AN ABSTRACT OF THE THESIS OF

Morgan Rose Emerson for the degree of Master of Science in Materials Science presented on June 12, 2009.

Title: <u>Bi-based Perovskite Solid Solutions for High Energy Density Thin Films</u>

Abstract approved:

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Abstract

Electrical energy storage devices are currently the main limiting factor in many electrical devices and with the increasing demands placed on electrical power over fossil fuels, high energy density materials are essential. Previous research by Huang et al. on bulk $(1-x)Bi(Zn_{1/2}Ti_{1/2})O_3$ -xABO₃ solid solution systems led to the discovery of an excellent dielectric material. The optimal compositions, which corresponded to morphotropic phase boundaries, were found to be $0.1Bi(Zn_{1/2}Ti_{1/2})O_3-0.9BaTiO_3$ and $0.3Bi(Zn_{1/2}Ti_{1/2})O_3$ -0.7NaNbO₃. Measurements, made on bulk ceramics, showed that these materials possess dielectric constants as high as 3000 at 10 KHz for BT-BZT and 1200 for NN-BZT with low loss tangents (tan $\delta < 0.01$) up to high temperatures $(T>400 \ ^{\circ}C)$. Most notably, these high dielectric constants persist to high fields (E<100 kV/cm) and the material exhibits a linear dielectric response at room temperature. Since most current and future applications of a high-K dielectric will require thin film geometry, we seek to duplicate these bulk properties in thin films. The purpose of this research was to investigate the dielectric properties of these two very promising compositions in thin film form in order to find a high-K material with low loss, minimal temperature dependence and a linear dielectric response.

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Bi-based Perovskite Solid Solutions for High Energy Density Thin Films

by Morgan Rose Emerson

A Thesis

submitted to

Oregon State University

in partial fulfillment of the requirements for the degree of

Master of Science

Presented June 12, 2009 Commencement June 2010 Master of Science Thesis of Morgan Rose Emerson presented on June 12, 2009.

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

Morgan Rose Emerson, Author

ACKNOWLEDGEMENTS

To Dr. Brady Gibbons: I have thoroughly enjoyed working with you. You quickly gained my trust and respect and made it clear that it was mutual. You let me be independent in the lab and pushed me to make my own conclusions but were always there the guide me and share your insights. I am honored to have had you as an advisor.

To Dr. David Cann: You have built a department that is capable of accomplishing great things but still keeps its sense of humor. I can't thank you enough for the opportunity to learn from you and be a part of this community.

To the materials science department: Coming to this department was one of the best decisions I have every made. The multidisciplinary environment was extremely conductive to expanding my knowledge base. Everyone in this department has always been more than friendly, welcoming and helpful and I will miss the family I have made. Chris Shelton: Although you are always modest, our many conversations have been a great help to me and it is clear that you have a solid knowledge base in thin films. I wish you all the luck and success in the world. Eric Patterson: You were always willing to help me in the lab even when you yourself were incredibly busy. Your guidance was always appreciated and at times, key to my success. Josh Hogg: I couldn't have asked for a better office-mate. Thank you for always listening and making me laugh.

To my parents: You have always made it clear that I can be the best in whatever field I choose and that the possibilities are endless. Mom: I am always thankful for your company and support. It is only when I share my successes with you that they feel real. I look forward to sharing many more.

To my husband: I am most grateful to you. Your support has never had any strings attached and I can always count on you to stand by me no matter what direction I decide to take. You are unfailingly patient and loving and I can't think of anyone else I would want to share my life with.

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I would like to dedicate this thesis to my husband Brice

Bi-based perovskite solid solutions for high energy density thin films

Chapter 1: Motivation and Objective

1.1 Motivation

One of the most important issues facing the United States and the world is reliance on fossil fuels for our growing energy needs. It is perhaps the single most important challenge to a sustainable future. Enormous amounts of scientific research have focused on developing alternative sources of energy to address this growing problem. Many of the sources being researched suffer from a 'time dependence.' That is, peak production of energy from these sources does not always coincide with peak demand. Therefore, in concert with alternative energy research, novel materials and mechanisms for electrical energy storage (EES) must be explored. The most recent Basic Energy Sciences and Advisory Committee (BESAC) report recognizes that "EES devices with substantially higher energy and power densities and faster recharge times are needed" [2]. This has spurred a large growth in research of high energy density materials and includes solutions such as lithium ion batteries and high permittivity capacitors. While each solution has its advantages, the overarching problem is the need for a dependable, affordable way to store and deliver large amounts of energy efficiently. New developments in thin film processing and materials chemistry in ceramics can allow for volumetrically efficient, high energy density devices that are expected to out-perform competing technologies such as batteries and electrochemical capacitors.

To meet these expectations, capacitors (which have high power densities), need to be modified to also achieve high energy densities of fuel cells and batteries. This is illustrated in figure 1.1 were the relative power and energy densities of various energy storage technologies are displayed.



Fig. 1.1 Comparison of energy density and power density of different energy storage technologies

Capacitors offer the advantage of short discharge times and longer lifetimes when compared to batteries, which is exhibited in table 1.1 along with typical values for relative power and energy densities.

Device	Energy Density	Power Density	Life Cycle	Discharge Time
	(Wh/m ³)	(W/m ³)	(cycles)	(Second)
Batteries	.0525	0.15	$1-10^{3}$	>1000
Capacitors	$5 \ge 10^{-5} - 5 \ge 10^{-3}$	$10^3 - 10^6$	$10^{5} - 10^{8}$	<1

Table 1.1 Comparison of energy and power densities, life cycles and discharge times of batteries and capacitors [3].

To outperform batteries while maintaining a high power density, high permittivity ceramic thin films are utilized to fabricate high energy density capacitors.

The benchmarks for high energy density capacitor materials are [4]:

- 1. High dielectric constant (>1000).
- 2. Minimal temperature dependence up to 400 °C.
- 3. Linear dielectric response up to fields of 100 kV/cm.
- 4. Low electrical losses (<1%)

A strategy to meet these benchmarks is outlined below.

1.2 Objective

One of the most effective approaches used to date starts with a very high permittivity (>1000) material such as $BaTiO_3$ and stabilizes the electric field and temperature dependences of the permittivity via substitution of another element for Ba

or Ti. While this lowers the dielectric constant, a more stable temperature/field response is achieved. Subsequently, thin film embodiments can be used to enhance the dielectric response and to provide a volumetrically efficient, compact and versatile design for device applications. However a material solution that reaches all of the required benchmarks has yet to be found.

Previous research on the $(1-x)Bi(Zn_{1/2}Ti_{1/2})O_3$ -xABO₃ system for lead free bulk piezoelectric applications resulted in the discovery of a new composition which exhibits promising behavior for use in high energy density capacitors. Based on ternary phase compositions, solid-solubility and the morphotropic phase boundary (MPB), optimal compositions were found to be $0.1Bi(Zn_{1/2}Ti_{1/2})O_3$ -0.9BaTiO₃ and $0.3Bi(Zn_{1/2}Ti_{1/2})O_3$ -0.7NaNbO₃. Since the majority of future applications of high-K dielectrics will require thin film geometries we seek to mimic and improve upon the early success seen in bulk materials using thin film geometries. The objective of this thesis is to investigate the dielectric properties of these compositions in thin film form and achieve a thin film with high volumetric efficiency for energy storage applications, low dielectric losses and a linear dielectric response.

Chapter 2: Introduction

2.1 Perovskites

The perovskite structure is defined as having the $A^{XII}B^{VI}X_3$ (roman numerals indicate coordination) structure with a small B cation at the center of an octahedron of X anions and the large A cations on the unit cell corners [1, 5]. The most common application of this structure is in its ferroelectric oxide form, ABO₃ as depicted in figure 2.1. This compound can be divided into $A^{1+}B^{5+}O_3$, $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$. $A^{2+}B^{4+}O_3$ is the most prolific compound since it encompasses the tianate-based materials that are used as high-permittivity ferroelectrics.



Fig. 2.1 The perovskite ABO₃ structure [6]

2.1.1 Stability

The stability of a perovskite can be defined by its lattice energy, which is a combination of static and vibrational energy. At room temperature and at low

pressures, vibrational energy is negligible and static energy is defined as the electrostatic and repulsion energy [7]. By focusing on the electrostatic energy we can effectively focus on what factors cause a perovskite to be stable or unstable.

$$E_{electrostatic} = NMZ^+Z^-e^2/r_{AB}$$
(2.1)

From equation 2.1 it is clear that the electrostatic energy depends on the number of particles (N), the Madelung constant (M), the valence of the cations and anions (Z^+ and Z^-), the charge of an electron (e) and finally the spacing between the A and B atoms (r_{AB}). The spacing between the atoms and the valence are thus crucial to the stability of the compound.

Based on work done on binary compounds, Goldschmidt [8] defined an ideal radius of the cation and the anion for the perovskite structure as shown in equation 2.2.

$$r_A + r_O = \sqrt{2}(r_B + r_O)$$
(2.2)

This work showed that the stability of the perovskite structure is determined by how the A atoms fit in octahedral interstice of the anions. The deviation from this ideal structure and thus the stability of the perovskite can be measured by a tolerance factor (t).

$$t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}$$
(2.3)

 r_A = Goldschmidt radius of cation A

 r_B = Goldschmidt radius of cation B

r_o= Goldschmidt radius of the oxygen anion

The ideal cubic perovskite structure has t = 1. For .88<t<1, the structure distorts to a orthorhombic or rhombohedral derivative and for 1<t<1.09 the structure distorts to a hexagonal or tetragonal derivative of the perovskite structure. Although the tolerance factor is a useful way to gauge the stability of a perovskite, Muller and Roy [1] developed Goldschmidt's work even further to describe perovskites consisting of A and B cations with different valences. Their work resulted in "structure field maps" (figure 2.2) that show which perovskite derivative structures are found depending on the cations involved.

These two methods are usually combined with information on the electronegativity. A larger difference in electronegativity results in a more polar bond and a more stable perovskite structure [7].



Fig. 2.2 Structure field map of $A^{3+}B^{3+}O_3$ and $A^{2+}B^{4+}O_3$ perovskites [1].

2.1.2 Ferroelectricity

When a dielectric material is placed in an electric field, the cations and anions in the structure shift position and the dipole moment is altered. In a linear dielectric, when the field is taken away the ions revert to their original positions and the center of positive and negative charge become coincident (zero dipole moment). A ferroelectric material is one in which there is an intrinsic dipole moment exists within the unit cell (with no applied field) and that dipole moment can be reoriented. In the case of BaTiO₃ at room temperature, for example, the Ti⁴⁺ ion shifts in one of the <001>directions while the O2- anions shift oppositely (very slightly) [9]. This distorts the structure from cubic to tetragonal, and results in a net dipole moment (polarization) within the unit cell (figure 2.3). Now, when a sufficiently high enough electric field is applied and removed, the dipole moment will align with the applied field and a remnant polarization will remain. If the field is then applied in the opposite direction, this remnant polarization can be reversed in direction (the shifting of the Ti^{4+} and O^{2-} are switched). Therefore, the polarization of the material can be switched from +P to -P by an applied field. This unusual behavior was first observed in Rochelle salt in the early 1920's [10]. As is shown in figure 2.3, BaTiO₃ goes through a progression of ferroelectric phases as a function of temperature. In each of these phases the dipole moment is directed along a different family of crystallographic directions.



Fig. 2.3 Phases of BaTiO₃ [9].

For a material to exhibit ferroelectricity, it must have a noncentrosymmetric structure and the centers of negative and positive charge distributions cannot be aligned as described above. Ferroelectricity occurs in ten of the twenty-one noncentrosymmetric point groups.

To characterize a ferroelectric material the polarization is measured as a function of the applied electric field. This is called the P-E hysteresis loop and the remnant polarization, P_r as well as the spontaneous polarization, P_s , is used to characterize the material. The coercive field, E_c can also be obtained from the graph

and is defined as the field required to re-orient the polarization vector [9]. A typical P-E loop is shown in figure 2.4 along with P_s , P_r and E_c .



Fig. 2.4 A typical hysteresis loop for a ferroelectric showing the spontaneous, remnant polarization and coercive field [11].

2.1.3 Curie temperature

A ferroelectric material will not maintain its intrinsic dipole moment at all temperatures. The temperature above which a ferroelectric loses its polarization is called the Curie temperature (T_C). In the case of BaTiO₃, the paraelectric (non-ferroelectric) cubic phase changes to a tetragonal phase upon cooling, then to a orthorhombic phase, and finally to a rhombohedral phase (see fig. 2.3) [9]. BaTiO₃ has a relatively low T_C of 120 °C which limits its use in high-power transducers but makes it an attractive dielectric for capacitive components [12]. At each phase transition, the dielectric properties go through a maximum. This is due to the relatively 'soft' nature

of the Ti⁴⁺ displacement at the phase transition. This also results in the strong temperature dependence of the dielectric response (not always desirable). For BaTiO₃ the Curie temperature can be adjusted by altering the cation composition. The resulting compound has a higher or lower T_C depending on the substituent as seen in figure 2.5.



Fig. 2.5 Transition temperature vs. concentration of isovalent substituents in BaTiO₃[9]. For example, Pb^{2+} raises T_C by about 150 °C while Zr^{4+} lowers it by the same amount [9]. This is thought to be due to regions in the dielectric with differing Curie points that effect the overall temperature dependence. By altering the Curie temperature, the operating limitations can be controlled. This is important for high permittivity

dielectrics since it has been shown that the dielectric constant follows the Curie-Weiss law [9].

$$\varepsilon_r = \frac{A}{T - T_C} \tag{2.4}$$

Where A is a material dependent constant.

It is also advantageous to broaden the temperature at which the dielectric constant peaks so that the material can be utilized in a wider range of temperatures. In $BaTiO_3$ this is commonly done by adding $CaZrO_3$ [13].

2.1.4 Morphotropic Phase Boundary

A phase transition that occurs based on composition instead of temperature is characterized by a morphotropic phase boundary (MPB). This occurs when one phase becomes relatively unstable compared to another at a critical composition. As is the case for BaTiO₃ going through a phase transition as a function of temperature, the dielectric, piezoelectric and ferroelectric properties exhibit a maximum at or near the MPB. This was explained by Ishibashi and Iwata in 1998 using the Landau-Devonshire potential and relative fourth order terms in the free energy function of tetragonal and rhombohedral phases for Pb(Zr,Ti)O₃ (PZT) [14]. They showed that the dielectric susceptibilities diverged at the MPB because one phase is more stable than the other due to the free energy. In the case of PZT, the MPB has been extensively studied [15-18]. PZT, depending on composition, can have tetragonal or rhombohedral symmetry [9]. When the Zr/Ti ratio is less than 52/48, PZT is tetragonal and when it is larger than 52/48, PZT is rhombohedral [19]. It is where this transition takes place that PZT exhibits a very high dielectric constant and strong piezoelectric effects due to the 14 possible polarization directions available (6 from the tetragonal phase and 8 from the rhombohedral phase) [9].

By combining knowledge of the tolerance factor, the Curie temperature and the MPB, a stable perovskite system can be designed. With these three parameters in mind, a specific system can be modified to achieve a stable perovskite with the desired temperature dependence and dielectric/ferroelectric properties. For example, the present study relies on work done on various perovskite compositions of Bi(B'B")O₃ - ABO₃. This system was investigated to find a composition with a tolerance factor close to 1 and the relative amounts of each were varied to locate the presence of a MPB. With that accomplished, the composition could be varied slightly or dopants could be selectively introduced to achieve a desirable T_c .

2.1.5 Relaxor Ferroelectrics

Stabilizing $BaTiO_3$ for use in high energy density dielectrics includes "thinning out" of the P-E loop such that a linear response is approached. A linear dielectric response in a nominally ferroelectric material can be attributed to relaxor behavior and

is desirable for energy storage materials. Relaxor ferroelectrics are a subset of ferroelectric materials that exhibit interesting behavior around the Curie point. As shown in figure 2.6, relaxors maintain their polarization above their transition temperature and usually exhibit a linear P-E response. Relaxor dielectrics have high dielectric constants and a broad permittivity vs. temperature dependence. Because of these characteristics, relaxors are widely used in high energy density dielectrics.

In normal ferroelectrics above the Curie temperature, the dielectric constant follows the Curie-Weiss law (eq. 2.4). In a relaxor ferroelectric the permittivity shows a quadratic dependence.

$$\frac{\varepsilon_{\max}}{\varepsilon(f,T)} = 1 + \frac{(T - T_m(f))^{\gamma}}{2\delta_{\gamma}^2} (1 \le \gamma \le 2)$$
(2.7)

Where ε_{max} is the permittivity at the Curie temperature, γ is the degree of dielectric relaxation where values greater than 1 indicate more relaxor behavior, and δ is a measure of the diffuseness of the transition peak [20].



Fig. 2.6 Comparison between a normal ferroelectric and a relaxor [21].

At high temperatures, the paraelectric (PE) phase exists (i.e. a linear dielectric) and when cooled, a relaxor transforms into an ergodic relaxor (ER). The temperature at which this occurs is lower than the Curie temperature and is called the Burns temperature (T_B). The phase transformation is not due to any change in the crystal structure but is instead thought to be due to polar nanoregions (PNRs) that are too small to react to an electric field like a normal ferroelectric [20]. There are two models to describe PNRs and are depicted in figure 2.7. In the first model they are thought to be due to local phase transitions that result in "polar islands" and the second model asserts that transitions occur throughout the crystal and results in low-symmetry nanodomains [20].



Fig. 2.7 Representation of two different models of polar nano-regions (PNRs) [20]. If the temperature is low enough, an intermediate non-ergodic state exists and the material is in the true relaxor state but when an electric field is applied here, the material becomes ferroelectric. This behavior can be exploited since it results in a broader temperature range at which the material is ferroelectric [11, 20, 22].

2.2 Energy Storage

The ability to store electrical energy is critical to the implementation of most electrical technologies and is usually done with batteries, inductors and capacitors. Each device is characterized by the ability to store and release energy, lifetime and implementation in larger electrically driven systems.

2.2.1 Batteries

Batteries are an electrochemical energy storage method and have been used since the 1800's. Batteries are based on converting chemical energy to electrical energy and typically store from 3.5 to 30 J/cm³ but usually have a limited lifetime, slow discharge times and a single discharge cycle [23]. The most basic design consists of thin sheets of various materials pressed together, rolled and encased in metal. The sheets consist of a positive and negative electrode and a separator that are all submerged in a solvent that acts as the electrolyte. While the design is fairly simple, the materials combinations are numerous.

One of the most promising advances within this area is lithium ion batteries. Lithium is a highly reactive element, which results in large energy storage within the structure with a very high energy density of 900-1900 J/cm³. They are also generally lightweight compared to other batteries. The positive electrode is made of $LiCoO_2$ and the negative electrode is carbon. The charging and discharging mechanism

involves moving lithium ions back and forth between the $LiCoO_2$ and the carbon through the electrolyte. Although lithium ion battery banks currently serve as the most popular power source in electric cars, they still have all the issues inherent to batteries. The average lifetime of these batteries is 3-5 years and while they have a much better cyclic performance normal batteries, they still do not meet the lifetime and discharge times of capacitors.

2.2.2 Capacitors

Capacitors address many of the problems found in batteries as they can be quickly discharged, have much longer lifetimes and recently have shown promising high energy densities and volumetric efficiencies [4]. The capacitor was invented in 1745 [24] by connecting a generator to a glass jar of water. Since then, the materials involved have changed but the basic design has stayed the same. A capacitor relies on two conducting parallel plates that act electrodes with a dielectric layer separating the two. The dielectric creates a charge separation and when the plates are connected a quick discharge occurs. Although the parallel plates are usually simple in terms of materials such as silver or gold, the insulating dielectric can be anything from air to a myriad of compounds. The dielectric in a capacitor is characterized in terms of its dielectric constant, K, which is a measure of the ability of the dielectric to store energy per unit volume compared to air. There are four main types of capacitors based on the materials involved and the fabrication method; electrolytic, film (paper/mica), ceramic, glass-ceramic and thin film. But to better understand these capacitors, two defining characteristics must first be defined: dielectric loss and strength.

2.2.3 Dielectric loss (dissipation factor)

The dielectric constant, ε_r can be defined in terms of a real part (ε_r ') and an imaginary part (ε_r ") [25].

$$\varepsilon_r = \varepsilon_r' - j\varepsilon_r'' \tag{2.9}$$

The real part represents the relative permittivity of the dielectric material and how well it can store energy. When an electric field is applied to a dielectric material, dielectric displacement occurs via different mechanisms including space charge, dipolar, ionic and electronic (atomic). Each mechanism contributes to the polarization up to a given frequency. Above that frequency, its contribution can no longer contribute and lowers the dielectric constant [13]. The general frequency range for each mechanism is shown below.


Fig. 2.8 The real and imaginary parts of the relative permittivity vs. frequency (Hz) [13]. The energy that is lost within the dielectric material is represented by the imaginary part and is defined using tanð. Starting from the basic equation for a capacitor where Q is the total charge in Coulombs and C is the capacitance in Farads we obtain the following:

$$\varepsilon_{r} = \frac{D}{\varepsilon_{o}E} = \frac{Q/A}{\varepsilon_{o}V/d}$$

therefore,
$$Q = \varepsilon_{o}\varepsilon_{r}\frac{A}{d}V = CV$$
(2.10)

Where A is the area, D is the dielectric displacement, V is the voltage, E is the electric field and d is the distance between parallel plates. Up to now, the electric field has

been assumed to be constant, but more commonly, V is sinusoidal so we must rewrite the above equations in terms of a time dependence, t where ω is the frequency of the applied field. The current can also be described as a time varying parameter that leads the voltage by 90°.

$$Q = CV_o e^{i\omega t}$$

$$I = V_o C\omega \cos(\omega t)$$
(2.11)

The cycles of charging and discharging can be described in terms of a current-voltage 'phasor' diagram (figure 2.9). For a perfect capacitor, the current will always lead the voltage by 90° . If power is lost during the cycle, this lead-lag angle starts to stray from 90° .



Fig. 2.9 Phasor diagrams for (a) perfect capacitor and (b) real capacitor where U is the voltage [13].

How much the angle strays from a perfect capacitor is expressed as tanô, the dissipation factor and defines how much power is dissipated as heat. The dissipated power density for a dielectric is defined as:

$$\frac{\overline{P}}{V} = \frac{1}{2} E_o^2 \omega \varepsilon_o \varepsilon_r \tan \delta$$
(2.12)

Where \overline{P} is the time average power dissipated. Clearly, it is desirable for all applications to minimize this dielectric loss.

2.2.4 Dielectric Strength (breakdown)

An important aspect in considering the dielectric properties of a high-K ceramic is its breakdown characteristics. This is sometimes referred to as the "strength" of a dielectric. There are three main breakdown mechanisms; thermal, electrical and discharge [9, 11, 13].

Thermal breakdown occurs when high frequency potentials are applied for a certain period of time. In this case, energy in the dielectric can be lost to heat, which results in an increase in the dissipation factor that in turn, generates more heat and causes a catastrophic breakdown event. Electrical breakdown occurs when a high enough electric field ($\sim 10^6$ - 10^7 V/cm) is applied. When subjected to an electric field, some electrons will gain enough energy to ionize other constituent ions, which leads to an avalanche effect due to the increasing number of electrons in the system. This is a result of the microstructure and grain size and is usually referred to as the "intrinsic" strength. It has been shown that the dielectric strength of a material (DS) is directly related to the thickness of the sample (d), where V_B is the breakdown voltage [13].

$$DS = \frac{V_B}{d}$$
(2.8)

Discharge breakdown is similar to electrical breakdown but its cause is more specific. In this type of breakdown, the electric field is greater in a flaw than in the rest of the dielectric. This will cause the flaw to discharge, which leads to charge leakage and breakdown.

Independent of the breakdown mechanism, the dielectric strength of a material is influenced by its composition, microstructure and testing conditions such as electrode configuration and sample thickness. By using thin films, the dielectric strength of a material can be increased dramatically due to more direct electrode contact with the dielectric and lower defect density.

Now that the characteristics of energy storage have been discussed, the four main types of capacitors will be introduced.

2.2.5 Electrolytic

Electrolytic capacitors use a conducting liquid as one of its electrodes and are usually made with very thin aluminum or tantalum oxides covered in an electrolyte and rolled into a cylinder as shown below.



Fig. 2.10 Drawing of a cylindrical electrolytic capacitor [26].

These are some of the most widely used capacitors and usually have a high capacitances (100-1000 μ F) and dielectric breakdown strength because of their uniformity and thin design. In aluminum electrolytic capacitors, an etched aluminum foil about 50 μ m thick is coated with a thin alumina layer and another layer of foil is impregnated with an electrolyte and acts as the top plate. The low cost of these capacitors makes them popular for simple electronic devices such as pocket calculators and digital clocks. Tantalum capacitors are similar except they can be made by either anodizing tantalum powder with sulphuric acid ('wet' method) or MnO₂ ('dry' method) and put in a tantalum container that acts as the cathode. This type of electrolytic capacitor operates in a greater range of temperatures and is highly reliable but it comes at a much higher cost than the aluminum capacitors. Recently, the CV of these capacitors has been increased by about 38% from 1540 to 2139 μ FV/cm² with a loss of about 30% using BaTiO₃- Al₂O₃ composites [27].

2.2.6 Thick Film capacitors (paper/polymer/oil)

These capacitors utilize a film made of paper, plastic or mica as the dielectric with evaporated electrodes and are either stacked or rolled into a cylinder. The paper and mica capacitors are typically impregnated with oil by saturation to replace any air that exists in the material. Because they are usually about .025 µm thick, they have very high energy densities. These have both low dielectric losses (~10%), high dielectric breakdown strength (5-8 MV/cm) and are typically used in high power electronics and high frequency filtering [11]. Current research also focuses on incorporating BaTiO₃ to increase energy density [11].

2.2.7 Ceramics

Due to the shortage of mica during World War II, capacitor technology switched focus from film-polymer capacitors to ceramic capacitors with high permittivity materials (2,000-30,000 at low electric fields). To achieve permittivities exceeding 1000, ferroelectric ceramics are used. Unfortunately, ferroelectric ceramics have much lower permittivities at high fields due to their hysteresic behavior. This is demonstrated below where the energy storage density, W_D , depends on the electric field, E, squared where ε is the relative permittivity.

$$W_D = \frac{1}{2}\varepsilon E^2 \tag{2.13}$$

The use of linear dielectrics can resolve this issue since their capacitance, C (dielectric constant), is not a function of voltage, V, which results in an energy storage density independent of electric field as seen below where W is the energy stored.

$$W = \frac{1}{2}CV^2$$
(2.14)

The other obstacle to using high permittivity ceramics is the strong temperature dependence. Fortunately, this can also be avoided by modifying the composition with substitution of other ions as described previously (although this typically results in a decreased dielectric constant).

2.2.8 Glass-ceramics composites

Since energy density relates to the electric field squared, it can be more effective to focus on increasing the breakdown strength of a material instead of increasing the dielectric constant. Recent interest in glass-ceramic capacitors is due to the low porosity of glass which can yield very high breakdown voltages [28]. The mechanical and dielectric breakdown strength of dielectrics has been shown to follow Wiebull statistics [29]. Therefore, it has been shown that the dielectric strength of a material is directly correlated with its mechanical strength and that new high strength glass-ceramic composites can meet this requirement. New glass-ceramics based on high-K Ba, Pb, and Na compositions have dielectric breakdown strengths of 400-800 kV/cm, dielectric constants up to 1000 and energy densities up to 10 J/cm³ [30-32].

Although glass-ceramic composites show promising initial results, a single composition and phase has yet to be found that has high dielectric strength and high dielectric constant, high energy density, low losses and low temperature dependence.

2.2.9 Thin Film Capacitors

New high permittivity ceramic dielectrics combined with well established thin film deposition techniques have made thin film capacitors popular for applications in fuel cells, sensors and ferroelectric memory technologies. Thin film embodiments open up new possibilities for high volumetrically efficient devices defined by the capacitance, C, over area, A, and depends on the permittivity of the dielectric and the square of the thickness of the film [13].

$$C = \varepsilon_r \varepsilon_o \frac{A}{t}$$

$$\frac{C}{V} = \frac{\varepsilon_r \varepsilon_o}{t^2}$$
(2.15)

Like paper or polymer capacitors, thin film capacitors have high volumetric efficiency but they also allow a wider range of materials to be used which opens up new possibilities to achieve large energy densities. Films can be made by various methods including evaporation, chemical vapor deposition (CVD), chemical solution methods, pulsed laser deposition and sputtering depending upon the material and the desired properties. Although stresses in the film can affect the structure (and therefore the electrical properties) thin film geometry has been shown to increase the breakdown field and energy density [33-36].

Factors that affect thin film properties are crystallographic texture, grain size and intrinsic stress, to name a few. It has been shown that increasing the film thickness minimizes the stresses between the film and the substrate and that increasing the grain size can minimizes stress within the film due to misorientations of domains across grain boundaries [34, 35] (figure 2.11). This was shown in the bulk with BaTiO₃ by Kinoshita and Yamaji with powders fired at different conditions [37].



Fig. 2.11 Relative permittivity of BaTiO₃ with grain size [37] (taken from Electroceramics, 2nd ed. [13].

2.3 High-K materials

Combining thin films capacitor technology with high-K materials results in high energy density and high breakdown field materials. High dielectric constant materials are used for capacitors in dynamic random-access memories (DRAM), nonvolatile ferroelectric random-access memories (NVFRAM), and piezoelectric MEMS [38]. While lead-based perovskites are used most in these devices, Ba and Bi-based devices are beginning to mature, as well as ceramic-glasses. There have been many advances in ceramic high-permittivity materials but they usually fall short when it comes to dielectric strength and loss [31, 39, 40].

2.3.1 Lead-based Ceramics

For use in high temperature devices such as some transducers, lead based ferroelectrics are used due to their high Curie temperature. (Pb, Zr)TiO₃ (PZT) and (Pb, Zr, La)TiO₃ thin films have been extensively studied for use in ferroelectric random access memories (FeRam) and gate insulators. PZT thin films possess a high dielectric constant at the MPB as discussed previously and low leakage current density. By substituting La²⁺ for Pb²⁺, the electrical resistivity of the material is increased [9]. These films are usually prepared using RF magnetron sputtering, MOCVD or wet chemical methods. Recently, Thomas *et al.* has shown that PLZT (8/65/35) possesses a lower dielectric constant than PZT (65/35) but has lower loss values, remnant polarization and coercive field [39]. Ma *et al.* recently fabricated

PLZT films on a foil substrate that exhibit a dielectric constant of 1300 with a dielectric loss of 5%, leakage current density of 1.4×10^{-9} A/cm² at 25 °C and an energy density of 17 J/cm³ [41] (figure 2.12). Similar results have also been obtained by Sigman *et al.* for PLZT on platinized silicon substrates [42].



Fig. 2.12 (a) Relative permittivity and dielectric loss as a function of applied field for PLZT on foil capacitor. (b) Dielectric response at room temperature of PLZT on foil capacitor with energy density shaded in blue [41].

While lead-based perovskites show promising results, the high permittivity is a direct result of their ferroelectric nature and is derived from domain contributions that saturate at relatively low fields. This results in energy storage densities of 10-20 J/cm³. There is also a general movement towards environmentally friendly materials and a demand for lead-free devices. This is where BaTiO₃- based materials have the advantage and as will be discussed, could possess energy storage densities as high as 100 J/cm³.

2.3.2 BaTiO₃ [5, 9]

The development and research of multilayer ceramic capacitors (MLCCs) increased exponentially with the discovery of the unusually high-K dielectric, barium titanate (K~1,100) in 1941 based on work by Thurnaeur and confirmed by several sources including Wainer and Soloman [43]. As described above, due to a shortage of mica during WWII, there was a high demand for a high-K dielectric and BaTiO₃ was found to be the best replacement due to its high dielectric constant and ferroelectric properties.

As mentioned previously, pure $BaTiO_3$ exhibits a high dielectric constant but is dependent upon temperature, electric field, frequency and stress [9]. To reduce the temperature and frequency dependent properties, $BaTiO_3$ is commonly combined with other materials, the most prevalent for high dielectric constant materials being Bi.

2.3.3 BaTiO₃ substitutions

As mentioned above it is common for $BaTiO_3$ to be substituted for a variety of ions [13]. Depending on the Curie point and electronic properties of the resulting compound, the temperature and electric field dependence can be controlled very effectively. When Zr or Sn is substituted for Ti, the transition from tetragonal to orthorhombic occurs at a higher temperature, which allows the piezoelectric properties to be utilized at room temperature [12]. By substituting various components, a ceramic capacitor can be obtained with dielectric constants as high as 3000 with low loss tangents (~1%) and good temperature stability [12].

2.3.4 BaZrTiO₃

When Zr is added, it occupies the B site in the perovskite structure, replacing the Ti [13]. This results in a lower dielectric constant but decreases the electric field dependence and the Curie temperature [44-47]. Independent of the preparation method, research has shown that BZT approaches a linear dielectric with the most promising results at a composition of Ba(Ti_{.85}Zr_{.15})O₃. Work by Zai *et al.* has also confirmed that increasing Zr content decreases the dielectric loss and temperature dependence as depicted in figure 2.13 [45].

Metal organic chemical vapor deposition (MOCVD) results in films with the highest dielectric constant with Tohma *et al.* reporting a maximum relative dielectric constant, ε_r of about 900 at 350K with a composition of Ba(Ti_{.85}Zr_{.15})O₃ [46]. Recently, a dielectric constant of 450 has been shown by Chen *et al.* (figure 2.14) using RF magnetron sputtering [44].



Fig. 2.13 (a) P-E loops of $BaZr_xTi_{1-x}O_3$ thin films with varying amounts of Zr. (b) The dielectric constant and dielectric loss of the same compound with a) x = 0, b) x = 0.05, c) x = .18, d) x = 0.35, as a function of temperature (1 kHz) [45].



Fig. 2.14 Dielectric constant and loss tangent as a function of the electric field for $BaZrTiO_3$ [44, 48].

2.4 Bi based perovskites

Research on bismuth-based perovskites gained popularity due bismuth's similarities to lead. Lead-based perovskites are used in many electronic devices for their ferroelectric and piezoelectric properties, however Pb is toxic and detrimental to the environment. Bi³⁺ has a similar electronic structure as Pb²⁺, has a low toxicity and goes into solid solution easily.

When Bi is substituted for Ba in $BaTiO_3$, a material with a high dielectric constant and minimal temperature dependence is achieved. This is due to a lowering of both the Curie temperature and the maximum permittivity [13]. Figure 2.15 shows that the permittivity changes depending on the amount of Bi and is always fairly high (~3 x 10³).



Fig. 2.15 The effect of adding Bi₄Ti₃O₁₂ and Bi₂O₃ to BaTiO₃ as A) 43cat%Ba-7cat%Bi-49 cat%Ti and B) 46 cat%Ba-5.5 cat%Bi-48 cat%Ti [13].

Adding Bi is thought to cause an inhomogeneous material since the ε_r –T peaks are diffuse which points to many different regions with different curie points. Similar

relaxor behavior has been shown in bismuth substituted $SrTiO_3$. This compound shows very high resistivity and dielectric constant (760 at room temperature) but also exhibits a high dissipation factor [49].

Recently, it has been shown that combining $Bi(ZnTi)O_3$ with $BaTiO_3$ or other compounds such as NaNbO₃ or $BiScO_3$ results in a material with high permittivity and broad temperature dependence [50, 51].

2.4.1 Bi(Zn_{1/2}Ti_{1/2})O₃ –ABO₃ perovskite solid solutions

While $Ba(Zr_xT_{1-x})O_3$ thin films show promising results, recent results in the bulk have shown that the composition $Bi(Zn_{1/2}Ti_{1/2})O_3$ -ABO₃ is one step closer to meeting the benchmarks sought for these applications. Huang *et al.* has shown that bulk $Bi(Zn_{1/2}Ti_{1/2})O_3$ -NaNbO₃ (BZT-NN) and $Bi(Zn_{1/2}Ti_{1/2})O_3$ -BaTiO₃ (BZT-BT) possess a very high dielectric constant, high breakdown strength (E ~ 100 kV/cm) and low temperature dependence up to 200 °C [50]. Based on previous studies on the enhancement of the dielectric breakdown strength in thin films [33, 36] and by extrapolating the bulk data, it is believed that this system is capable of exhibiting an unmatched energy density as high as 100 J/cm³.

2.4.2 Bulk data

An extensive study on the $(1-x)Bi(Zn_{1/2}Ti_{1/2})O_3-xABO_3$ found that loss, temperature dependence and dielectric response improved dramatically with

increasing BZT content [50, 52]. As expected for BZT-BT, pure $BaTiO_3$ exhibits the highest dielectric constant but has a very strong temperature dependence. In comparison, when 0.5BT is added, the temperature dependence is much more desirable and the dielectric constant remains relatively high (~1400).



Fig. 2.16 (a) Dielectric constant as a function of temperature for various amounts of BZT in (1-x)BZT-xBT (b) P-E data for (1-x)BZT-xBT [50, 52].

Further testing shows that the dielectric response flattens out and the loss tangent is lower as more BZT is added. This is indicated in figure 2.16 where all of the benchmarks for a high energy density material including low temperature dependence, low loss, linear dielectric response and a high dielectric constant are met. However, the volumetric efficiency can only be addressed by duplicating these results in thin film form.

2.5 Deposition techniques

The preferred deposition techniques for ceramic thin film fabrication are sputtering, pulsed laser deposition (PLD), MOCVD and sol-gel. These three methods have consistently been the method of choice not just for ceramics and ferroelectrics but more importantly for oxides in general. In the research environment, PLD and sputtering are preferred because they generally provide stoichiometric material transfer over a small area. The reactions in MOCVD are more complicated and harder to predict but can be used to coat large areas for industrial applications.

2.5.1 Sputtering

Sputter deposition has been used for ferroelectric and piezoelectric materials including BaTiO₃, PbTiO₃, BaSrTiO₃, Pb(Zr)TiO₃ (PZT) and Pb(La,Zr)TiO₃ (PLZT) [53]. Sputtering involves removing atoms from a target surface via kinetic energy transfer between the target and ions in a plasma. A basic sputter deposition setup includes a target with an applied negative bias, which acts as the cathode, a substrate located some distance away and a background gas, which provides the ions that interact with the target to create the characteristic plasma. The plasma is created when electrons ionize the background gas atoms. The ions are accelerated to the negatively charged target and knock out the target atoms, which are then deposited on the substrate. This is a self sustaining reaction since the ionization process results in the creation of electrons that subsequently ionize other gas atoms [54].

This is a popular method to create ferroelectric oxide thin films but the process must be modified to work properly with an insulating target. Radio frequency (RF) sputtering at 13.56 MHz allows for this [53]. While heavy gas ions cannot respond to the RF bias, the electrons can and the reaction is sustained. Argon is usually used as the background gas and to ensure stoichiometry, an oxygen mix up to 20% is common.

Advantages to sputtering include the availability of a wide variety of useful target materials, good substrate adhesion and a variety of parameters such as type of background gas to control film stoichiometry [53]. Some disadvantages include controlling film thickness and morphology and matching film and target composition since the stoichiometric transfer of sputtered ions depends on their reactivity (especially true for the complex compositions discussed here). One last modification routinely used is applying a magnetic field to the target so that the plasma is confined; this is referred to as "magnetron" sputtering [54].

2.5.2 Pulsed Laser Deposition

Pulsed laser deposition is a form of evaporation where atoms from a target are flash evaporated with a high-energy laser focused laser pulse. The laser is focused from outside of a vacuum chamber by a lens onto the target that is rotated. In most cases PLD results in stoichiometric films but it can become more complicated. An excimer laser with particular gas mixtures to achieve desired wavelengths such as Ar/F (193 nm), Kr/F (248 nm) is focused to achieve the desired energy density $(2-4 \text{ J/cm}^2)$ [54]. When the laser hits the target, the target atoms are electronically excited and results in flash evaporation. This is usually done with 20-200 mTorr of O₂ or N₂ and results in a deposition rate of 0.2-2 Å/pulse. This method is not generally applicable to industry but is widely used in research environments. PLD has become popular in fabrication of complex ceramic thin films since it provides a method to achieve stoichiometric films.

Chapter 3 Experimental Procedures

3.1 Powder processing and target fabrication

Ceramic targets of composition $0.3Bi(Zn_{1/2} Ti_{1/2})O_3$ -0.7BaTiO₃ and $0.1Bi(Zn_{1/2} Ti_{1/2})O_3$ -0.9NaNbO₃ were fabricated using solid state reaction methods. Batched oxide powders (table 3.1) were mixed and the relative amounts were determined by stoichiometry.

Chemical	CAS#	Description	
BaCO ₃	513-77-9	99.5%, Fisher# B30-500	
Bi ₂ O ₃	1304-76-3	99.9%, Aldrich Chemicals #223891	
Na ₂ CO ₃	497-19-8	Fisher # S78419	
Nb ₂ O ₅	1313-96-8	99.99%, Aldrich # 208515-500g	
TiO ₂	13463-67-7	98.0-100.5%, Fisher # AC27737-0010	
ZnO	1314-13-2	Fisher # S80249	

Table 3.1 Component oxides used in this study

To anticipate a loss of Bi during the thin film deposition process, non-stoichiometric targets were also prepared with 5, 10 and 20 molar % excess Bi. The powders were then vibratory milled for 6 hours (M-18 grinding mill, 37 SWECO Inc., Florence, KY)

in a Nalgene bottle with 85 vol% ethanol and yttria-stabilized zirconia media. The powders were then dried by evaporating the ethanol overnight in a 65 °C oven. Subsequently, the dried powders were put into crucibles, ramped at 3 °C/min and calcined in air at 920 °C for 6 hours. An additional 800 °C/ 6 hour step was used for the NaNbO₃ powders to reduce impurity contamination. The calcination step results in agglomerated powder so it must be pulverized in a mortar followed by a second milling and drying step to reduce particle size to a nm scale.

With the desired composition in powder form, a sputtering target is fabricated. Depending on the predicted density of each composition and the desired target dimensions, a calculated amount of the calcined powders were mixed in a mortar with 3 wt% polyvinyl butral (PVB) binder until dry and poured into a 1.125" stainless steel die. A plunger is inserted on top of the powder and cold-pressed uniaxially at 15,000 psi for 3 minutes. To sinter the target and eliminate the binder, the target is placed in a closed ceramic container, covered with excess calcined powder to prevent the loss of Bi and placed in a furnace. Binder burnout is performed at 400 °C for 12 hours and the target is subsequently sintered at 1120 °C for 4 hours (heated at a rate of 3 °C/min) and oven cooled. This results in target diameters between 0.94"-0.96" and 0.15"-0.20" thick. To obtain a desired thickness of 0.125" and a smooth and level surface, the targets were polished on a mechanical lapping machine using 240 µm, 400 µm and 600 µm grit sandpaper. The final dimensions of each target were measured to ensure

parallel surfaces and correct thickness.

3.2 Thin film preparation

Thin films were primarily made by RF-Magnetron sputtering with a 1" target onto varying conductive substrates. For most of the films tested, platinized-silicon substrates were used (Nova Electronic Materials) while initial system calibration was done on plain silicon. The substrates were bonded to a thermocoax-based inconel heater with silver paint and placed at a distance of 4 cm from the target surface. The chamber was pumped down to 1×10^{-7} Torr and backfilled with the desired gas pressure. Ultra high purity (UHP) argon was mainly used as the sputtering gas, however in some cases the argon was mixed with 10 - 20% UHP oxygen to incorporate more oxygen in the film and assist in achieving stoichiometric material transfer. The target was pre-sputtered for 5 minutes to clean the target prior to each deposition. The majority of depositions were made with an energy density of 2.14 W/cm^2 (power setting of 40 W) while manually rotating the substrate 90° every 15 minutes to insure uniformity. The film was crystallized in situ by keeping the substrate at 600 °C during deposition and cooled in the chamber atmosphere until the temperature reached 70 °C. To explore the effect of temperature on the growing film, films were deposited with a substrate temperature of 575 °C, 600 °C, 650 °C and 700 °C. 600 °C was used as a base temperature for films deposited in oxygen atmospheres. To account for oxygen deficiency, some films were subsequently

annealed in a tube furnace at 500 °C in a flowing oxygen environment.

Films were also deposited using pulsed laser deposition (PLD). These films were deposited in an ambient pressure of 200 mTorr of O₂ in a chamber with a base pressure of 1×10^{-7} Torr and at a substrate temperature of 600 °C. A KrF laser (Lambda Physik Compex 201, λ =248 nm) was used at a measured power output and energy density of 170 mJ/pulse and 4 J/cm², respectively. It was operated at 10 Hz with 5,000 pulses to obtain films 150-200 nm thick. A small piece of quartz served as a shadow mask to maintain access to the bottom electrode and the target was constantly rotated and rastered to maintain a uniform target ablation.

3.3 Film Characterization

3.3.1 Structure and surface morphology

The film thickness was measured using visible wavelength reflectance data with a fitting program (filmetrics). These measurements were confirmed for 2 samples by spectroscopic ellipsometry (JA Woollam M-2000F) and found to be correct within 10%. Attainment of the perovskite structure was verified using grazing incidence Xray diffraction (XRD: Bruker D8 Discover, 40 kV, 40 mA) with a Cu K_{α} source. Surface morphology was characterized using contact mode atomic force microscopy (AFM: Digital Instruments Nanoscope IIIa) and scanning electron microscopy (SEM: FEI Quanta 3D FEG).

3.3.2 Electrical measurements

After structural and optical characterization, a capacitor configuration was achieved by depositing silver electrodes via thermal evaporation at 1.5×10^{-5} Torr at 10 A for 30 seconds using an aluminum shadow mask to create the desired electrode pattern.

To measure the dielectric response a probe station was connected to analytical software (Vision 4.1.1, Radiant Technologies). While one side is contacted with the bottom conducting substrate and the other with one of the top Ag electrode, an electric field is applied and the resulting polarization is measured at a period of 100 Hz. A LCR meter (Model 4284A, Agilent) was used to measure capacitance and loss vs. frequency from 100 Hz - 1Mhz with an oscillating voltage of 50 mV on top of a constant voltage from 1-100 V. The dielectric constant (K) is calculated using the directly measured area of the electrode used (A), film thickness (t), the permittivity of free space (ε_0) and measured capacitance (C) (eqn. 3.1).

$$K = \frac{Ct}{A\varepsilon_o} \tag{3.1}$$

Chapter 4 Results

4.1 Target Material

Matching the target materials to those fabricated by C.-C. Huang [50] was achieved. X-ray diffraction (XRD) results confirm that the targets prepared are identical to the previously tested bulk samples. The diffraction patterns of both $0.1Bi(Zn_{1/2}Ti_{1/2})O_3$ -0.9BaTiO₃ (BZT-BT) and $0.3Bi(Zn_{1/2}Ti_{1/2})O_3$ -0.7NaNbO₃ (BZT-NN) are shown in figure 4.1 for targets with 20% excess Bi.



Fig. 4.1 XRD data for BZT-NN and BZT-BT 20% excess Bi targets used for this study.

BZT-BT and BZT-NN exhibit a BaTiO₃ and NaNbO₃ pattern, respectively, with a second phase of Bi_2O_3 . All peaks have been indexed using the powder diffraction database numbers 01-077-0873 (NaNbO₃) [55], 01-089-2475 (BaTiO₃) [56] and 01-071-0465 (Bi₂O₃) [57].

4.2 Pulsed laser deposition (PLD)

Initial films were deposited via PLD. By varying the number of laser pulses from 3,000 to 10,000 the thickness of the films was varied and electrical tests were carried out. The average deposition rate was 0.4 Å/pulse and tests were carried out on BZT-BT and BZT-NN films 140 nm – 800 nm thick. The substrate was not rotated during deposition, which resulted in non-uniform thicknesses. Although the films were annealed in oxygen, they had dielectric losses up to 20% that increased at high frequencies (1 MHz). The majority of the films were made from targets with 10% excess Bi and resulted in films with a dielectric constant around 1500. When a 20% excess Bi target was used, the loss dropped by about 10% and the dielectric constant stayed high (~1600).

Film	Average Thickness	Average tanb	Average Dielectric constant
	(±10 nm)		
PN-1 (BZT-NN, 10% excess Bi)	177	.25	1530
PN20-1 (BZT-NN, 20% excess Bi)	221	.13	1640
PB-1 (BZT-BT, 10% excess Bi)	789	.08	30
PB20-1 (BZT-BT, 20% excess Bi)	190	.07	13

Table 4.1 Comparison of PLD films made from 10% and 20% excess bismuth targets at1KHz.

BZT-BT gave similar results but comparing 10% excess and 20% excess films were more difficult since one film is much thicker than the other. There is still a decrease in the loss when a 20% excess Bi target is used (PB20-1) and the dielectric constant is comparable to the 10% excess film (PB-1). Overall, the dielectric constant was much less than the BZT-NN films. For more flexibility in deposition conditions

and to explore a different technique, the remainder of the films was deposited via sputtering. The effect of thickness is further investigated using this deposition method as described below.

4.3 Sputtering

Based on the results from PLD, the sputtered films were made exclusively with 20% excess bismuth targets. A study on how pressure, gas and temperature affects the structure and electrical properties was carried out. Films were made at 50 mTorr and 70 mTorr with background gasses of pure Ar, 10% O₂/Ar, 20% O₂/Ar at a temperature of 575 °C, 600 °C, 650 °C and 700 °C. By using different combinations of these parameters, it was hoped to find the optimal process that results in thin films with low loss, linear P-E response and a high dielectric constant.

4.3.1 AFM

From atomic force microscopy (AFM) the surface morphology for different processing conditions was explored. As expected, the grain size increased with increasing substrate temperature. The progression of growth for both compositions and at both pressures is shown in figures 4.2 and 4.3. Drifting of the AFM tip can be observed in some images, for this reason, all grain size measurements were taken for isotropic grains.



Fig. 4.2 AFM images of BZT-NN prepared at 70 mTorr with different substrate temperatures (a) 575 °C (b) 600 °C (c) 650 °C (d) 700 °C and at 50 mTorr: (e) 575 °C (f) 600 °C (g) 650 °C and (h) 700 °C. All images have a scale of 1 μ m.

For BZT-NN, the resulting surfaces from different pressures are very similar. BZT-BT is slightly different with a pressure of 50 mTorr resulting in a more granular, rough surface than at 70 mTorr.

Depositing in an oxygen atmosphere generally resulted in films with smaller grains and increased roughness and growth in the z-direction than those deposited in pure argon. Figures 4.4 and 4.5 AFM images of BZT-BT and BZT-NN films deposited at in 0%, 10% and 16% oxygen at a constant pressure.



Fig. 4.3 AFM images of BZT-BT deposited at different substrate temperatures at 70mTorr: (a) 575 °C (b) 600 °C (c) 650 °C (d) 700 °C and at 50 mTorr: (e) 575 °C (f) 600 °C (g) 650 °C and (h) 700 °C. All images have a scale of 1 μ m.



Fig. 4.4 AFM images of BZT-BT deposited at 600 °C with various amounts of oxygen at 70 mTorr: (a) 0%, (b) 10%, (c) 16% and at 50 mTorr (d) 0%, (e) 10%, (f) 16%. All images have a scale of 1 μ m.



Fig. 4.5 AFM images of BZT-NN deposited at 600 °C with various amounts of oxygen at 70 mTorr: (a) 0%, (b) 10%, (c) 16% and at 50 mTorr (d) 0%, (e) 10%, (f) 16%. All images have a scale of 1 μ m.

The effect of oxygen annealing at 500 °C for 1 hour can also be investigated using AFM. Examples are shown below in figure 4.6 for BZT-BT samples XB6 (70 mTorr, 600 °C) and XB11 (70 mTorr, 575 °C). Before annealing, the surface is relatively flat. After annealing, the grains appear to exhibit some roughening.



Fig. 4.6 Comparison of AFM images before and after annealing in oxygen at 500°C for 1 hour for XB11: (a) before (b) after and XN4: (c) before (d) after (All images have a scale of 1 μ m).

Scanning electron microscopy (SEM) was done on a sampling of films. SEM images include a comparison between a 60 nm and a 180 nm film to characterize features as a function of thickness. An image was also taken of a film deposited in 20% oxygen. The SEM images of these films are shown in figure 4.7. The structural difference between the films is pronounced.



Fig.4.7 SEM images of (a) BZT-BT film 180 nm thick (scale of 2 μ m), (b) BZT-BT film 90 nm thick (scale of 1 μ m) and (c) a film deposited in a 20% O₂/Ar atmosphere (scale of 500 nm).

Fig. 4.8 summarizes the AFM results as they relate to the processing conditions. This includes the root mean square (RMS) value used to quantify roughness. For BZT-BT at 50 mT and 700 °C (figure 4.8), the RMS value is clearly incorrect since it is on the order of the film thickness. This error is most likely due to drifting in the AFM image. The grain size for BZT-BT films deposited at 50 mTorr were not calculated due unclear grain boundaries and more complex surface formations.



Fig. 4.8 Average grain size and surface roughness (RMS) as a function of temperature. Grain size calculated from 1μ m AFM images. RMS values taken from 10μ m AFM images.

4.3.2 X-ray Diffraction

There are several things to consider in terms of the structure of the films. XRD data can give us information on the structure of the as-tested films, the films before being oxygen annealed and the differences between films deposited at different temperatures, pressures and gas compositions.

Figures 4.9 and 4.10 compare XRD results for BZT-NN films deposited at 70 mTorr and 50 mTorr, respectively, at different substrate temperatures. All scans were done at grazing incidence with an incident angle of 4°. The peaks present in most of the scans are of the substrate; Si and Pt, the top electrodes (Ag) and perovskite peaks that match those of the targets. It can be seen that for varying deposition

parameters, the intensity of the peaks change and is thought to have a large effect on the electrical properties of the film. For both materials, the perovskite structure is the most defined for films deposited at 650 °C. Figures 4.11 and 4.12 show the same data for BZT-BT.



Fig. 4.9 XRD of BZT-NN films deposited at 70 mTorr. (*) denotes the substrate.


Fig. 4.10 XRD of BZT-NN films deposited at 50 mTorr. (*) denotes the substrate.



Fig. 4.11 XRD of BZT-BT films deposited at 70 mTorr. (*) denotes the substrate.



Fig. 4.12 XRD of BZT-BT films deposited at 50 mTorr. (*) denotes the substrate.

Figures 4.13 and 4.14 show how the structure of the film changes when deposited in partial oxygen atmospheres.



Fig. 4.13 BZT-BT deposited in 50 mTorr and 70 mTorr with 10% and 16% oxygen at 600 °C. (*) denotes the substrate.



Fig. 4.14 XRD of BZT-NN deposited in 50 mTorr and 70 mTorr with 10% and 16% oxygen at 600 °C. (*) denotes the substrate.



Fig.4.15 XRD of a BZT-BT sample before and after being annealed in oxygen at 500°C for 1 hour. (*) denotes the substrate.

XRD was also used to understand the effect of annealing in oxygen (figure 4.15). Scans were taken of several films before and after annealing. The only difference that can be seen between the two is that a peak at 59° (2 θ) that matches a Bi₂O₃ peak appears before annealing.

4.3.3 Electrical properties

Initial films made by sputtering had extremely high losses that indicated the presence of conducting behavior. After the films were annealed at 500 $^{\circ}$ C for 1 hour in constant oxygen flow, the loss decreased dramatically to an average tan δ value of

0.03 and an average dielectric constant of 62 at a measuring frequency of 1 KHz. Although the dielectric constant is much lower than desired, the loss was at an acceptable value and served as a base from which the rest of the films were made. By increasing the thickness from 174 nm to 300 nm, the dielectric constant was almost doubled from 62 to 116 while the loss stayed at ~ 0.01 . This effect is could be due to pinholes in the film as the dielectric constant should not be dependent on thickness (unless very thin) if all other parameters are kept constant. A summary of the processing conditions along with the average loss, dielectric constant, grain size, breakdown voltage and film thickness is shown in tables 4.2 and 4.3.

Depositing in partial oxygen atmospheres gave mixed results. When these films were annealed in oxygen, they exhibited conducting behavior. When the annealing step was omitted, partial success was achieved. XB20 was the only film of this set for which data could be obtained. The data for this film shows that depositing BZT-BT in 10% oxygen at 70 mTorr results in very low losses with a breakdown voltage and dielectric constant nearly equal to films deposited in pure argon. Unfortunately, all others films deposited in partial oxygen (XN10, 11, 12, 13 and XB7,18, 19, 20) could not be measured due to their conductive nature.

Film	Р	Backgrnd	Substrate	Average	Breakdown	Average	Thickness	Leakage
			temp (°C)	tanð	field	Dielectric	(nm, ±10%)	current
	(mTorr)	Gas		(1 KHz)	(kV/cm)	Constant		(µA)
		(UHP)						
								at 4 V
1010	70			0.42	205	1.57	2.00	1.62
XN3	70	Argon	575	.043	385	157	260	.163
XN1	70	Argon	600	.022	233	115	215	.476
XN4	70	Argon	650	.079	179	206	280	.482
XN5	70	Argon	700	.150	167	237	300	
XN6	50	Argon	575	.048	111	145	450	.020
XN7	50	Argon	600	.035	465	172	430	.068
XN8	50	Argon	650	.048	135	148	370	.500
XN9	50	Argon	700	.120	143	244	350	.484

Table 4.2 Data for BZT-NN samples made with different background gasses, pressures and substrate temperatures.

Film	Р	Backgrnd	Substrate	Average	Breakdown	Average	Thickness	Leakage
			temp (°C)	tanð	field	Dielectric	(nm, ±10%)	current
	(mTorr)	Gas		(1 KHz)	(kV/cm)	Constant		(µA)
		(UHP)						
								At 4 V
VD11	70	A	575	021	541	100	105	00012
ABII	70	Argon	575	.021	541	100	185	.00013
VDC	70		600	020	014	<i>c</i> 1	164	105
XB6	70	Argon	600	.020	914	64	164	.485
VD 10	70		650	000	1250	100	104	00115
XB12	70	Argon	650	.009	1359	108	184	.00115
ND 10	70		700	027	1010	1.67	1.65	00172
XB13	70	Argon	700	.037	1212	167	165	.00172
VD 17	50		<i></i>	022	022	017	100	00002
XB15	50	Argon	575	.033	833	217	180	.00092
VD 10	50		600	020	C 41	174	195	04640
XB10	50	Argon	600	.029	541	174	185	.04640
VD16	50		650	022	000	201	170	00017
XB10	50	Argon	650	.022	882	201	170	.00017
VD17	50	A	700	000	2424	107	165	00014
AB1/	30	Argon	700	.009	2424	127	105	.00014
VD20	70	10% 0 /	600	004	1212	117	165	00021
лВ20	70	10% O ₂ /	000	.004	1212	117	105	.00021
		Ar						

Table 4.3 Data for BZT-BT samples made with different background gasses, pressures and substrate temperatures.

The highest breakdown voltage achieved in BZT-NN films was 20 V while the BZT-BT films had much better performance - up to 40 V. The breakdown field as a function of deposition temperature for each set of films is shown in figure 4.16 and the capacitance and loss as a function of voltage is shown in figure 4.17 for a representative BZT-BT film. The breakdown field is only an approximation since measurements are taken every 5 V and there exists error in the thickness measurements as stated previously.



Fig.4.16 Approximate breakdown field vs. substrate temperature for all four sets of films.



Fig. 4.17 Capacitance and loss as a function of applied voltage for sample XB17 (50 mT, 700 °C).

As a bias is applied to the film, the capacitance decreases from 306 pF to 231 pF and the loss stays constant up to 15 V after which it increases to 0.51 at 35 V. A breakdown voltage of 40 V for sample XB17 translates into a breakdown field of:

$$\frac{V}{thickness} = \frac{.04kV}{1.65 \times 10^{-5}cm} = 2,424\frac{kV}{cm}$$
(4.1)

It should be clarified that the bias was applied in increments of 5 V and all breakdown fields cited are approximate. For each film, the breakdown field cited is a slow breakdown and not a catastrophic failure.

4.3.4 Dielectric response

Most samples exhibited a linear dielectric response. BZT-NN Films deposited at 70 mTorr did not exhibit desirable P-E loops and the film deposited at 700 °C (XN5) could not be measured. Films deposited at 50 mTorr all exhibited more linear behavior than those deposited at 70 mTorr. The same trend is observed in BZT-BT. Within both compositions and pressures, the P-E loop generally becomes less linear as temperature is increased. The P-E behavior for BZT-NN is shown in figures 4.18 and 4.19 while BZT-BT is shown in figures 4.20 and 4.21.



Fig. 4.18 P-E loop for BZT-NN for samples deposited at 50 mTorr at various substrate temperatures. All measurements taken at 100 Hz except for XN9, which was taken at 1000 Hz. (XN6: 575 °C; XN7: 600 °C; XN8: 650 °C; XN9: 700 °C).



Fig. 4.19 P-E loop for BZT-NN deposited at 70 mTorr at various substrate temperatures. All measurements taken at 100 Hz (XN3: 575 °C, XN1: 600 °C; XN4: 650 °C).



Fig. 4.20 P-E loop for BZT-BT deposited at 70 mTorr at various substrate temperatures. All measurements taken at 100 Hz (XB11: 575°C; XB6: 600°C; XB12: 650°C; XB13: 700°C).



Fig. 4.21 P-E loop for BZT-BT deposited at 50 mTorr at various substrate temperatures. All measurements taken at 100 Hz (XB15: 575°C; XB10: 600°C; XB16: 650°C; XB17: 700°C).



Fig. 4.22 P-E loop for BZT-NN at several operating frequencies (sample XN6: 70 mTorr, 600 °C).



Fig. 4.23 P-E loop for BZT-BT at several operating frequencies (sample XB12: 70 mTorr, 650 °C).

The 70 mTorr samples also maintain their linearity with varying frequencies. Shown above is the P-E loop for a BZT-NN film taken at several frequencies (figure 4.20). A similar plot for BZT-BT is in figure 4.23.

Chapter 5 Discussion

5.1 Surface Morphology (AFM/SEM)

While the goal of this study is to identify processing parameters that yield desirable electronic properties for high energy density materials, understanding the microstructure of the film and how it is influenced by processing is paramount to interpreting the electrical data.

5.1.1 Temperature and pressure effects

As expected, the substrate temperature and chamber pressure directly affect surface morphology as seen from the AFM and SEM data. This is largely a result of thermodynamic effects in film growth, specifically heterogeneous nucleation and growth. By considering the equations for nucleation and growth, one can further understand how deposition parameters affect the film morphology. For a nucleus depositing on a surface of a different material, we can roughly define the critical nuclei size necessary for growth (r^{*}) and a critical energy barrier to form these nuclei (ΔG^*) [1].

$$r^{*} = \frac{-2(a_{1}\gamma_{fv} + a_{2}\gamma_{fs} - a_{2}\gamma_{sv})}{3a_{3}\Delta G_{V}}$$
$$\Delta G^{*} = \frac{4(a_{1}\gamma_{fv} + a_{2}\gamma_{fs} - a_{2}\gamma_{sv})^{3}}{27a_{3}^{2}\Delta G_{V}^{2}}$$
(5.1)

Where a_1 , a_2 and a_3 are geometric constants dependent on the shape of the nucleus and the various γ are surface energies between the surface, substrate and vapor. This approximation does not account for the anisotropy of the surface energy in a crystalline structure. ΔG_V is the change in chemical free energy per unit volume (from conversion to solid from vapor) and is defined as:

$$\Delta G_{V} = -\frac{k_{B}T}{\Omega} \ln \left(\frac{\dot{R}}{\dot{R}_{e}}\right)$$
(5.2)

Where k_B is Boltzmann's constant, T is the temperature, Ω is the atomic volume, \dot{R} is the deposition rate and \dot{R}_e is the equilibrium re-evaporation rate. If we take the derivative of r^{*} and ΔG^* with respect to temperature, holding the deposition rate constant, we arrive at four inequalities.

$$\left(\frac{\partial r^*}{\partial T}\right)_{\dot{R}} > 0$$

$$\left(\frac{\partial \Delta G^*}{\partial T}\right)_{\dot{R}} > 0$$
(5.3)

Similarly, the derivative of r^* and ΔG^* with respect to the deposition rate, holding temperature constant:

$$\left(\frac{\partial r^*}{\partial \dot{R}}\right)_T < 0$$

$$\left(\frac{\partial \Delta G^*}{\partial \dot{R}}\right)_T < 0$$
(5.4)

These four inequalities contain basic information about how the film morphology can change with temperature and pressure.

The inequalities above indicate the following: as temperature is increased, the critical radius needed for nucleation increases. At the same time, the energy barrier for nucleation also increases. This translates into fewer but larger nuclei, which results in large grained films [1]. This progression can be seen from the AFM images taken of samples grown at different substrate temperatures (figs. 4.2 and 4.3). The grain sizes are much larger when grown at 700 °C than at 575 °C. The plot in figure 4.8 shows that the grain size increases with substrate temperature for both materials.

There are also differences in films deposited at different pressures. BZT-BT at 50 mTorr has a much larger grain size than the same material deposited at 70 mTorr. This could be due to the higher energies of the arriving species at a lower pressure.

The occurrence of collisions within the plasma decreases with pressure, which results in more energetic particles reaching the substrate. This bombardment energy can act as an enhancement to surface diffusion and change the ultimate morphology of the deposited film. A lower pressure also means that the sputtered atoms are not thermalized as effectively in crossing the plasma, affecting growth behavior. There are many different interactions occurring during the sputtering process that relate to pressure and will all contribute to a varied surface morphology [2].

The second set of inequalities relate to the arrival rate. As arrival rate increases, the critical radius and the energy barrier decrease. This will result in more, smaller nuclei and fine-grained films. It is interesting to see that while both BZT-NN and BZT-BT follow the expected trend for grain size, there are differences in surface roughness. Figure 4.8 shows that roughness reaches a maximum at 650 °C for BZT-NN films while the roughness of BZT-BT films continue to increase past this point for the deposition parameters explored. There are many variables that could explain this behavior. One possible explanation is the density of the targets. The targets made from BZT-NN were less dense than those of BZT-BT (~ 4.7 g/cm³ compared to ~ 6.2 g/cm³). Since they are both assumed to be 100% theoretically dense, the density shouldn't directly effect thin film surface morphology. Instead, it is most likely due to differences in sputter yield between the two compositions. Another possible explanation is a difference in sticking coefficients between the two compositions,

which would change the rate at which the film grows and covers the substrate, as it is well known that the sticking coefficient for a given atom will vary with pressure [1].

While heterogeneous nucleation theory is a simple approximation, it can be applied to any thin film deposition technique. The trends seem to show that it can be generally applied here with some surprising differences between the two materials.

5.1.2 Oxygen incorporation

A parameter not yet addressed is the effect of oxygen partial pressure. This study included films deposited in a 10% and 16% oxygen – balance argon mix as well as films which had a post-deposition anneal in oxygen. When deposited with an oxygen/argon mix, the films tend to have smaller grains. Oxygen in commonly used in reactive sputtering and can cause the formation of precipitates when deposited at high temperatures. It can also result in an enhancement of the film crystallinity [3-5]. From the XRD results in figures 4.13 and 4.14, it can be seen that an atmosphere of 10% oxygen results in different peaks becoming more pronounced. Unlike argon, oxygen will form a negative ion in the plasma, which is accelerated away from the target and towards the substrate, which results in a "re-sputtering" of the film. Based on previous findings, it is possible that 10% oxygen is excessive for this system and that 5% or lower would be optimal [6-8].

After the samples are annealed in oxygen at 500 °C, considerable roughening is observed. This could be due to a combination of increased energetic bombardment and the incorporation of oxygen. The XRD results in figure 4.15 show that the oxygen anneal results in the existence of a sharp BiTiO₃ peak. The main contribution is likely an incorporation of oxygen into the film, which reduces defects. This leads to reduced conductivity and dielectric loss.

5.2 X-ray Diffraction

By comparing XRD data from the films and the targets, it becomes clear that some conditions such result in films with a more defined structure than others. In BZT-NN (figures 4.9 and 4.10) the Bi_2O_3 peak becomes especially pronounced as temperature increases but the (220) peak is all but lost. BZT-BT films exhibit the sharpest peaks at 600 °C. A shift in crystallographic texture can also be seen in some of the films. This is also a result of the thermodynamics and kinetics of thin film growth. Detailed elemental analysis of the films could help elucidate some of the processes occurring in the growth of these materials.

5.3 Electrical properties

5.3.1 Dielectric constant, breakdown voltage and dielectric loss

Interpretation of the electrical data must be done with care since thickness has been shown to have an unexpected effect. As mentioned previously, film thickness can change the electrical response. This could be explained by voids or "pinholes" that exist in the film. Pinholes are common in sputtered films and it has been shown that they can depend on substrate temperature (depending on the material being deposited) [2, 9, 10]. Further research needs to be carried out to characterize this phenomenon with different processing conditions. SEM and AFM data suggest that the different processing conditions result in very different microstructures. More uniform coverage would optimize electronic transport and would explain why doubling the thickness results in a higher yield of successful capacitors. However, this data alone is not sufficient to characterize voids in the film or substrate coverage.

As explained previously, films deposited at higher substrate temperatures exhibit larger grain sizes. Based on models of the breakdown field as mentioned in chapter 2, this would suggest that these films should have higher breakdown fields than those with smaller grains. A plot of substrate temperature vs. breakdown field for all films is shown in figure 4.16. This plot shows that BZT-BT generally follows the expected trend while BZT-NN does not. This result is surprising and suggests another breakdown mechanism such as discharge breakdown due to defects or dislocations in the microstructure that is influencing the breakdown behavior in BZT-NN films. These flaws could be inherent in the development of the NaNbO₃ structure during sputtering or they could be due pressure and temperature variables for this specific composition. Higher substrate temperatures have been shown to effect the development of grain boundaries according to the model by J.A. Thornton [11]. The "transition zone" microstructure described by Thornton and shown in figure 5.1 has a high dislocation density and is common in sputtered films [1, 12]. In general, the zone structures shown below are formed depending on the temperature of the substrate compared to the melting temperature of the material (T_s/T_m), known as the "reduced temperature".



Fig. 5.1 Sketch of the cross section of the four basic structural zones [13]. Although this model is based on metals, it provides clues as to why there are differences in surface morphology between the two compositions.

It should also be noted that the observed differences in breakdown field vs. temperature between the two compositions can be correlated to differences in surface roughness vs. temperature in figure 4.8. As mentioned above, roughness increases with temperature in BZT-BT while BZT-NN reaches a maximum at 650 °C. While this behavior is almost identical to the breakdown behavior in figure 4.16, there is not enough data to make a definite conclusion.

Overall, the breakdown voltage exceeded that of the bulk material and that of PLZT thin films [14]. A graphical comparison is shown below with the potential performance of BZT-BT and BZT-NN thin films represented by the dashed line with an estimated breakdown field of about 1500 kV/cm (figure 5.2). Based on these preliminary results, BZT-BT and BZT-NN exhibit an average breakdown field of 1102 kV/cm and 227 kV/cm, respectively. While BZT-NN falls short of this estimation, BZT-BT is much more desirable and surpasses PLZT thin films. This raises the possibility that with careful thin film engineering, this benchmark can be met while maintaining a linear P-E response and low losses.



Fig. 5.2 Polarization vs. Electric field for PLZT thin films (red, blue and green) [14], BZT-BT bulk material (black) and the desired behavior for BZT-BT (dashed). The asterisk marks where the material would posses an energy density of (100 J/cm²) [15].

The average dielectric loss for BZT-BT and BZT-NN was 0.02 and 0.07, respectively. This is a very promising result as many films had dielectric losses of $\sim 2\%$ and below. Figure 4.17 also shows that as a bias is applied, the loss stays low up to high voltages (i.e., 25 V for XB17).

While films deposited via PLD had higher losses, they also resulted in some films with a much higher dielectric constant. This suggests that PLD could offer an alternative to sputtering in order to minimize stoichiometry concerns. These results also show that it is possible to make BZT-BT and BZT-NN films with a high dielectric constant. It remains to be seen what processing conditions in sputtering give similar results in terms of dielectric constant while maintaining a low dielectric loss.

5.3.2 Polarization vs. electric field

Figures 4.18 - 4.23 present the P-E loops for each sample set. The polarization response is fairly linear for most of the samples tested. BZT-NN exhibited strong linear behavior for samples deposited at both pressures and only XN9 (50 mTorr, 700 °C) had polarizations of more than 25 μ C/cm². This is characteristic of relaxor behavior and could suggest the existence of polarized nano-regions (PNRs) as mentioned previously. This is supported by the existence of an MPB and could mean that there are disordered regions rich in each cation that prevents the material from transitioning fully to the ferroelectric structure. Both compositions maintained their linearity as frequency was varied from 25 - 1000 Hz (figures 4.22 and.4.23). Additionally, the leakage current stayed low for all samples, especially BZT-BT with an average leakage current of 0.06 μ A (table 4.3).

Chapter 6 Conclusions

Both of these materials exhibited low dielectric losses, a linear P-E response and relatively high breakdown fields. The dielectric constant, on the other hand, was lower than desired. There remain promising opportunities to alter these films such that all of the benchmarks for a high energy density material can be met.

6.1 Future Work

This research is meant to be a starting point in optimizing thin film processing for high energy density dielectrics. The materials presented here, 0.1BZT-0.9NN and 0.3BZT-0.7BT, are just two perovskite compounds of the family Bi(B'B'')O₃ + ABO₃. Temperature, pressure and atmosphere were varied to observe structural and electronic changes in the material. This was carried out to understand the sputtering process and how it relates to these Bi compounds. This resulted in useful data on how the materials respond to various sputtering conditions but is far from comprehensive. There remain many more variables to be tested. One such variable is a target of different stoichiometry (5%, 10% and stoichiometric). It is well known that Bi is a reactive element and needs to be replenished during the sputtering process, but it is possible that 20% extra Bi is excessive. A better understanding of the resulting film composition would be greatly helped by energy dispersive X-ray spectroscopy (EDS) to obtain an elemental analysis of the film. This would also help in characterizing oxygen deficiency. Another variable is target composition. The composition of these materials was chosen based on previous research on bulk materials. While 0.3BZT-0.7BT and 0.1BZT-0.9BT is within the MPB, there is an "envelope" of compositions around the MPB that could be explored. Thin films also allow for a wider range of compositions since surface contributions change the required equilibrium. There also exist several similar systems under consideration for high energy density dielectrics. These systems are shown in figure 6.1 along with their tolerance factors and electroneutrality numbers.

IJ	nstable perc	ovskite	Stable perovskite			
	Bi(B'B'')O ₃		+A	BO ₃		
	B´=2+, B´´=4+					
	Bi(Zn _{1/2} Ti _{1/2})O ₃	t=0.97		BaTiO ₃	t=1.06	EN=2.23
	Bi(Ni _{1/2} Ti _{1/2})O ₃	t=0.98		KNbO ₃	t=1.05	EN=2.23
	Bi(Mg _{1/2} Ti _{1/2})O ₃	t=0.98		KTaO3	t=1.05	EN=2.28
	B´=3+	,,		$Bi_{1/2}K_{1/2}TiO_3$	t=1.04	EN=1.96
	BiGaO3	t=1.00		AgNbO ₃	t=1.02	EN=1.68
	BiScO ₃	t=0.94		$K_{1/2}Na_{1/2}NbO_3$	t=1.01	EN=1.96
	BiYO ₃	t=0.88		$Bi_{1/2}Na_{1/2}TiO_3$	t=0.98	EN=1.93
	BiYbO ₃	t=0.84		NaNbO3	t=0.97	EN=2.18
	L	1		La _{1/2} Zn _{1/2} TiO ₃	t=0.94	EN=2.09

Fig. 6.1 Compositions of Bi(B'B")O₃ + ABO₃ under consideration for high energy density dielectrics.

It also appears that lower pressures not only yield a higher deposition rate but better electronic properties as well. Exploring pressure effects further would be a useful exercise. A surprising result came from the films deposited in 10% and 16% oxygen. Adding oxygen to the chamber when sputtering oxides is a common practice and is expected to increase film quality. Our results indicate the opposite for both of these materials. When oxygen was incorporated into the chamber, the films consistently had extremely high loss characteristic of a conductor and a less defined perovskite structure. The success of XB20 suggests that it is possible to obtain data for these films without annealing in oxygen but the results are inconclusive. Further study is needed on films deposited in a partial oxygen atmosphere to obtain clearer results.

An important benchmark for high energy density dielectrics that has not been addressed is temperature dependence. In the bulk, the dielectric and loss tangent for BZT-NN and BZT-BT have been shown to have minimal temperature dependence. This characteristic is important for a wide range of applications and needs to be characterized in the thin films of the same composition.

Current work is being conducted in the bulk to explore the reasons behind the observed electrical behavior, focusing on BZT-NN. While thin films can be unpredictable, understanding these systems in the bulk will yield useful information on how to optimize them in thin film form.

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