick as the 230 nm film deposited at 100 mTorr. The surface morphology of the film at 400 mTorr looks like an agglomerate of small grains, possibly because the 550 °C substrate temperature was insufficient to allow surface diffusion of adatoms arriving from the target. This results in a rougher surface with similarly shaped grains compared with the film deposited at 100 mTorr.

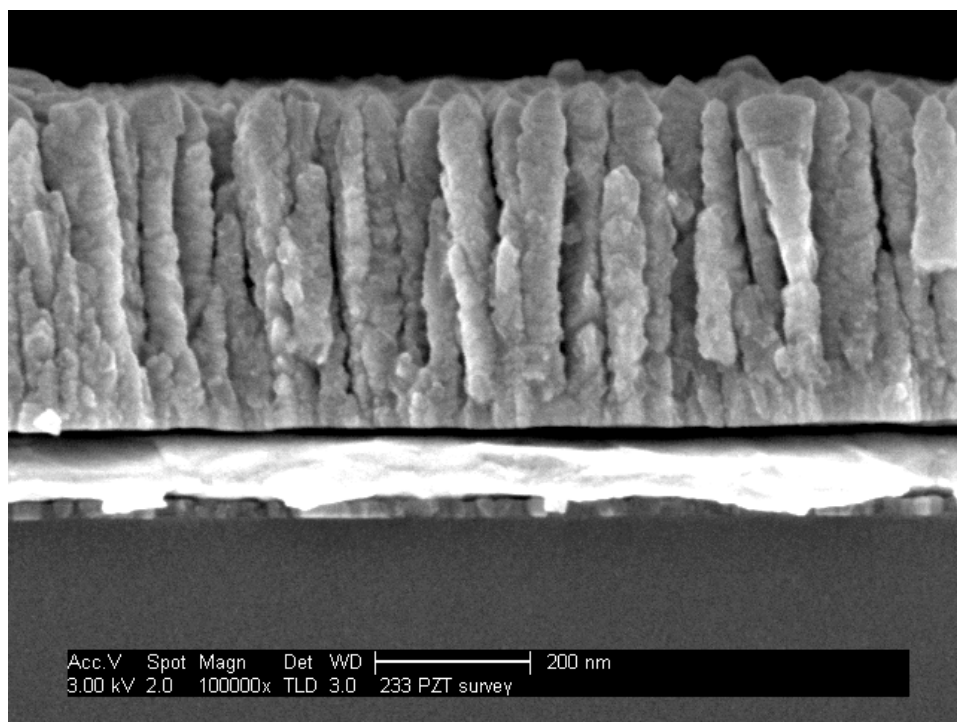


Figure 4.8 Cross-sectional SEM image of the film deposited at 550 °C and 100 mTorr

Cross-sectional SEM for the film fabricated at 500 °C and 100 mTorr is displayed in Figure 4.8. The film displays a columnar growth morphology with

grains 60 ~ 70 nm in width. However, the film was not well densified as small grains piled up at given processing condition. Some voids between columns were also observed. TEM micrographs in Figure 4.9 illustrate the porous microstructure of the film. Figure 4.9 (a) shows the bright field image where light colored areas indicate voids. The porous microstructure is visible in the secondary electron image of (b) clearly showing voids between or along the columnar grains. Worse dielectric and ferroelectric properties are likely related to this microstructure. Additionally, this may explain why polarization hysteresis loops at low frequency(<1 kHz) and high electric field (>300 kV/cm) were not obtained.

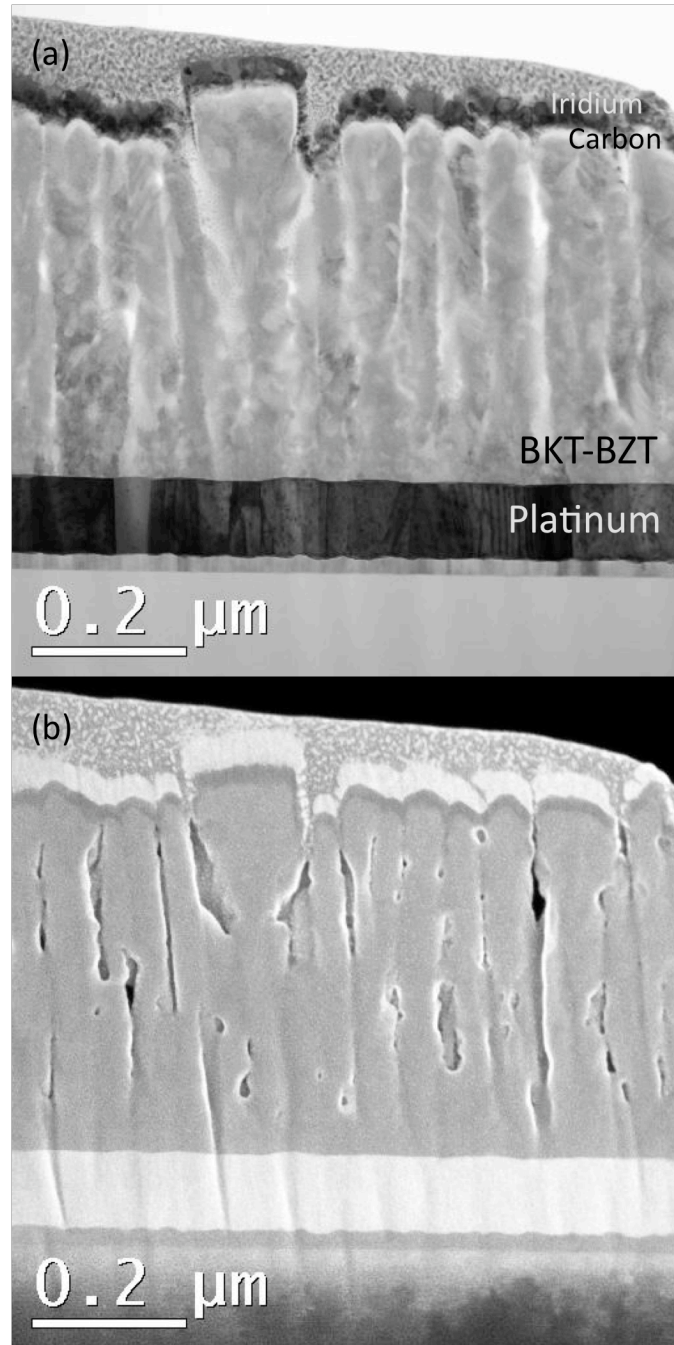


Figure 4.9 TEM cross-sectional micrograph film deposited at 550 °C and 100 mTorr:

(a) bright-field image; (b) secondary electron image

TEM-EDS analysis also verifies the low density of 0.95BKT – 0.05BZT thin films deposited at 550 °C and 100 mTorr. Figure 4.10 depicts elemental distribution throughout the film. Although EDS confirms that Zn is present in the film, the concentration of Zn is not sufficient to map. Areas that appear as voids in the secondary electron image, however, clearly do not contain O, Ti, K, or Bi. To enhance the electrical properties of 0.95BKT – 0.05BZT films densification of the microstructure and better crystallization will also be required.

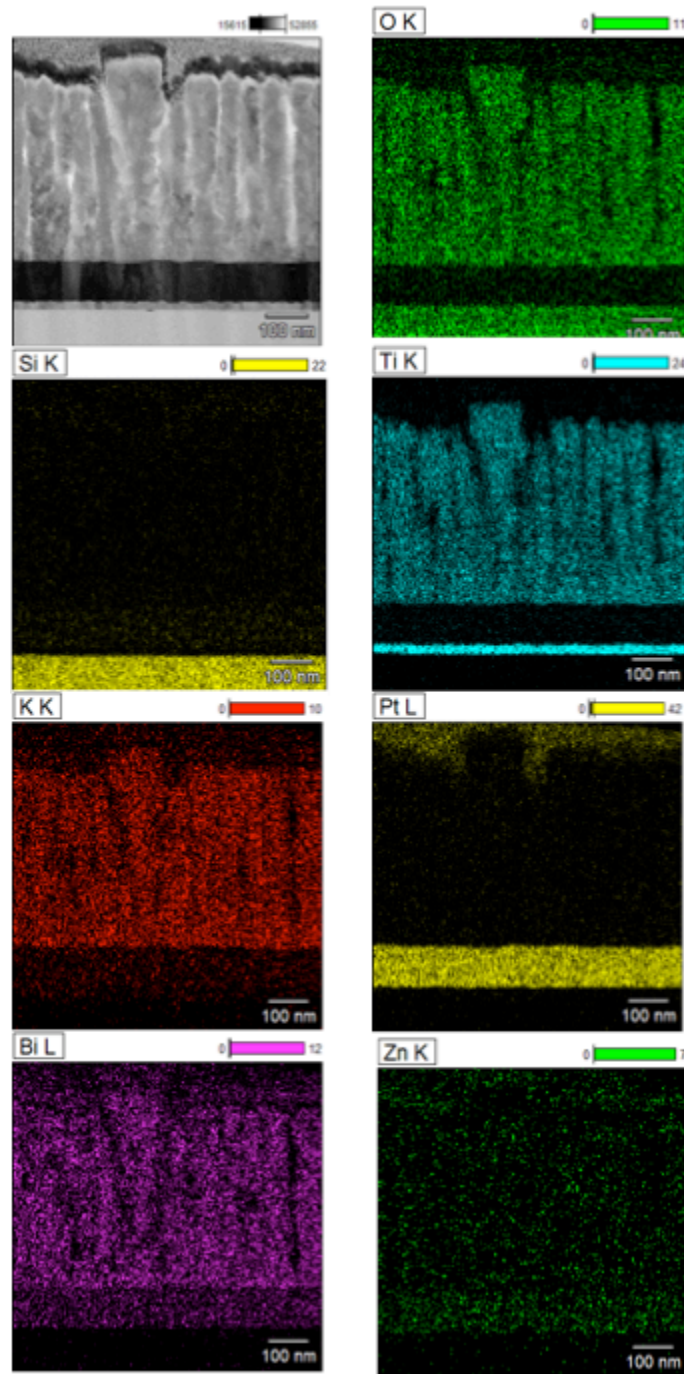


Figure 4.10 The elemental distribution by TEM-EDS for 0.95BKT – 0.05BZT deposited at 550 °C and 100 mTorr

4.4. Conclusions

In summary, this research investigates the crystal structure as well as dielectric and ferroelectric properties of lead-free polycrystalline 0.95BKT – 0.05BZT thin films by PLD. Larger target-substrate distances and higher temperatures with stoichiometric targets produced Bi and K deficient films. Due to the loss of these volatile cations the perovskite phase was not observed. However, by adjusting deposition parameters, phase pure perovskite films with broad XRD peaks were deposited by *in-situ* methods. Dielectric constants for these films were lower than that of bulk 0.95BKT – 0.05BZT and the dielectric loss for all films was higher than 10% over the frequency range from 100 Hz to 1 MHz. Hysteresis loops of the thin films showed linear dielectric behavior with a maximum polarization of about 8.5 $\mu\text{C}/\text{cm}^2$ at fields greater than 200 kV/cm. Poor electrical response of 0.95BKT – 0.05BZT thin films could be the result of poor crystallinity as indicated by the broad XRD peaks as well as possible off-stoichiometry due to A-site volatility. SEM and TEM revealed less dense microstructures with voids between grown columns and EDS confirmed that there were elements missing in those areas. Lead-free BKT – BZT thin films have the potential to be a high performance, environmentally friendly ferroelectric and piezoelectric materials but further investigations will be required to eliminate compositional problems along with density issues for improvement of their electrical properties.

4.5. References

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Chapter 5. Ferroelectric properties and compositional investigations of 0.8 BNT – 0.2 BKT thin films prepared by chemical solution deposition

5.1. Introduction

Lead zirconate titanate, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT), and its related solid solutions are currently by far the most widely used high strain piezoelectric materials and have found numerous applications in actuators, transducers, resonators, sensors, and random access memories due to their outstanding piezoelectric and ferroelectric properties.^[1-4] However, recent environmental concerns about the toxicity of lead have increased the need for alternative lead-free piezoelectric materials.^[5] Some promising candidates include Bi-based perovskite materials such as $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) and its solid solutions. A ferroelectric material with rhombohedral symmetry, bulk BNT has a remanent polarization (P_r) of $38 \mu\text{C}/\text{cm}^2$.^[6, 7] This system has been widely investigated because it forms a solid solution with a morphotropic phase boundary (MPB) when mixed with tetragonal perovskite materials like BaTiO_3 (BT), PbTiO_3 (PT), and $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (BKT).^[8] Hiruma *et al.* investigated the $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) - $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (BKT) system and found a MPB between rhombohedral and tetragonal phases at 0.8 BNT-0.2 BKT.^[8] This system was reported to have over $30 \mu\text{C}/\text{cm}^2$ of remanent polarization and a relatively high d_{33} piezoelectric coefficient of over $150 \text{ pC}/\text{N}$. Despite numerous studies of BNT-based bulk ceramics, including BNT - BKT, there are still very few reports of high quality thin films. This deficiency is likely due to difficulty controlling stoichiometry with multiple volatile cations such as K^+ , Na^+ , and Bi^{3+} .^[5] Previous work has shown that the vapor pressures of K_2O and Na_2O under typical thin film processing conditions are comparable to that of PbO .^[9, 10] Additionally, Bi is known to readily

interact with Pt and Pd, as has been demonstrated for catalyst applications and in standard ceramic processing of Bi-based ceramics.^[11, 12] Therefore, it is highly likely that the film is losing Bi to both the atmosphere and the substrate during processing.

A large number of groups have reported on the dielectric and ferroelectric properties of BNT-based thin films fabricated by various routes such as chemical solution deposition (CSD), pulsed laser deposition (PLD), and RF sputtering, but the great majority of them thus far are characterized by low permittivity values and electrically-leaky, non-saturating hysteresis loops whose measuring frequencies were either unreported or were recorded at high frequencies, often over 10 kHz.^[13-22] Charge transport within lossy dielectrics can manifest as artifacts in polarization-electric field measurements which could be incorrectly represented as polarization reversal;^[23] such reports are particularly prevalent within the Pb-free piezoelectric thin film literatures. The characteristics of previous hysteresis loops of lead-free thin films or the necessary use of high measurement frequencies are consistent with lossy dielectric response. Given the presence of multiple highly volatile cations in many of these systems, it is likely that many of these loss issues are indicative of poor control of stoichiometry and defect equilibria.

The goal of this work is to address these previous deficiencies by synthesizing high-quality BNT – BKT thin films with high dielectric constants, low dielectric losses, and saturating polarization hysteresis loops at previously unreported, and potentially technologically relevant, low frequencies. To achieve this, BNT – BKT thin films on Pt/TiO_x/SiO₂/Si were prepared by chemical solution deposition (CSD). To understand the role of stoichiometry on ferroelectric and dielectric response, solutions with excess cations (overdoped) were prepared to compensate for volatile species. With optimal overdoping,

varying annealing and drying conditions were investigated to adjust the film morphology and properties to optimize the ferroelectric response.

5.2. Experimental Procedure

Bismuth acetate ($\text{Bi}(\text{OOC}_2\text{H}_3)_3$, Alfa Aesar), sodium acetate trihydrate ($\text{Na}(\text{OOC}_2\text{H}_3) \cdot 3\text{H}_2\text{O}$, Alfa Aesar), potassium acetate ($\text{K}(\text{OOC}_2\text{H}_3)$, J.T. Baker), and titanium isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, Alfa Aesar) were used as solution precursors. First, titanium isopropoxide was chelated with acetic acid in a ratio of 1:4 inside of a dry argon atmosphere to prevent deleterious reaction with H_2O . Dissolution of bismuth acetate is difficult in many solvents, including acetic acid. In this work, we found that bismuth acetate is easily dissolved at room temperature in propionic acid. Sodium acetate trihydrate and potassium acetate were dissolved separately in methanol. The ratio of two solvents, propionic acid and methanol, for dissolving different acetates was 2:1 respectively. To compensate for the volatilization of Bi, Na, and K at processing temperatures, three overdoped solutions (relative to the stoichiometric amount of each cation) were prepared: 1) +20% Na, +20% K; 2) +5% Bi, +20% Na, +20% K; and 3) +10% Bi, +20% Na, +20% K. The Bi, Na and K solutions were added drop-wise to the Ti solution to reach the final desired stoichiometry. As mentioned previously, the vapor pressure of K_2O and Na_2O are similar to that of PbO , and for PZT thin films via CSD, it was reported that up to 30% excess PbO can be added.^[3, 24] Although it is well-known that Bi_2O_3 is volatile, it has a lower vapor pressure than PbO .^[12, 25] Thus, adding less excess bismuth than sodium and potassium was deemed appropriate. The 0.3M final solution was stable for more than one month without precipitation. The precursor solution was spin-coated on a 100 nm Pt/33 nm TiO_x /500 nm SiO_2 /Si substrate at 3000 rpm for 30 sec. After each spin cast layer, the film was pyrolyzed at 300 °C for 5 minutes and annealed in a preheated furnace at 700 °C in air for times between 10 min and 30 min. The coating, drying, and annealing steps were repeated 6 times for all films in this study,

resulting in a total film thickness of approximately 300 nm. The phase purity of the films was determined by X-ray diffraction (XRD, Bruker, AXS D8 Discover, Cu $K\alpha$ radiation). Variable angle spectroscopic ellipsometry (J. A. Woollam, V-VASE) was used to obtain the film thicknesses (confirmed with scanning electron microscopy for selected samples). Silver top electrodes, 0.2 mm in diameter, were thermally evaporated to measure the dielectric and ferroelectric properties. Dielectric constant and loss (50 mV oscillation level) and polarization hysteresis loops were obtained using an impedance analyzer (HP 4192A) and ferroelectric tester (Radiant RT66B), respectively. The film morphologies, both planar and cross-sections, were observed via scanning electron microscopy (SEM, FEI Quanta 600F).

Quantitative compositional analysis of films was conducted with electron probe for microanalysis (EPMA, Cameca SX50). For high accuracy, the system was calibrated with standard materials (Pt metal, Bi metal, Ti metal, Si metal, MgO for Mg and O, Albite for Na, Orthoclase for K) for each element using four wavelength dispersive (WDS) Bragg spectrometers. Four different locations on each film were analyzed with three accelerating voltages (12, 16, and 22 keV). X-ray counts from each location were converted to film composition while considering the k -ratio between the films and standard materials at each accelerating voltage, as well as the thickness and density of underlying layers (Pt, TiO_x and SiO_2).^[26] X-ray photoelectron spectroscopy (PHI Quantera Scanning ESCA) was used to determine the distribution of the cations as a function of film depth. The spectrometer used a monochromatic aluminum x-ray source (1486.6 eV). The samples were cleaved and a section of each was analyzed without further preparation. Each sample was mounted under a 3×3 mm mask and analyzed with a 100 μm diameter photon beam. A low spectral resolution survey spectrum was acquired from each area of interest on the sample. Higher spectral resolution data were acquired from the detected elements to determine the

surface chemistry and composition. The data were charge corrected to carbon 1s at 284.8eV. The quantification calculation was made using standard elemental RSF values, which do not account for the preferential sputtering effects that may occur during the analysis. The depth profiles were acquired by alternately sputtering and acquiring spectral data. The samples were sputtered using a 2kV Ar⁺ ion beam with a sputter rate of about 5 nm/min relative to SiO₂.

5.3. Results and discussion

The θ -2 θ XRD patterns of 0.8 BNT – 0.2 BKT films are plotted logarithmically in Figure 5.1 to highlight the presence of any second phases. Under identical processing conditions (300 °C/5 min pyrolysis and 700 °C/10 min anneal each layer) the three films display a well-crystallized perovskite phase with random orientation. The perovskite peaks have similar sharpness and intensity, regardless of precursor stoichiometry. A second phase is found in films prepared without excess Bi. It is difficult to identify this second phase with only one peak present, but possibilities include potassium sodium titanate (KNaTiO₃) or potassium sodium oxide (KNaO). Nevertheless, the perovskite phase is still dominant. Additional bismuth (+5%) eliminates this second phase, and higher Bi concentrations appear to have little effect on the phase and crystallinity development. This suggests that the 0.8 BNT – 0.2 BKT system can tolerate a fairly wide range of Bi³⁺ overdoping in solution and still form the perovskite phase.

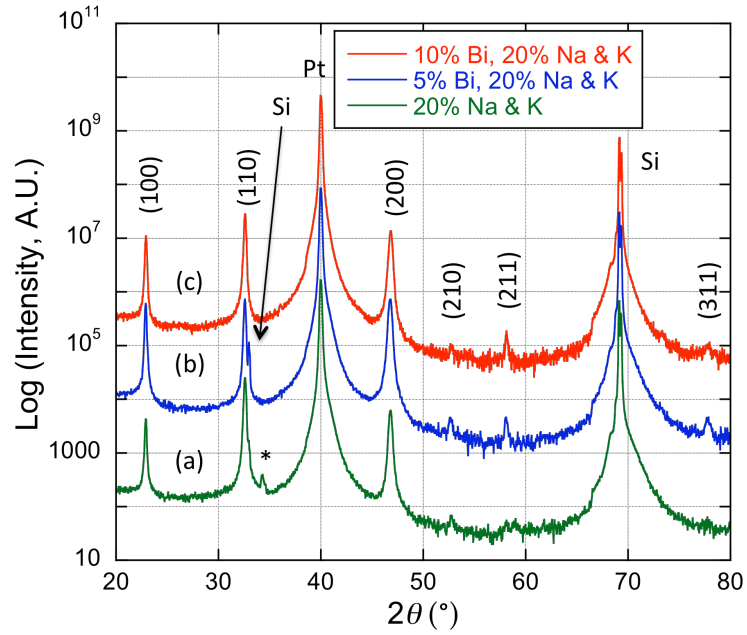


Figure 5.1. XRD θ - 2θ pattern ($\text{Cu K}\alpha$) for 0.8 BNT – 0.2 BKT thin films synthesized with different excess cation concentration in solution: (a) +20% Na and +20% K; (b) +5% Bi, +20% Na, and +20% K; (c) +10% Bi, +20% Na, and +20% K. Asterisk indicates second phase

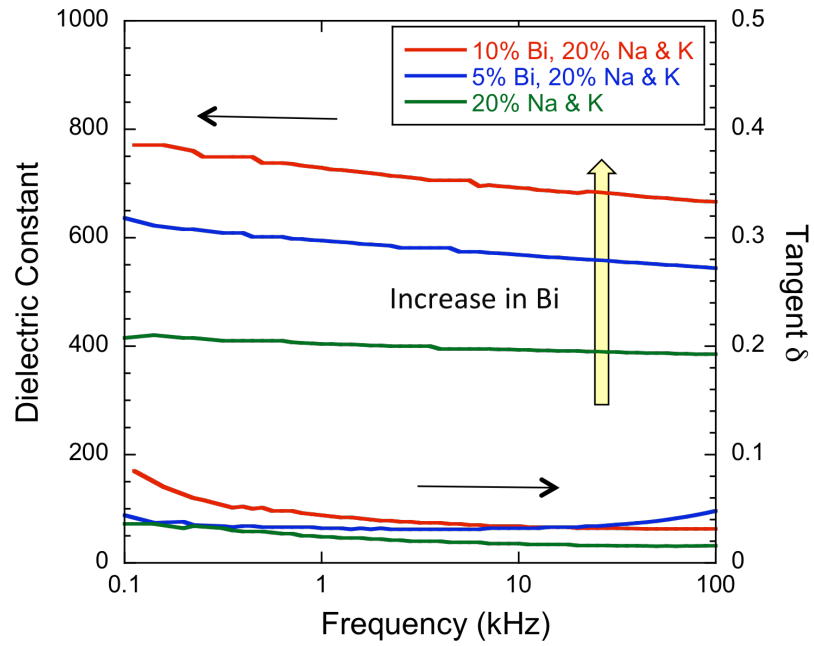


Figure 5.2. Dielectric constant and loss of 0.8 BNT – 0.2 BKT thin films fabricated with 20% excess of Na and K and different excess of Bi

Figure 5.2 shows the dielectric constant and loss versus frequency from 100 Hz to 100 kHz for 0.8 BNT – 0.2 BKT thin films. All films have acceptable loss (less than 8%) over the entire frequency range and from 2 - 4% at 1 kHz, which indicates minimal space charge contributions to the dielectric response. Addition of bismuth enhances the dielectric constant from 400 to 600 and 750 for +5% and +10% bismuth, respectively. These improved dielectric properties are likely not due to improvement in crystallinity or crystallographic texturing, as evidenced by the nearly identical polycrystalline XRD patterns for all three compositions. Compensating the loss of Bi, Na, and K by adding excess cations might induce the improvement in dielectric property. Previous researchers have reported dielectric constants of BNT – BKT thin films of 300-400 at 1 kHz.^[19, 21] The lowest dielectric constants in this work are similar to those previously reported, while the optimally Bi-overdoped films have dielectric properties nearly double the best previous reported. Two primary differences are apparent between this and previous reports of BNT-BKT thin films; first different cation precursors and solvents were used, and second overdoping was used for preparation of the precursor solutions. As precursor and solvent selection is not explicitly investigated in this report, it is not clear if their selection will have a large impact on the dielectric and ferroelectric properties. It seems likely, at least, that the excess cation concentrations added to the precursor solution to compensate for the loss of bismuth, sodium, and potassium could explain the enhanced dielectric response.

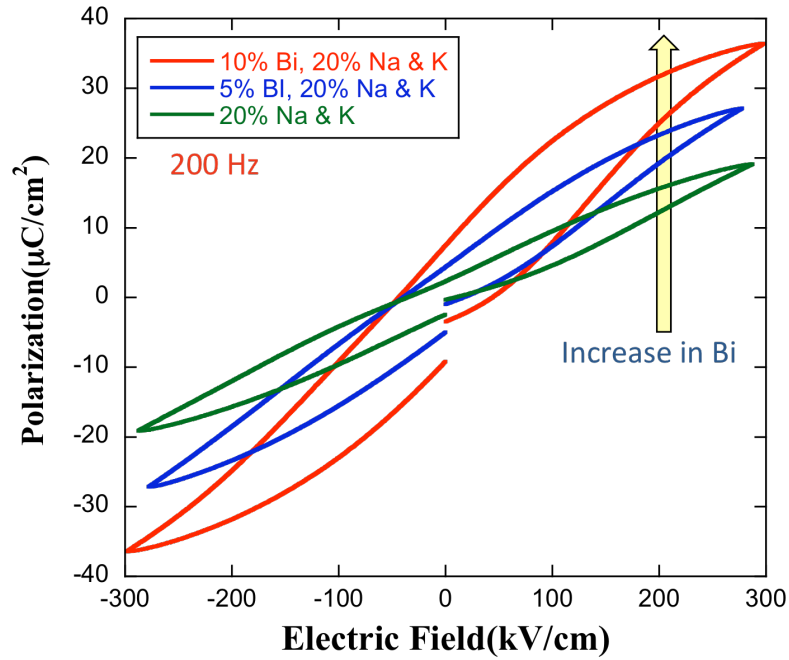


Figure 5.3. PE loops of 0.8 BNT – 0.2 BKT thin films fabricated with 20% excess of Na and K and different excess of Bi

Figure 5.3 displays polarization-electric field hysteresis loops for these BNT-BKT films. All of the polarization hysteresis measurements in this work were performed at 200 Hz which, to date, is the lowest reported measurement frequency for thin films within this material system. With increased excess bismuth in solution, remanent and maximum polarization increased from 3 $\mu\text{C}/\text{cm}^2$ to 8 $\mu\text{C}/\text{cm}^2$ and from 19 $\mu\text{C}/\text{cm}^2$ to 36 $\mu\text{C}/\text{cm}^2$, respectively under an electric field of approximately 300 kV/cm. Additionally, the shape of the loop becomes more well-developed and characteristic of ferroelectric response. In the case of no excess bismuth in solution, the loop displays nearly linear behavior and does not saturate. The loop additionally shows a slightly pinched character, which may be related to a built-in field resulting from defect dipoles within the film (likely due to the presence of some cation vacancies). Loops from films prepared with excess bismuth saturate better and display less pinching.

Compared to previous work on 0.8 BNT-0.2 BKT reported by other groups,^[19, 21] which showed hysteresis at higher frequencies, the present work has significantly higher remanent polarization with better saturation at much lower measurement frequency. The shapes of the hysteresis loops presented here are clearly indicative of a less electrically leaky ferroelectric material.

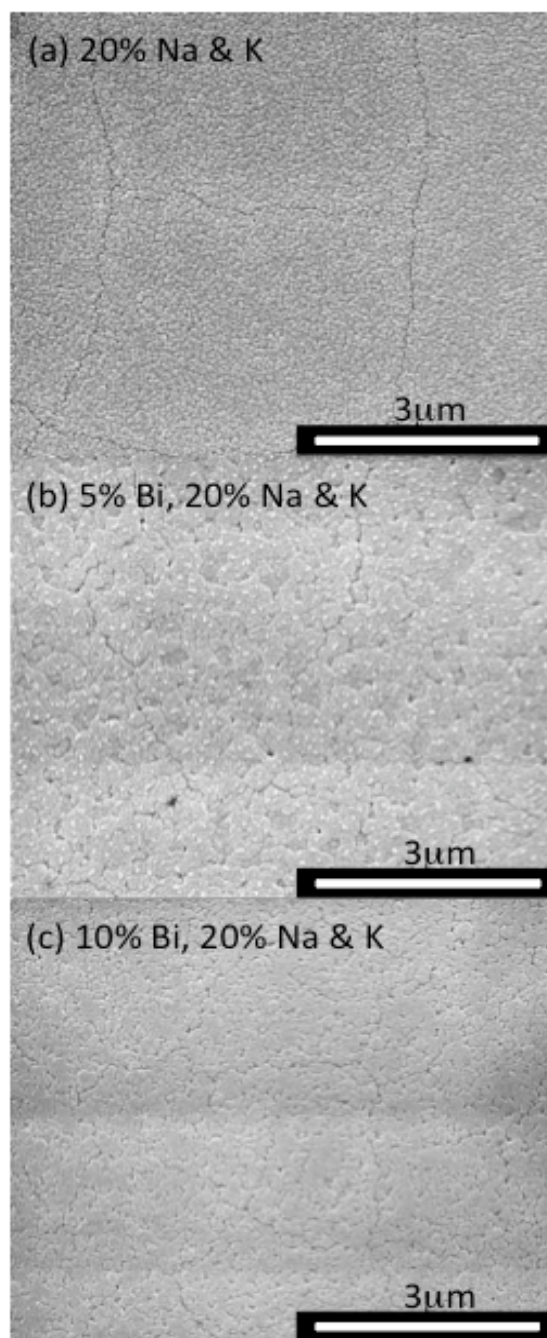


Figure 5.4. Plan view SEM images for 0.8 BNT – 0.2 BKT thin films: (a) +20% Na and +20% K; (b) +5% Bi, +20% Na, and +20% K; (c) +10% Bi, +20% Na, and +20% K

Figure 5.4 shows the surface morphologies of the 0.8 BNT - 0.2 BKT thin films. Without excess bismuth, there are interconnected micro-cracks present on the surface. Films prepared with 5% excess bismuth show small nano-sized features on the top of grains. The appearance of this surface phase does not coincide with the 2nd phase peak detected in x-ray for films without excess bismuth. Further investigation of the relationship between the cation overdoping and second phase formation is required. An increase in the amount of excess bismuth, however, does reduce the density of micro-cracks as shown in Figure 5.4(b) and (c).

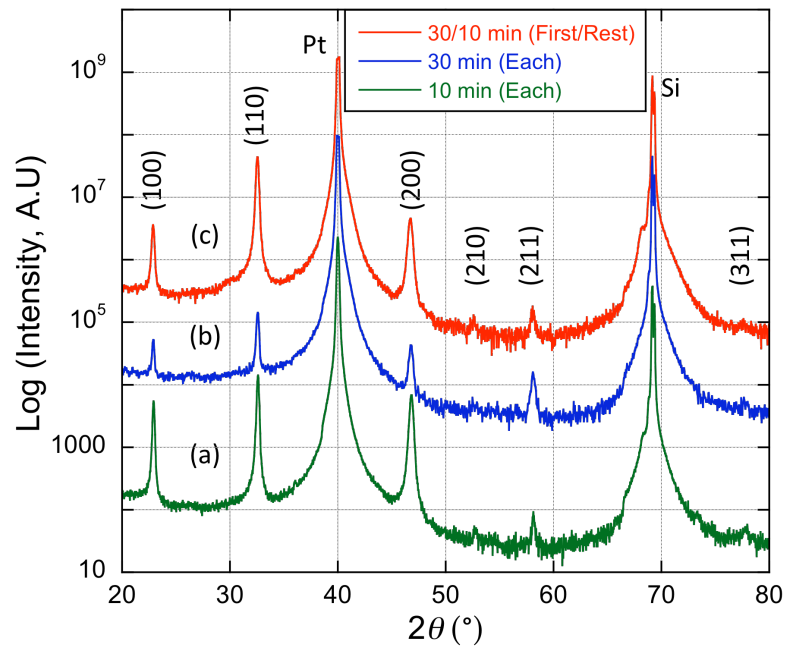


Figure 5.5. XRD patterns of 0.8 BNT – 0.2 BKT thin films: annealed (a) 10 min each layer; (b) 30 min each layer; and (c) 30 min first layer and 10 min each additional layer

Clearly films fabricated with 10% excess Bi show significantly improved electrical properties and morphologies. Generally it is believed that higher annealing temperatures and longer holding times are helpful in achieving higher

quality thin films, as higher thermal budgets encourage improved crystallinity with larger grain sizes.^[16, 27, 28] To examine this relationship, the annealing conditions were adjusted while maintaining a constant overdoping (+10% Bi, +20% Na, and +20% K), pyrolysis temperature (300 °C), and pyrolysis time (5 min). First the effect of longer annealing time was examined. Films were spin-cast and pyrolyzed as normal and were annealed at 700 °C for either 10 or 30 min each layer. Figures 5.5(a) and (b) show XRD θ -2 θ patterns for films annealed for 10 and 30 minutes per layer, respectively. The intensities of the perovskite peaks are significantly reduced for the films annealed for longer time per layer. This is confirmed by examining the normalized perovskite (110) peaks against the Pt (111) peak. The normalized value for 10 minutes/layer annealing is 0.6% but for 30 minutes/layer it is reduced to 0.07%. Although the film remains phase pure perovskite by XRD, the film for 30 minute/layer had lower dielectric property and lossy polarization hysteresis loop (not shown) compared to the film for 10 minutes/layer. This deterioration in dielectric constant may be the result of loss of volatile cations during the longer anneal. The film, however, remains phase pure perovskite by XRD. SEM micrographs of films annealed 30 minutes each layer are shown in Figure 5.6. Longer annealing times typically allow development of larger grains and this particular film has grains approximately 200 - 300 nm in diameter. The film surface in Figure 5.6(a) appears to display some minor porosity, however the cross-section indicates a dense morphology. It is conceivable that, although the lack of micro-cracking and larger grains were found in this film, possibility of the increased loss of volatile elements and apparent less dense surface degrades the dielectric and ferroelectric properties.

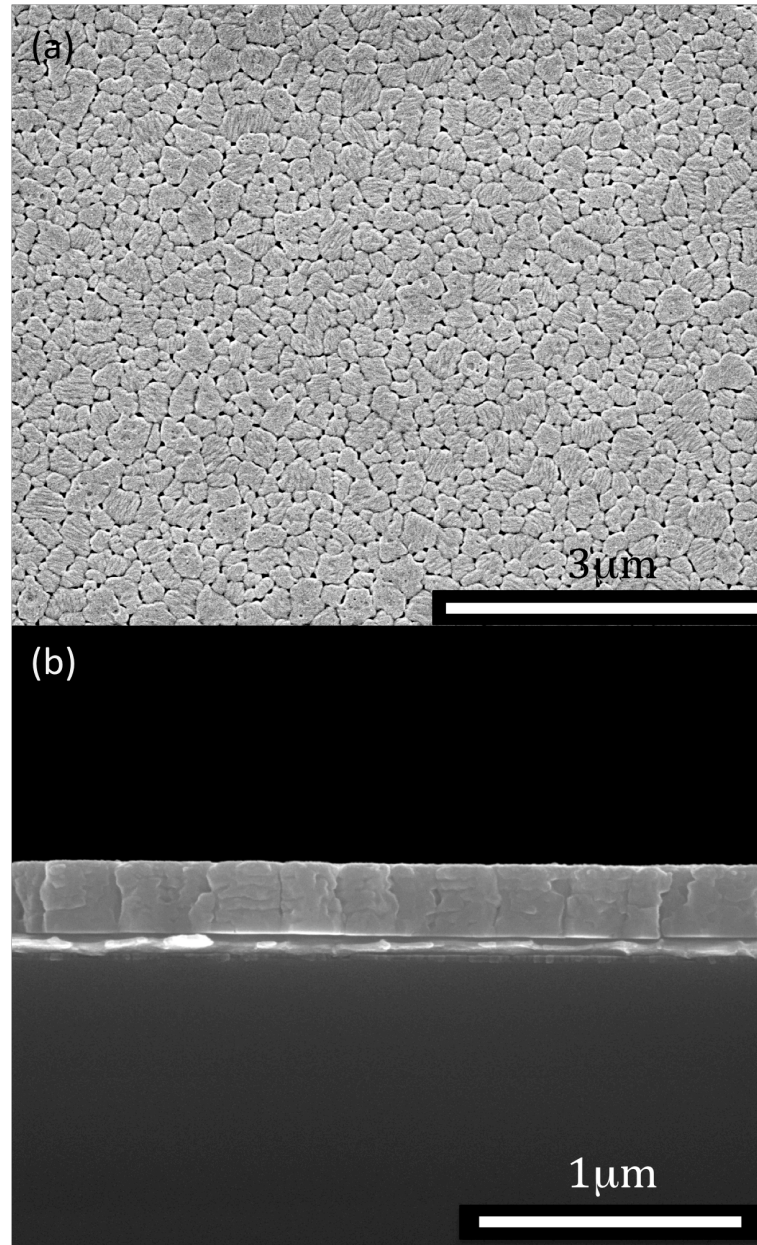


Figure 5.6. Plan view (a) and cross-section (b) SEM image of 0.8 BNT – 0.2 BKT thin film annealed at 700 °C for 30 min each layer

It was found that when the film was annealed for 30 minutes each layer, larger grain sizes developed, which is desirable for better electrical properties. However, a less dense surface and the corresponding loss of volatile elements

appear to deteriorate the electrical response. To minimize these adverse effects, while still producing crack-free, large grained films, a first 30 minute annealed layer was utilized as a template/seed layer annealed at 700 °C while subsequent layers were annealed for 10 min. Figure 5.5(c) shows the XRD pattern for this annealing process. Note the intensity of the perovskite peaks are significantly increased and are comparable to films annealed for 10 min each layer. Under this varied-time annealing process, a more dense film surface was observed as seen in Figure 5.7 (a) with grain sizes approximately 100 – 150 nm. Unlike the film annealed for 30 minutes each layer (shown in Figure 5.6(b)) the cross-section of this varied-time annealed film shown in Figure 5.7(b) displays some degree of columnar growth. The textured columnar growth of PZT thin films is well known to be nucleation controlled.^[29, 30] The initial layer in the BNT-BKT case, annealed for 30 minutes, may function as a seed layer allowing the film to grow in a columnar fashion. Further investigation is required to elucidate the effect of orientation and grain growth on microstructure.

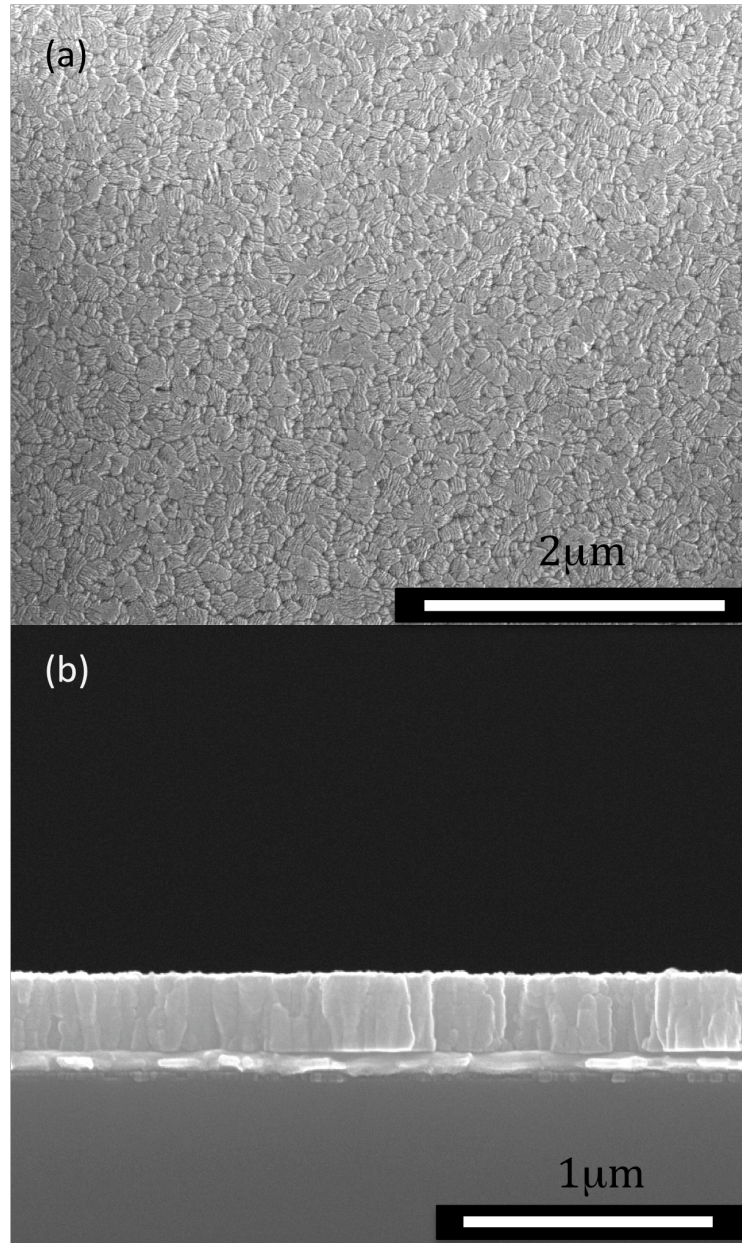


Figure 5.7. Plan view (a) and cross-section (b) SEM image of 0.8 BNT – 0.2 BKT thin film annealed at 700 °C for 30 min (first layer) and 10 min (subsequent layers).

Figure 5.8 shows the dielectric and ferroelectric properties of 0.8 BNT – 0.2 BKT films prepared in this study with varied-time annealing conditions. The

dielectric constant at 1 kHz is 580 which is inferior to those annealed for 10 minutes per layer. Nested hysteresis loops were obtained at 200 Hz and are shown in Figure 5.8(b). At 200 Hz, the film annealed under varied-time conditions could withstand up to 530 kV/cm due to the more dense cross-sectional morphology. This resulted in increased maximum and remanent polarization of $45 \mu\text{C}/\text{cm}^2$ and $16 \mu\text{C}/\text{cm}^2$, respectively due to improved saturation. The corresponding coercive field is approximately 70 kV/cm. Considering both dielectric and ferroelectric properties, the film synthesized at 700 °C with varied-crystallization time per layer showed the most promising properties. Although the remanent polarization of $16 \mu\text{C}/\text{cm}^2$ is very encouraging, it is still about half that of bulk-BNT-BKT ceramics and the shape of the hysteresis loop of these films are not as well formed as the bulk ceramic.^[7] Optimization between loss of volatile elements versus the enhancement of microstructure from longer or adjusted annealing times will be required to achieve maximum quality 0.8 BNT – 0.2 BKT thin films, although those presented here appear to be of the highest quality presented thus far.

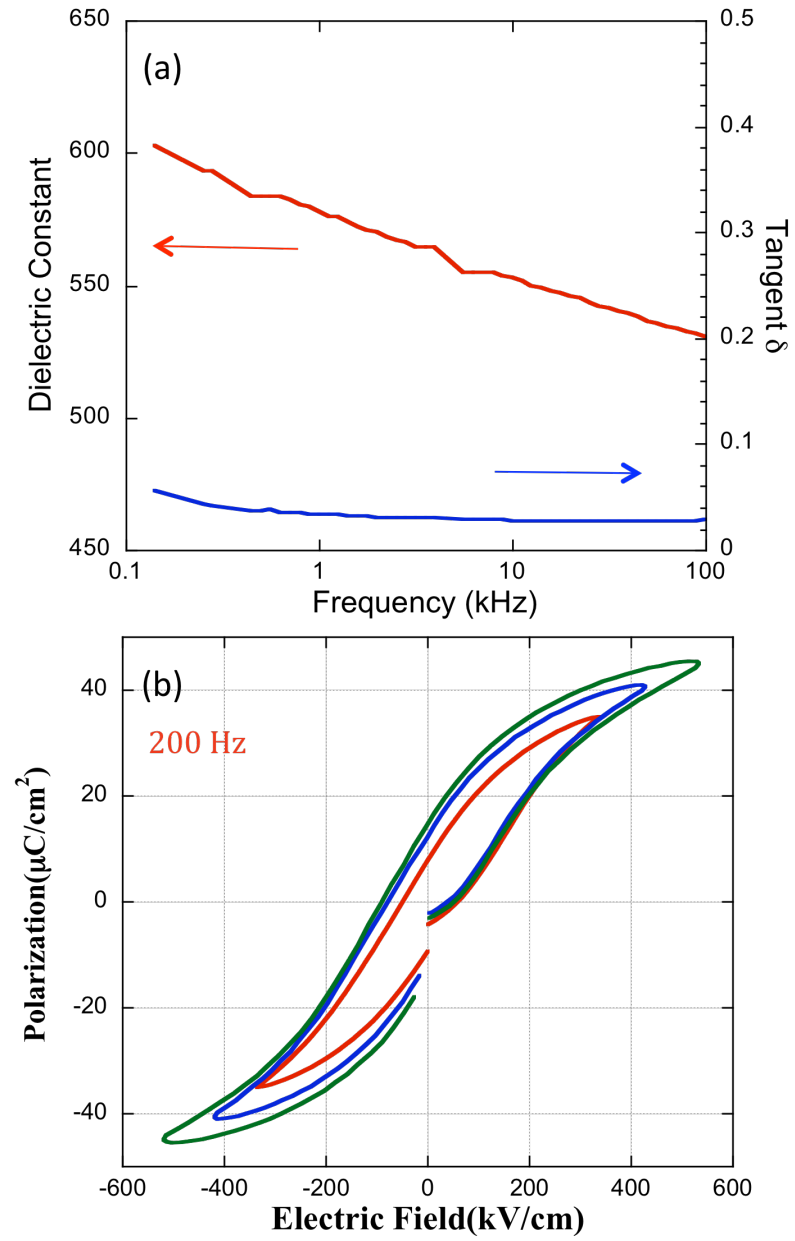


Figure 5.8. Dielectric properties (a) and polarization hysteresis loop (b) for 0.8 BNT - 0.2 BKT thin film annealed at 700 °C for 30 min (first layer) and 10 min (subsequent layers)

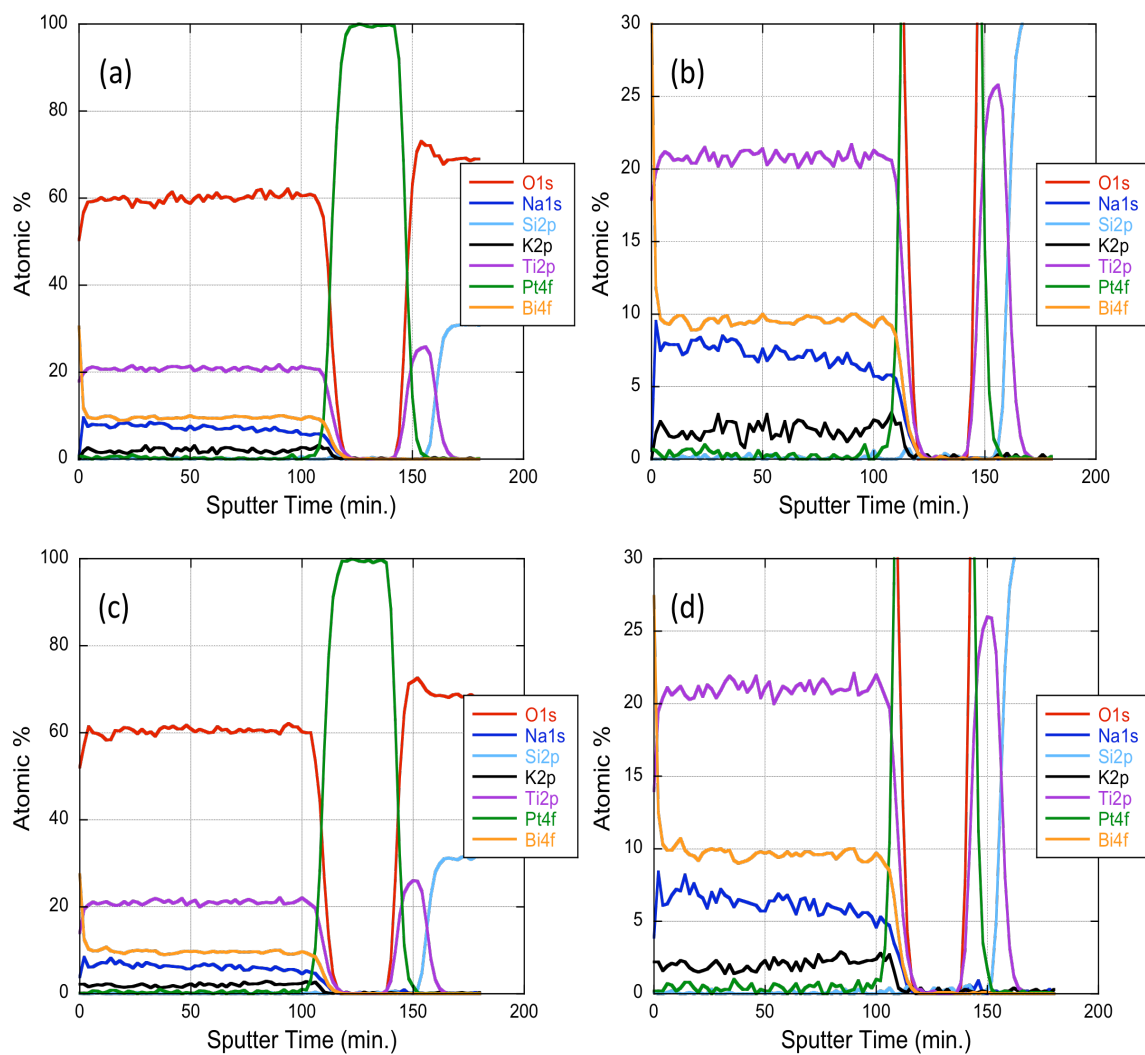


Figure 5.9. XPS depth profiles of 0.8 BNT – 0.2 BKT thin films: annealed at 700°C for (a) & (b) 10 min each layer; (c) & (d) 30 min first layer and 10 min each additional layer

	Bi (at%)	Na (at%)	K (at%)	Ti (at%)	O (at%)
Ideal atomic ratio	10	8	2	20	60
700 °C for 10 min (Each)	10.1	9	1.9	19.9	59.2
700 °C for 30 min (first) and 10 min(subsequent)	10.2	9	1.9	20.2	58.8

Table 5.1. Average atomic percentages of 0.8 BNT – 0.2 BKT thin films annealed under various conditions determined with EPMA

The compositional depth profiles of samples were obtained via XPS. These can be seen (to the SiO₂ layer) in Figure 5.9. Figure 5.9 (a), (b), (c) and (d) show the profiles for films annealed for 10 minutes/layer and for the film annealed with varied time conditions in different y-scale respectively. Overall a relatively uniform distribution of each elements through the film thickness can be seen in Figure 5.9(a) and (c) but non-uniformity for Na cation distribution is also observed. The atomic percentage of Na cation gradually decreases as it gets close to the interface between the film and substrate for both films as seen in Figure 5.9(b) and (d). Although this trend is found in both films, the ratio between Bi and Na is different. For the film annealed with varied time conditions, relative atomic percentage of Na is lower than that of the film annealed for 10 minutes/layer as two has almost same level of relative atomic percentage of Bi. This might cause some difference in dielectric property. As XPS is only an indicator of relative atomic ratios, it is important to complement it with a technique that can measure stoichiometry. Table 5.1 summarizes the average atomic percentage for each film determined using EPMA (along with the ideal

values). It can be seen that the films show near ideal stoichiometric compositions for all annealing conditions. For the EPMA data analysis it was assumed that the Pt, TiO_x , and SiO_2 remained intact during film fabrication. This assumption may cause a small discrepancy in atomic percentage for some elements. Considering the values given in Table 5.1 and the depth profiles, the optimized overdoping levels used (+10% Bi, +20% Na, +20% K) result in films with near ideal atomic ratios.

5.4. Conclusions

Lead-free 0.8 BNT – 0.2 BKT thin films were successfully synthesized via chemical solution deposition. The importance of overdoping in the precursor solution was confirmed by comparing XRD patterns and electrical properties. With the same amounts of excess Na and K, dielectric constant and ferroelectric properties were greatly improved by increasing the amount of excess bismuth. Annealing conditions were also investigated and dielectric constants ranged from 580 to 730 with low dielectric loss (<5%) depending on annealing conditions. All films in this work had measurable polarization hysteresis loops at the lowest frequency currently reported (200 Hz). Films where the first layer was annealed at 700 °C for 30 min as a template with subsequent layers annealed for shorter times (10 min) at the same annealing temperature resulted in the best ferroelectric properties with E_c , $P_{\max}$, and P_r of 70 kV/cm, 45 $\mu\text{C}/\text{cm}^2$ and 16 $\mu\text{C}/\text{cm}^2$ respectively. XPS compositional depth profiling revealed a somewhat non-uniform cation distribution through the thickness of films annealed under different conditions. EPMA data additionally confirmed that the levels of overdoping selected in this work results in films with near ideal stoichiometry. Our results suggest that carefully processed 0.8 BNT – 0.2 BKT thin films may be promising candidates for lead-free piezoelectric thin films.

5.5. References

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Chapter 6. Ferroelectric properties of 85BNT - 10BKT - 5BT perovskite Pb-free piezoelectric thin films via chemical solution deposition

6.1. Introduction

In the past few decades, lead-based piezoelectric materials, represented by $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) and PZT-based solid solutions have been widely used in many electronic devices because they show the highest performing piezoelectric properties.[1-3] However, recent environmental legislation in the EU, such as Waste from Electrical and Electronic Equipment (WEEE), Restriction of Hazardous Substances (RoHS), and End-of Life Vehicles (ELV), have sought to limit the usage of toxic elements.[4] The toxicity of lead oxide in PZT and its high vapor pressure during processing has led researchers to develop new, environmentally benign piezoelectric materials to replace PZT and its solid solutions.

Bismuth sodium titanate, $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) was one of the earliest candidates as a lead-free piezoelectric material. In bulk form it exhibits good ferroelectric properties, with $P_r = 38 \mu\text{C}/\text{cm}^2$ and was long thought to have rhombohedral symmetry.[5, 6] Recently Aksel *et al.* reported that BNT actually has monoclinic crystal structure.[7] However, BNT ceramics do not readily exhibit very high piezoelectric properties because of the difficulty to pole the material due to its large coercive field, $E_c (=73 \text{ kV}/\text{cm})$. [8] To improve the piezoelectric properties, BNT-based solid solutions formed with many other perovskite materials such as BaTiO_3 (BT), $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$, NaNbO_3 (NN), $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BZT), and $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ have been developed.[8-12] Hiruma *et al.* reported good piezoelectric performance with a high d_{33} of 181 pC/N and k_p of 0.56 in BNT – BKT – BT ternary solid solutions.[13] When the composition was 88BNT – 8BKT – 4BT near morphotropic phase boundaries (MPB), large P_r (40

$\mu\text{C}/\text{cm}^2$) was obtained.[14] Achieving this behavior in bulk materials is promising, however many of the ultimate applications of these systems will be in thin film form (i.e., MEMS devices). Thus, it is important to verify this performance can also be achieved in thin film embodiments.

Due to the inherent anisometric nature of thin films, and the difficulty in controlling the stoichiometry because of the inherently volatile A-site elements (Bi, Na, and K) an increased conductivity is often observed. As a result, obtaining a large and reliable piezoelectric response is often challenging in thin films.[15, 16] In previous work on BNT –BKT thin films, high quality films on Pt/TiO_x/SiO₂/Si were fabricated by chemical solution deposition using an appropriate amount of excess cations (overdoping). These films showed good maximum and remanent polarization values at low frequency (200Hz), P_{MAX} of 45 $\mu\text{C}/\text{cm}^2$ and P_r of 16 $\mu\text{C}/\text{cm}^2$, respectively.[17] For the closely related BNT-BKT-BT ternary system, Abazari *et al.* reported on 88BNT – 8BKT – 4BT epitaxial thin films synthesized by pulsed laser deposition on SrRuO₃ coated SrTiO₃ substrate. These showed a saturated polarization hysteresis loop with a large P_r = 30 $\mu\text{C}/\text{cm}^2$. [18] Polycrystalline thin films of BNT – BKT – BT, however, have not yet been investigated. In this study, 85BNT – 10BKT – 5BT thin films were synthesized on Pt/TiO_x/SiO₂/Si substrates via chemical solution deposition and their structural and electrical properties were investigated.

6.2. Experimental Procedure

For preparation of the 85BNT – 10BKT – 5BT solution, bismuth acetate Bi(OOC₂H₃)₃, sodium acetate trihydrate Na(OOC₂H₃)•3H₂O, potassium acetate K(OOC₂H₃), barium acetate Ba(OOC₂H₃)₂, and titanium isopropoxide Ti[OCH(CH₃)₂]₄ were used as the precursors. Acetic acid and propionic acid were chosen as solvents. First, titanium isopropoxide was chelated with acetylacetone

in a molar ratio of 1:2 in a dry atmosphere to prevent hydrolysis. Next, potassium acetate, sodium acetate trihydrate, and barium acetate were dissolved in acetic acid at 70 °C. Bismuth acetate was dissolved separately in propionic acid at room temperature. As previously reported [11], to compensate for the volatility of the A-site cations, 20 mol% excess potassium and sodium and 10 mol% excess bismuth were added to their corresponding solutions. The final mixture was achieved by pipetting an appropriate weight of the Bi, Na, K and Ba solution into the Ti solution in order to achieve a final concentration of approximately 0.3 molarity.

The precursor solution was spin-cast on 100 nm Pt/33 nm TiO_x/500 nm SiO₂/Si substrates at a 3000 rpm for 30 seconds. After each spin, the film was pyrolyzed at 300 °C for 5 min on a hot plate and annealed in air at 700 °C in a preheated furnace for varying times. The annealing conditions were adopted from previous work on BNT – BKT thin films [17], with the first layer annealed for 30 min and subsequent layers were annealed for 10 min each. The films were comprised of 6 total spin cast layers. The phase purity of the films was confirmed using X-ray diffraction (XRD, Bruker, AXS D8 Discover). The film thickness was obtained via variable angle spectroscopic ellipsometry (J. A. Woollam, V-VASE). 0.2 mm diameter thermally evaporated silver electrodes were deposited through a shadow mask for electrical measurements. An impedance analyzer (HP 4192A) was used to obtain dielectric properties at a 50mV oscillation level. Polarization hysteresis loops up to 125 °C were recorded using a ferroelectric tester (aixACCT Systems GmbH, TF Analyzer 2000HS system). The microstructure of the crystallized films was observed via scanning electron microscopy (SEM, FEI Quanta 600F)

6.3. Results and discussion

A representative X-ray diffraction θ - 2θ pattern of a 85BNT – 10BKT – 5BT film is logarithmically plotted in Figure 6.1. Perovskite phase with no second phase formation was observed, with the pattern indexed according to a pseudo-cubic perovskite structure. Similar to previous work on BNT – BKT thin films[17], the (110) peak showed the strongest intensity, with the films having an overall random orientation. The thickness of the crystallized film was approximately 240 nm.

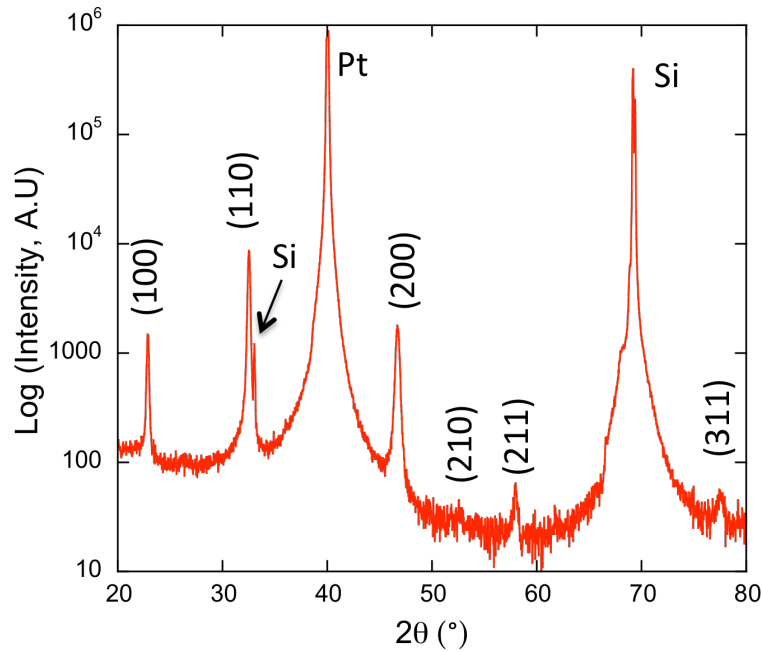


Figure 6.1. XRD θ - 2θ pattern for 85BNT – 10BKT – 5BT thin film synthesized with excess cation concentration in solution (+10% Bi, +20% Na, and +20% K)

Figure 6.2 shows the dielectric constant and loss as a function of frequency for a typical 85BNT – 10BKT – 5BT thin film at room temperature. As frequency increases from 100 Hz to 100 kHz, the dielectric constant decreases from 640 to 550. Meanwhile dielectric loss remains relatively stable over the

frequency range, with only a slight increase at lower frequencies. Dielectric constant and loss at 1 kHz are 610 and $\sim 3.5\%$, respectively. Compared to the work reported by Abazari *et al.* the permittivity at 1 kHz is similar but loss tangent here is lower.[18] It is difficult, however, to compare directly with these previously reported BNT – BKT – BT films as the two films were grown on different substrates with very different orientations (epitaxial vs. polycrystalline). Lower dielectric loss ($<6.5\%$) over the frequency range measured here indicates a lower defect concentration in these films.

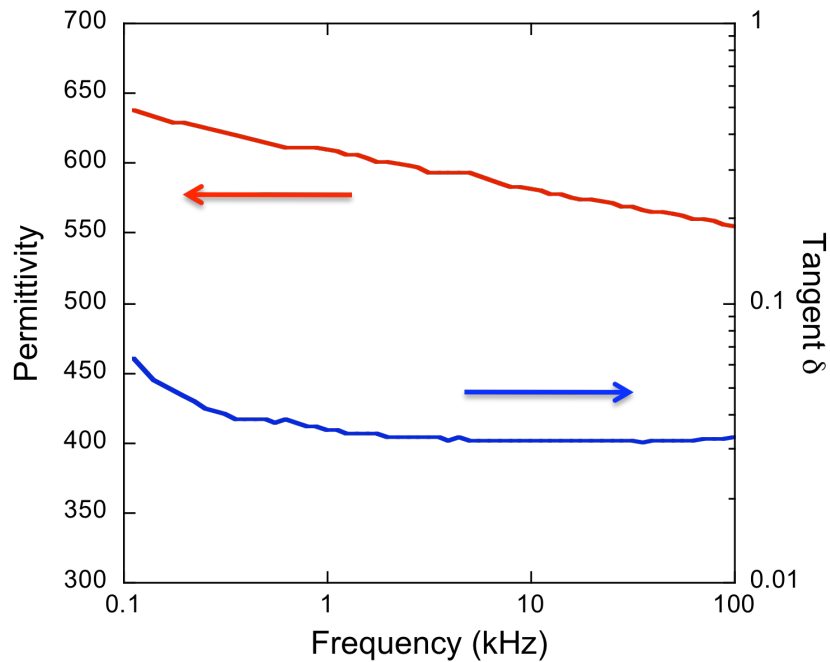


Figure 6.2. Dielectric constant and loss of 85BNT – 10BKT – 5BT thin film as a function of frequency

Figure 6.3 shows polarization-electric field hysteresis loops (PE loops) at different measuring conditions. First, in Figure 6.3(a), PE loops at room temperature were measured at 200 Hz. The shape of the loop indicates good ferroelectric behavior, however full saturation is not achieved. Maximum and remanent polarizations at about 360 kV/cm were $31 \mu\text{C}/\text{cm}^2$ and $6 \mu\text{C}/\text{cm}^2$

respectively. Considering that the P_r of bulk BNT – BKT – BT is typically over 30 $\mu\text{C}/\text{cm}^2$, here the value is only 20% of that of the bulk ceramic. [19, 20]

Polarization hysteresis loops taken at about 370 kV/cm and 500 Hz as a function of temperature up to 125 °C are displayed in Figure 6.3(b). The polarization values for these 85BNT – 10BKT – 5BT thin films were very stable as a function of temperature, and the shape of loops remained relatively unchanged. Both P_{max} and P_r at room temperature and 125 °C were nearly identical at approximately 32 $\mu\text{C}/\text{cm}^2$ and 6 $\mu\text{C}/\text{cm}^2$, respectively. Hysteresis loops above this temperature range ($> 125^\circ\text{C}$) became highly rounded in shape, which is indicative of conduction and defect migration beginning to occur.

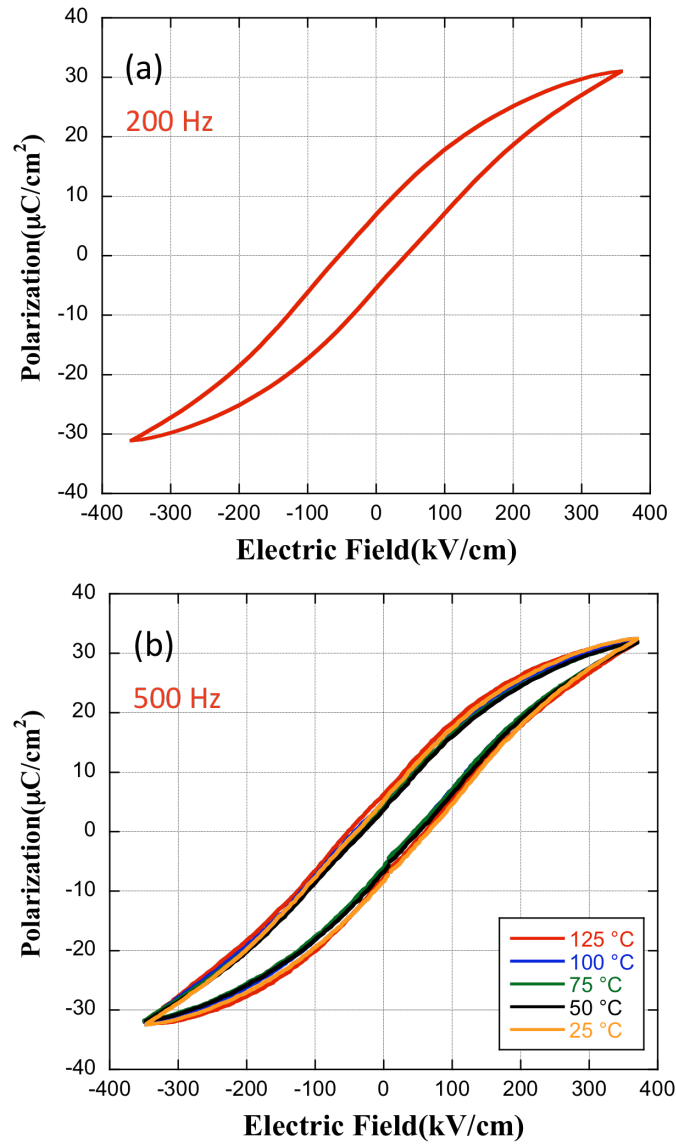


Figure 6.3. PE loops of 85BNT – 10BKT – 5BT thin film (a) at room temperature and 200 Hz (b) as a function of temperature up to 125 °C at 500 Hz

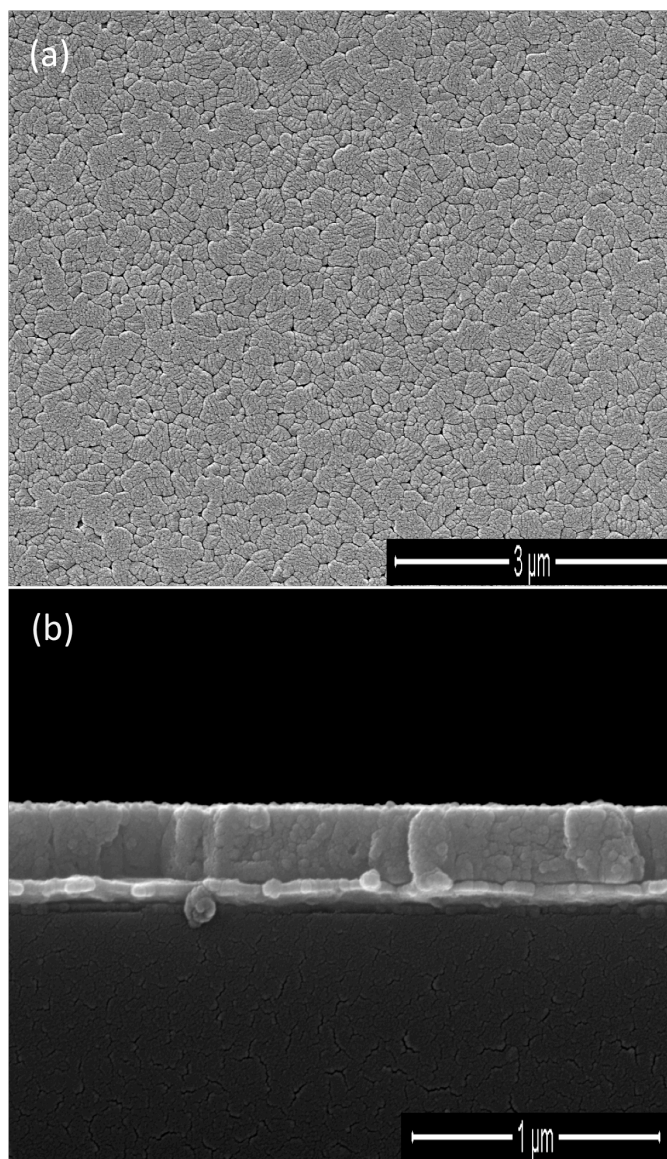


Figure 6.4. Plan view (a) and cross-section (b) SEM images of a 85BNT – 10BKT – 5BT thin film

Figure 6.4 shows the surface morphology and cross-sectional images of a 85BNT – 10BKT – 5BT thin film by SEM. There are many “clusters” present on the film surface, which consist of small grains. Outside of these clusters, the grain size is about 80 - 100 nm. Pores or voids, which could result from solvent evaporation or carbon oxidation during heat treatment of the film, were not observed.

Previous work on 80BNT – 20BKT showed some degree of columnar growth from cross-sectional SEM images, however these 85BNT – 10BKT – 5BT thin films did not. Instead, more equiaxed growth was observed. Columnar grain growth can be achieved when a heterogeneous nucleation event at the substrate is favored over a homogenous nucleation events within the amorphous gel.[21] To be favored over a homogenous nucleation event, increased crystallization temperatures could lower the driving force for crystallization on the substrate surface. Additionally, this type of equiaxed microstructure has been observed in CSD BaTiO₃ thin films, indicating even 5% BaTiO₃ can alter the nucleation and growth mechanism in the films shown here .[21, 22] Previously it was reported that BaTiO₃ developed different microstructures varying from columnar to fine-grained morphologies depending on the thickness of the individually crystallized layers.[23] In this study the dependence of the film microstructure on changing solution molarity (and hence thickness of each spin-cast layer) was not explored, but could potentially alter the film morphology from equiaxed to columnar. Using higher annealing temperatures to do this could cause two potential issues. First, increasing the crystallization temperature would likely have an adverse effect of the film stoichiometry due to increased volatilization of A-site cations (Bi, Na, and K). Second, delamination and hillock formation from diffusion of the TiO_x adhesion layer due to thermophysical instabilities of the plantinized silicon are known to be issues at higher temperatures (>700 °C) [24]

6.4. Conclusions

Pb-free 85BNT – 10BKT – 5BT thin films were synthesized via chemical solution deposition. By adopting the processing conditions from previous 80BNT – 20BKT thin films, phase pure perovskite films were achieved as confirmed by XRD. Good dielectric properties over the frequency range of 100 Hz to 100 kHz were obtained. The observed dielectric constant and loss at 1 kHz were 610 and 3.5%, respectively. Polarization hysteresis loops were obtained at 350 kV/cm

and 200 Hz with P_r of $6 \mu\text{C}/\text{cm}^2$ and P_{max} of $31 \mu\text{C}/\text{cm}^2$. SEM images revealed fine-grained homogenous film growth. Future investigation of this system should include using higher annealing temperatures on alternative substrates and the effects of varying solution molarity. The results of this current work suggest that BNT – BKT – BT thin films are a promising candidate for thin film piezoelectric applications.

6.5. References

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Chapter 7. Large piezoresponse and ferroelectric properties of 72.5BNT – 22.5BKT – 5BMgT thin films prepared by chemical solution deposition

7.1. Introduction

Recently many researchers have focused on the development of new, environmentally benign piezoelectric materials as potential replacements for lead zirconate titanate ($\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ or PZT) and its related solid solutions.[1] Potential materials are often Bi-based perovskites as Bi^{3+} has a similar electronic configuration to Pb^{2+} . [2] One of the more promising candidates is the A-site complex perovskite $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) and its solid solutions, including ternary systems with other perovskites such as BaTiO_3 (BT), $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (BKT), $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BZT), $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN), $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BMgT), and $\text{Bi}(\text{Ni}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BNiT). [3-8]

The Bi-based BNT, BKT and BNT-BKT binary systems are well-known materials systems studied by many research groups.[5-9] In the case of the binary system, compositions near 0.8BNT – 0.2BKT form a morphotropic phase boundary (MPB) between rhombohedral and tetragonal perovskite phases and have shown promising piezoelectric properties. Recently there have been several investigations on ceramics formed from BNT – BKT based ternary systems.[7, 10, 11] Jarupoom *et al.* studied the compositional dependence of the piezoelectric behavior for BNT – BKT – BMgT and BNT – BKT – BNiT ternary systems. The polarization hysteresis loops for these compositions were ‘pinched’ and had relatively low remanent polarization (less than $5 \mu\text{C}/\text{cm}^2$), however they exhibited large electromechanical strains with effective d_{33}^* for BNT – BKT – BMgT system as high as 570 pm/V at about 50 kV/cm. The mechanism for such high values is not fully understood, but based on the measured properties, these systems seem promising for piezoelectric microelectromechanical systems

(MEMS) applications. To explore the suitability of these materials they must be synthesized in thin film embodiments.

Various techniques such as pulsed laser deposition (PLD), RF sputtering, and chemical solution deposition (CSD) have been utilized to create BNT – based thin films. [12-20] but most of this work has focused on pure BNT, BNT – BKT, or BNT – BT binary compositions. Recently, Abazari *et al.* reported on 88BNT – 8BKT – 4BT epitaxial thin films on SrRuO₃/SrTiO₃ single crystal substrates that showed high remanent and maximum polarizations, P_r of 30 $\mu\text{C}/\text{cm}^2$ and P_{max} of about 50 $\mu\text{C}/\text{cm}^2$ respectively. [12] However, research on BNT – based ternary systems, especially polycrystalline thin films, was not explored much. In this work, high quality, polycrystalline 72.5BNT – 22.5BKT – 5BMgT thin films are synthesized on platinized silicon substrates and their dielectric and piezoelectric properties are assessed for suitability in piezoelectric-MEMS devices.

7.2. Experimental Procedure

Bismuth acetate $\text{Bi}(\text{OOC}_2\text{H}_3)_3$, sodium acetate trihydrate $\text{Na}(\text{OOC}_2\text{H}_3) \cdot 3\text{H}_2\text{O}$, potassium acetate $\text{K}(\text{OOC}_2\text{H}_3)$, magnesium acetate tetrahydrate $\text{Mg}(\text{OOC}_2\text{H}_3)_2 \cdot 4\text{H}_2\text{O}$ and titanium isopropoxide $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ were used as solution precursors. First, titanium isopropoxide was stabilized with acetic acid in a 1:4 of molar ratio in a dry atmosphere to prevent the reaction of the titanium precursor with H_2O . Subsequently, bismuth acetate was dissolved in propionic acid at room temperature. Sodium, potassium, and magnesium acetates were dissolved separately in methanol. Twice as much propionic acid by volume was used to dissolve the bismuth acetate compared to the amount of methanol used to dissolve all of the other separate cation acetates. Next, an appropriate weight of the Bi, Na, K, and Mg solutions was carefully dropped into the Ti solution using a syringe to achieve a 0.3M final solution molarity. To compensate for the high volatility of the cations, varying amounts of

excess cations were added when making the solutions (overdoping). Two solutions with a slight variation in overdoping were prepared; 1) +10% Bi, +20% Na/K excess and 2) +10% Bi, +20% Na/K, +5% Mg excess. It is well known that bismuth, sodium, and potassium are all volatile (especially at process temperatures typical of perovskite crystallization). The vapor pressure of K_2O and Na_2O are especially high, being comparable to that of PbO , but it has been shown that Bi_2O_3 is not as volatile as PbO [21-23]. Although magnesium is not a highly volatile element, a small amount of evaporation was observed during processing in previous work [24].

The solutions were spin cast on a 100 nm Pt/33 nm TiO_x /500 nm SiO_2 /Si substrate at 3000 rpm for 30 sec. After each spin, the wet film was pyrolyzed at 300 °C for 5 min and then annealed in air for 10 min at varying temperatures ranging from 600 °C to 700 °C. These steps were repeated 6 times, with all films approximately 260 nm ~ 270 nm thickness measured via variable angle spectroscopic ellipsometry (J. A. Woollam, V-VASE). Phase purity was confirmed via X-ray diffraction (XRD, Bruker, AXS D8 Discover, $Cu K\alpha$ radiation). For the top electrode, silver was thermally evaporated using 0.2mm diameter shadow mask. Dielectric constant and loss were obtained using an impedance analyzer (HP 4192A, 50 mV oscillation level). Ferroelectric and piezoelectric property measurement systems (aixACCT Dual Beam Laser Interferometer, DBLI, and TFAalyzer systems) were used to record polarization and strain hysteresis loops at room temperature and polarization hysteresis up to 100 °C. For the measurement of displacement and temperature dependence of the ferroelectric properties, iridium was sputtered via shadow mask for 0.01mm² top electrodes. The microstructures of crystallized films were observed via scanning electron microscopy (SEM, FEI XL30S-2) and transmission electron microscopy (TEM, JEOL 2500SE) and they were also used to confirm the thickness of the films. Compositional depth profiling of the films was accomplished by X-ray

photoelectron spectroscopy (XPS, PHI Quantera Scanning ESCA). Quantitative compositional analysis of films was performed via electron probe microanalysis (EPMA, Cameca SX50).

7.3. Results and Discussion

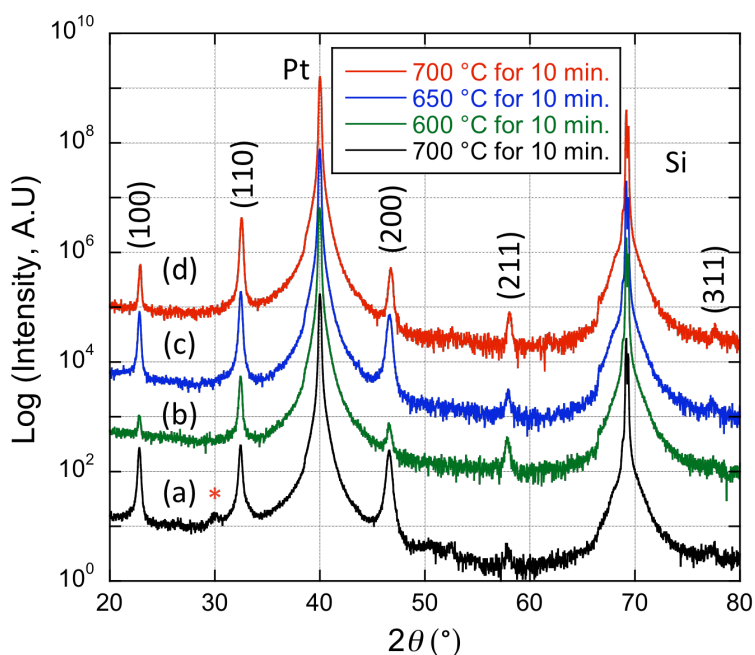


Figure 7.1. XRD θ - 2θ pattern ($\text{Cu K}\alpha$) for 72.5BNT – 22.5BKT – 5BMgT thin films: (a) without adding excess Mg precursor; (b) Annealed at 600 °C for 10 min; (c) Annealed at 650 °C for 10 min; (d) Annealed at 700 °C for 10 min. Asterisk indicates second phase

Figure 7.1 shows the logarithmic plot of θ - 2θ XRD patterns for 72.5BNT – 22.5BKT – 5BMgT films synthesized with the different solutions and annealed at different temperatures. As seen in Figure 7.1 (a), when the film was deposited using the solution without excess Mg precursor, a small second phase peak is apparent prior to the perovskite (110) peak. With the additional Mg (+ 5%), all films annealed at different temperature showed pure perovskite phases with

random orientation, as observed in Figure 7.1 (b)-(d). This XRD comparison between films made with and without overdoping of the Mg precursor suggests that the loss of some Mg is likely occurring during the crystallization step. The film annealed at 600 °C displayed overall lower intensity compared to those of the films annealed at higher temperatures. When normalizing (110) peaks of 72.5BNT – 22.5BKT – 5BMgT against Pt (111) peaks, the normalized value for 600 °C, 650 °C, and 700 °C were 0.08%, 0.25%, and 0.27% respectively. Lower XRD intensity for films of similar thickness while using the same scanning condition indicates a lower degree of crystallinity for the films processed at 600 °C.

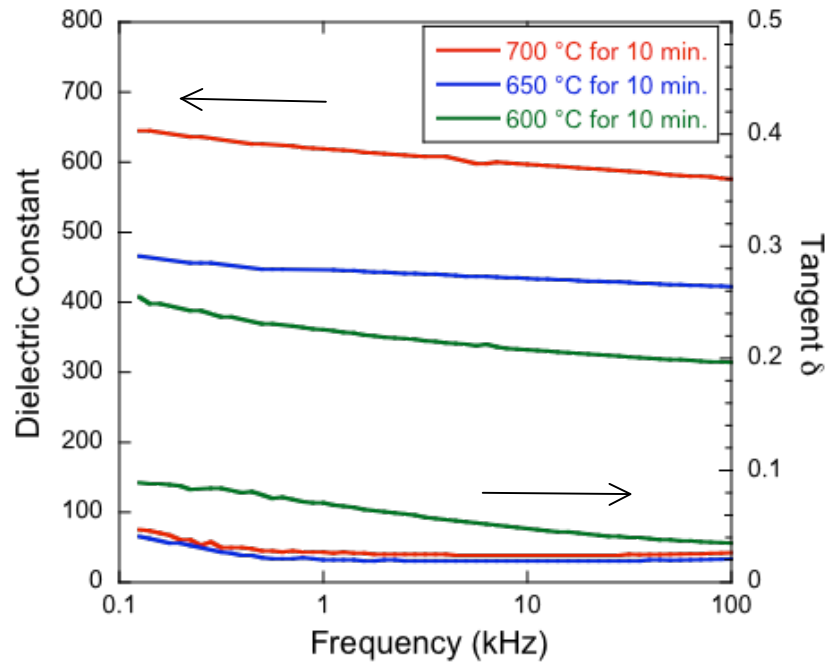


Figure 7.2. Dielectric constant and loss of 72.5BNT – 22.5BKT – 5BMgT thin films fabricated with +10% Bi, +20% Na/K, +5% Mg excess solutions at different annealing conditions

Figure 7.2 shows the dielectric constant and loss from 0.1 kHz to 100 kHz for 72.5BNT – 22.5BKT – 5BMgT films annealed at different temperatures. The film synthesized from the solution without excess Mg was not measured due to the presence of a second phase. As annealing temperature increased, the dielectric constant also increased and, especially for 700 °C, a high value was observed. At 1 kHz, the dielectric constant for films annealed 600 °C, 650 °C, and 700 °C were 360, 450, and 720, respectively. The film annealed at 600 °C showed higher dielectric loss (> 8%) at low frequencies compared to the other two films (3~4%). Although 600 °C is the lowest temperature to result in phase-pure perovskite 72.5BNT – 22.5BKT – 5BMgT, it may not be high enough to fully crystallize the system for the time used here, 10 min for each layer. This likely resulted in the higher loss with lower dielectric constant in the film annealed at 600 °C.

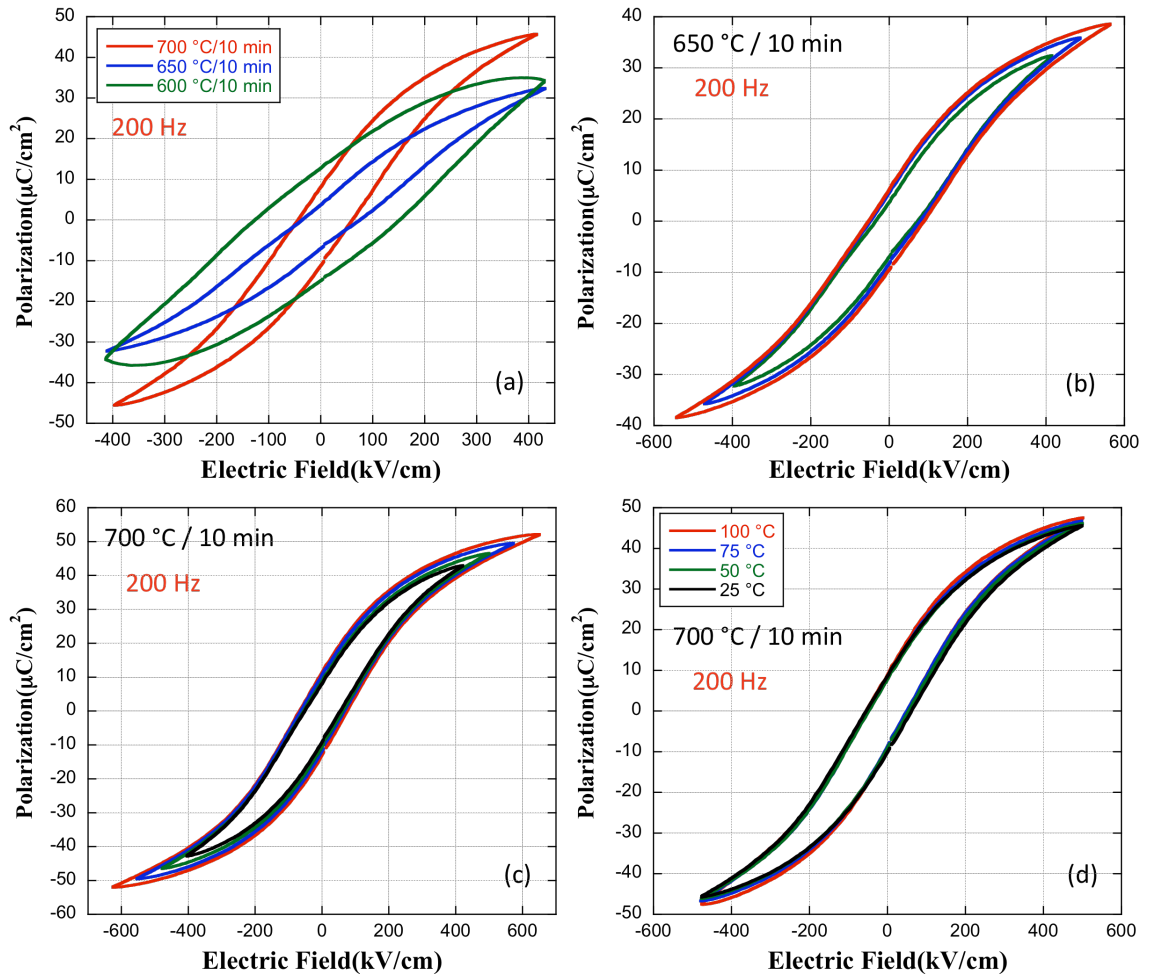


Figure 7.3. PE loops of 72.5 BNT – 22.5 BKT – 5 BMgT thin films fabricated with +10% Bi, +20% Na/K, +5% Mg excess solutions: (a) effect of annealing temperature; (b) annealed at 650 °C; (c) annealed at 700 °C; (d) as a function of temperature up to 100 °C.

Figure 7.3 displays the polarization-electric (PE) field hysteresis loops for these 72.5BNT – 22.5BKT – 5BMgT films at various measurement conditions. Figure 7.3(a) shows the hysteresis loops for all 3 films at the same level of electric field and frequency, about 400 kV/cm and 200 Hz, respectively. For the film annealed at 600 °C, as expected from the structural and dielectric properties, a rounded shape indicative of electrically lossy behavior was observed, but the

other two films show better PE hysteresis loops with high maximum polarization. Figure 7.3(b) shows nested hysteresis loops for the film annealed at 650 °C for increasing applied fields up to about 560 kV/cm with corresponding $P_{\max}$ and P_r of 38 $\mu\text{C}/\text{cm}^2$ and 8 $\mu\text{C}/\text{cm}^2$, respectively. When annealed at 700 °C, the ferroelectric properties were further improved as seen in Figure 7.3(c). The $P_{\max}$ increased to 52 $\mu\text{C}/\text{cm}^2$ and P_r was 12 $\mu\text{C}/\text{cm}^2$ at 200 Hz. This is significant as a $P_{\max}$ of over 50 $\mu\text{C}/\text{cm}^2$ was measured at 200 Hz, and high polarization values at such low measuring frequency have not previously been reported in BNT-based thin films. [13-20] Unlike the work of bulk 72.5BNT – 22.5BKT – 5BMgT ceramics, the thin films did not display pinched loops and had 65% and 240% higher $P_{\max}$ and P_r compared to those of bulk. [7] As mentioned earlier, this bulk system had large field-induced strains, one theory proposed to explain this was an electric field induced phase transition from a non-polar to a polar phase. In this work the amount of stress the films experience during processing was not directly investigated, but it is known that large stresses are generally anticipated for thin film synthesis and have been known to affect the nature of phase transitions in the film. [25, 26] Thus if the pinched-loop in bulk materials at lower electric fields is the result of a non-polar phase, a large film stress could induce the phase transition of the BNT-BKT-BMgT thin film to the polar phase and the pinched-loop may be less likely to be observed in thin films. Furthermore the lower $P_{\max}$ of about 30 $\mu\text{C}/\text{cm}^2$ reported in the bulk system was obtained at only 50 kV/cm, meaning that the response at higher electric fields for bulk BNT-BKT-BMgT is not available for a more direct comparison with this work.

The PE hysteresis loop for the 700 °C annealed film as a function of temperature up to 100°C at a fixed electric field of 500 kV/cm is also shown in Figure 7.3(d). Clearly the shape of the loop at 100 °C remains satisfying and does not show any sign of increased electrically lossy behavior which could result from unwanted mobile defect contribution. Comparing PE loops at 25 °C and

100 °C, it is found that $P_{\max}$ increases slightly from 46 $\mu\text{C}/\text{cm}^2$ to 48 $\mu\text{C}/\text{cm}^2$ and the values of P_r remain the same. Only a minor reduction in coercive field, E_c , from 57 kV/cm to 51 kV/cm was observed. From these data it is clear that the 72.5BNT – 22.5BKT – 5BMgT thin film can withstand up to 100°C while maintaining good ferroelectric behavior.

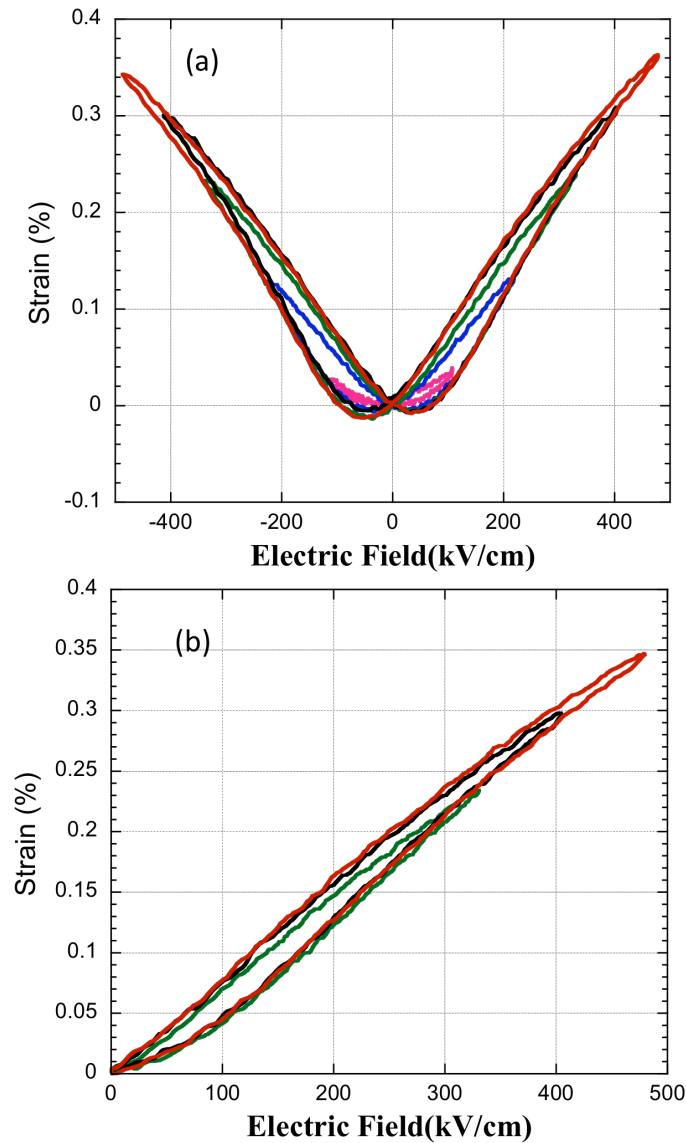


Figure 7.4. The electromechanical strain loops of 72.5 BNT – 22.5 BKT – 5 BMgT thin film annealed at 700 °C: (a) bipolar loop; (b) unipolar loop

The effective piezoelectric coefficient $d_{33,f}$ is can be given by[27]:

$$d_{33,f} = 2Q_{eff}\epsilon_0\epsilon_rP_s \quad (7.1)$$

where Q_{eff} , ϵ_0 , ϵ_r , and P_s are the effective electrostriction coefficient, vacuum permittivity, relative dielectric permittivity, and spontaneous polarization respectively. It is common that the ferroelectric material, which has higher P_{max} , possesses large P_s , and previous work showed that the change in $d_{33,f}$ followed the change of P_s . [27] Among BNT – BKT – BMgT samples, the higher P_{max} of thin film should result in a larger electromechanical strain upon application of similar maximum electric field. Therefore the 700 °C film, due to its enhanced dielectric and ferroelectric properties was selected for electromechanical strain hysteresis loop analysis (calculated from displacement measurements) via double beam interferometry at 1 kHz under increasing electric field levels. Prior to the measurement, the backside of the substrate was carefully polished after depositing the film. Figures 7.4 (a) and (b) show bipolar and unipolar strain loops measured up to a maximum applied field of 500 kV/cm, respectively. The bipolar strain loop had a highly symmetric shape, but exhibited some degree of negative displacement which deviates from pure parabolic behavior. This phenomenon is slightly different from work on bulk 72.5BNT – 22.5BKT – 5BMgT.[7] But it is similar to strain results shown in the related bulk ternary system of BNT-BKT-BZT [10]. Both the bulk and thin films showed very similar maximum strain values as high as ~0.34 % at high electric field. Effective $d_{33,f}$ was calculated from the unipolar strain loop to be 75 pm/V at ~500 kV/cm, which is large but somewhat inferior to the values of some PZT thin films. [28-30]

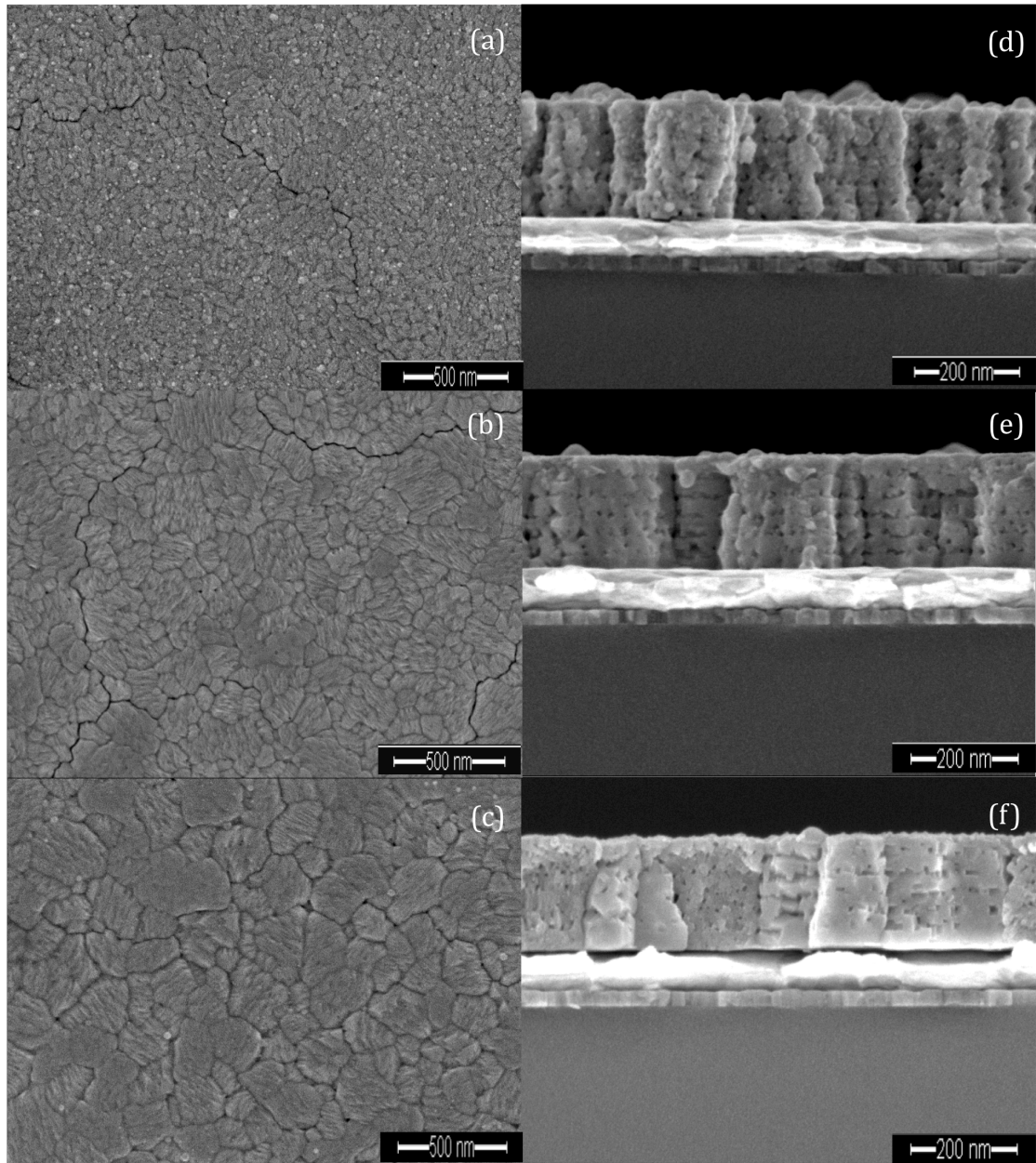


Figure 7.5. Plain view and cross-sectional SEM images for 72.5BNT – 22.5BKT – 5BMgT thin films: annealed (a)&(d) at 600 °C; (b)&(e) at 650 C; and (c)&(f) at 700 °C

Figure 7.5 shows the microstructures of 72.5BNT – 22.5BKT – 5BMgT thin films annealed at different temperatures. Some very small features on the surface of the film annealed at 600 °C were observed. These could be a second phase resulting from using too low of an annealing temperature (although this was not noted in the XRD). It has been reported that the perovskite phase could not be crystallized fully at 600 °C if acetate groups are used as precursors [31] and it is likely that 600 °C is not high enough to volatilize all of the excess cations in a ten minute per layer anneal time. It is clearly observed that larger grains developed as the temperature was increased, with the film annealed at 700 °C having the largest grains of about 200 ~ 250 nm. Microcracks on the surface of thin films annealed at 600 °C were found, but the origin of their formation is not clearly understood. Cross-sectional SEM images are shown in Figure 7.5 (d) ~ (f). All films are composed of relatively dense microstructures within each layer, and it was found that at higher annealing temperature increasingly dense individual layers were crystallized. However some voids were present in all of the films. These small voids or grooves are more highly concentrated at the interfaces between any two given layers. To confirm this, TEM images for the film annealed at 700°C were taken and are displayed in Figure 7.6. In these images what appear to be cubic-shaped defects are clearly seen at the interface between successive layers. As the presence of these voids or defects could alter the mechanical clamping of the film (perhaps reducing it), the measured effective piezoelectric coefficient, $d_{33,f}$ may be somewhat artificially high. Aside from these interfaces, a dense microstructure was confirmed from TEM imaging. Interestingly, the first layer of 72.5BNT – 22.5BKT – 5BMgT thin films appeared to be a nearly defect- or void-free. Two factors could explain this phenomenon; 1) the first layer was effectively annealed 6 times and longer annealing may densify the layer more than subsequent layers, and 2) the first layer was deposited directly on the Pt electrode but the remaining layers were deposited on the top of the perovskite phase. The difference between the smoothness of the platinum and the top of a

perovskite layer for subsequent spin-casting might result in different wetting behavior of the solution. To fully understand why these defects form at the interfaces and how to eliminate them, further investigation is required.

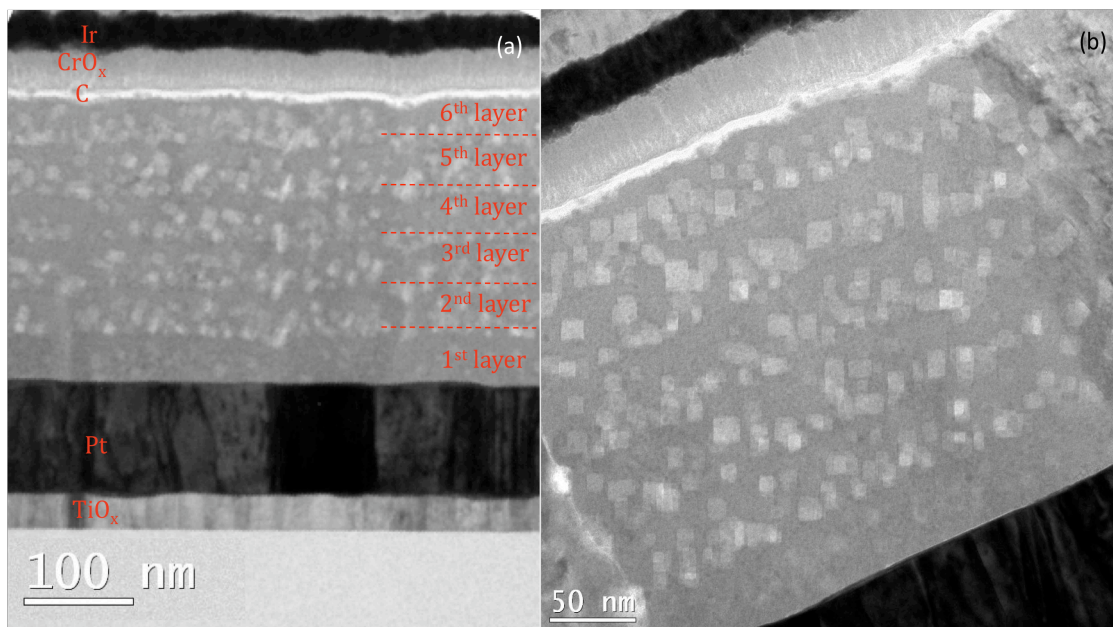


Figure 7.6. TEM image of 72.5BNT – 22.5BKT – 5BMgT thin film annealed at 700 °C

The compositional depth profiles to the SiO₂ underlying layer for the samples were obtained via XPS and are shown in Figure 7.7. The overall distributions of all elements through the film thickness were reasonably uniform, as seen in Figure 7.7 (a) ~ (c). In expanded y-scale (excluding Ti), however, cation compositional fluctuations were observed in Figure 7.7(d) ~ (f). The sample annealed at 600 °C has a slight increase in the average Bi atomic percentage close to the bottom of the film, but the rest of the cations do not have any significant overall change in atomic percentage. Depending on the annealing temperature, different relative atomic ratios between Bi and Na were found. The ratio of Na/Bi for an ideal composition is 0.69. After taking an average atomic percentage of each film, excluding the regions near the surface and near the bottom electrode,

the current measured ratios of the films annealed at 600°C, 650°C, and 700°C were 0.57, 0.69, and 0.70 respectively. This could explain the difference in ferroelectric response and microstructure for the film annealed at 600 °C. In general, the fluctuation of cations, especially for Bi, aligns closely with the boundaries between the 6 separate layers deposited. Figure 7.8 shows the depth profile of only bismuth and schematically how each layer is indicated by each peak (represented by dotted lines). This is consistent when compared to the previous SEM and TEM analysis. Additionally, as it was confirmed from TEM images that the voids are very concentrated between any two layers, the fluctuation of the bismuth through the film thickness in the XPS depth profile is likely related to the locations of these voids. There were some observable signal levels for the cations within the Pt layer in Figure 7.7, however those signals are artifacts due to the fact that the Pt XPS signal dominates in this layer. Any other signals in this layer resulted from the non-linear least squares fitting of the XPS spectra.

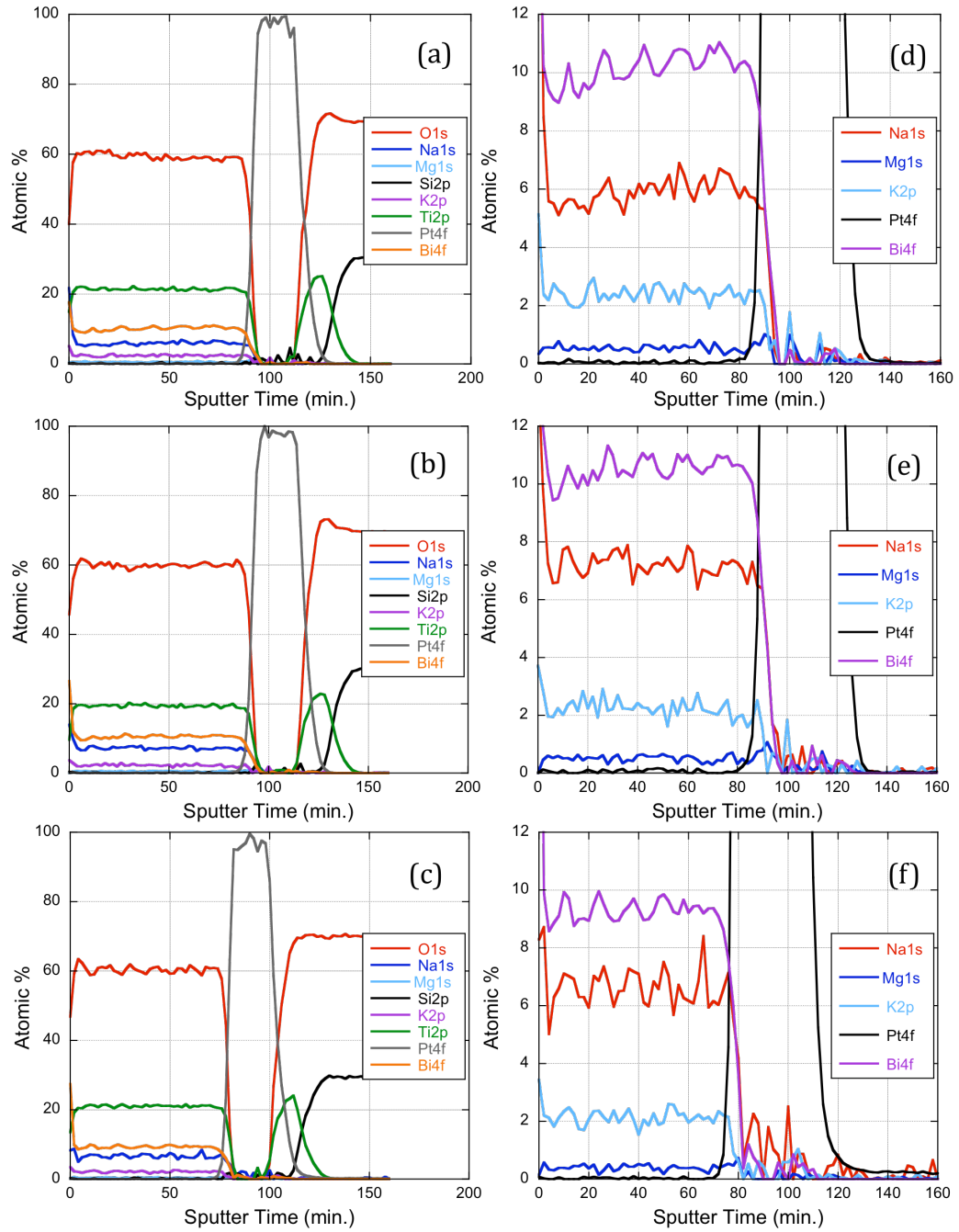


Figure 7.7. XPS depth profiles of 72.5BNT – 22.5BKT – 5BMgT thin films: annealed
(a)&(d) at 600 °C; (b)&(e) at 650 °C; and (c)&(f) at 700 °C

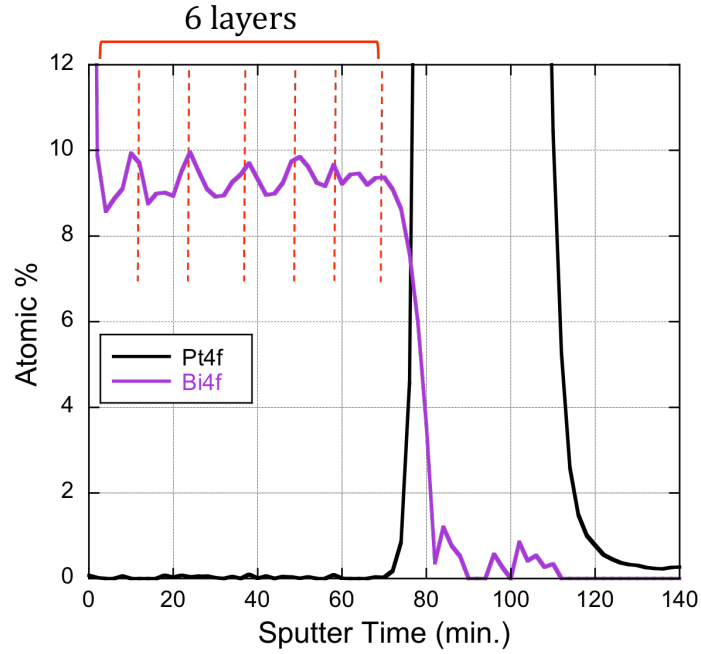


Figure 7.8. Bi elemental distribution of 72.5BNT – 22.5BKT – 5BMgT thin film annealed at 700 °C

		Bi (at %)	Na (at %)	K (at %)	Mg (at %)	Ti (at %)	O (at %)
Ideal		10.5	7.25	2.25	0.5	19.5	60
EPMA	650 °C/10min	10.54	8.38	2.19	0.49	19.52	58.88
	700 °C/10min	10.38	8.43	2.16	0.48	19.37	59.18

Table 7.1. Average atomic percentages of 72.5BNT – 22.5BKT – 5BMgT thin films annealed at different temperatures

Finally, EPMA was used to measure the overall stoichiometry of 72.5BNT – 22.5BKT – 5BMgT thin films annealed at 650 °C and 700 °C that had shown good electrical response. Table 7.1 summaries the average atomic percentage for the

samples along with the ideal values for the stoichiometric composition. It was found that the two films have almost identical atomic ratios for all elements and was very close to the ideal stoichiometric composition. This implies that the overdoping levels used for the different cations in this work were appropriate and helped to ensure the films had the correct atomic ratios at the given processing conditions. For the EPMA data analysis, two assumptions were made. 1) Underlying layers such as Pt, TiO_x and SiO_2 were not damaged from the film processing such that their initial thicknesses were unchanged, and 2) TiO_x was dealt with as being equivalent to TiO_2 . These assumptions may introduce a small discrepancy in the atomic ratios for some elements. Interestingly, the two films annealed 650 °C and 700 °C have almost identical compositions but showed significantly different electrical properties as seen Figures 7.2 and 7.3. Due to their nearly identical compositions, this can be largely attributed to the differences in the morphologies of the two films.

7.4. Conclusions

In summary, this research demonstrated the synthesis of lead-free 72.5BNT – 22.5BKT – 5BMgT thin films via chemical solution deposition. With the appropriate amount of overdoping (+10% Bi, +20% Na/K, +5% Mg), an each-layer annealed approach enabled the formation of phase pure perovskite films from 600 °C to 700 °C. As annealing temperature was increased, a distinct improvement of the dielectric and ferroelectric properties was observed. The 72.5BNT – 22.5BKT – 5BMgT thin film annealed at 700 °C performed the best, exhibiting properties such as a P_{max} of 52 $\mu\text{C}/\text{cm}^2$ and P_r of 12 $\mu\text{C}/\text{cm}^2$ respectively. The XPS compositional depth profiles revealed a cation distribution through the thickness of films annealed at different temperature that corresponded to the thicknesses of the 6 layers deposited. Analysis of the XPS and EPMA data indicated that films annealed at 650 °C and 700 °C had near ideal atomic ratios. A high effective piezoelectric coefficient ($d_{33,f}$) of about 75 pm/V

was obtained via double laser beam interferometry. Microstructural imaging revealed that some voids existed and were concentrated at the interfaces between each layer of the film. This suggests that removing those voids might reduce the variation of cation fluctuation as seen in the XPS depth profile and increase the density and therefore electrical response. Considering the current properties obtained and strong possibility for further improvement, 72.5BNT – 22.5BKT – 5BMgT thin films can be considered an attractive candidate for piezoelectric actuators in microelectromechanical systems (MEMS).

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Chapter 8. Dielectric nonlinearity in BNT – BKT and BNT – BKT – BMgT thin films

8.1. Introduction

Ferroelectric materials have been investigated for many years for applications such as sensors, actuators, non-volatile ferroelectric random access memory (FERAM), and microelectromechanical systems (MEMS). [1-3] The correlated dielectric and piezoelectric properties of these materials can be attributed to two mechanisms: intrinsic and extrinsic contributions. The intrinsic part is associated with the crystal lattice and the extrinsic part is due to domain wall motion and phase boundaries.[4] Rayleigh analysis was originally developed to study ferromagnetic materials under weak field conditions, but it has more recently been applied to ferroelectric materials in order to separate intrinsic and extrinsic contributions to the dielectric and piezoelectric response in ferroelectric ceramics, thin films, and even single-crystals including $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT), $\text{Pb}(\text{Yb}_{0.5}\text{Nb}_{0.5})\text{O}_3 - \text{PbTiO}_3$ (PYN – PT), BiFeO_3 (BFO), and $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (BZT).[4-14] The validity of Rayleigh analysis was confirmed through those researches. The Rayleigh relationships as given in equations (8.1) - (8.3) describe the dielectric response as a function of ac electric field under sub-switching conditions.

$$\varepsilon' = \varepsilon'_{init} + \alpha'E_0 \quad (8.1)$$

$$\varepsilon'' = \alpha'' E_0 = \frac{4}{3\pi} \alpha' E_0 \quad (8.2)$$

$$P(E) = (\varepsilon'_{init} + \alpha' E_0) E \pm \frac{\alpha'}{2} (E_0^2 - E^2) \quad (8.3)$$

where ε' , ε'_{init} , α' , E_0 , ε'' , α'' , and P are the real part of relative permittivity, the reversible (intrinsic) component of the permittivity, the irreversible (extrinsic) Rayleigh coefficient, the amplitude of the driving electric field $E = E_0 \sin(\omega t)$, the imaginary part of relative permittivity, imaginary irreversible Rayleigh coefficient, and polarization, respectively.

Bismuth sodium titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) and its solid solutions have been investigated for many years to replace lead zirconate titanate PZT, widely used for many piezoelectric applications, because of the toxicity of lead. [15, 16] Previously, good quality of BNT – BKT and BNT – BKT – BMgT thin films were achieved via chemical solution deposition, however the dielectric and piezoelectric nonlinearities have not been explored via Rayleigh analysis. It is important to understand the intrinsic and extrinsic contributions in these materials, and to compare them to PZT. Thus in this research, the nonlinear dielectric response of solution-derived BNT – BKT and BNT – BKT – BMgT thin films is investigated with Rayleigh analysis under sub-switching electric fields.

8.2. Experimental Procedure

80BNT – 20BKT and 72.5BNT – 22.5BKT – 5BMgT thin films were prepared via chemical solution deposition. The solution preparation is described in chapters 5 and 7 for each composition. The precursor solutions for both systems were spin-cast on Pt/TiO_x/SiO₂/Si substrates at 3000 rpm for 30 seconds. After spinning each layer, the wetted films were pyrolyzed at 300 °C for 5 minutes followed by annealing in a preheated furnace at 700 °C in air. These steps were repeated 6 times for each film. Variable angle spectroscopic ellipsometry (SE, J. A. Woollam, V-VASE) was used to obtain the film thickness. X-ray diffraction (XRD, Bruker, AXS D8 Discover) with Cu K α radiation was utilized to determine the phase purity of the crystallized films. Silver top electrodes, 0.2 mm in diameter, were thermally evaporated to measure the dielectric properties of each film with an impedance analyzer (HP 4192A). Polarization hysteresis loops were obtained from a ferroelectric tester (Radiant Premier II).

8.3. Results and discussion

The phase pure perovskite structure of BNT – BKT and BNT – BKT – BMgT films was confirmed by XRD (refer to chapters 5&7) and the thickness of those samples as measured by spectroscopic ellipsometry was 260 ~ 265 nm. Figure 8.1 shows the ac electric field dependence of the dielectric properties at 5 kHz and 10 kHz for BNT – BKT and BNT – BKT – BMgT films. Similar dielectric behavior for each composition was observed. The initial dielectric permittivity at

both frequencies was constant until ac field amplitude reached a threshold field (E_{th}) which indicates the degree of domain wall pinning.[10] The samples had E_{th} of approximately 10 kV/cm. Beyond this, the dielectric constant increased linearly. Since Rayleigh-like behavior in dielectric response can be valid up to 1/2 or 1/3 of coercive field, using equation (8.1), the linear region for both systems from 11 kV/cm to 40 kV/cm which is about half of coercive field of two systems was used to fit to Rayleigh behavior.

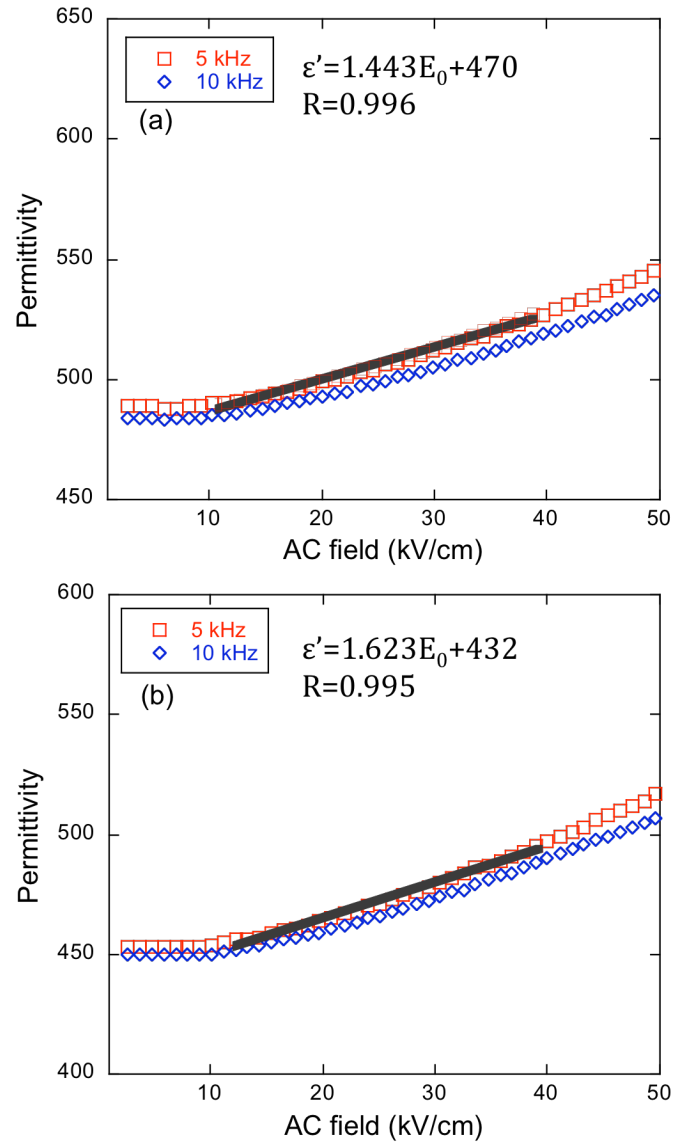


Figure 8.1 ac field dependence of the relative permittivity for (a) BNT – BKT film and (b) BNT – BKT – BMgT film.

Table 8.1 summarizes Rayleigh parameters of these systems at 5 kHz and other materials for comparison.[9-12] According to the Rayleigh relationship, the term $\alpha'E_0$ represents irreversible domain wall or phase boundary displacements

at the electric field. By comparing irreversible Rayleigh parameters, the degree of the extrinsic contribution to the permittivity can be inferred. BNT – BKT and BNT – BKT – BMgT films had α' of 1.443 cm/kV and 1.623 cm/kV, respectively. These values are lower compared to other materials aside from the BFO film. The very limited irreversible Rayleigh parameter for BFO resulted from specifically engineered domain structures.[11] However, for a better comparison the thickness of the BFO films and the measuring frequency should be considered as changes in α' were observed as the film thickness and frequency were changed.[6] At a fixed field, the ratio of the irreversible to reversible Rayleigh contributions describes the relative increase of the dielectric constant per unit of electric field. BNT – BKT and BNT – BKT – BMgT films showed approximately 0.31% and 0.37% contribution per unit of electric field.

Materials	α' (cm/kV)	ϵ'_{init}	α'/ϵ'_{init}	Ref.
BNT - BKT	1.443 $\pm$ 4.0E-4	470	3.07E-3	This work
BNT - BKT - BMgT	1.623 $\pm$ 1.1E-4	432	3.76E-3	
PZT	18	890	0.02	[9]
PYN - PT	19.5 $\pm$ 0.4	1147*	0.017	[10]
BFO	0.12 $\pm$ 5.3E-4	92.6 $\pm$ 1.4E-2	1.29E-3	[11]
BZT	7.7	708	10.9E-2*	[12]

Asterisk represents the calculated values using two other parameters because those were not present in previous works

Table 8.1 The Rayleigh parameters for BNT – BKT, BNT – BKT – BMgT, and other thin film materials.

Validity of the Rayleigh law for BNT – BKT and BNT – BKT - BMgT was confirmed by comparing the expected polarization from equation (8.3) and the actually measured polarization from ferroelectric tester. The positive sign in equation (8.3) was used to predict the polarization in the direction of decreasing field and the negative sign was used for increasing field. There is a slight discrepancy between measured and calculated polarizations, however overall good agreement was observed.

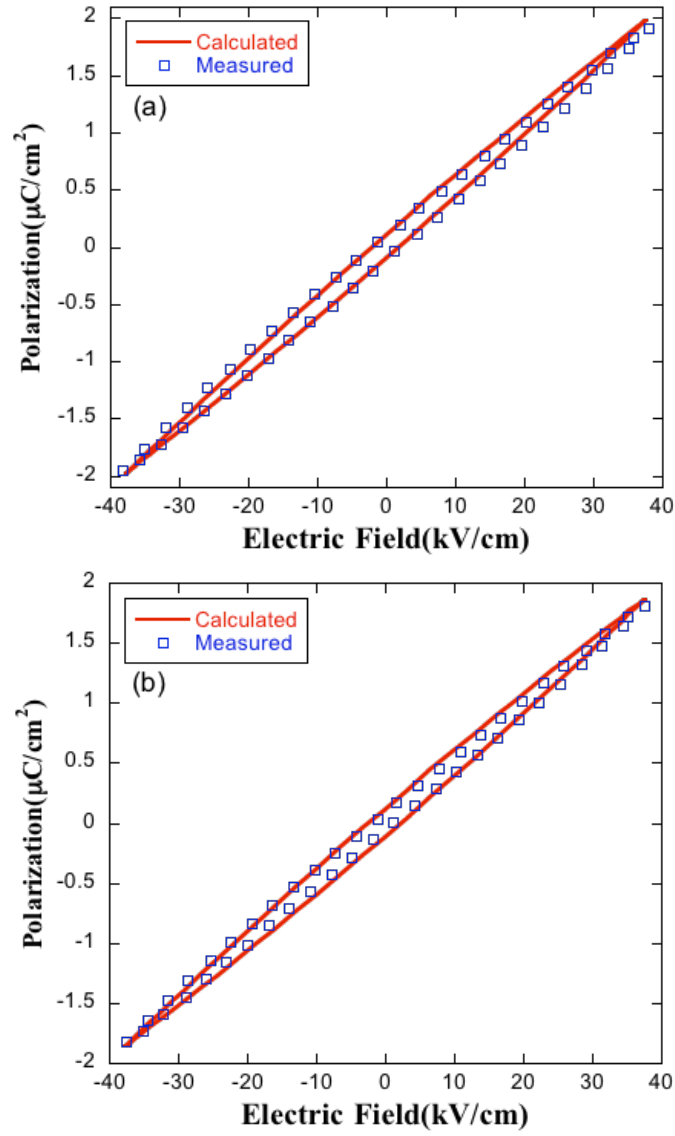


Figure 8.2 The measured and calculated hysteresis loops for (a) BNT – BKT and (b) BNT – BKT – BMgT thin films

8.4. Conclusion

The nonlinearity of the dielectric response for solution-derived BNT – BKT and BNT – BKT – BMgT thin films was studied utilizing Rayleigh analysis. Both

material systems had a very similar increase in permittivity as a function of increasing ac field amplitude. Slightly higher mobility or higher concentration of domain wall contribution was found in BNT – BKT – BMgT thin film. However, the ratio of the irreversible to reversible Rayleigh contributions for the two systems revealed that both had low extrinsic contribution to the dielectric permittivity. To verify the validity of Rayleigh law, the calculated polarization from the impedance measurements and the polarization measured from hysteresis were compared and an overall good fit between the two curves was found. These results suggest that Rayleigh analysis can also apply to lead-free BNT-based ferroelectric materials.

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Chapter 9. Conclusions and future work

This research demonstrated the fabrication of high quality bismuth based piezoelectric thin films via pulsed laser deposition (PLD) and chemical solution deposition (CSD). The manner in which electrical properties are linked to processing conditions was elucidated.

9.1. Conclusions

Lead-free polycrystalline 0.95BKT – 0.05BZT thin films were synthesized via PLD. Controlling for the A-site cation volatility was critical to achieving phase pure perovskite thin film. The dielectric constant of the films was lower than that of bulk 0.95BKT – 0.05BZT ceramics with a higher loss tangent ($>10\%$) over the frequency range from 100 Hz to 1 MHz. Hysteresis loops of the films were linear with a maximum polarization of $\sim 8.5 \mu\text{C}/\text{cm}^2$ at fields over 200 kV/cm. Poor electrical response of 0.95BKT – 0.05BZT thin films could be related to possible off-stoichiometry due to A-site volatility, which adversely affected crystal structure and phase purity. A porous microstructure was observed and EDS confirmed elements missing in those voids.

Chemical solution deposition was utilized to fabricate lead-free 0.8BNT – 0.2BKT thin films with a composition near the MPB region. The importance of overdoping to compensate the loss of Bi, Na, and K was observed by comparing XRD patterns and electrical properties. With an optimized the level of doping

(+10% Bi, +20% Na/K), it was found that annealing conditions affected the dielectric constant, which varied from 580 to 730. This could be related to the thermal budget for crystallizing and the loss of A-site cations under some given conditions. Films where a first layer, or template, was annealed at 700°C for 30 min with subsequent layers annealed for 10 min at the same annealing temperature showed the best ferroelectric properties with P_r of 16 $\mu\text{C}/\text{cm}^2$ and P_{max} of 45 $\mu\text{C}/\text{cm}^2$. Compositional analysis revealed that overdoping selected for 0.8BNT – 0.2BKT thin films with near ideal stoichiometry.

85BNT – 10BKT – 5BT ternary system was synthesized into thin film via CSD. For the deposition, the processing conditions from previous BNT – BKT works were adopted including annealing temperature, annealing time and amount of excess cations. Polarization hysteresis loops at 350 kV/cm & 200 Hz showed P_r of 6 $\mu\text{C}/\text{cm}^2$ and P_{max} of 31 $\mu\text{C}/\text{cm}^2$. The hysteresis loops were stable until 125 °C. A different microstructure from BNT – BKT film was observed. Fine-grained growth might be attributed to the introduction of BT.

Duplicating the solution process and deposition condition from BNT – BKT film enabled the formation of phase pure perovskite of 72.5BNT – 22.5BKT – 5BMgT films. On increasing the annealing temperature from 600 °C to 700 °C, a larger dielectric constant was obtained. The 72.5BNT – 22.5BKT – 5BMgT film annealed at 700°C performed the best, exhibiting properties such as a P_r of 12 $\mu\text{C}/\text{cm}^2$ and P_{max} of 52 $\mu\text{C}/\text{cm}^2$. A high effective piezoelectric coefficient ($d_{33,f}$) of

about 75 pm/V was obtained via DLBI. However, microstructure analysis by TEM and SEM revealed some voids concentrated at the interface between layers and it was found that those voids could be correlated to the fluctuation of elemental distributions.

Lastly, the nonlinearity of the dielectric response for solution-derived BNT – BKT and BNT – BKT – BMgT thin films was studied by utilizing the Rayleigh law. The ratio of the irreversible (α') to reversible (ϵ'_{init}) Rayleigh contributions for both the BNT – BKT and BNT – BKT – BMgT systems were 3.07E-3 and 3.76E-3, respectively. Compared to other materials, lower extrinsic contribution to the dielectric constant was observed in both films. The measured polarization from the ferroelectric tester and the calculated polarization from the Rayleigh analysis were compared and overall good agreement between them confirmed the validity of Rayleigh analysis for BNT – BKT and BNT – BKT – BMgT thin films.

9.2. Future work

Intensive investigation on lead-free piezoelectric thin films was performed throughout this thesis. To understand structure – property relationships and enhance the electrical properties, more studies need to be carried out. Several avenues to continue the work presented in this thesis are suggested.

1. Improving the *in situ* deposition process is required to achieve better crystallinity and electrical response of bismuth based piezoelectric thin films. Use

of solution-derived bismuth-based perovskite as a buffer or seed layer may enhance nucleation and result in a more well-crystallized thin film. Similarly, after *in situ* deposition, putting down one top layer of thin film by CSD could be helpful. With cation rich solution, off-stoichiometry could be healed and the microstructure might be densified further through an additional annealing step. The chemical solution deposition was well established as shown in chapter 5~7 so combining PVD and CSD methods could be interesting.

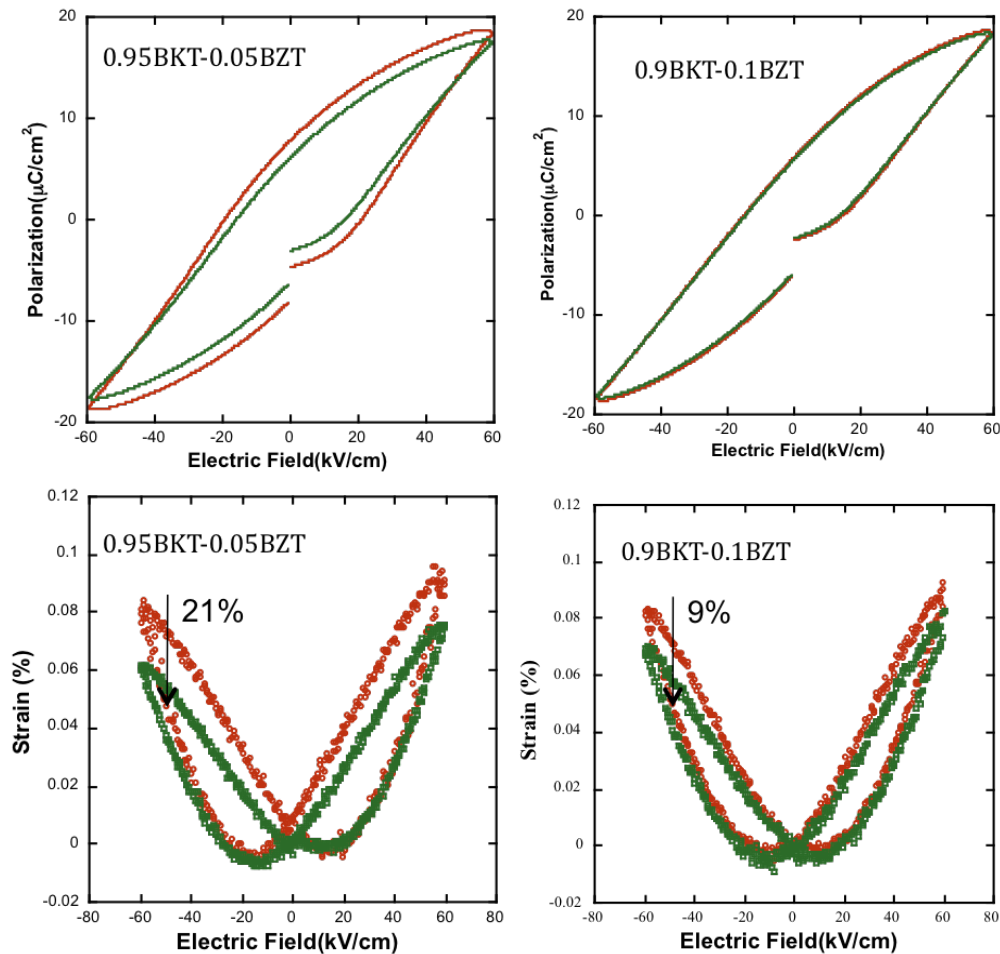
2. The effect of solution molarity on the development of microstructure and the dielectric properties should be explored. Depending on the thickness of a single layer, different grain growth can be displayed. For this research, however, the amount of excess cations might be adjusted accordingly

3. Annealing each layer was critical to obtaining phase pure perovskite of solution-derived thin films. One possible reason is difficulty in nucleation for perovskite phase. Ease of nucleation could be achieved via use of different substrates such as IBAD and single crystal substrate (SrTiO_3). Putting seed layers on Pt/Ti/SiO₂/Si substrate before deposition of bismuth-based thin film may also be helpful. As seen in the microstructure of BNT – BKT – BMgT films, defects like voids or pinhole are easily created by each layer annealing process. Incorporating the substrate or seed layer into the fabrication process might allow a single annealing step to achieve the perovskite structure with less cation loss.

4. Fatigue characterization for these thin films needs to be performed. Higher fatigue endurance could be another advantage versus PZT, so comparing fatigue behaviors under various conditions could be a key experiment from the perspective of real device applications.

Appendix A. Bipolar Fatigue of BKT – BZT ceramics

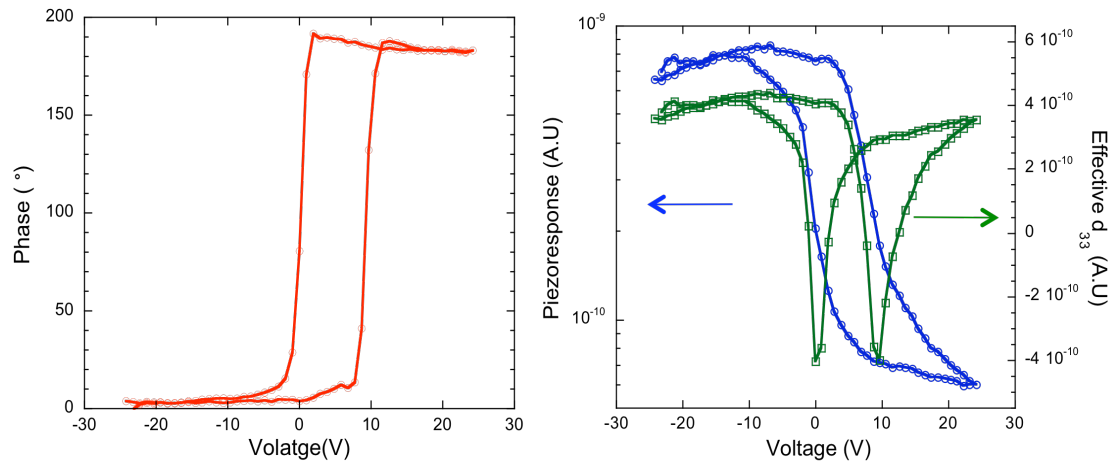
(0.95,0.9)BKT – (0.05,0.1)BZT ceramics were fatigued under a high electric field ~ 60 kV/cm with a triangular waveform at 10 Hz until reaching $1E6$ cycles. Simultaneously field induced strain was also measured. Both are shown in Figure below. For the 0.95BKT-0.05BZT sample, degradation of both the maximum and remanent polarization was observed after 1 million cycles. The maximum polarization decreased 4.9% and the remanent polarization decreased 22%. Correspondingly, the maximum total strain was also reduced after one million cycles. In contrast, the 0.9BKT-0.1BZT showed excellent fatigue characteristics. The maximum polarization $P_{\max}$ only decreased 1% from an initial value of $18.3\mu\text{C}/\text{cm}^2$ to $18.1\mu\text{C}/\text{cm}^2$ after 1 million cycles. The remanent polarization likewise remained relatively unchanged from the initial $5.85\mu\text{C}/\text{cm}^2$ to $5.65\mu\text{C}/\text{cm}^2$ after fatigue. While the polarization remained stable in 0.9BKT-0.1BZT, there was some loss in the electric field induced strain.



Appendix B. Piezo Force Microscopy of BNT – BT & BNT – BKT – BMgT Films

Local hysteresis loops and piezoresponse for 94BNT – 6BT and 72.5BNT – 22.5BKT – 5BMgT thin films were obtained via piezo force microscopy (PFM). Drive voltage up to 24V superimposed with 1 V_{ac} was utilized at 200 mHz. Clear switching of domain was observed and corresponding piezoresponse including effective d_{33} was obtained for both systems.

94BNT – 6BT



72.5BNT – 22.5BKT – 5BMgT

