

ACOUSTIC AND ELECTRICAL PROPERTIES OF
BISMUTH SODIUM TITANATE –BASED MATERIALS

By

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ABSTRACT OF THE DISSERTATION

Acoustic and Electrical Properties of Bismuth Sodium Titanate-based Materials

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In this research, an attempt has been made to develop and characterize lead-free ceramics, transducers, and thin films based on $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) compositions.

BNT-based ceramics with different compositions were prepared by mixed oxide route. The electromechanical and acoustic properties of the ceramics were studied. 0.88BNT-0.08BKT-0.04BT (BNKLT88) and 0.076BNT-0.20BKT-0.04BLT (BNKLT76) ceramics showed relatively high values of piezoelectric coefficient ($d_{33} \sim 170\text{-}175 \text{ pC.N}^{-1}$), dielectric constant (850-950), and planar coupling coefficient ($k_p \sim 0.32\text{-}0.37$). On the other hand, BNKLT88 ceramics with a rhombohedral structure exhibited high mechanical quality factor ($Q_m \sim 420$). Acceptor dopants such as Mn and Fe were doped in BNKLT88 ceramics. By optimizing the powder processing and sintering temperature, Q_m values as high as 900-975 were obtained in 1.5 mol.% Fe or Mn-doped ceramics sintered at 1100 °C. This composition showed the maximum vibration velocity (0.6 m.s^{-1}), minimum heat generation, minimum input power, and the best efficiency among the studied compositions.

High frequency ultrasonic transducers for medical imaging were designed and fabricated based on the BNKLT88 ceramics. The focused transducer with a center frequency of 23 MHz, exhibited a -6dB bandwidth and insertion loss of 55% and -32.1 dB, respectively. B-mode images of a wire phantom (30 μm in diameter) were produced by the transducer.

BNT-based thin films with four different compositions in BNT-BKT-BT as well as BNT-BKT-BLT systems were deposited on (001)-oriented SrRuO₃/SrTiO₃ substrates by pulsed laser deposition technique. The effects of deposition parameters on the microstructure, chemical composition, and electrical properties of thin films were evaluated. Under optimized condition, BNKLT88 thin films exhibited a remnant polarization of about 30 $\mu\text{C}\cdot\text{cm}^{-2}$ and coercive field of 85 $\text{kV}\cdot\text{cm}^{-1}$. The dielectric constant and loss tangent at 1 kHz were measured to be 645 and 0.052, respectively. The leakage current of epitaxial BNKLT88 thin films measured at different temperatures was matched with the Lampert's triangle bounded by three straight lines of different slopes. It was shown Mn-doping suppressed the leakage current by more than two orders of magnitude. The remnant polarization and dielectric constant (at 10 kHz) of Mn-doped BNKLT76 film deposited at 400 mtorr were measured to be 23 $\mu\text{C}\cdot\text{cm}^{-2}$ and 660, respectively.

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1 Research Objectives and Scope of the Dissertation

1.1 Statement of the Problem

Lead-based materials are the most widely used piezoelectrics for variety of applications such as sensors, actuators, and transducers. Ceramics, thin films and single crystals based on lead-containing compositions such as $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) and $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{-PbTiO}_3$ (PMN-PT) exhibit outstanding electromechanical properties. The longitudinal piezoelectric charge coefficient (d_{33}) as high as 700 pC.N^{-1} for ceramics and 2500 pC.N^{-1} for lead-based single crystals have been reported. Despite their excellent properties, lead-based piezoelectrics contain a considerable amount of lead which is known as a toxic element. Due to the low vapor pressure of PbO , high temperature processing of these materials is accompanied by lead evaporation. Releasing the lead to the environment has several detrimental effects on the ecosystem and living tissues of human body. There are also serious environmental issues associated with the disposal and recycling of lead-based materials. These matters have triggered global concern to find lead-free compositions as replacements for lead-based piezoelectrics. Legislations have been established on restriction of hazardous materials (ROHS) and end of life vehicle (EOV) by European Union and Japan. Legislation of waste from electrical and electronic equipment (WEEE) in Europe requires the manufacturers to be responsible for recycling of their waste products. Japan and China have also set similar legislations which restrict the use of lead-based materials in electronic industry. These legislations necessitate the search for lead-free composition with high electromechanical properties.

During past fifteen years, tremendous amount of research has been carried out in the field of lead-free piezoelectrics. The number of publications focused on this area has been increased remarkably. New compositions based on different lead-free materials such as bismuth sodium titanate (BNT) and potassium sodium niobate (KNN) particularly in the vicinity of the morphotropic phase boundary (MPB) have been developed. Despite all the efforts taken to find and modify new lead-free compositions, the electromechanical properties of these materials are still inferior to their lead-based counterparts. There are many reports on electrical properties of A-site substituted BNT-based ceramics. However, there are only limited studies on B-site substituted BNT ceramics. Similar to PZTs, incorporation of acceptor dopants on the B-site is expected to induce hard piezoelectric characteristics demanded for high power applications. The performance of hard-lead free ceramics under high drive condition needs to be understood.

A major part of the research on lead-free piezoelectrics has been devoted to ceramics while less attention has been paid to thin film growth and characterization. In order to deposit high quality and reliable thin films, it is required to systematically study the effect of processing parameters on the properties of lead-free films. One of the major issues leading to poor ferroelectric performance in lead-free thin films is their low resistivity. A high leakage current in these thin films prevents achievement of saturated P-E hysteresis loops and results in a low polarization. Basically, the electrical conductivity originates from volatilization of A-site elements leading to deviation from stoichiometry. It is vital to decrease the leakage current of lead-free thin films through optimization of the processing parameters or addition of appropriate dopants.

Another field of interest for using lead-free piezoelectrics is medical ultrasonic transducers for medical and therapy purposes. Especially, in some invasive therapeutic or diagnostic applications such as intravascular ultrasound where the transducer is embedded in the human body, lead-free piezoelectrics are the safest option. In order to achieve that goal, the knowledge and technology of fabrication of ultrasonic transducers based on lead-free piezoelectrics needs to be developed.

1.2 Research Objectives

The scope of this dissertation is to study and develop lead-free BNT-based ceramics, thin films, and ultrasonic and high power transducers. The main objectives of this study can be mentioned as follows:

1- To study and examine the electromechanical and acoustic properties of BNT-based ceramics with compositions in tetragonal and rhombohedral sides of Morphotropic phase boundary (MPB) as well as the MPB composition. The aim was to tailor the electrical properties as needed for various applications such as actuators, medical ultrasonic transducers, and high power transducers. It was also desired to establish reliable processing condition for preparation of ceramics with reproducible properties. Furthermore, compositions with promising electromechanical properties were selected as targets for the development of BNT-based thin films.

2- To develop hard BNT-based ceramics for high power applications. The objective was to study the effect of acceptor dopants such as Mn and Fe on electromechanical properties and high power characteristics of these ceramics. The effect

of vibration velocity on the mechanical quality factor and efficiency of hard BNT-based ferroelectrics was also studied.

3- To design and fabricate high frequency single element BNT-based ultrasonic transducers. The acoustic performance and imaging capability of single element transducers were investigated.

4- To study and understand the effects of deposition parameters on the microstructure, chemical composition, dielectric, and ferroelectric properties of BNT-based thin films prepared by pulsed laser deposition. Another objective was to optimize the deposition parameters of the thin films including substrate temperature, oxygen pressure, and laser repetition rate to enhance ferroelectric properties of the films.

5- To study the electrical conduction mechanisms in BNT-based thin films by evaluation of the leakage current behavior at different temperatures.

6- To decrease the leakage current and dielectric loss of BNT-based thin films by Mn-doping and controlling the oxygen pressure during the deposition.

1.3 Outline of the Dissertation

In Chapter 2, fundamentals of piezoelectricity and ferroelectricity are reviewed. This chapter also provides a literature review on bismuth sodium titanate (BNT) materials. Chapter 3 presents the dielectric and piezoelectric properties of BNT-based ceramics with different compositions. Chapter 4 provides processing-property relationship and high drive characteristics of acceptor-doped BNT-based ceramics and transducers. Acoustic performance of high frequency BNT-based ultrasonic transducers is presented in chapter 5. Chapter 6, 7, and 8 are assigned to the processing, electrical

properties, and leakage current behavior of BNT-based thin films deposited by pulsed laser deposition. In chapter 6, the processing-property relationship in BNT-BKT-BT thin films is discussed. Chapter 7 demonstrates the leakage current mechanisms in BNT-based thin films. And finally, chapter 8 presents the effect of composition, Mn-doping and oxygen pressure on microstructure and electrical properties of BNT-BKT-BLT thin films. Chapter 9 provides conclusions and summary of the results achieved in this study. In chapter 10, few suggestions are made to carry out further research on BNT-based materials and devices.

2 Introduction and Background

2.1 Dielectric Materials

In dielectric materials, the constituent atoms are ionized to a certain degree and are positively or negatively charged. The dielectric constant or relative permittivity (K or ϵ_r) is defined as the ratio of the permittivity of a material (ϵ) to the permittivity of free space ($\epsilon_0 = 8.854 \times 10^{-12} \text{ F.m}^{-1}$), $K = \epsilon / \epsilon_0$. Due to the dielectric polarization, the charges stored in an electroded dielectric material are higher than the charges stored in free space between the same electrodes separated by an identical distance [1]. The dielectric displacement with the SI unit of C.m^{-2} is sum of the charges stored on the electrodes plus those originating from polarization (P) as shown in Fig. 2.1. [2, 3]:

$$D = E\epsilon_0 + P = E\epsilon\epsilon_0 \quad (2.1)$$

where E is the applied electric field (V.m^{-1}).

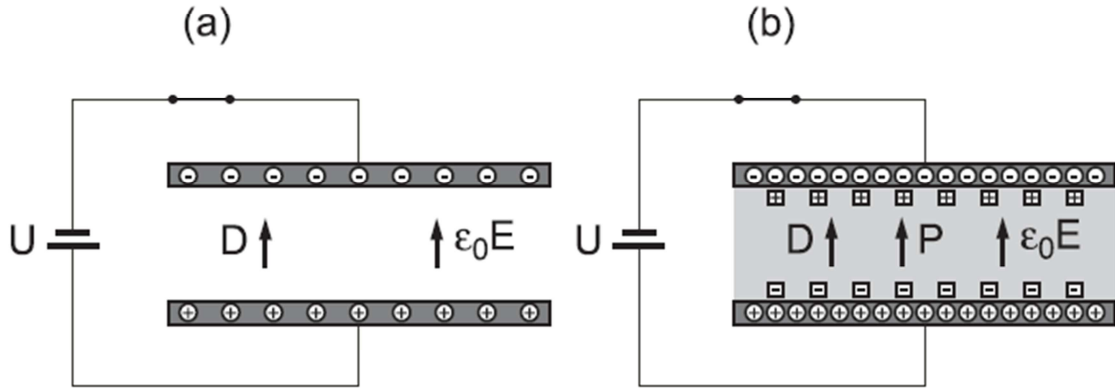


Fig. 2. 1. Parallel plate capacitors (a) vacuum separating two electrodes without any dielectric materials in between (b) filled with a dielectric material [3].

The dielectric constant is directly proportional to the capacitance (C_p). While the capacitance is a function of the thickness (t) and the electrode area (A), the dielectric constant is a material's property independent of the geometry (eq. 2.2).

$$\epsilon_r = \frac{C_p \cdot t}{A \cdot \epsilon_0} \quad (2.2)$$

There are four major types of polarization mechanisms which contribute to the dielectric properties: the electronic, ionic, molecular, and space charge polarization as schematically illustrated in Fig. 2.2 [2].

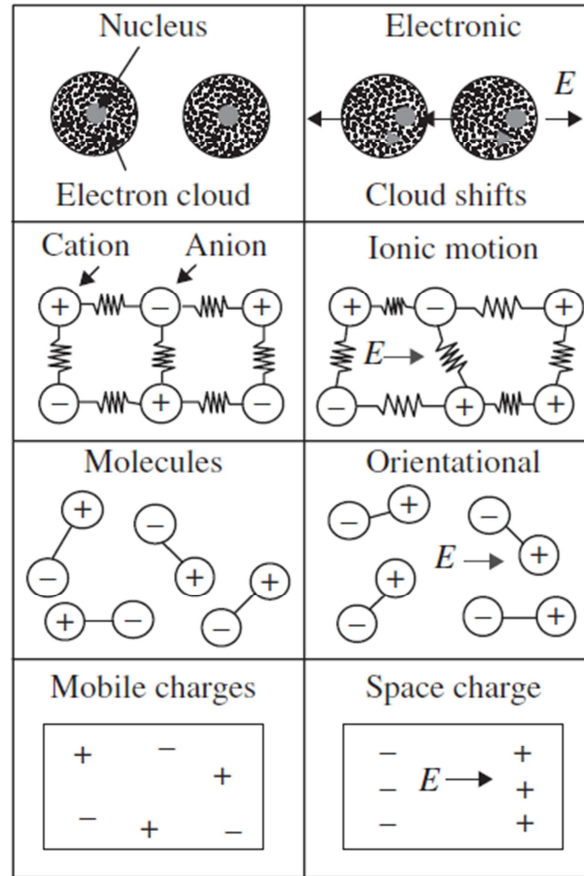


Fig. 2. 2. Different polarization mechanisms leading to the dielectric displacement [2].

The electronic part comes from the displacement of the electron cloud around the nucleus under application of an external electric field. The ionic contribution is associated with the relative movement of cations and anions toward the cathode and anode under an electric field. The molecular or orientational polarization arises from reorientation of molecular dipoles in the direction of electric field. The space charges are mobile charge carriers such as free electrons or ions which can migrate under applied electric field. Each polarization mechanism is active up to a certain range of frequencies. Fig. 2.3 displays the frequency dependence of the real and imaginary parts of dielectric constant (K' and K'' , respectively). The dielectric loss or dissipation factor is defined as the ratio of the imaginary (out of phase) part of the dielectric constant to the real (in phase) part [1, 2]. Space charges, for example, can only contribute at low frequencies (kHz range). Electrons have very small mass and are able to follow the electric field up to very high frequencies (optical range). At the optical range, the electronic polarization is the only dominant mechanism. For this reason, the dielectric constant at high frequencies is also called as optical dielectric constant which is proportional to the refractive index (n) of a material ($\epsilon_r = n^2$). Ionic polarization can follow alternating fields with frequencies up to GHz-THz. Permanent dipoles respond to frequencies only up to MHz-GHz range [4].

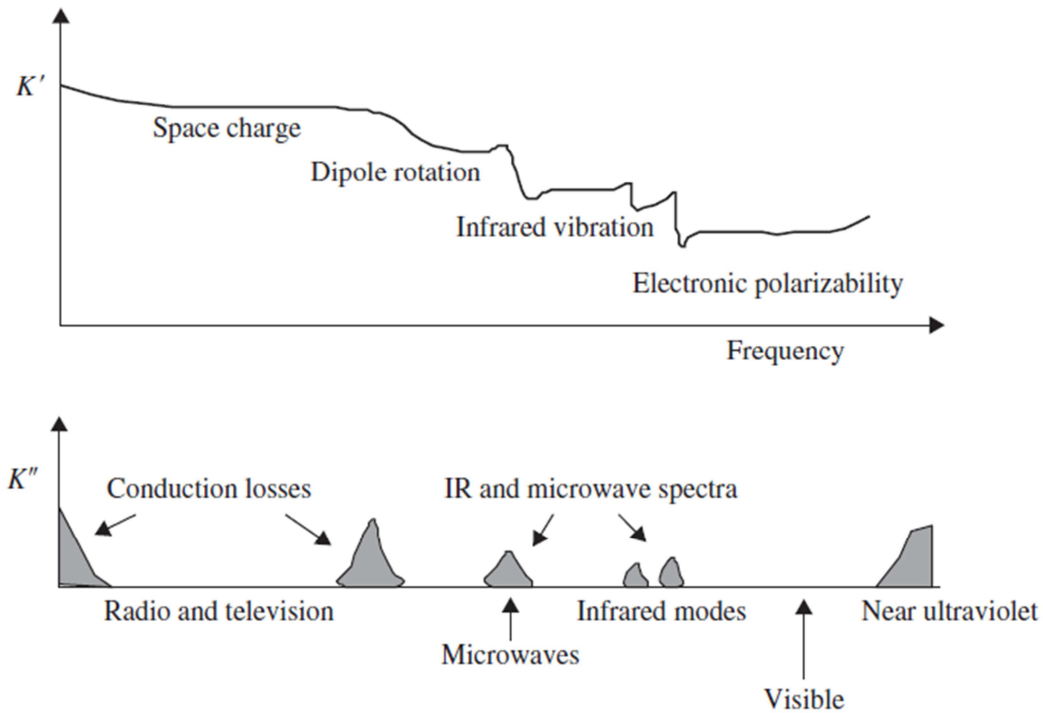


Fig. 2. 3. Variations of the real (K') and imaginary (K'') parts of the permittivity with frequency.

Dielectric materials can be categorized in three different groups based on the available polarization mechanisms [5]:

(a) Nonpolar dielectrics: In these materials, application of electric field only shifts the electron cloud (basically valence electrons). Therefore, only the electronic polarization is observed in these dielectrics. Diamond is one of the materials belonging to this group.

(b) Polar dielectrics: Ionic crystals, alkali halides, and some oxides belong to this category. In addition to the electronic polarization, the displacement of ions creates an extra (ionic) contribution to the total polarization. The molecules of these materials do not contain permanent dipoles (dipole moments summed over the different directions give a null total moment).

(c) Dipolar dielectrics: These materials contain permanent dipole moments which can be oriented under electric field to create the orientational polarization.

2.2 Piezoelectric Materials

Piezoelectricity (piezo is a Greek word meaning pressure) was discovered by Nobel Laureates Pierre and Jacques Curie in 1880 during their study of the effects of pressure on the generation of electrical charge by crystals such as quartz, tourmaline, and Rochelle salt [6].

Piezoelectrics are polar materials in which electrical charge can be produced by application of a mechanical stress (direct piezoelectric effect). The created charge is proportional to the force but it has opposite signs for tensile and compressive forces. The proportionality constant relating the generated charge to the applied force is called piezoelectric coefficient. In the longitudinal direction, the piezoelectric charge coefficient is known as d_{33} with units of pC.N^{-1} . Alternatively, if an electric field is applied to a piezoelectric material, the material shows a mechanical displacement or strain (converse piezoelectric effect). The direct and converse piezoelectric coefficients essentially have the same numerical values; however, they may be expressed in two different units (pm.V^{-1} vs pC.N^{-1}). Piezoelectricity is only observed in non-centrosymmetric point groups. Out of 32 crystal classes or point groups, 21 lack a center of symmetry. 20 out of the 21 non-centrosymmetric classes show piezoelectricity in practice (432 point group is an exception). Piezoelectrics are anisotropic materials i.e. their properties vary in different crystallographic directions. The number of independent piezoelectric coefficients in a third rank piezoelectric tensor depends on the symmetry elements of a specific point

group. Poled ceramics with $\infty\infty m$ symmetry have only three independent piezoelectric coefficients d_{33} , d_{31} , and d_{15} [2, 6]. One of the most important parameters which measures the efficiency of a piezoelectric material is the electromechanical coupling factor (k). When an electric field is applied, k^2 measures the fraction of the electrical energy converted to mechanical energy (and vice versa). Depending on the geometry, and position of electrodes in respect to the poling direction, a piezoelectric resonator can resonate in different fundamental modes as shown in Fig. 2.4.

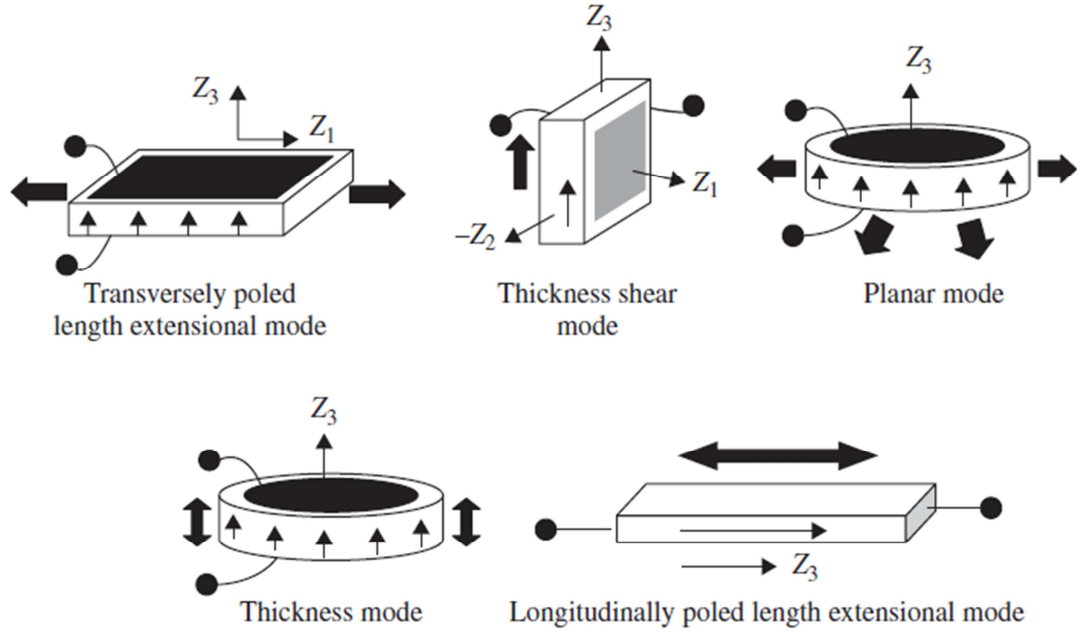


Fig. 2. 4. Different vibration modes in a piezoelectric resonator [2].

The natural vibration fundamental frequency (f_r known as the resonance frequency) is only a function of the resonator's dimension and the sound velocity in the material (see eq. 2.3). For each resonance frequency, there are harmonic oscillations which are odd multiples of the fundamental frequency. Eq. 2.3 expresses the relation

between f_r , sound velocity (v), length of the resonator (l), the elastic compliance (s^E), and the density (ρ) [7]:

$$f_r = \frac{v}{2l} = \frac{1}{2l} \sqrt{\frac{1}{s^E \rho}} \quad (2.3)$$

2.3 Ferroelectric Materials

Among the 20 piezoelectric point groups, 10 groups show a spontaneous polarization. The spontaneous polarization originates from permanent dipole moments existing in the crystal. The primary feature distinguishing ferroelectrics from other polar materials is that the direction of spontaneous polarization can be switched by an electric field. Ferroelectrics crystallize in different structures such as perovskite, tungsten-bronze, and bismuth layer structure. Significant numbers of ferroelectrics used in practical applications have a perovskite structure. The general formula for a perovskite is ABO_3 , in which A is a large cation with valence of 1+, 2+ and 3+ and B is a small cation with valences of 3+, 4+ and 5+. Figs. 2.5 (a),(b) show the perovskite structure with cubic and tetragonal symmetries in lead titanate. Oxygen atoms occupy the faces of the unit cell, forming an oxygen octahedron. The tilting and distortion of this oxygen octahedron, which happens to lower the Ti-O binding energy, has a considerable effect on properties of perovskite ferroelectrics [2, 8]. Small B cation (e.g. Ti^{4+} , Nb^{5+} , Zr^{4+}) with a six-fold coordination is placed in the center of the octahedron and large A cations with 12-fold coordination (e.g. Pb^{2+} , Ba^{2+} , Bi^{3+} , Na^{1+}) occupy the corner of the unit cell, as shown in Fig. 2.5. The B-site cations such as Ti^{4+} and Nb^{5+} or other d^0 cations are highly polarizable and play an important role in promoting the ferroelectric and piezoelectric properties [2, 8]. Another group of active elements contributing to polar distortion in

oxide dielectrics are the lone-pair ions having two electrons outside a closed shell in an asymmetric hybrid orbital. Pb^{2+} and Bi^{3+} are most significant lone-pair ions in ferroelectrics [2].

The Curie temperature T_C is the maximum temperature that a ferroelectric material shows ferroelectricity. Above T_C , dipoles are vanished and a ferroelectric material converts to a paraelectric (nonpolar) phase. At temperatures higher than T_C , the crystal adapts a cubic structure (point group $m\bar{3}m$) in which the centers of negative and positive charges are coincident and therefore, charges cancel each other out (Fig. 2.5 (a)). The permanent dipoles in ferroelectrics form due to an offset between the center of positive and negative charges (Fig. (2.5 (b))). As a ferroelectric material is cooled down the Curie temperature, sequences of displacive phase transitions occur. The dipoles form as a result of relative displacement of the cations and anions in the unit cell. Cooling a ferroelectric material below the Curie temperature is accompanied by a reduction in symmetry elements of the unit cell. Crystal symmetries such as orthorhombic (point group $mm2$), tetragonal (point group $4mm$) or rhombohedral (point group $3m$) are common in ferroelectrics below the T_C . In each type of ferroelectric phases, the number and directions of polar axes are unique. The polar axes in orthorhombic, tetragonal, and rhombohedral phases are $[110]$, $[001]$, and $[111]$, respectively. The number of equivalent directions in the unit cell is 12, 6, and 8, respectively. The spontaneous polarization in ferroelectrics is coupled with a spontaneous strain (shape change) in the unit cell through the intrinsic piezoelectric effect. In ferroelectric distortions, the crystal elongates parallel to the spontaneous polarization direction and contracts perpendicular to it. Similarly, application of an external electric field which increases the polarization, elongates the

crystal in that direction [8]. In the case of cubic to tetragonal phase transformation, the oxygen is shifted towards the crystallographic c-axis, while the positive ions are displaced towards the opposite direction. The transition causes expansion of the unit cell in $\langle 001 \rangle$ direction, along with a contraction in $\langle 100 \rangle$ and $\langle 010 \rangle$ directions. The dipole is either parallel or antiparallel with the c-axis as shown in Fig 2.5 (b).

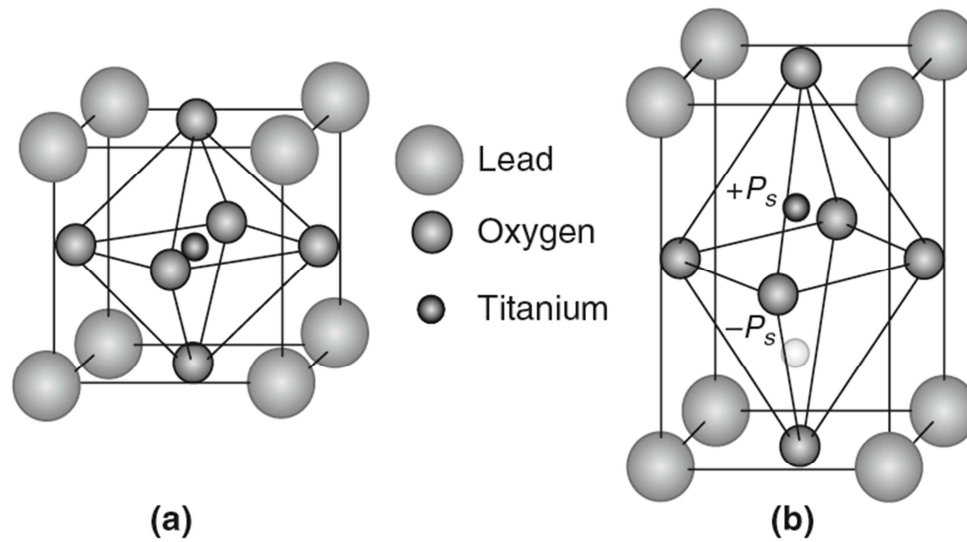


Fig. 2. 5. (a) The perovskite crystal structure of PbTiO_3 with a cubic symmetry above T_C and (b) off-center displacement of Ti along $[001]$ below the T_C in the tetragonal phase [9].

The ferroelectric phase transitions in BaTiO_3 with a T_C of about 120°C are shown in Fig. 2.6. Phase transitions are accompanied by a sharp rise/drop in the dielectric constant and polarization during the heating/cooling. At Curie temperature, the P_s abruptly drops to zero. From practical point of view, it is important for a ferroelectric material to retain its high dielectric constant over a wide range of temperature. Relaxor ferroelectrics, show broad peaks rather than sharp peaks at the phase transition temperatures which are believed to be resulted by compositional fluctuations in a microscopic scale. $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) are examples of

relaxor ferroelectric materials. In relaxor ferroelectrics, the transition temperatures as well as the peak capacitance are functions of the frequency (dielectric relaxation). Fig. 2.7 shows the dielectric properties of relaxor-type $(\text{Pb}_{0.92}\text{La}_{0.08})(\text{Zr}_{0.7}\text{Ti}_{0.3})\text{O}_3$ ceramics as a function of temperature. Note that the maximum dielectric constant decreases and the dielectric maximum temperature increases with increasing the frequency. Due to their very high permittivity and diffuse phase transitions (temperature-insensitive properties), relaxor ferroelectric have been utilized in fabrication of compact chip capacitors [4].

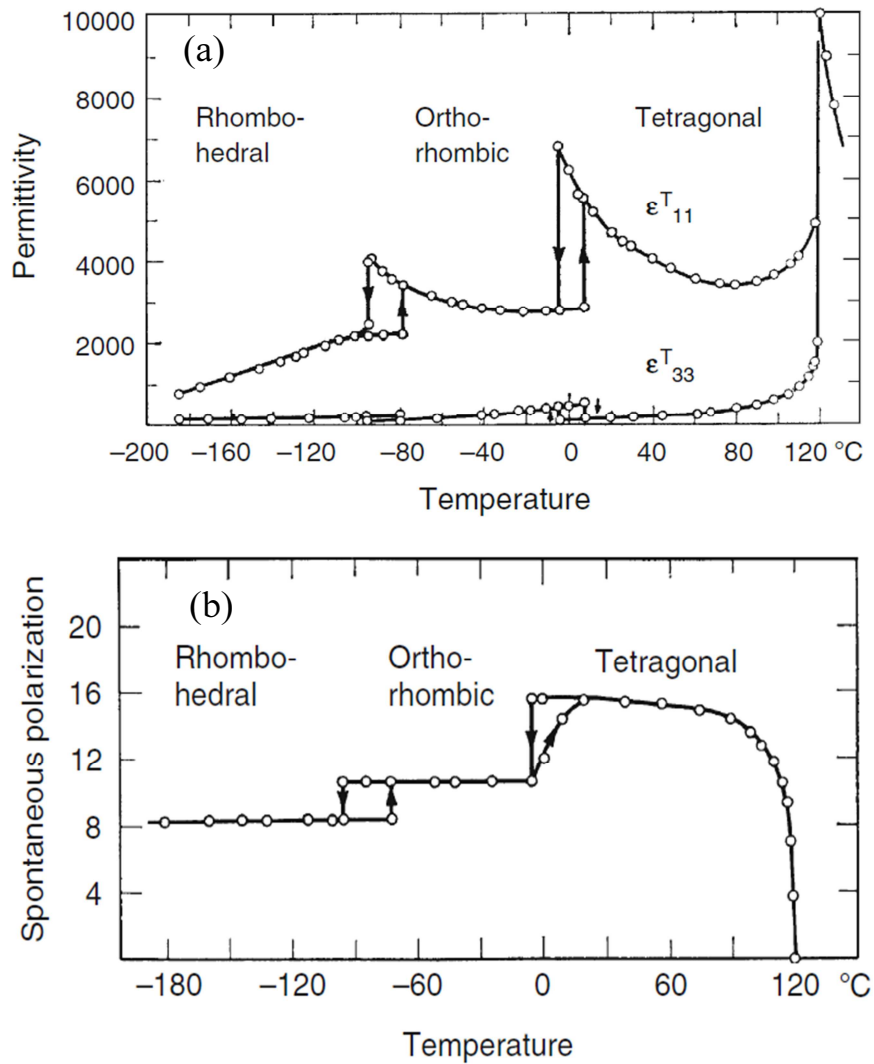


Fig. 2. 6. Phase transitions in BaTiO_3 crystal under the Curie temperature. Variations of (a) dielectric constant (b) spontaneous polarization with temperature [10].

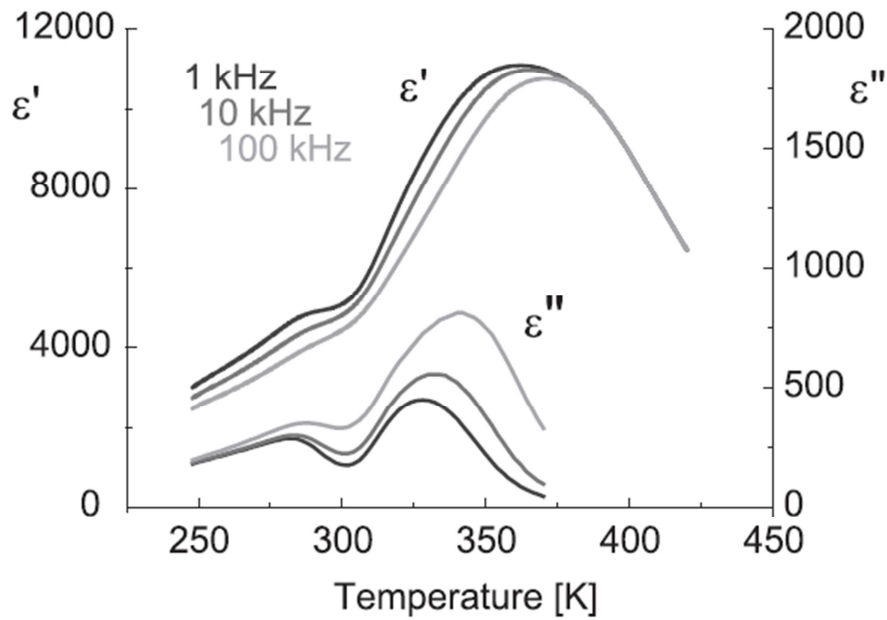


Fig. 2. 7. Dielectric behavior of relaxor-type $(\text{Pb}_{0.92}\text{La}_{0.08})(\text{Zr}_{0.7}\text{Ti}_{0.3})\text{O}_3$ ferroelectrics known as PLZT [3].

One of the other characteristics of ferroelectric materials is the polarization and strain hysteresis upon application of electric field. The hysteresis corresponds to an energy loss. This energy is required to nucleate and grow ferroelectric domains with opposite polarization direction [9]. Fig. 2.8 shows the typical polarization – electric field (P-E) hysteresis loops for paraelectric, ferroelectric, and antiferroelectric materials. In paraelectrics, there is a linear relationship between the polarization and electric field. Due to the lack of ferroelectric domains and permanent dipoles, there is no remnant polarization and hysteresis loops in the paraelectric state.

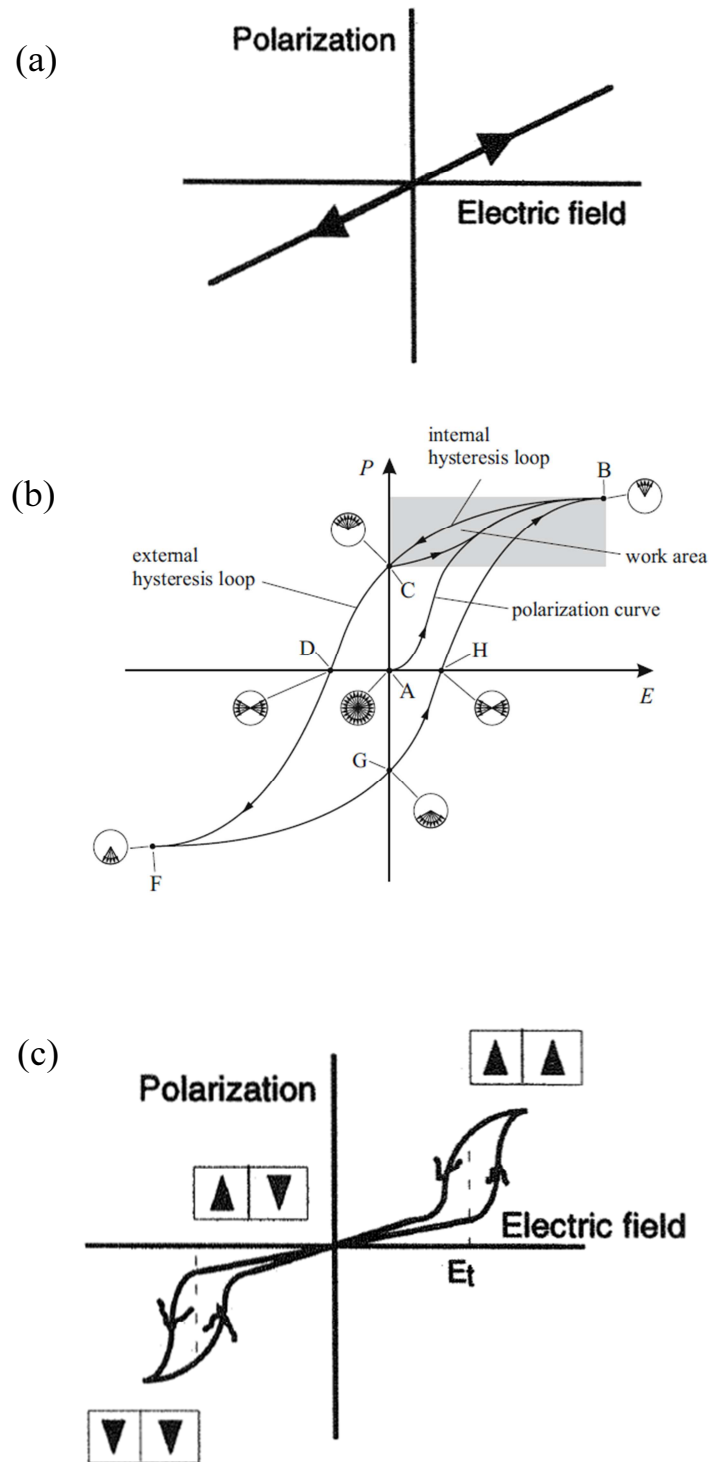


Fig. 2. 8. Typical P-E hysteresis loops of (a) paraelectric (b) ferroelectric (c) and antiferroelectric materials [4, 11].

Ferroelectric materials contain microscopic regions called domains. Within each domain, the dipoles are oriented in the same direction. In as-sintered polycrystalline ferroelectrics, the domains are randomly distributed. Consequently, the polarization vectors from different domains cancel each other out and result in a zero net polarization (Point A in Fig. 2.8 (b)). Due to the clamping effect of neighboring grains, the formation of domains in ceramics is different than single crystals. The grain size also affects the domain twinning in ferroelectric ceramics. A simple lamellar domain structure is favored in fine-grained ceramics, while banded lamellar structure is observed in coarse-grained ferroelectrics [10]. Upon application of electric field, dipoles are aligned in the direction of the polar axis which is closest to the direction of applied field. As the dipoles in different domains become oriented, the polarization is increased up to a saturation point called the saturation polarization P_s (point B). When the electric field is removed, some of the dipoles switch back to their original direction (due to the internal stress) but most of them retain their aligned orientation leading to a remnant polarization P_r at zero electric field (point C). To obtain a zero polarization, a certain amount of electric field called the coercive field E_c needs to be applied in the negative direction (point D) [11]. The coercive field is a measure of the internal friction opposing the domain wall motion.

Antiferroelectrics are antipolar crystals in which the dipoles are aligned in an anti-parallel pattern. Under application of an electric field, antiferroelectrics become a polar crystal by parallelizing the dipole configuration. After removal of the field, the crystal goes back to its anti-polar state and hence, no remnant polarization is observed. Antiferroelectrics are recognized by a double hysteresis curve as illustrated in Fig. 2.8. (c).

Fig. 2.9 demonstrates the electric field-induced strain in a ferroelectric material. The ceramic is initially poled in negative direction (point 1), and the electric is applied in positive direction. Since the direction of the applied field is opposite to the polarization, the crystal initially shrinks (from pint 1 to point 2). At the coercive field (point 2), the domains in different grains start to reorient in positive direction. At electric fields higher than the coercive field, the material expands up to $E_{\max}$ (point 3). When the field is removed, the strain decreases monolithically. The final state (point 5) is similar to the initial state with the polarization direction reversed [4].

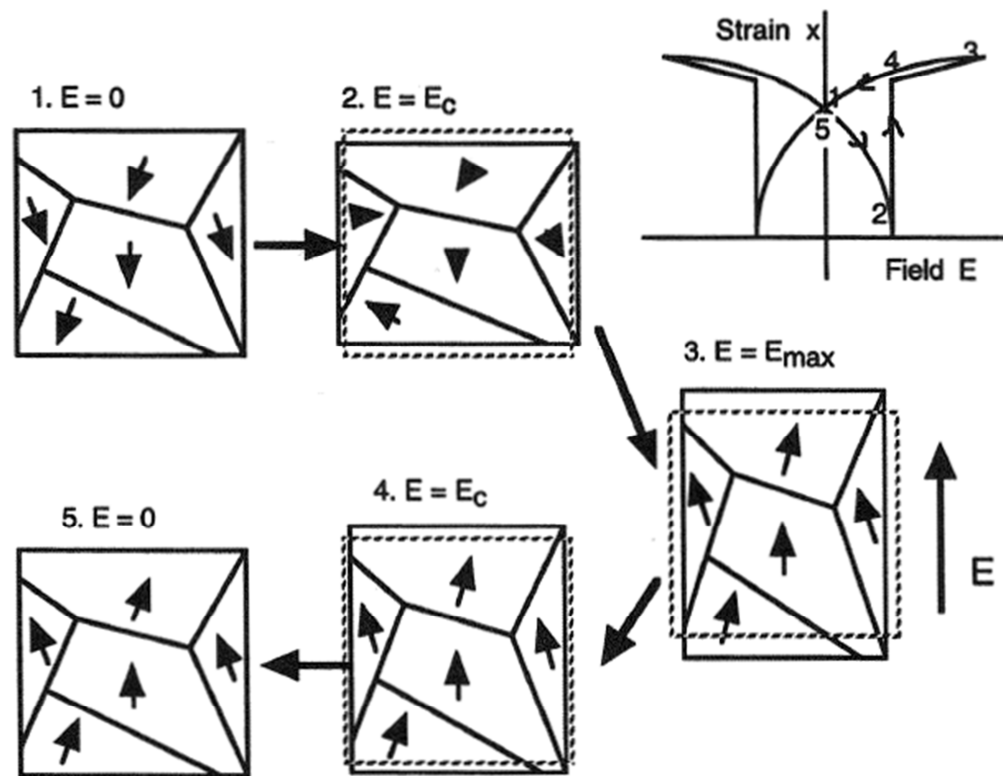


Fig. 2. 9. Electric field-induced strain in a ferroelectric material (so-called butterfly hysteresis loop). Corresponding reorientation of the polarization state has also been shown [4].

As mentioned above, domains appear in ceramics and single crystals when the material is cooled down the Curie point in order to minimize the electric and elastic energy of the system. The boundary separating two adjacent domains is called the domain wall. Depending on the angle between the dipoles in two adjacent domains, the domain walls are categorized into two types: 180° and non- 180° . Fig. 2.10 schematically depicts the domain configuration in tetragonal and rhombohedral crystals. In a tetragonal crystal, 90° and 180° domain walls form to decrease the free energy of the system. The 90° domain walls change to 71° and 109° in a rhombohedral phase due to the crystal distortions.

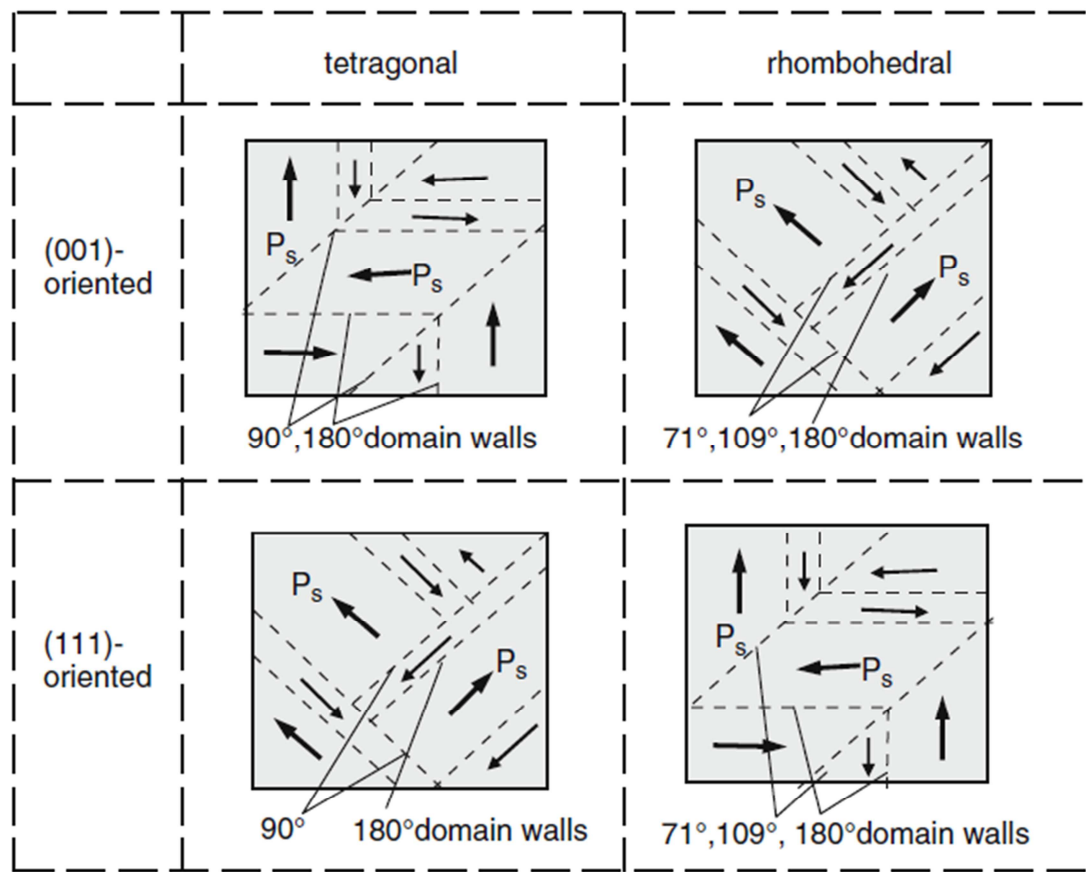


Fig. 2. 10. Ferroelectric domains in tetragonal and rhombohedral crystals grown in (001) and (111) directions [10].

There are intrinsic and extrinsic mechanisms contributing to the ferroelectric and piezoelectric properties of a crystal. The intrinsic part comes from the displacement of the cation and anions as explained earlier. The extrinsic part is brought by the domain wall motion. About 60-70% of piezoelectric coefficient values may originate from extrinsic contributions [10]. In soft ferroelectrics with a low coercive field, domain walls can easily move leading to high piezoelectric and ferroelectric properties. These materials are used in sensor applications. The electric field-induced strain and the shape change are resulted by non-180° domain wall motion. Fig. 2.11 shows 90° domain wall in a tetragonally distorted perovskite ferroelectric. The motion of the domain wall across the domains with different strain states contributes to the shape change observed in the crystal. 180° domain walls basically do not contribute to the strain but play a significant role in generation of polarization. The domain wall motion causes nonlinearity in ferroelectrics [8]. The displacement of domain walls contributes to the dielectric, mechanical, and piezoelectric losses. The movement of domain walls can be inhibited by pinning defects. The mobility of these defects influences the time variation of dielectric and piezoelectric properties, a phenomenon called aging. In hard ferroelectrics, the extrinsic contribution, the strain hysteresis, non-linearity and electric field dependence of properties are reduced because the domains walls are pinned by defects such as oxygen vacancies. Hard ferroelectrics are used in high power actuators to decrease the electric field dependence of material properties such as the coupling coefficient and mechanical quality factor. Since the domain wall mobility decreases with decreasing the temperature, at very low temperatures only intrinsic contribution becomes significant, and the properties of soft and hard ferroelectrics converge as shown in Fig. 2.12.

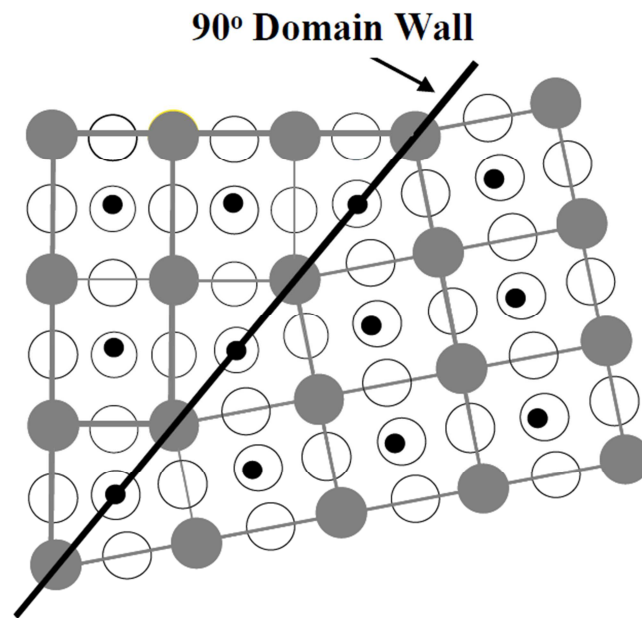


Fig. 2. 11. 90° domain wall in a tetragonally distorted ferroelectric. The domain wall motion contributes to the shape change of the crystal under an applied electric field [8].

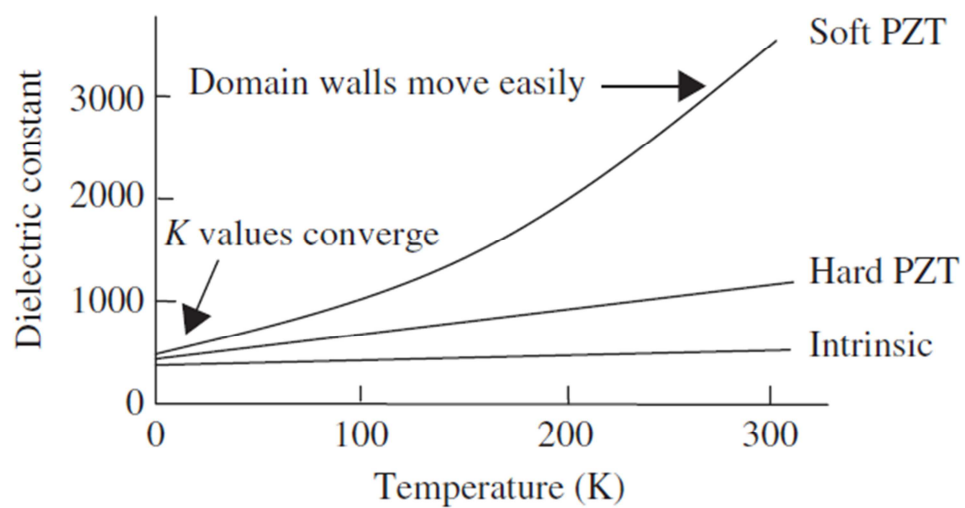


Fig. 2. 12. Effect of the temperature on the dielectric constant of soft and hard ferroelectrics (PZT) showing the concept of intrinsic and extrinsic contribution [2].

The maximum piezoelectric and ferroelectric properties in solid solutions occur at morphotropic phase boundary (MPB). In an MPB composition, two different phases such as the tetragonal and rhombohedral phases coexist. In the phase diagram, the MPB region appears as a nearly vertical line which is very sensitive to small variations of the composition but not the temperature (Fig. 2.13). An MPB occurs because of the instability of one phase (such as the ferroelectric tetragonal phase) in respect to another phase (such as the ferroelectric rhombohedral phase) at a critical composition where two phases are energetically very similar but elastically different [12]. The enhanced properties in the vicinity of MPB composition originates from increased number of polar axes. Monoclinic phases near the MPB has been recently found to be another reason of enhanced piezoelectricity particularly at low temperatures [6]. In monoclinic phases, 24 spontaneous polarization directions are possible. The larger the number of possible orientations for the spontaneous polarization, the more likely there is an allowed direction that is nearly parallel to the applied electric field. As a result, poling tends to be more complete in systems with more polarization directions such as MPB and monoclinic phases [8]. Fig. 2.13 displays the phase diagram of the most famous ferroelectric $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT). At room temperature, in solid solutions containing about 48% Ti and more, the tetragonal ferroelectric distortion is observed. On the other hand, Zr-rich solutions adopt a rhombohedral distortion. The boundary between these two phases is the MPB composition with a monoclinic phase at low temperatures [8]. Fig. 2.14 demonstrates the composition dependence of the dielectric constant and coupling coefficient in PZT system. The maximum properties are achieved at MPB composition as discussed above.

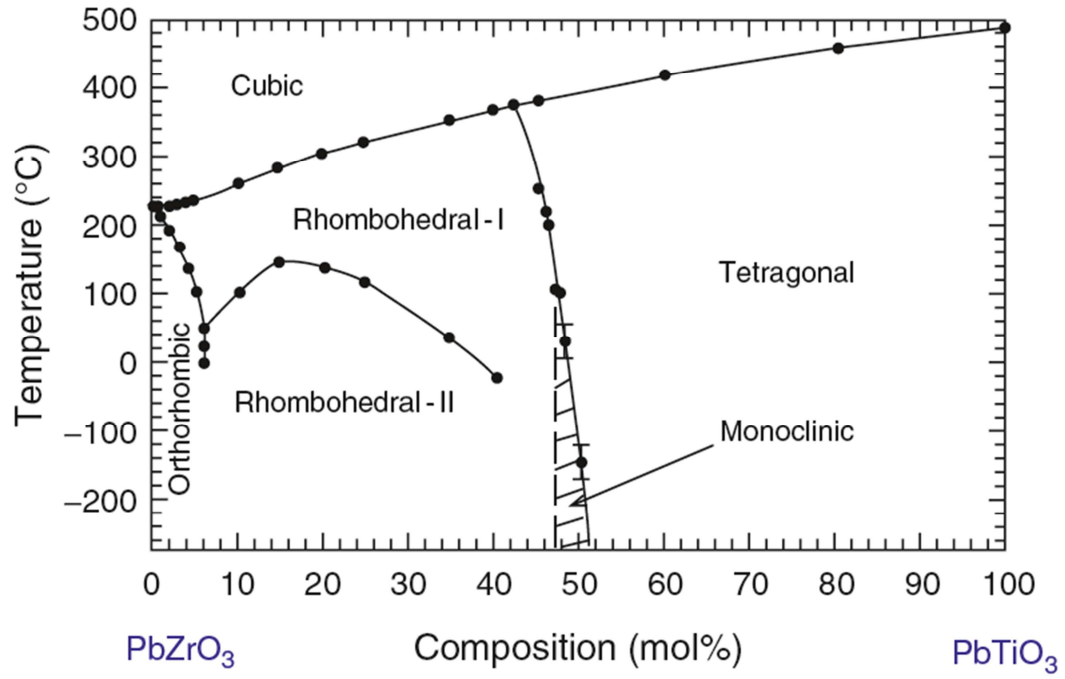


Fig. 2. 13. Phase diagram of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) solid solution.

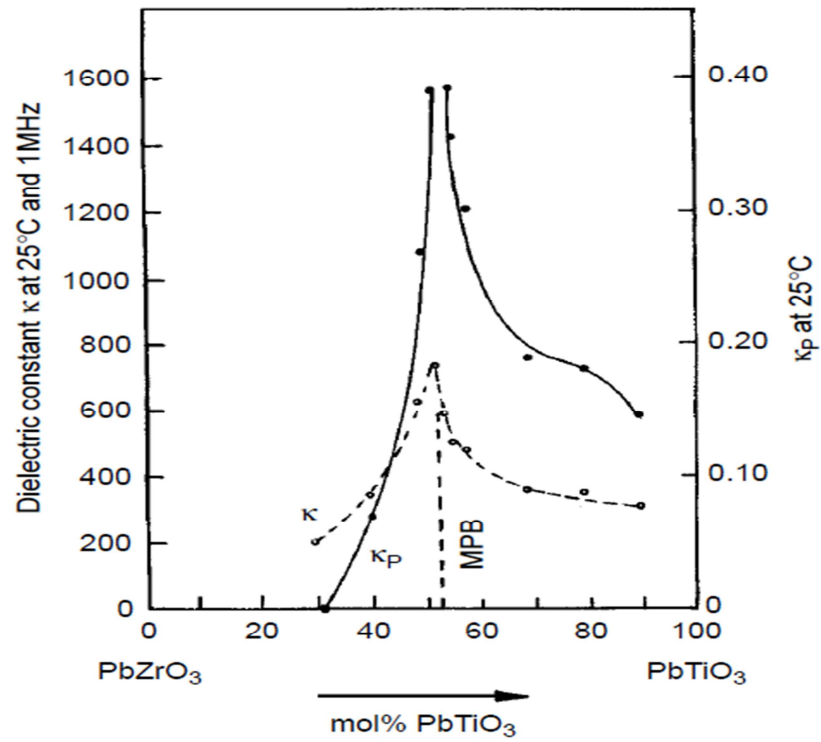


Fig. 2. 14. Composition dependence of the dielectric constant and planar coupling coefficient (k_p) in PZT ceramics [12].

Formation of a pure perovskite phase is in competition with other phases especially pyrochlore phases. The stability of the perovskite phase is dictated by Goldschmidt tolerance factor (t):

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (2.4)$$

The perovskite structure is stable if the tolerance factor is in the range of 0.8 to 1.06. The MPB compositions often form near tolerance factors of 0.97 to 1.02 [8].

2.4 Applications of Piezoelectric and Ferroelectric Materials

Piezoelectric materials nowadays are extensively used in hundreds of applications with a market turnover of billions of dollars. In the field of frequency control, signal processing, and filtering, piezoelectric materials such as quartz, LiNbO_3 , and LiTaO_3 single crystals, hard PZT, AlN, and ZnO thin films are used for fabrication of surface and bulk acoustic devices. In the area of sound and ultrasound, microphones and speakers, hydrophones, ultrasonic transducers for medical imaging and therapy, high power shock wave generators, atomizers, and buzzers are manufactured based on hard and soft PZT plates, films, or composites. Single layer and multilayer ferroelectrics have found many applications in the form of motors and actuators used in printers, transformers, micropumps, fuel valves, fine positioners and optics. Piezoelectric sensors are utilized in sensing the acceleration, pressure, temperature, and mass. Gas and fuel ignition, vibration and noise cancelation, adaptive control, capacitors, and non-volatile random access memories can be named as some of the numerous applications of ferroelectric materials [13].

2.5 Motivation for Development of Lead-free Piezoelectrics

Due to their excellent piezoelectric properties, lead-based ferroelectrics are the most widely used materials for fabrication of piezoelectric actuators, sensors and transducers. Because of the lead toxicity, however, there is rising concern over the recycling and disposal of devices containing lead. The lead oxide vaporizes during the high temperature processing. Lead stays in the environment for a long time. It can be absorbed and accumulated in the human body causing damage to the brain and nervous system. Besides the environmental issues, there is also an interest in developing biocompatible piezoelectric materials [14-17]. Various lead-free compositions based on bismuth sodium titanate and potassium sodium niobate have been developed during past 15 years. Despite all the progress made in processing and development of new lead-free compositions, the dielectric, piezoelectric, and ferroelectric properties of lead-based ceramics is still much higher than their lead-free counterparts. Fig. 2.15 compares the coupling coefficient, dielectric constant, and piezoelectric coefficient of several lead-based and lead-free ceramics. While the maximum dielectric constant and piezoelectric coefficient in majority of lead-free compositions are in order of 1300 and 250 pC.N^{-1} , these values in lead-based ferroelectrics reach as high as 10000, and 800 pC.N^{-1} . This comparison shows that more extensive research is needed to develop lead-free compositions with competitive properties. The fabrication of lead-free piezoelectric devices is also at its initial stage. In the following section of this chapter, different BNT-based materials reported in the literature have been reviewed.

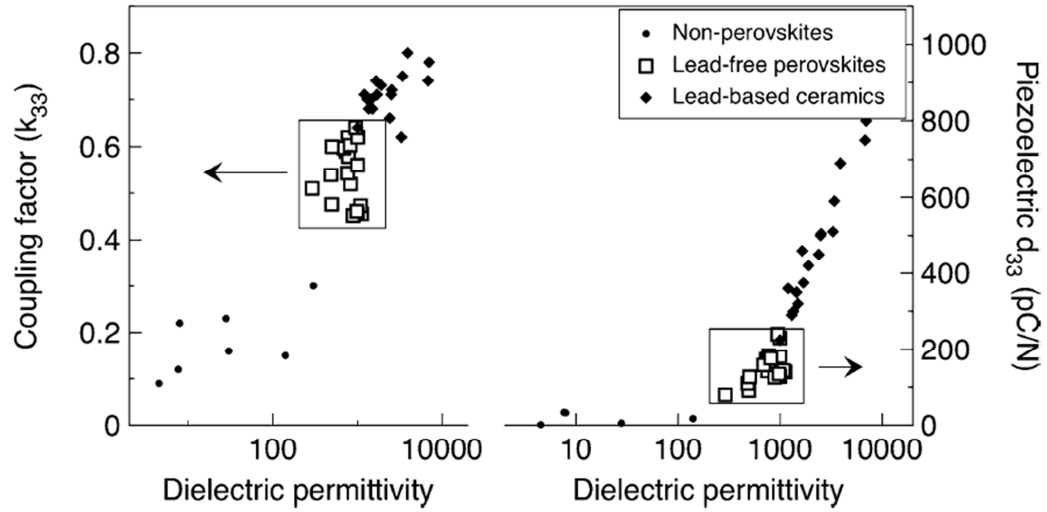


Fig. 2. 15. The coupling coefficient, dielectric constant, and piezoelectric coefficient of several lead-based and lead-free ceramics [18].

2.6 BNT-based Ceramics

Bismuth sodium titanate, $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) is one of the most studied lead-free ferroelectrics with perovskite structure discovered by Smolenskii et al [19]. At room temperature, it has a rhombohedral symmetry (R3c). Recent studies by high resolution XRD have revealed a monoclinic structure with Cc space group [20]. BNT ceramics show relaxor-type ferroelectricity with diffuse peaks in variations of the dielectric properties with temperature. This material has a high remnant polarization $P_r = 38 \mu\text{C}.\text{cm}^{-2}$ and high Curie temperature $T_C = 320^\circ\text{C}$ [21-28]. Phase transitions in BNT are complicated and the nature of some of these transitions is not clear yet. With increasing the temperature, a rhombohedral to tetragonal ($T_{R-T} \sim 300^\circ\text{C}$) phase transition occurs which is then followed by a tetragonal to cubic phase transition at 320°C . Due to the low tetragonality ($c/a=1.002$), the R-T phase transformation was not identified previously. In majority of ferroelectric materials, the working temperature can be as high as the half of the Curie temperature. However, despite having a high Curie temperature, the working

temperature of BNT ceramics is limited to a temperature called the depolarization temperature ($T_d \sim 190^\circ\text{C}$) [21, 23, 27, 29-31]. It is suggested that a ferroelectric to antiferroelectric transition occurs at this temperature. The phase transitions for a BNT-BKT ceramics is illustrated in Fig. 2.16. The T_d of BNT ceramics can be identified from variations of the dielectric loss with temperature as shown in Fig. 2.16.

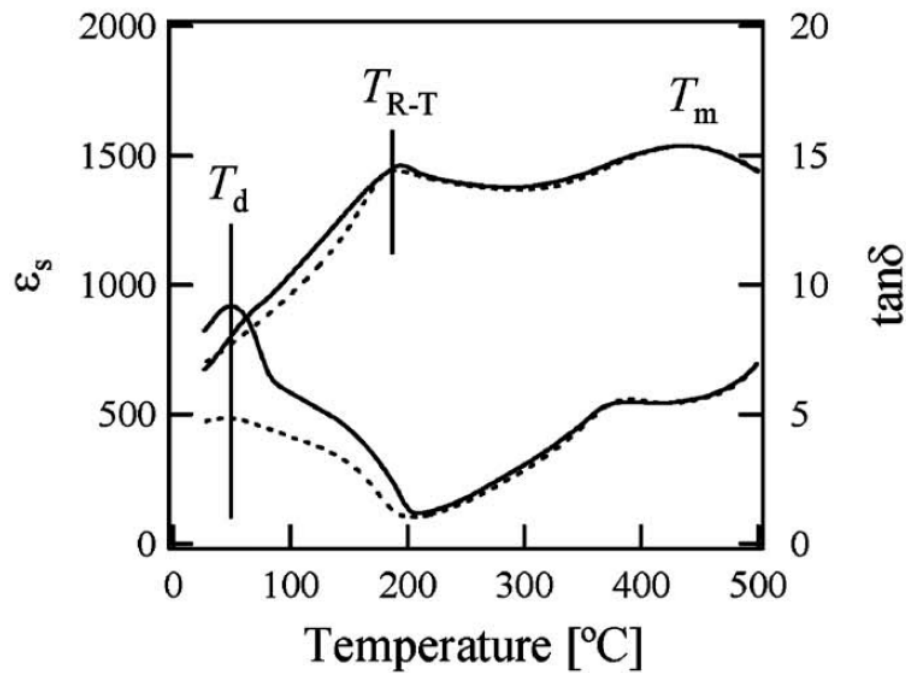


Fig. 2. 16. The phase transitions in 0.9BNT-0.1BKT ceramics [32].

One of the other challenges in processing of BNT ceramics originates from their high coercive field ($E_c = 73 \text{ kV.cm}^{-1}$) and high conductivity [21, 22, 27, 33, 34] which prevent complete poling of these ceramics. In addition, in order to obtain dense samples, pure BNT ceramics need to be sintered at temperatures higher than 1200°C [15]. It is known that the Bi-loss becomes noticeably high at temperatures higher than 1030°C

[15]. To alleviate the bismuth volatilization problem, addition of extra Bi_2O_3 (0.3 wt.%) or using hot-press technique has been suggested. Due to all these inherent limitations, pure BNT ceramics have not attracted attention for practical applications. However, binary and ternary BNT-based solid solutions have been reported to be potential alternatives for lead-based ferroelectrics. A-site substituted BNT-based ceramics exhibit a lower coercive field, lower sintering temperature and higher resistivity compared to pure BNT. It has been found that solid solutions of BNT with BKT, BLT, and BT form MPB compositions between rhombohedral and tetragonal phases [15, 17, 24, 31, 33-35]. Figs. 2.17 (a),(b) display the phase diagram of BNT-BKT and BNT-BT ceramics. The MPB at BNT-BT ceramics occurs at 6% BT with a d_{33} of about 130 pC.N^{-1} . Similarly, the MBP composition in BNT-BKT system is found to exist around 18-20% BKT with a dielectric constant of about 1030, $k_p \sim 0.314$, and $d_{33} \sim 170 \text{ pC.N}^{-1}$ [15, 21, 34-39].

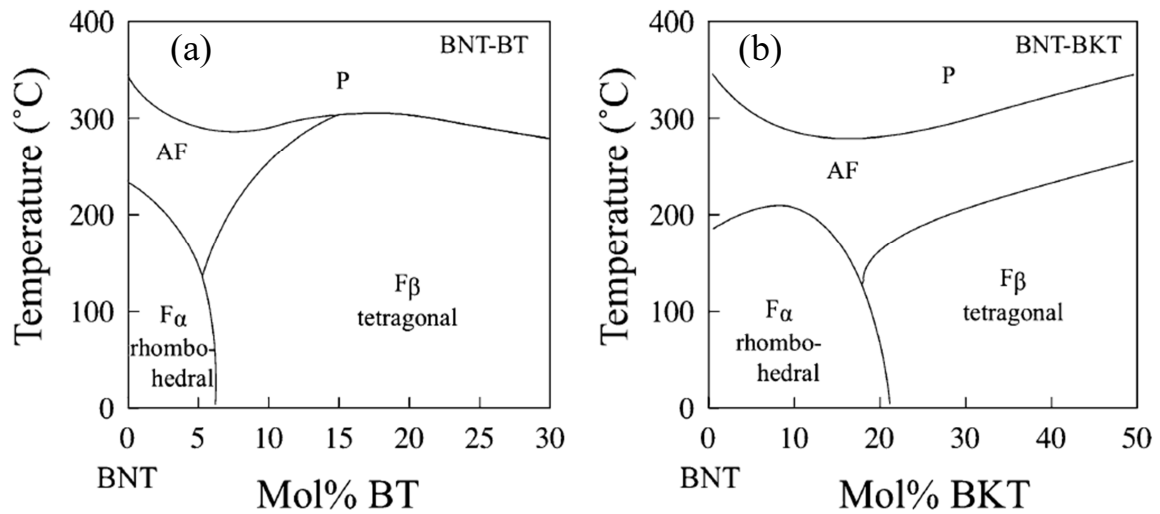


Fig. 2. 17. The phase diagram of (a) BNT-BT [24] (b) BNT-BKT ceramics [18].

The electrical properties of the $[\text{Bi}_{1-z}(\text{Na}_{1-x-y-z})\text{K}_x\text{Li}_y)0.5] \text{Ba}_z\text{TiO}_3$ ($\text{BN}_{1-x/y/z}$) were evaluated by Lin et al. The maximum piezoelectric constant d_{33} of 178 pC.N^{-1} was obtained at $x = 0.15$. The maximum value of the d_{33} (198 pC.N^{-1}) of the $\text{BN}_{0.15/0.10/z}$ ceramic occurs at $z = 0.02$. The ceramics with $x = 0.15$ - 0.20 and $z = 0.01$ - 0.04 provide better piezoelectric properties, which may be attributed to the compositions near the MPB where the number of spontaneous polarization directions is enhanced [40]. The MPB compositions in BNT-based ceramics exhibit relatively high piezoelectric and ferroelectric properties. However, they suffer from low depolarization temperature [29]. For example, the MPB composition in 0.88BNT - 0.08BKT - 0.04BT system shows a high piezoelectric constant, d_{33} of about 180 pC.N^{-1} , $\epsilon_r \sim 1000$ °C, and high $T_C \sim 301$ °C, but the T_d is as low as 113 °C [17, 21, 41]. One of the other compositions with relatively high piezoelectric properties ($k_p=0.31$, $k_t=0.476$, $d_{33}=220 \text{ pC.N}^{-1}$) is 85.25BNT - 10.995BKT - 3.755BT ceramic which again suffers from a low T_d (157 °C) [33]. Substitution of small amounts of monovalent cations such as Li^+ and K^+ in the A-site of BNT increases the T_d up to 200 - 220 °C [22, 31, 42-44]. Li^+ also increases the polarization and dielectric constant of BNT ceramics [26, 45]. It is reported that the variation of T_d is correlated with the rhombohedrality and tetragonality of the unit cell [31, 42, 44]. Unfortunately, there is a tradeoff between d_{33} and T_d [30, 44] as shown for various BNT-based ceramics in Fig. 2.18. An increase in the depolarization temperature is accompanied by a decrease in piezoelectric coefficient. The rhombohedral composition 0.88BNT - 0.08BKT - 0.04BLT system shows a high T_d (~ 220 °C) and a high mechanical quality factor (~ 400) [31, 41, 46].

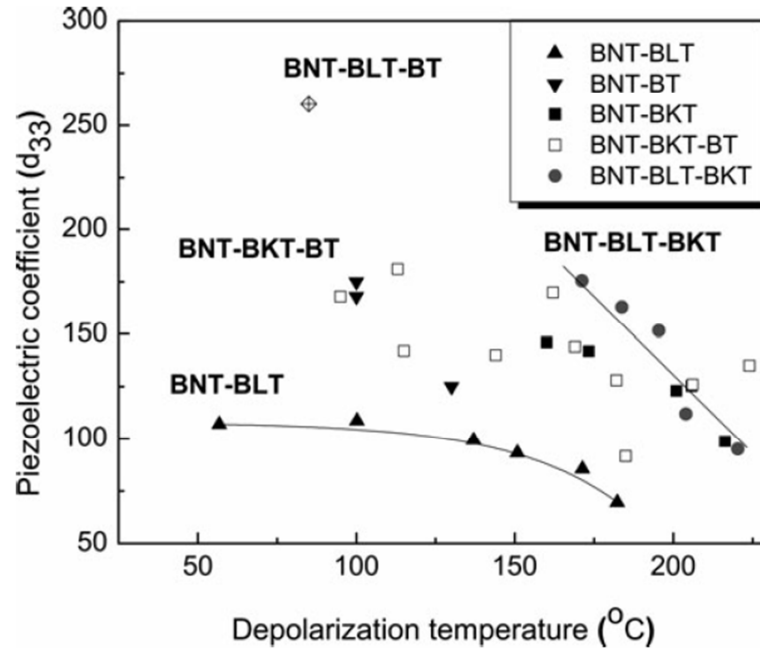


Fig. 2. 18. Relation between the depolarization temperature and piezoelectric coefficient in different BNT-based ceramics [18].

2.7 BNT-based Thin Films

BNT-based thin films have been deposited by different techniques such as pulsed laser deposition, sputtering, sol-gel, and metalorganic solution deposition [47-66].

Deposition of BNT-BT ($x = 0.06$) thin films with high dielectric constant was reported by Dinescu et al. Films were grown on (100)-MgO substrates at a temperature of 600-650°C using a Nd:YAG laser. The dielectric constant changed between 1230 and 1330 depending on the deposition temperature and cooling regime. The best results were obtained for films grown at 650°C in 0.5 mbar oxygen [67]. BNT-BT thin films with different BT contents in the range 0.02-0.44 have been deposited by a modern PLD-based combinatorial technique on (001) LaAlO_3 (LAO) substrates, by using a KrF excimer laser [47]. Deposition was performed sequentially from BNT-BT targets using three quaternary masks, at room temperature, and the ratio of BNT and BT was estimated by

the growth time. To obtain homogeneous crystallized films, a post-annealing treatment was adapted. The films showed (101) oriented growth. It was found that the dielectric constants reached the maximum value at $x=0.09$ ($\epsilon_r=327$). The BT concentration at which the MPB was observed in BNT-BT thin films was higher than that in ceramics where the MPB occurs at $x=0.06$. This indicated that the MPB in BNT-BT thin films was located at a slightly higher BT content than in bulk materials. The reason might be the additional stress applied by the substrate on the film as well as intrinsic unrelaxed strain developed during the film growth [59]. Unrelieved strain also shifts the phase transitions to higher temperatures in comparison to ceramic samples. Similar results were obtained for the MPB composition by growing films from a BNT-BT ($x=0.09$) ceramic target at a substrate temperature of 750°C, without post-annealing treatment [47]. Scarisoreanu et al. reported the growth of 0.94BNT-0.06BT thin films on Pt/Si substrates by PLD and radiofrequency beam discharge assisted PLD (RF-PLD) [59]. (001)-oriented films were grown by using the RF-PLD technique. The difference of RF-PLD from a conventional PLD system is the presence of the RF discharge produced by a generator working at 13.5 MHz and a maximum power of 1000 W. The discharge is generated in flowing oxygen between two parallel electrodes and it expands into the ablation chamber through a small aperture in the bottom electrode. The enhanced reactivity at the substrate surface decreases the concentration of oxygen vacancies at the electrode-film interface and reduces the oxygen deficiency in thin films. It was shown that the films prepared by PLD were randomly oriented with coexistence of tetragonal and rhombohedral phases at the MPB composition. On the other hand, films deposited by RF-PLD had rhombohedral structure and were grown in $\langle 001 \rangle$ direction. However, the ferroelectric properties of

these films were not remarkable. P-E hysteresis loop showed very low values of the remnant polarization (below $3 \mu\text{C}\cdot\text{cm}^{-2}$) and coercive field ($5 \text{ kV}\cdot\text{cm}^{-1}$). These values are much lower than bulk values for the same composition ($P_r = 33.6 \mu\text{C}\cdot\text{cm}^{-2}$ and $E_c = 57.6 \text{ kV}\cdot\text{cm}^{-1}$). Due to the high leakage current, porous microstructure, and low breakdown voltage, P-E loops were not saturated. Dielectric constants were reported to be as high as 850 and 1100 for PLD and RF-PLD grown films, respectively [59]. Among BNT based systems, $[\text{Bi}_{0.5}(\text{Na}_{0.7}\text{K}_{0.2}\text{Li}_{0.1})_{0.5}\text{TiO}_3]$ ceramics exhibit a high piezoelectric properties with $d_{33}=231 \text{ pC}\cdot\text{N}^{-1}$, $k_t=0.505$, and $T_d= 130 \text{ }^\circ\text{C}$. Wang et al deposited polycrystalline films with the mentioned composition on Pt/Ti/SiO₂/Si substrates using the PLD technique [56]. P-E loops of the films are depicted in Fig. 2.19. It is seen that the hysteresis loops resemble lossy ferroelectrics and show an offset in the vertical direction, which may be caused by non-switchable domains pinned near the electrode-film interface. The observed remnant polarization P_r was much lower than the ceramic (13.9 versus $37.5 \mu\text{C}\cdot\text{cm}^{-2}$. See inset in Fig. 2.19).

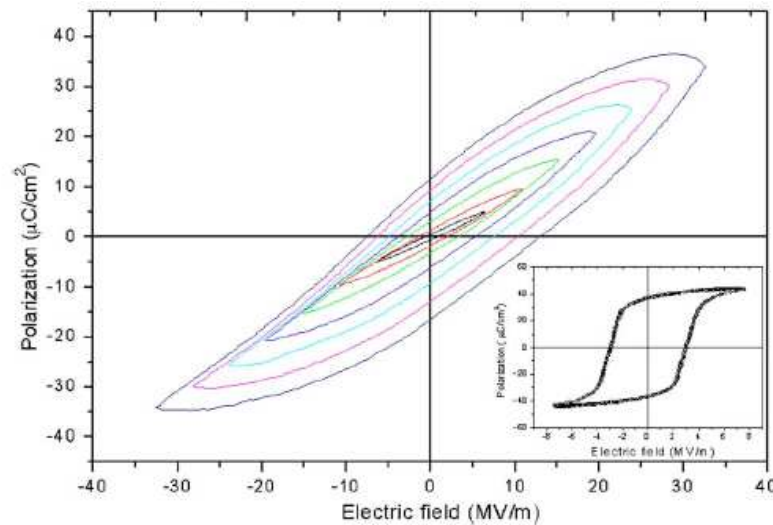


Fig. 2. 19. P-E hysteresis loops of the BNKLT thin film grown on Pt/Ti/SiO₂/Si substrate. The inset is the P-E hysteresis loop of the BNKLT bulk ceramic [56].

Polycrystalline BNT thin films have been deposited on Pt/Ti/SiO₂/Si substrates by sol-gel process using rapid thermal annealing (RTA) [58]. Dielectric constant and dielectric loss at 100 kHz were 277 and 0.02, respectively. The observed remnant polarization and coercive field were 8.3 $\mu\text{C}\cdot\text{cm}^{-2}$ and 200 $\text{kV}\cdot\text{cm}^{-1}$, respectively. Fig. 2.20 shows the surface morphology of the BNT film. It can be seen that the grain sizes ranged from 50 nm to 200 nm. Intergranular porosities were also observed in the film.

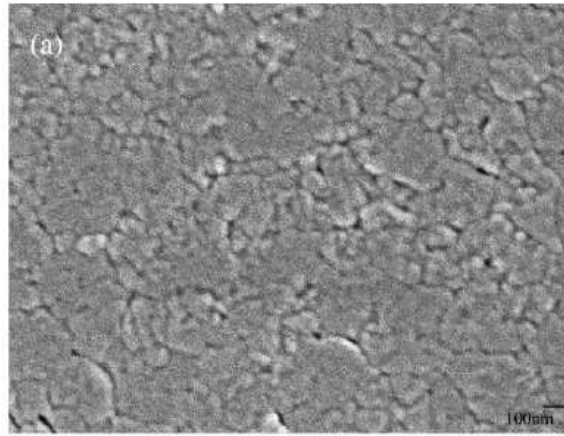


Fig. 2. 20. SEM micrograph showing the top surface of the BNT thin film deposited by sol-gel annealed at 650 °C using RTA [58].

Yu et al also deposited (1-x) BNT-xBKT ($x=0.1, 0.15, 0.18, 0.2$) films by the sol-gel method [68]. They found that at $x=0.15$, films showed better crystallinity, larger grain size, and a relatively high dielectric constant ($\epsilon_r=360$) and remnant polarization (13.8 $\mu\text{C}\cdot\text{cm}^{-2}$). Fig. 2.21 shows the dielectric constant and $\tan\delta$ of these films as a function of frequency.

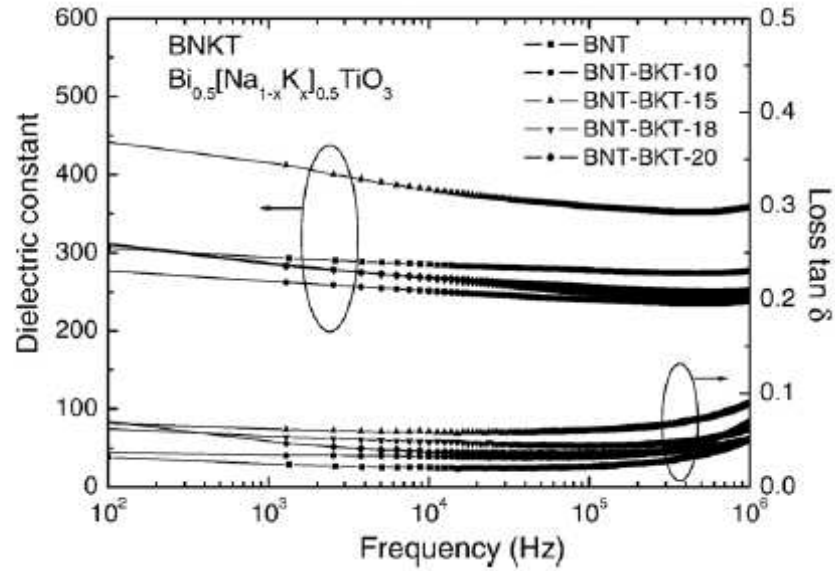


Fig. 2. 21. Dielectric constant and $\tan\delta$ of $(1-x)\text{BNT}-x\text{BKT}$ films ($x=0, 0.1, 0.15, 0.18$ and 0.2) as a function of frequency [68].

Guo et al deposited (001)-oriented $0.94\text{BNT}-0.06\text{BT}$ films on $\text{LaNiO}_3/\gamma\text{-Al}_2\text{O}_3/\text{Si}$ substrates using the chemical solution route. A dielectric constant of 740 and a loss tangent of 5% (at 100 Hz) were obtained (Fig. 2.22 (a)). The remnant polarization was about $15 \mu\text{C}\cdot\text{cm}^{-2}$ as shown in Fig. 2.22 (b) [49].

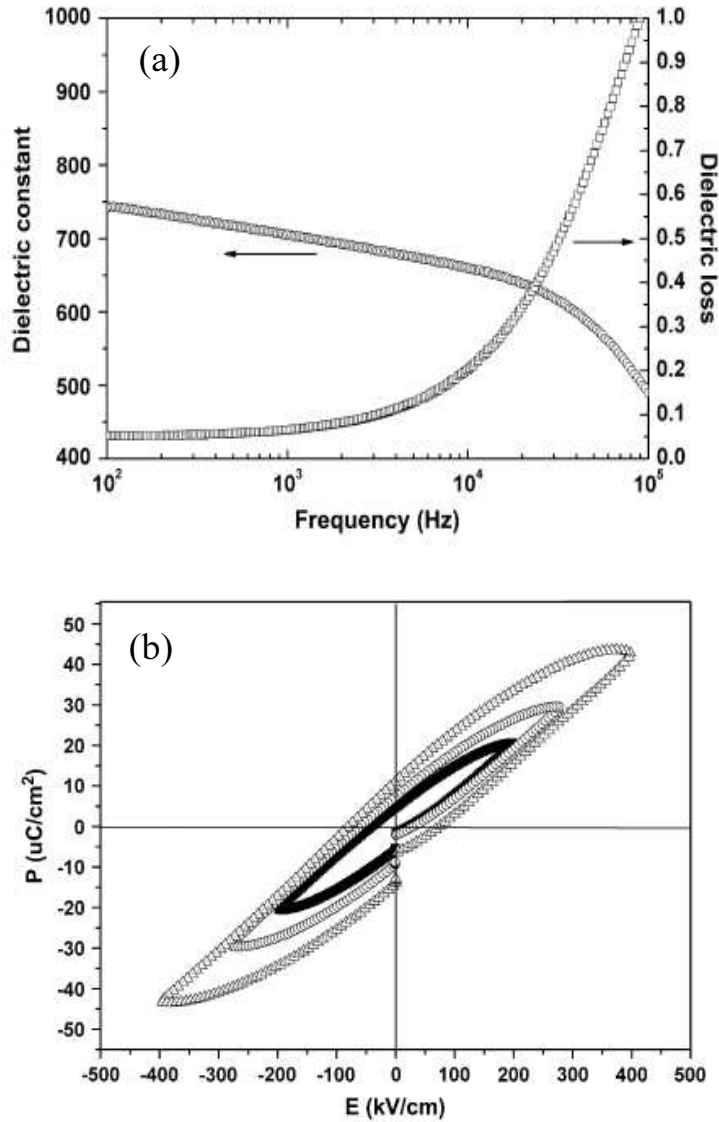


Fig. 2. 22. (a) Frequency dependence of dielectric constant and loss tangent in (001)-oriented 94BNT-6BT thin film (b) P-E hysteresis loop [49].

Guo et al enhanced the electrical properties of 94BNT-6BT on Si substrates by using a trilayer structure rather than a monolayer film. They deposited a thin layer (25 nm) of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ under and above the BNT-BT film. Remnant polarizations of $16 \mu\text{C}\cdot\text{cm}^{-2}$ and pyroelectric coefficient of $4.8 \times 10^{-4} \text{ C m}^{-2} \text{ K}^{-1}$ were reported for the trilayer film [51].

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3 Preparation and Characterization BNT-based Piezoelectric Ceramics

Abstract

Ceramics with six different compositions in ternary systems of BNT-BKT-BT (BNKBT) and BNT-BKT-BLT (BNKLT) were prepared by mixed oxide route and conventional sintering. The dielectric, piezoelectric and electromechanical properties of these ceramics were studied. It was found that 0.88BNT-0.08BKT-0.04BT and 0.76BNT-0.20BKT-0.04BLT ceramics exhibited soft piezoelectric characteristics, i.e. high piezoelectric coefficient, high dielectric constant, high coupling coefficients, and low mechanical quality factor. These ceramics showed a $d_{33} \sim 175 \text{ pC.N}^{-1}$, $\epsilon_r \sim 1000$, and $k_p \sim 0.37$. The main drawback of these compositions was their high dielectric loss. On the other hand, 0.88BNT-0.08BKT-0.04BLT ceramics exhibited hard characteristics i.e. the lowest dielectric and mechanical losses. The mechanical quality factor of this composition was measured to be as high as 400 for the planar vibration mode.

3.1 Introduction

Bismuth sodium titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ abbreviated to BNT) is a ferroelectric material with a perovskite structure. This material was originally reported to possess a rhombohedral symmetry at room temperature. Recent studies by high resolution X-ray diffraction suggested a monoclinic symmetry for this composition [1]. Pure BNT crystals and ceramics show a relatively high Curie temperature ($\sim 320^\circ\text{C}$) and remnant polarization ($\sim 38 \mu\text{C}\cdot\text{cm}^{-2}$). High conductivity along with a very high coercive field ($\sim 73 \text{ kV}\cdot\text{cm}^{-1}$) are major challenges in poling and processing of pure BNT materials [2-14]. To alleviate the poling problem and enhance the piezoelectric and electromechanical properties, binary and ternary solid solutions with different materials such as BaTiO_3 (BT), $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BKT), and $\text{Bi}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ (BLT) have been developed [4, 10, 13, 15, 16]. The morphotropic phase boundary (MPB) compositions separating rhombohedral and tetragonal phases exhibit the highest electromechanical properties which are suitable for soft piezoelectric applications. On the other hand, the rhombohedral structure shows higher mechanical quality factor which is desired for high power applications [12-14, 17].

This chapter presents electromechanical properties of BNT-based ceramics. Six different compositions in ternary systems of BNT-BKT-BT (BNKTBT) and BNT-BKT-BLT (BNKLT) were prepared by mixed oxide route. Compositions with soft and hard piezoelectric characteristics were identified. High power BNT-based transducers, high frequency ultrasonic transducers and BNT-based thin films were developed based on the materials studied in this chapter. The results pertaining to the BNT-based transducers and thin films are provided in the following chapters.

3.2 Experimental Procedures

3.2.1 Powder Synthesis

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based powders with desired compositions were synthesized via conventional mixed oxide route. Table 3.1 shows different compositions studied in this research. Raw materials including high purity oxides and carbonate powders; Bi_2O_3 (Alfa Aesar, 99%), Na_2CO_3 (Alfa Aesar, 99.997%), K_2CO_3 (Alfa Aesar, 99.997%), BaCO_3 (Acros, 99.99%), Li_2CO_3 (Sigma-Aldrich, 99.99%), and TiO_2 (Sigma-Aldrich, 99.9%); were dried overnight at 120 °C in an oven. Then, powders with appropriate molar ratios were milled in acetone and zirconia balls for 24 hours. The batch was then dried and calcined at 800 °C for 3 hours with a heating rate of 300 °C.hr⁻¹. The calcined powders were ball milled again for 12 hours to obtain a uniform homogenous powder.

Table. 3. 1. Chemical composition of synthesized powders and ceramics in this research.

Chemical Composition	Abbreviation
0.88 BNT- 0.08 BKT- 0.04 BT	BNKTB88
0.94 BNT- 0.04 BKT- 0.02 BT	BNKTB94
0.78 BNT- 0.15 BKT- 0.07 BT	BNKTB78
0.76 BNT- 0.20 BKT- 0.04 BLT	BNKLT76
0.88 BNT- 0.08 BKT- 0.04 BLT	BNKLT88
0.68 BNT- 0.28 BKT- 0.04 BLT	BNKLT68

3.2.2 Consolidation and Sintering

8wt.% Poly Vinyl Alcohol solution (PVA) binder was added to the synthesized powder and then sieved through a mesh size of 100. The binder was prepared by stirring and dissolving 20 wt.% of PVA in water at 60 °C. Disk shape samples were uniaxially pressed by a hydraulic machine at 150 MPa in a steel die with diameter of 14 mm. The binder was removed at 550 °C for 2 hours and then samples were sintered at 1150 °C for

2 hours with a heating rate of $300\text{ }^{\circ}\text{C.hr}^{-1}$. The density was calculated by weighing and measuring the dimensions of samples.

3.2.3 Characterization of Ceramics and Powders

X-ray diffraction technique (Cu $K\alpha$ radiation, Panalytical, Model # PW3040, Netherlands) was employed to study the phase and crystal structure of calcined powders and sintered ceramics. The scan was carried out with a step-size of 0.01 degrees and dwell time of 8s per step. The particle size of the powders was evaluated by a laser particle size analyzer (Zetasizer, Nano ZS, Malvern Instruments, UK).

3.2.4 Evaluation of Electrical Properties

Ceramics were mechanically polished to a thickness of less than 1 mm and then were electroded using high temperature silver paste (PELCO®, Ted Pella, CA) diluted in n-Butyl Acetate. The electroded samples were fired at $550\text{ }^{\circ}\text{C}$ for 15 min. Samples were poled by a DC power supply under an electric field of $3.5\text{-}5\text{ kV.mm}^{-1}$ for 15 minutes at a temperature range of $70\text{-}100\text{ }^{\circ}\text{C}$ in silicon oil bath. The electrical properties were measured 24 hours after poling. The dielectric constant ($\epsilon_r = \epsilon_{33}^T / \epsilon_o$) and dielectric loss were measured at 1 kHz by an impedance analyzer HP4194A at an oscillation level of 1 volt. Berlincourt piezo-meter (Channel Products Inc., OH) was utilized to measure the longitudinal piezoelectric charge coefficient (d_{33}) at 100 Hz. Piezoelectric planar and thickness coupling coefficients (k_p and k_t , respectively) were calculated from the resonance and antiresonance frequencies of the impedance traces, based on the IEEE and IRE standards [18, 19]:

$$k_t^2 = \frac{\pi f_s}{2 f_p} \tan \left(\frac{\pi \Delta f}{2 f_p} \right) \quad (3.1)$$

$$\frac{k_p^2}{1 - k_p^2} = \frac{\Delta f}{f_s (1 + \sigma_p)} \left[\left(\sigma_p^2 - 1 + \eta^2 \right) \right] \quad (3.2)$$

Where f_s and f_p are series (resonance) and parallel (antiresonance) frequencies, σ_p is the planar Poisson's ratio and η is frequency constant of disk resonator. The longitudinal coupling coefficient, k_{33} , was estimated from the thickness and planar coupling coefficients according to eq. 3.3:

$$k_{33}^2 = k_p^2 + k_t^2 - k_p^2 k_t^2 \quad (3.3)$$

The clamped dielectric constant ($\epsilon_{33}^s/\epsilon_o$) was also calculated by:

$$\left(\frac{\epsilon_{33}^s}{\epsilon_o} \right) = \left(\frac{\epsilon_{33}^T}{\epsilon_o} \right) (1 - k_t^2) (1 - k_p^2) \quad (3.4)$$

The planar mechanical quality factor (Q_m) at the radial resonance frequency was calculated based on the IRS and IEEE standard with using the following equation:

$$Q_m^{-1} = 2\pi f_s |Z_m| (C_o + C_l) \left(\frac{f_p^2 - f_s^2}{f_p^2} \right) \quad (3.5)$$

Where Z_m is the minimum impedance of the sample, and C_o and C_l are shunt and series capacitance, respectively. The mechanical quality factor was also measured by eq. 3.6:

$$Q_m = \frac{1}{R} \sqrt{\frac{L}{C_a}} \quad (3.6)$$

where R , L and C_a are the resistance, inductance and capacitance of the Van dyke equivalent circuit of a piezoelectric resonator at the resonance frequency as shown in Fig. 3.1. The Van Dyke Model is a parallel connection of a series RLC representing

mechanical damping, mass, and elastic compliance, and a capacitor representing the electrostatic capacitance between the two parallel plates of the piezoelectric patches.

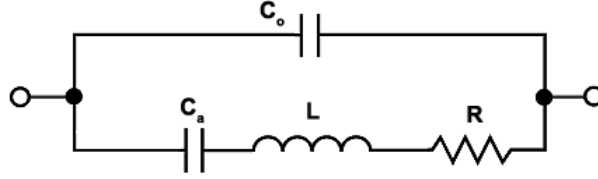


Fig. 3. 1. Van-dyke equivalent circuit of a piezoelectric resonator.

The third method for measuring the Q_m is based on the following equation:

$$Q_m = \frac{f_r}{f_2 - f_1} \quad (3.7)$$

where f_r is the resonance frequency, f_2 and f_1 are the frequencies 3 dB down from the maximum admittance. The results showed that the Q_m values obtained by any of these three methods were very close to each other ($\pm 5\%$). However, the last method seems to be more accurate since the Q_m is directly measured from width of the admittance spectrum and the approximations in obtaining the equivalent circuit parameters are eliminated.

Planar and thickness frequency (N_p and N_t , respectively) constants were obtained from resonance frequency spectra based on the following equations:

$$N_p = f_s^p \cdot 2r, \quad N_t = f_s^t \cdot t \quad (3.8)$$

where r and t are the radius and thickness of a disk-shape piezoelectric resonator. The planar and longitudinal sound velocities (V_p and V_t , respectively) were calculated from antiresonance frequencies and dimension of the sample (l):

$$V = 2f_p \cdot l \quad (3.9)$$

Hysteresis loops were measured using Sawyer-Tower circuit at a pulse width of 200 ms (0.5 Hz frequency) using a triangular wave signal.

For each composition, 5-8 samples were characterized and the average values of electrical properties are reported here.

3.3 Results and Discussion

3.3.1 Calcined Powders

Fig. 3.2 illustrates the X-ray diffraction patterns of BNKLT powder with different chemical compositions calcined at 800 °C for 3 hours. All powders had perovskite structure. BNKLTBT powders also had similar XRD pattern with pure perovskite structure.

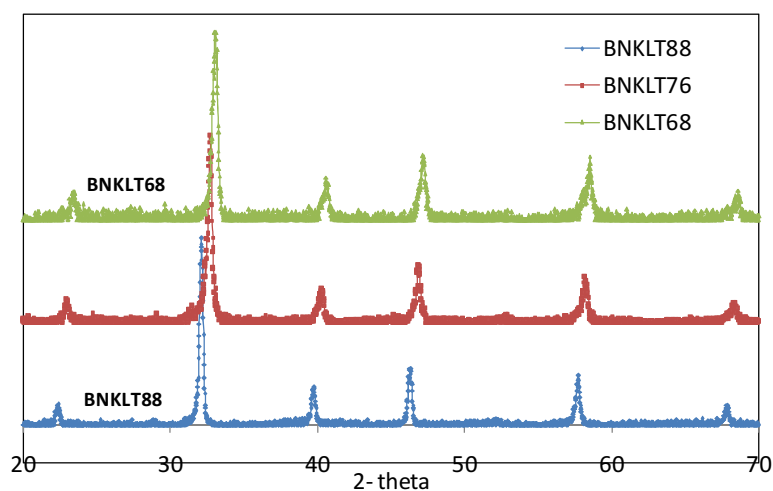


Fig. 3. 2. X-ray diffraction of synthesized BKNLT powder with different compositions calcined at 800 °C for 3 hours.

Fig. 3.3 shows the particle size distribution of BNKLT88 powders. The synthesized powder had an average particle size of about 600 nm. The particle size for powders with other compositions was in the range 550-650 nm.

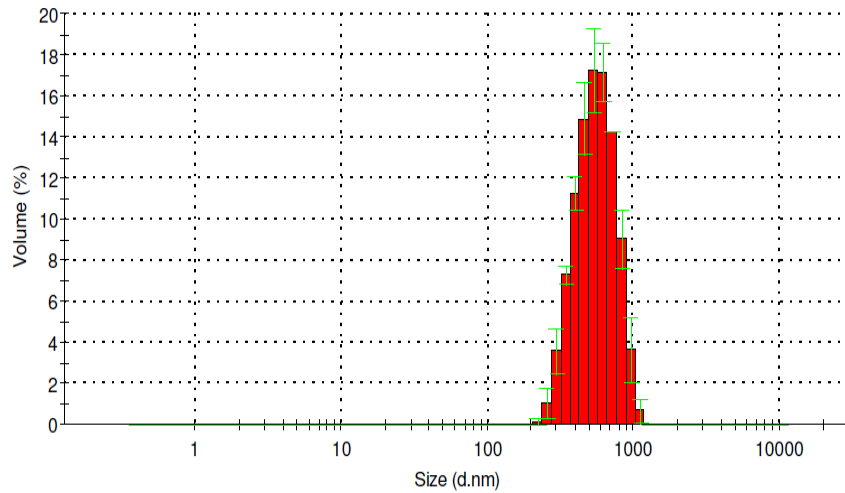


Fig. 3. 3. The particle size distribution of BNKLT88 calcined powders.

3.3.2 BNT-BKT-BT Ceramics

Figs. 3.4 (a)-(c) show the compositional dependence of piezoelectric and dielectric properties in BNKLTBT ceramics. As can be observed in Fig. 3.3 (a), d_{33} increased from 144 to 174 pC.N^{-1} as the composition changed from BNKLTBT78 to BNKLTBT88. Further increase of the BNT concentration declined the d_{33} value to 94 pC.N^{-1} at BNKLTBT94 composition. It was also noticeable that the value of mechanical quality factor (Q_m) for planar mode monolithically increased with BNT concentration in these ceramics. Highest value of Q_m in this ternary system was found to be around 162 which belonged to BNKLTBT94 composition. Variations of thickness and planar coupling coefficients with BNT concentration was similar to d_{33} , i.e. the coupling coefficients were

maximized at BNKTBT88 composition. Values of k_p and k_t for this ceramic were measured to be 0.323 and 0.515, respectively. According to Takenaka [13], BNKTNT88 is the MPB composition between rhombohedral and tetragonal phases in BNT-BKT-BT solid solutions. Therefore, this composition showed the maximum piezoelectric constant and coupling coefficients in this ternary system.

Fig. 3.4 (c) displays the effect of BNT concentration on dielectric properties of BNKTBT ceramics. As the BNT molar fraction increased from 0.78 to 0.94, the dielectric constant and dielectric loss decreased continuously. BNKTBT78 ceramics exhibited the highest dielectric constant ($\epsilon_r \sim 967$), however, a high value of the dielectric loss ($\tan \delta \sim 3\%$) is a drawback for using this ceramic in practical applications. BNKTBT88 composition, on the other hand, showed a relatively high dielectric constant ($\epsilon_r \sim 849$) and a moderate loss ($\tan \delta \sim 2\%$). This composition also showed high values of k_p and k_t and therefore, can be used for soft applications such as sensors.

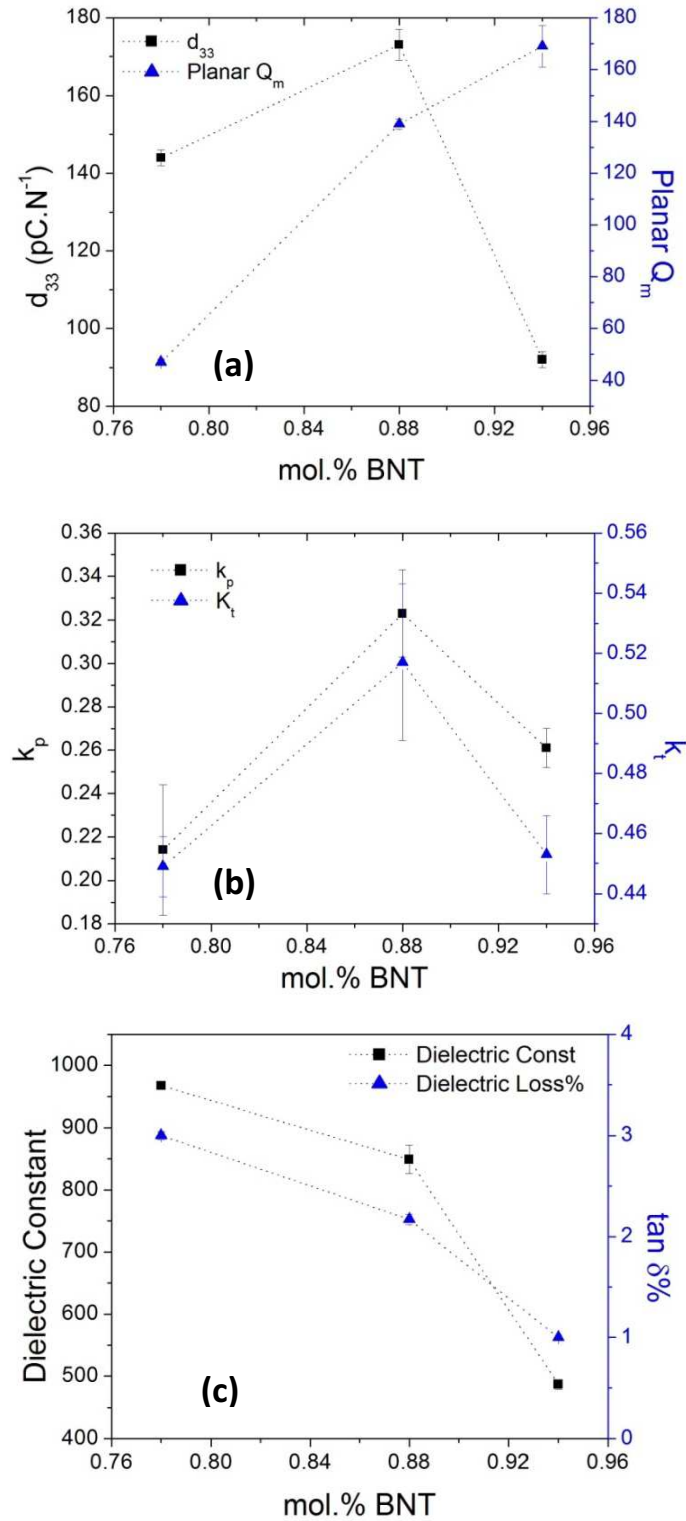


Fig. 3. 4. Effect of BNT molar fraction on (a) piezoelectric charge coefficient (d_{33}) and mechanical quality factor (Q_m), (b) planar coupling coefficient (k_p) and thickness coupling coefficient (k_t), and (c) dielectric properties of $x\text{BNT}-2/3(1-x)\text{BKT}-1/3(1-x)\text{BT}$ ceramics.

3.3.3 BNT-BKT-BLT Ceramics

Figs. 3.5 (a)-(c) illustrate the compositional dependence of planar and thickness coupling coefficients in BNKLT ceramics. k_p and k_t were maximized to 0.367 and 0.522 by increasing the BNT content from 0.68 to 0.76 and then they were dropped to 0.262 and 0.486 at BNKLT88 composition. It has been confirmed that BNKLT76 ceramics is the MPB composition between rhombohedral and tetragonal phases [14]. Similar to BNKLTBT ceramics, the dielectric constant and loss in BNKLT system decreased with BNT concentration. The highest dielectric constant of 1220 was obtained in BNKLT68 composition with a loss tangent of about 4%. On the other hand, BNT-rich composition (BNKLT88) showed the lowest dielectric loss ($\tan\delta \sim 1.1\%$) and dielectric constant ($\epsilon_r \sim 380$). The permittivity and dielectric loss of BNKLT76 composition which had the highest values of coupling coefficients were slightly less than BNKLT68 composition. The effect of BNT concentration on d_{33} and Q_m values of BNKLT ceramics is depicted in Fig. 3.5 (c). As observed in this figure, there was a trade-off between d_{33} and Q_m . The BNKLT76 composition showed characteristics of a soft piezoelectrics with a high d_{33} of 175 pC.N^{-1} and a low Q_m value of 97. The BNKLT76 and BNKLTBT88 compositions are potential alternative replacements for lead-based materials in sensor applications. On the other hand, BNKLT88 ceramic exhibited the highest value of Q_m (~ 400) among all studied composition while the d_{33} was measured to be 92 pC.N^{-1} . This hard piezoceramic with a relatively low dielectric loss of about 1.1% is suitable for high power applications such as ultrasound motors and transformers where high mechanical quality factor and low dielectric loss are desired to minimize the heat generation and mechanical loss during the operation.

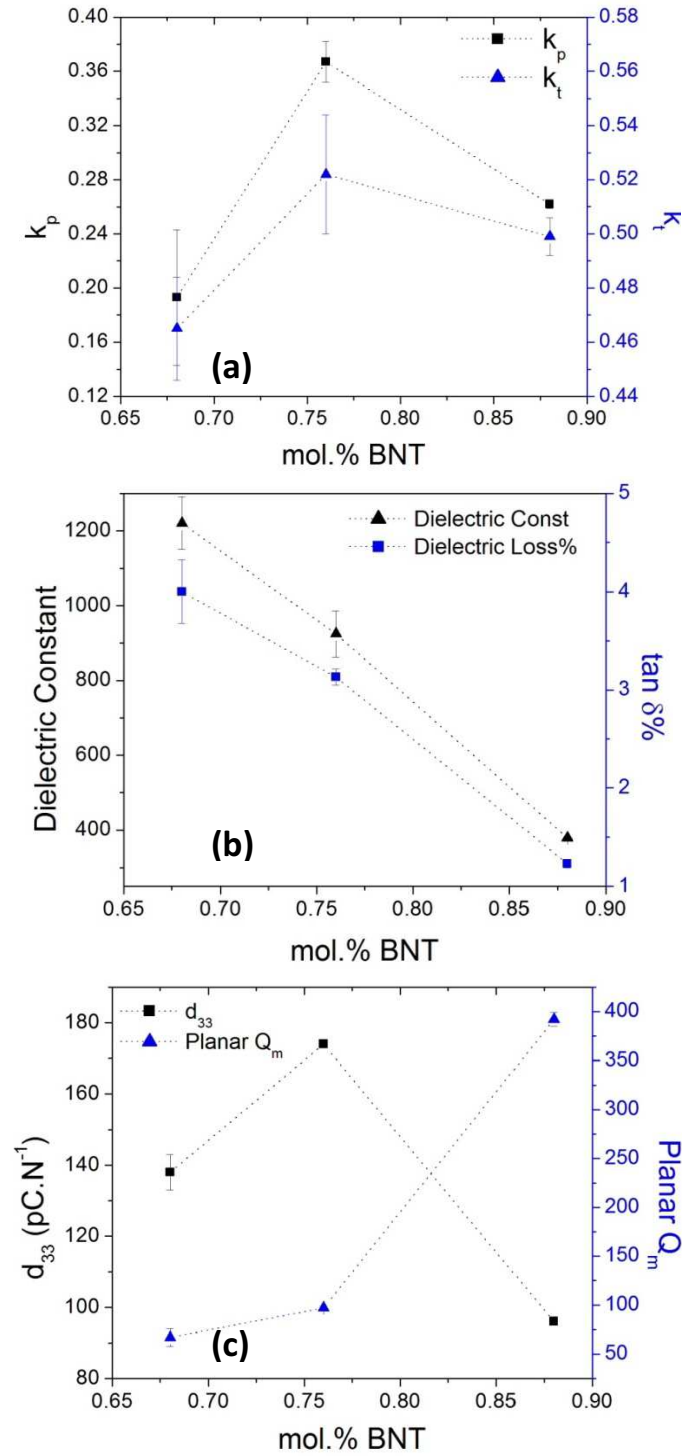


Fig. 3. 5. Effect of BNT molar fraction on (a) planar coupling coefficient (k_p) and thickness coupling coefficient (k_t), (b) dielectric properties, and (c) piezoelectric constant (d_{33}) and mechanical quality factor (Q_m) of xBNT-(0.96-x)BKT-0.04BLT ceramics.

Fig. 3.6 shows the P-E hysteresis loops of BNKLT88 and BNKLT76 ceramics at room temperature. The ceramic with composition on the rhombohedral side of the phase diagram (BNKLT88) showed higher coercive field ($E_c \sim 47 \text{ kV.cm}^{-1}$) and lower polarization compared to the MPB ceramics (BNKLT76). The remnant polarization for rhombohedral and MPB compositions were 35 and $41 \mu\text{C.cm}^{-2}$, respectively. The coercive field for BNKLT76 composition was 27 kV.cm^{-1} .

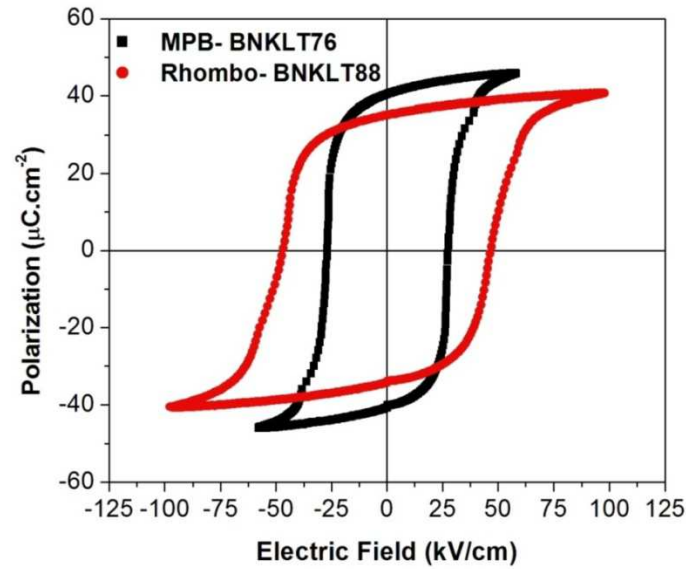


Fig. 3. 6. The P-E hysteresis loops of BNKLT88 and BNKLT76 ceramics at room temperature.

3.4 Summary

In Fig. 3.7, the relationship between d_{33} and Q_m has been mapped for all compositions studied in this work. Ceramics with high d_{33} and low Q_m fall in the upper left side of the figure. These compositions are suitable for sensors and actuators applications where maximum sensitivity is required. On the other hand, the BNKLT88 ceramic with a high Q_m , low d_{33} , (also high depolarization temperature ($\sim 220^\circ\text{C}$) [13], and high E_c) is placed on the lower right side of the graph. This composition can be used in high power applications such as ultrasonic motors where minimal heat generation and high output power are demanded.

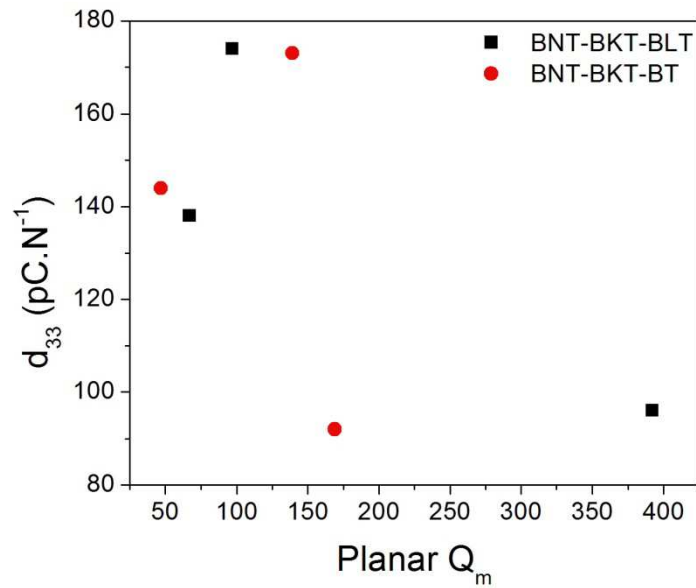


Fig. 3. 7. Piezoelectric charge coefficient (d_{33}) versus mechanical quality factor (Q_m) in BNT-based ceramics.

Table 3.2 summarizes the piezoelectric, dielectric and the acoustic properties of BNKLTBT and BNKLT ceramics. The electrical properties are similar to those reported by Takenaka and Hiruma et al [13, 14]. Substitution of Li in the A-site of BNT-based

ceramics not only enhanced the dielectric and piezoelectric properties, but also increased the mechanical quality factor. The only disadvantage of BNKLT ceramics compared to BNKLTBT is higher dielectric loss at the MPB composition. The electrical properties of lead-free BNKLT system can be tailored by changing the ratio of Li, Na, and K monovalent cations to achieve hard or soft piezoelectric characteristics. These ternary systems can be regarded as promising candidates for both high power and actuator applications.

Table. 3. 2. Piezoelectric, dielectric and acoustic properties of lead-free BNKLT and BNKLTBT ceramics.

Composition	BNKLT68	BNKLT76	BNKLT88	BNKLTBT78	BNKLTBT88	BNKLTBT94
Density (g.cm ⁻³)	5.68±0.05	5.89±0.05	5.76±0.01	5.77±0.03	5.80±0.04	5.83±0.05
$\epsilon_{33}^T/\epsilon_0$	1220±70	925±62	379±2	967±3	849±23	487±8
$\epsilon_{33}^S/\epsilon_0$	920±46	581±24	271±4	737±5	559±16	361±5
tan δ%	4±0.32	3.13±0.08	1.23±0.04	3±0.04	2.17±0.05	1.00±0.02
d₃₃ (pC.N⁻¹)	138±5	174±1	96±1	144±2	173±4	92±2
k_t	0.465	0.522	0.499	0.449	0.517	0.453
k_p	0.193	0.367	0.262	0.214	0.323	0.261
k₃₃	0.495	0.606	0.547	0.488	0.573	0.489
Planar Q_m	67±9	97±2	392±7	47±1	139±2	169±8
V_t (m.s⁻¹)	5206±24	5298±36	5520±31	5085±28	5209±15	5312±33
Z (M Rayl)	29.25±0.19	31.20±0.26	31.78±0.16	29.35±0.15	30.21±0.36	30.96±0.48
N_t (m.Hz)	2329±38	2401±26	2463±31	2316±9	2443±30	2499±23
N_p (m.Hz)	3019±5	3113±6	3161±5	2981±3	3039±4	3051±5

* The standard deviation for k_t, k_p, and k₃₃ is about 0.02, 0.01, and 0.02, respectively.

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4 Processing, Electromechanical Properties, and High Power

Characteristics of Hard BNT-based Ceramics

Abstract

This chapter presents the results pertaining to the development of hard lead-free BNT-based piezoceramics. Different amounts of Mn (0.01, 0.014, 0.015, 0.016, 0.017, 0.02, and 0.022) or Fe (0.0125, 0.015, 0.0175) were added to the $0.88[\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3]$ - $0.08[\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3]$ - $0.04[\text{Bi}_{0.5}\text{Li}_{0.5}\text{TiO}_3]$ ceramics prepared by mixed oxide route either in form of a dopant (B-site substitution) or an additive. Samples were sintered at different temperatures (1075-1150 °C) to achieve the highest density and mechanical quality factor (Q_m). It was found that Mn-addition did not exhibit any hardening effect and in fact led to a significant increase in the dielectric loss. On the other hand, Mn or Fe-doping resulted in a considerable enhancement of Q_m in both planar and thickness vibration modes. A planar Q_m of about 970 and $\tan\delta$ of 0.88% were obtained in 1.5 mol.% Mn-doped ceramics sintered at 1100 °C. In Fe-doped ceramics, planar Q_m as high as 900 was achieved. Acceptor dopants also resulted in decreasing coupling coefficients, piezoelectric charge coefficient, and dielectric constant. The performance of the undoped and Mn-doped transducers for high power applications was studied using a constant vibration velocity set-up. The high drive measurements showed that Mn-doping remarkably reduced the heat generation and resulted in a higher maximum vibration velocity compared to the undoped samples. The BNKLT88 ceramic doped with 1.5 mol.% Mn exhibited the best performance under high drive conditions with a maximum vibration velocity of 0.6 m.s^{-1} .

4.1. Introduction

For high power applications such as ultrasonic motors and cleaners, high power sonar, piezoelectric transformers, high intensity focused ultrasound (HIFU), and actuators, minimum heat generation and maximum output power are desired. Piezoelectric ceramics with a high mechanical quality factor, low dielectric and mechanical losses, a high coercive field, and increased energy density (reduced size) are suitable materials for high power applications [1]. The low mechanical and dielectric losses in hard ferroelectrics prevent dissipation of energy in form of the heat and hence, increase the efficiency of the device. According to the eq. (4.1), the power loss per unit volume (w) is inversely proportional to the mechanical quality factor [2]:

$$w = \frac{1}{2} \omega s^E T^2 Q_m^{-1} \quad (4.1)$$

where ω is angular resonance frequency, T is stress, and s^E is elastic compliance.

In lead-based ceramics such as PZT, hard compositions have been developed by adding acceptor dopants such as $\text{Mn}^{2+,3+}$, $\text{Fe}^{2+,3+}$, and Cr^{3+} particularly in the B-site of the perovskite structure [3-5]. Acceptor dopants with a lower valance than the host cations (e.g. Zr^{4+} and Ti^{4+}) create oxygen vacancies to maintain the charge neutrality. Oxygen vacancies are interconnected with the oxygen atoms located at the octahedral sites. The oxygen vacancies, therefore, are able to diffuse to the domain walls during the sintering or even at lower temperatures [5, 6]. These positively charged oxygen vacancies may also form oriented dipoles with negatively charged acceptor sites. These defect dipoles are known to reduce the extrinsic ferroelectric contribution by pinning the domain walls [2, 5-7]. The domain wall pinning in acceptor-doped piezoelectrics is accompanied by formation of wavy domains instead of a regular domain configuration [5]. Consequently,

addition of acceptor dopants decreases the piezoactivity of the ferroelectrics but results in a considerable enhancement of the mechanical quality factor as well as the coercive field. A built up internal bias field in the direction of the spontaneous polarization also increases the mechanical quality factor through stabilization of the ferroelectric domains [4-9]. The diffusion of the oxygen vacancies is necessary for building up the internal bias. Since the diffusion phenomenon is a thermally activated process, the generation of the internal bias takes up to several hours [6, 7]. The internal bias field prohibits the domain wall motion and is recognized by an imprint or a horizontal shift in P-E hysteresis loops [8, 10]. Donor dopants such as Nb^{5+} , on the other hand, induce soft piezoelectric characteristics by creating A-site vacancies and randomly distributed point defects [5]. Donor-doped electroceramics possess high electromechanical and piezoelectric coefficients but low coercive field and mechanical quality factor which are not desired for high power applications. These materials are suitable for sensors and acoustic transducers where a wide bandwidth (wide range of receiving signals) is required [6].

The mechanical quality factors of piezoceramics reported in the literature are measured under low drive condition (0.5-1 V) by an impedance analyzer. In order to utilize these materials in high power applications, their performance under high drive conditions needs to be studied. The figure of merit for high power applications is the vibration velocity which is proportional to the product of mechanical quality factor and electromechanical coefficient. High values of vibration velocity are desired for high power applications to decrease the temperature rise and obtain a high output power. The vibration velocity (v_0) is defined as the product of angular resonance frequency (ω) and the root mean square (rms) of maximum vibration amplitude ϵ_m [2, 5, 7, 11, 12]:

$$v_o = \frac{1}{\sqrt{2}} \omega \epsilon_m = \frac{4}{\pi} \sqrt{\frac{\epsilon_{33}^T}{\rho}} (k_{31} Q_m) \cdot E \quad (4.2)$$

where ρ is the density, ϵ^T is the relative permittivity, and E is the driving electric field.

In the longitudinal vibration mode, the off-resonance displacement is equal to $d_{33} \cdot E \cdot L$ (where L is the length of the sample). At the resonance frequency, the displacement is amplified by a factor of $8/\pi Q_m$ which again shows the importance of Q_m for high power applications at the resonance frequency [6, 7, 11, 12]. Materials with a high Q_m , high E_c , low $\tan \delta$ and high k_{ij} values are the best candidates for high power applications. However, it is vital for a hard piezoceramic to maintain its high Q_m and low $\tan \delta$ at high vibration velocities i.e. under application of a high electric field. It is known that the Q_m abruptly decreases as the vibration velocity surpasses a critical value. Materials with a high vibration velocity at lower AC fields are preferred for high power applications [5]. The decline of the Q_m and heat generation at high levels of vibration are accompanied by a sharp increase in the dielectric, mechanical and piezoelectric losses. Fig. 4.1 shows the mechanical quality factor and temperature rise as a function of vibration velocity in PZT samples excited at 31 mode [11, 13]. In this figure, the curves labeled A and B correspond to the mechanical quality factors measured at the resonance (Q_A) and antiresonance (Q_B) frequencies, respectively. After a certain level of vibration velocity (about 0.1 m.s^{-1}), Q_m decreased abruptly and there was a steep temperature rise on the surface of the sample. At higher vibration velocities with increasing the applied electric field, the input power converts to the heat and therefore, there is no increase in the output power. In PZT materials, it is reported that with increasing the vibration level, the contribution of the dielectric loss becomes more significant than mechanical loss. In other words, the vibration velocity dependence of dielectric loss is higher than the

mechanical loss [11]. It is notable that less heat is generated in antiresonance mode compared to the resonance mode. This is useful in fabrication of devices with low driving current and high driving voltage [13].

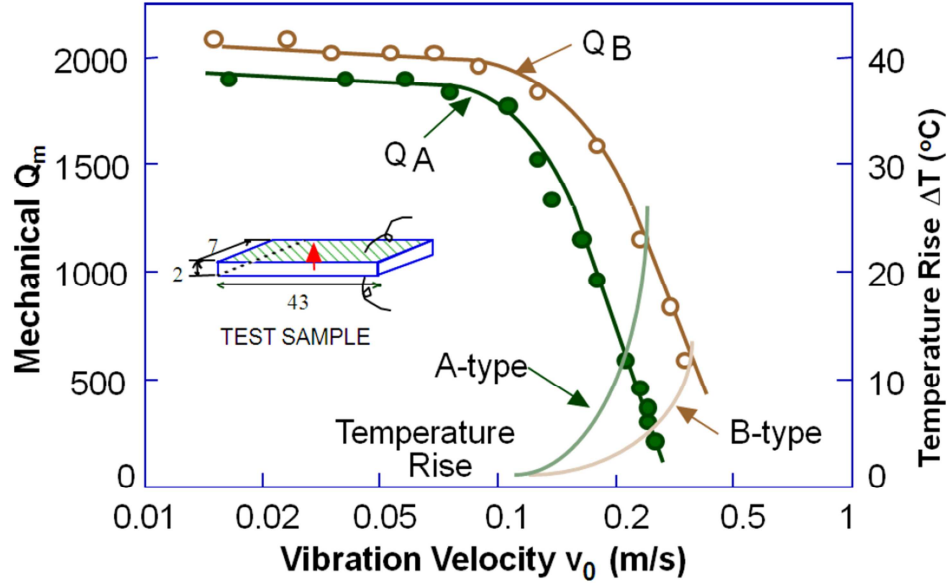


Fig. 4. 1. Vibration velocity dependence of the mechanical quality factors Q_A and Q_B , and corresponding temperature rise for resonance and antiresonance frequencies of a PZT ceramic vibrating at 31 mode [11, 13].

In general, there are three types of losses in piezoelectrics including the mechanical (elastic), dielectric and piezoelectric (electromechanical) losses [12-14]. In the phenomenological theory of piezoelectrics, these dissipation factors are taken into account by introduction of complex functions containing an imaginary part. The loss is expressed in form of a phase delay in the imaginary part of the complex function. [6, 13]. In this context, the intensive properties refer to those measured while an external force (such as stress or electric field) is kept constant. From thermodynamics point of view, the

intensive properties are independent of the size of the system. On the contrary, the extensive properties represent those measured while a response (such as the strain or electric displacement) is maintained constant during the measurement [14]. In practice, intensive losses are measurable [6]. Equations 4.3 (a)-(c) describe the intensive dielectric, elastic, and piezoelectric losses, respectively

$$\varepsilon^{X*} = \varepsilon^X (1 - j \tan \delta') \quad (4.3 \text{ a})$$

$$s^{E*} = s^E (1 - j \tan \phi') \quad (4.3 \text{ b})$$

$$d^* = d (1 - j \tan \theta') \quad (4.3 \text{ c})$$

where ε^X is the permittivity measured at constant stress, s^E is the elastic compliance measured at constant electric field, d is the piezoelectric coefficient, δ' , ϕ' , and θ' are the phase delays between the drive and the response in D-E (stress-free condition), x-X (Electric field constant), and x-E (stress-free condition) or D-x (Electric field constant) hysteresis loops, respectively [12, 14]. In this context, D is electric displacement, x is strain, X is stress, and E is electric field. The tangent of these phase delays are defined as intensive losses. For an instance, the intensive dielectric loss $\tan \delta'$ is related to the D-E hysteresis loop shown in Fig. 4.2.

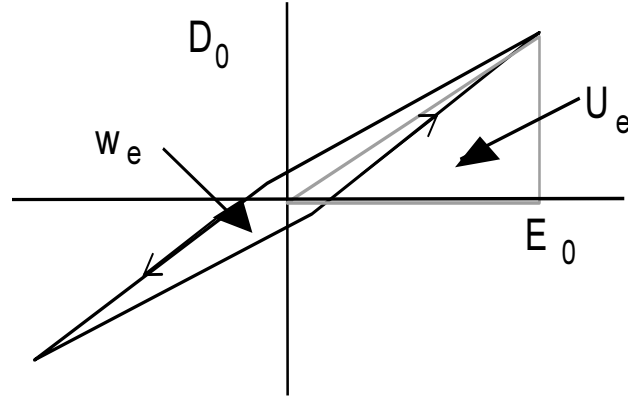


Fig. 4. 2. Electric displacement-electric field (D-E) hysteresis loop in a stress-free condition for obtaining the intensive dielectric loss [13, 14].

The hysteresis area W_e correspond to the energy loss during one cycle of electric field application on a dielectric material.

$$w_e = - \int D dE = - \int_0^{2\pi/\omega} D \left(\frac{dE}{dt} \right) dt = \pi E_0 D_0 \sin \delta' = \pi \varepsilon'' \varepsilon_0 E_0^2 = \pi \varepsilon' \varepsilon_0 E_0^2 \tan \delta' \quad (4.4)$$

In the absence of any phase delay, the dielectric energy loss will be equal to zero. This phase delay will also appear in the polarization response which oscillates with the same frequency as the applied field:

$$E^* = E_0 e^{j\omega t} \quad (4.5)$$

$$D^* = D_0 e^{j(\omega t - \delta')} \quad (4.6)$$

The stored energy in one cycle of the D-E loop is equal to $4U_e$ (Fig 4.2):

$$4U_e = 1/2(2E_0)(2\varepsilon' \varepsilon_0 E_0) = 2\varepsilon' \varepsilon_0 E_0^2 \quad (4.7)$$

With comparing the equations (4.4) and (4.7) it is concluded that the $\tan \delta'$ can be experimentally measured from the D-E hysteresis curve as follows [13]:

$$\tan \delta' = \left(\frac{1}{2\pi} \right) \left(\frac{W_e}{U_e} \right) \quad (4.8)$$

with considering the complex nature of D^* and E^* , the dielectric property will be essentially a complex function as pointed out earlier:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad (4.9)$$

$$\frac{\varepsilon''}{\varepsilon'} = \tan \delta' \quad (4.10)$$

Similar analysis can be applied to correlate the intensive mechanical and piezoelectric losses to the hysteresis loops. A detailed mathematical treatment can be found in Refs [6, 12, 13].

If the hysteresis measurements are carried out under different boundary conditions (i.e. constant electric displacement and constant strain instead of constant electric field and constant stress), then the extensive losses can be defined in a similar manner to the intensive losses. The extensive dielectric loss $\tan \delta$, for example, can be expressed as:

$$\varepsilon^{x*} = \varepsilon^x (1 - j \tan \delta) \quad (4.11)$$

It can be proved that the intensive and extensive losses are related through the electromechanical coupling coefficient (k): [6, 12]

$$\tan \delta' = \frac{1}{1-k^2} [\tan \delta + k^2 (\tan \emptyset - 2 \tan \theta)] \quad (4.12)$$

$$\tan \emptyset' = \frac{1}{1-k^2} [\tan \emptyset + k^2 (\tan \delta - 2 \tan \theta)] \quad (4.13)$$

$$\tan \theta' = \frac{1}{1-k^2} [\tan \delta + \tan \emptyset - (1 + k^2) \tan \theta] \quad (4.14)$$

It is notable in these equations that any individual intensive loss is correlated to all extensive dissipation factors i.e. the extensive dielectric, mechanical and piezoelectric losses. It is experimentally demonstrated that among different extensive losses, the dielectric loss increases more rapidly with an applied electric field [6, 12].

These losses basically origin from domain wall motion, the lattice contribution (mono domains), microstructure (polycrystalline ceramics), and conductivity in ohmic ceramics [6]. In piezoelectric ceramics, the internal friction caused by domain wall motion is more significant than the other mechanisms. With increasing the vibration velocity, the contribution of individual loss mechanisms to the overall loss is changed. The elastic nonlinearity at high electric fields also become significant [12, 15]. Since the dominant loss mechanisms under low and high vibration velocities are different, it is possible that a high Q_m material at low electric field loses its hard characteristics at high electric fields. In PZT system, for example, the mechanical quality factor was measured as a function of Zr molar fraction as shown in Fig. 4.3 [6, 11].

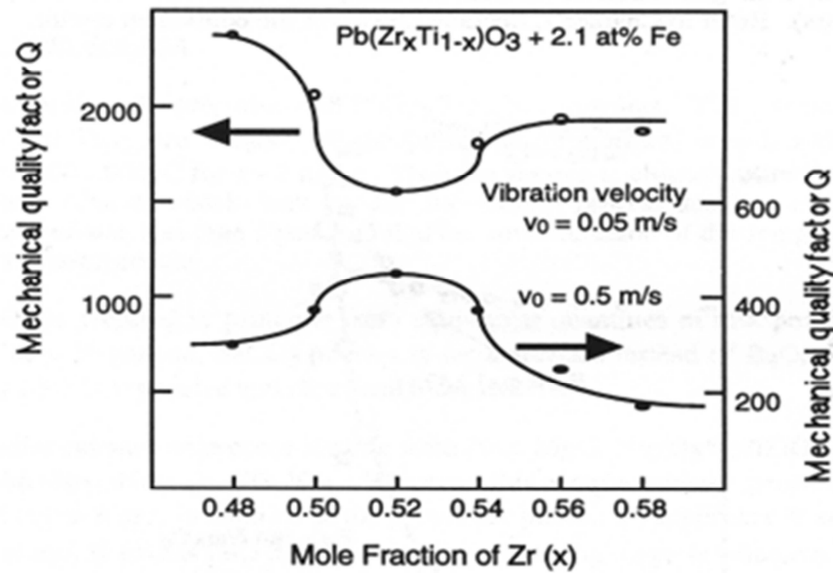


Fig. 4. 3. The composition dependence of the mechanical quality factor in Fe-doped PZT ceramics under low (0.05 m.s^{-1}) and high (0.5 m.s^{-1}) vibration velocities [11].

At a low vibration velocity, the lowest Q_m occurred in the vicinity of the morphotropic phase boundary. However, at a high vibration velocity, the MPB composition showed the highest Q_m compared to other compositions. In other words, composition with the lowest Q_m under low drive condition became the best material (highest Q_m) under high drive condition. This happens due to the fact that different mechanisms become responsible for the loss as the vibration velocity is increased. Under low drive conditions, the extensive mechanical loss is the dominant mechanism. The mechanical loss is basically originated from the motion of non- 180° domain walls. The extensive mechanical loss is less sensitive to the variations of an external force. On the other hand, the extensive dielectric loss becomes prevailing at high levels of vibration velocity [12]. The movement of 180° domain walls is accountable for extensive dielectric loss. Fig. 4.4 shows the effect of vibration velocity on the motional resistance (R_m) and

damped resistance (R_d) of the equivalent circuit of a piezoelectric material. Note that R_d is related to the dielectric loss and R_m is inversely proportional to the mechanical quality factor and directly proportional to the mechanical loss. The damped resistance sharply increases with the vibration velocity indicating that the overall loss at a high vibration level is mainly attributed to the dielectric loss [11, 12].

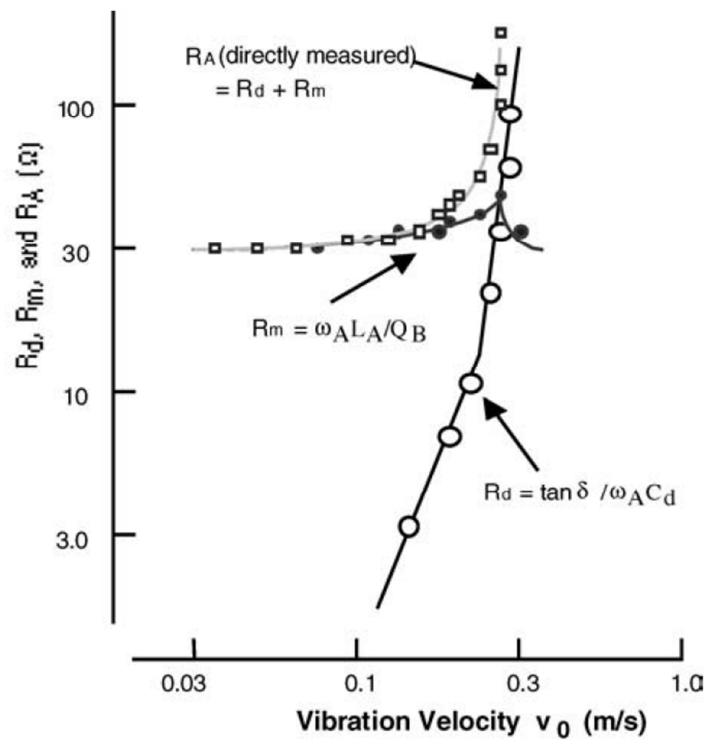


Fig. 4. 4. The influence of the vibration velocity on the motional resistance (R_m) and damped resistance (R_d) of the equivalent circuit of a piezoceramic [11].

This is agreement with the polarization reversal model proposed by Uchida-Ichida as illustrated in Fig. 4.5. This model shows the concept of domain reversal for 180° and 90° domain walls under application of an electric field. The vertical axis shows the percentage of the domain reversal which is an indication of polarization and strain

evolution for 180° and 90° domains, respectively [16]. While the 90° domains are switched gradually, the reversal of the 180° domains occurs rapidly when an electric field is applied. The suppression of the domain wall motion is, therefore, the essential key for high power applications. This can be achieved either by the domain wall pinning or through development of internal bias field [5]. Grain boundaries in a polycrystalline ceramic have similar pinning effect as dipole defects. Therefore, the grain size refinement can be considered as another method for enhancing the mechanical quality factor and the vibration velocity under an applied electric field [15].

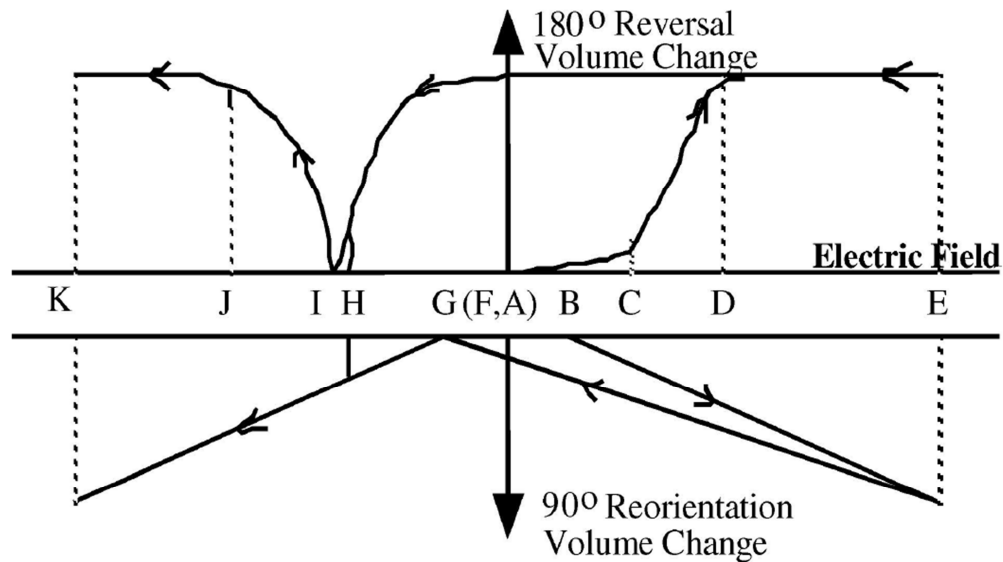


Fig. 4. 5. Uchida-Ichida model illustrating the 180° and 90° domains reorientation in polycrystalline ferroelectrics subjected to an applied electric field.

Based on the aforementioned discussion, the Q_m measurement by an impedance analyzer does not provide an accurate insight on high power performance of materials.

Consequently, it is required to directly evaluate the performance of hard piezoelectrics under high vibration velocities.

It has been demonstrated that the temperature rise in PZT ceramics can be suppressed by addition of acceptor dopants while it is increased through addition of donor dopants [11]. Acceptor dopants such as Mn and Fe [17-19], therefore, improve both low-drive and high-drive characteristics of hard piezoceramics. In lead-free materials such as BNT and KNN based compositions, the mechanical quality factor can be similarly enhanced by addition of acceptor dopants [20]. In KNN-based ceramics, Cu-doping and addition of sintering aids such as $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$ (KCT), $K_4CuNb_8O_{23}$ (KCN), and $K_{1.94}Zn_{1.06}Ta_{5.19}O_{15}$ (KZT) has been reported to improve the densification by forming a liquid phase during the sintering step. Q_m values as high as 1500 have been achieved in these ceramics [4, 8, 21]. However, there is limited information available on hard BNT-based ceramics. Tou et al [22] reported a Q_m of about 500, Curie temperature of 260 °C and a dielectric constant of 520 in $0.82(Bi_{0.5}Na_{0.5})TiO_3$ - $0.15BaTiO_3$ - $0.03(Bi_{0.5}Na_{0.5})(Mn_{1/3}Nb_{2/3})O_3$ solid solution. This composition was successfully used in fabrication of ultrasonic cleaners [22]. Nagata [20] and Takenaka [23] showed that the mechanical quality factor of BNKLT88 ceramics with a depolarization temperature of 220 °C [24] was increased up to 700 by Mn addition. However, in their paper, no detailed explanation on the processing of those ceramics was provided. Furthermore, it was not clear if Mn was incorporated into the lattice as an acceptor dopant or whether it was added as an additive. Mn has been added or doped into several BNT-based ceramics with MPB composition. However, the Q_m of these materials was not higher than 150-300 [25-29]. Very recently, 1 wt.% Co_2O_3 -doped $0.83BNT$ - $0.084BKT$ - $0.03BLT$ - $0.056BT$

ceramics with a mechanical quality factor of about 800 were developed [2]. This was the highest Q_m value reported in BNT-based ceramics till publication date of this chapter.

In this chapter, a systematic and comprehensive processing-property relationship in acceptor-doped BNKLT88 ceramics is reported. Mn^{2+} and Fe^{3+} were added as acceptors. Different amounts of Mn were added to the $0.88[Bi_{0.5}Na_{0.5}TiO_3]-0.08[Bi_{0.5}K_{0.5}TiO_3]-0.04[Bi_{0.5}Li_{0.5}TiO_3]$ ceramics prepared by mixed oxide route. Mn was added either in form of a dopant (B-site substitution) or an additive (added as extra amount). Fe-doped ceramics were also prepared to compare the results with Mn-doped samples. The high power characteristics of Mn-doped ceramics were also evaluated. The resonance frequencies, mechanical quality factor, and heat generation were measured under high drive conditions.

4.2 Experimental Procedure

4.2.1 Powder and Ceramic Preparation

BNKLT88 powders were prepared via mixed oxide route by calcination at 800 °C for 3 hours with the same conditions as explained in chapter 2. Several batches containing Mn or Fe were prepared. Mn and Fe were added in two different forms:

I) Manganese as an additive: In this case, Mn was added as an extra additive. In other words, the addition of Mn was not compensated by a reduction in Ti amount. The synthesized composition was $(BiNa_{0.88} K_{0.08} Li_{0.04})_{0.5}TiO_3 + x \text{ mol.}\% \text{ Mn}$ ($x=0.01$ and 0.02). Manganese was added either in form of $MnCO_3$ (Alfa Aesar, 99.9%) or MnO_2 (Fisher, 99%) before the calcination step.

II) Manganese or iron as a dopant: In this case, the B-site element (Ti) was partially replaced by an acceptor dopant (Mn or Fe). The synthesized compositions were $(\text{BiNa}_{0.88} \text{K}_{0.08} \text{Li}_{0.04})_{0.5} \text{Ti}_{1-x} \text{Mn}_x \text{O}_3$ ($x=0.01, 0.014, 0.015, 0.016, 0.017, 0.02, 0.022$) and $(\text{BiNa}_{0.88} \text{K}_{0.08} \text{Li}_{0.04})_{0.5} \text{Ti}_{1-x} \text{Fe}_x \text{O}_3$ ($x=0.0125, 0.015, 0.0175$). MnCO_3 was used as source of Mn and was mixed with other raw materials before the calcination. Fe was added in form of Fe_2O_3 .

Calcined powders were mixed with 8 wt.% PVA solution and pressed at 150 MPa. The pellets were sintered at different temperatures (1075, 1100, 1125, and 1150 °C) for 2 hours after the binder removal at 550 °C.

4.2.2 Evaluation of Electrical Properties

The ceramics were prepared for electrical characterization as described in chapter 3. Samples were poled at 85-95 °C under an applied electric field of 5 kV.mm⁻¹ for 15 minutes. The dielectric and electromechanical properties were measured by an impedance analyzer as explained in the previous chapter.

4.2.3 High Power Measurements

High power measurements can be implemented at different modes such as transient (burst) and equilibrium (continuous). Continuous excitation mode can be implemented by keeping voltage, current, power, and vibration velocity constant. Ref [13] explains the advantages and disadvantages of each technique. The constant voltage and constant current modes can be utilized to measure the Q_m at antiresonance (Q_A) and resonance (Q_B) frequencies, respectively. However, in practice, the current and voltage

are not perfectly constant at these fundamental frequencies [13]. In general, the constant vibration velocity mode is preferred over other techniques because of the higher accuracy, elimination of admittance spectrum distortion (which was observed under constant voltage mode), and the opportunity to simultaneously measure the resonance and antiresonance frequencies in a single set of experiments. Therefore, the constant vibration velocity technique was selected to study the high power characteristics of hard BNT-based piezoceramics in this research. The experimental setup of high power measurements is schematically shown in Fig. 4.6.

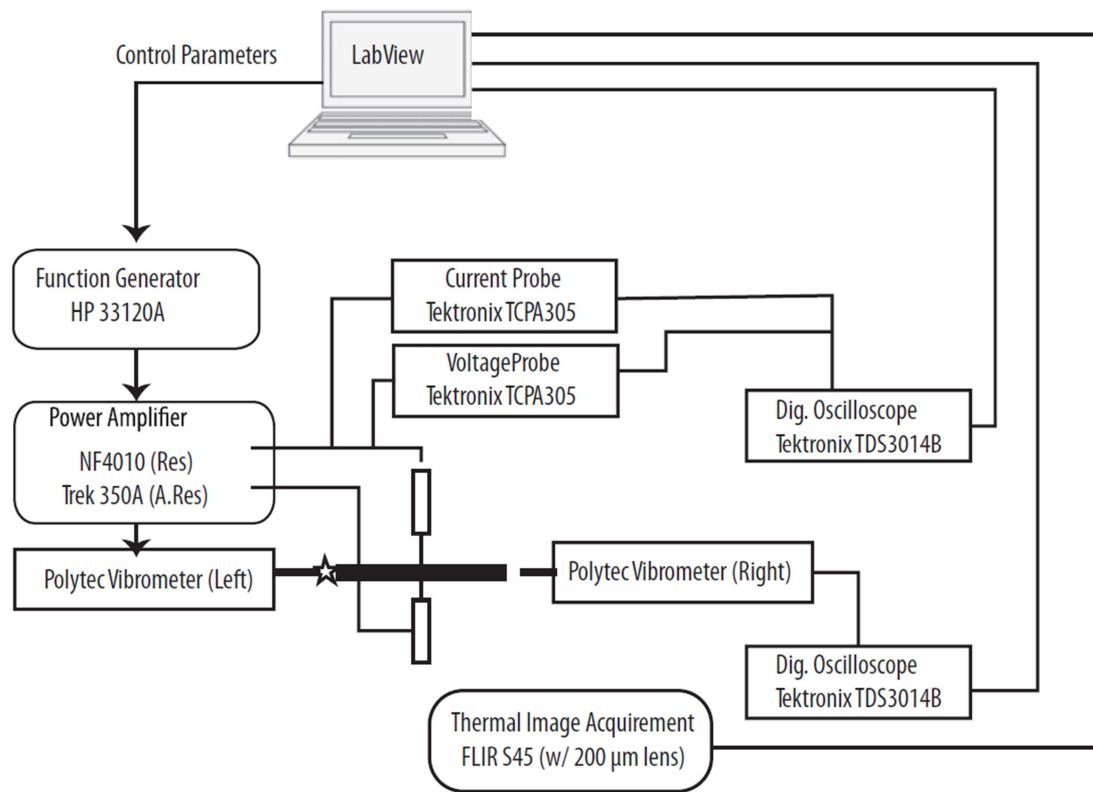


Fig. 4. 6. Schematic diagram of high power piezoelectric characterization system under constant vibration velocity.

Disk-shape transducers with thickness of 1.1 mm and diameter of about 12 mm were used for doing the measurements. Undoped and Mn-doped BNKLT88 transducers (Mn=1.4, 1.5, and 1.6 mol.%) were selected for the high power tests. The frequency sweep was done with a step size of 50 Hz per step. A sinusoidal signal was generated by a function generator (HP 33120A, Hewlett-Packard, Palo Alto, CA) and amplified by a power amplifier (NF 4010, NF Corporation, Yokohama, Japan). The sample current was detected by a clamp-on AC current sensor (Tektronix TCP 305). Vibration amplitudes (v_{rms}) on the edges of the piezoelectric disks were measured using laser interferometer (Polytec PI, Model OFV-511, Polytec Inc., Irvine, CA). The voltage, current, and displacement waveforms of the piezoelectric disks were monitored by two digitizing oscilloscopes (Tektronix TDS 3014B, Beaverton, OR). The temperature on the surface of the sample was monitored by an IR thermometer (Hioki 3445, Japan) and observed by an IR thermal camera (FLIR Systems Therma-CAM S40, FLIR Systems, Boston, MA). The driving voltage and current were automatically adjusted using a LabVIEW controlled computer to maintain a constant vibration velocity over the whole range of frequencies. The mechanical quality factor at the resonance (Q_A) and antiresonance (Q_B) were measured from the impedance curves at each vibration velocity by using 3dB up/down method [14] as shown in Fig. 4.7.

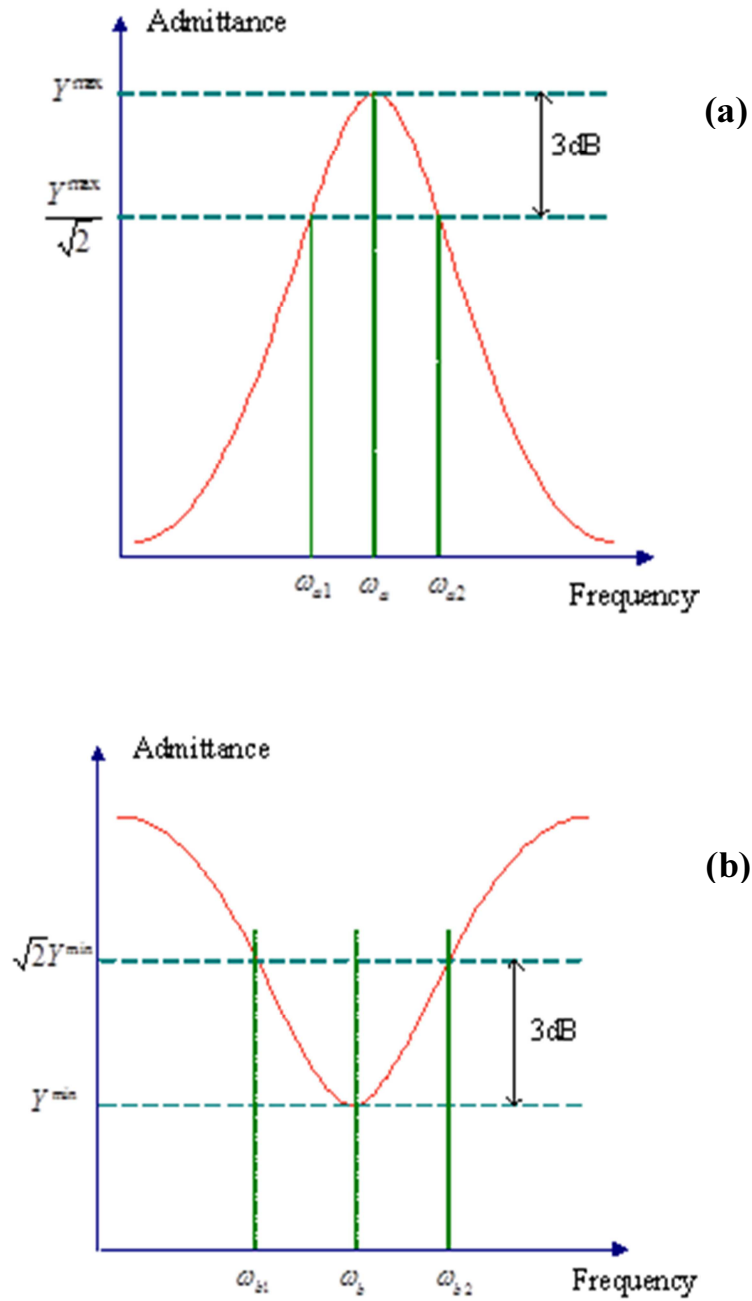


Fig. 4. 7. Measurement of mechanical quality factors from admittance spectra through 3dB down/up method (a) at resonance frequency $QA = \omega_a / (\omega_{a2} - \omega_{a1})$ (b) at antiresonance frequency $QB = \omega_b / (\omega_{b2} - \omega_{b1})$.

4.3 Results and Discussion

4.3.1 Phase Analysis

Fig. 4.8. shows the XRD patterns of undoped and Mn-doped BNKLT88 ceramics sintered at 1100 °C. According to the Rietveld refinement ($R=6.4\%$, $E=0.99\%$) shown in Fig. 4.9, these samples possessed a Perovskite structure with a rhombohedral symmetry. The structure of the ceramics was similar to the pure BNT single crystal (PDF# 36-0340). The variation of the lattice parameter and rhombohedrality with concentration of Mn is provided in Fig 4.10. Mn-doping up to 1.5 mol.% resulted in the shrinkage of the unit cell. At higher levels of Mn-dopant, the lattice parameters almost remained constant. The shrinkage of the unit cell can be attributed to the oxygen vacancies formed following the occupation of B-sites by Mn cations [30].

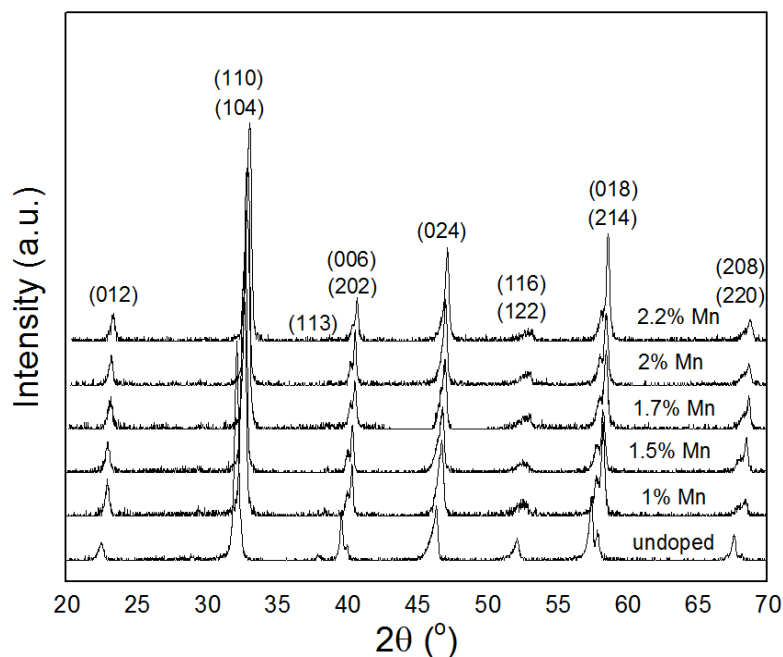


Fig. 4. 8. XRD patterns of undoped and Mn-doped BNKLT88 ceramics sintered at 1100 °C.

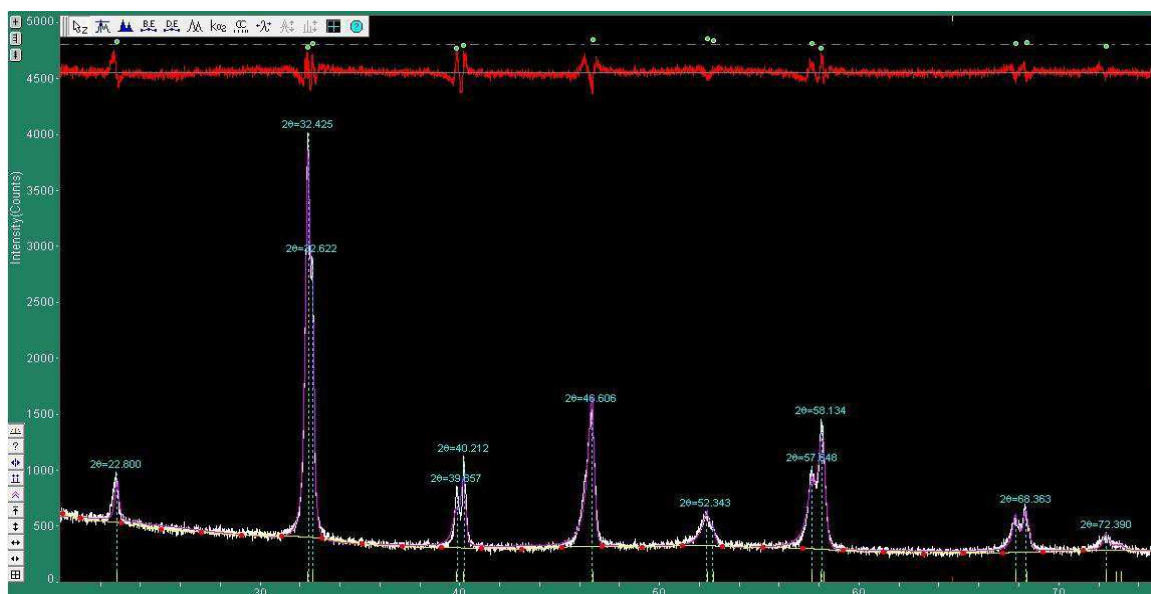


Fig. 4. 9. Rietveld refinement of undoped BNKLT88 ceramic by JADE software showing a rhombohedral structure.

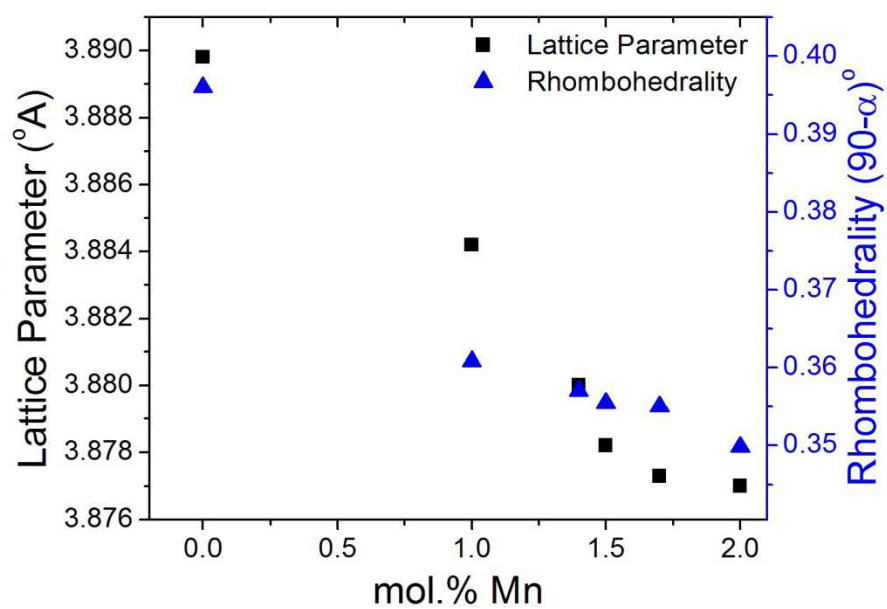


Fig. 4. 10. Effect of Mn content on the lattice parameter and rhombohedrality of BNKLT88 ceramics.

4.3.2 Low Drive Properties

4.3.2.1 Mn-added ceramics

Figs. 4.11 (a)-(b) show the dielectric and electromechanical properties of $(\text{BiNa}_{0.88}\text{K}_{0.08}\text{Li}_{0.04})_{0.5}\text{TiO}_3 + x \text{ mol.}\% \text{ Mn}$ ($x=0.01$ and 0.02) ceramics sintered at 1150, 1125, and 1100 °C. Mn was added in form of carbonate (MnCO_3). The density of all samples was higher than 5.7 g.cm^{-3} (96% of the theoretical density). It was found that adding MnCO_3 to BNKLT88 ceramics decreased the mechanical quality factor compared to the undoped ceramic. The quality factor degradation was accompanied by a remarkable increase in the dielectric loss. The $\tan\delta$ of 1% and 2% Mn-added samples were 2.6-3.5% and 5.2-6.2%, respectively, which is considerably higher than that of undoped ceramics ($\tan\delta$ about 1%). In samples sintered at 1100 and 1125 °C, the dielectric constant increased with increasing the Mn content which was in agreement with increasing the $\tan\delta$. It was speculated that the increase in the relative permittivity was caused by space charges and structural defects created as a result of Mn-addition. With increasing the Mn concentration, the piezoelectric charge coefficient as well as the coupling coefficients were decreased. Accumulation of Mn around grain boundaries [26, 27], and generation of space charges might be the reasons for degradation of dielectric and electromechanical properties of Mn-added ceramics.

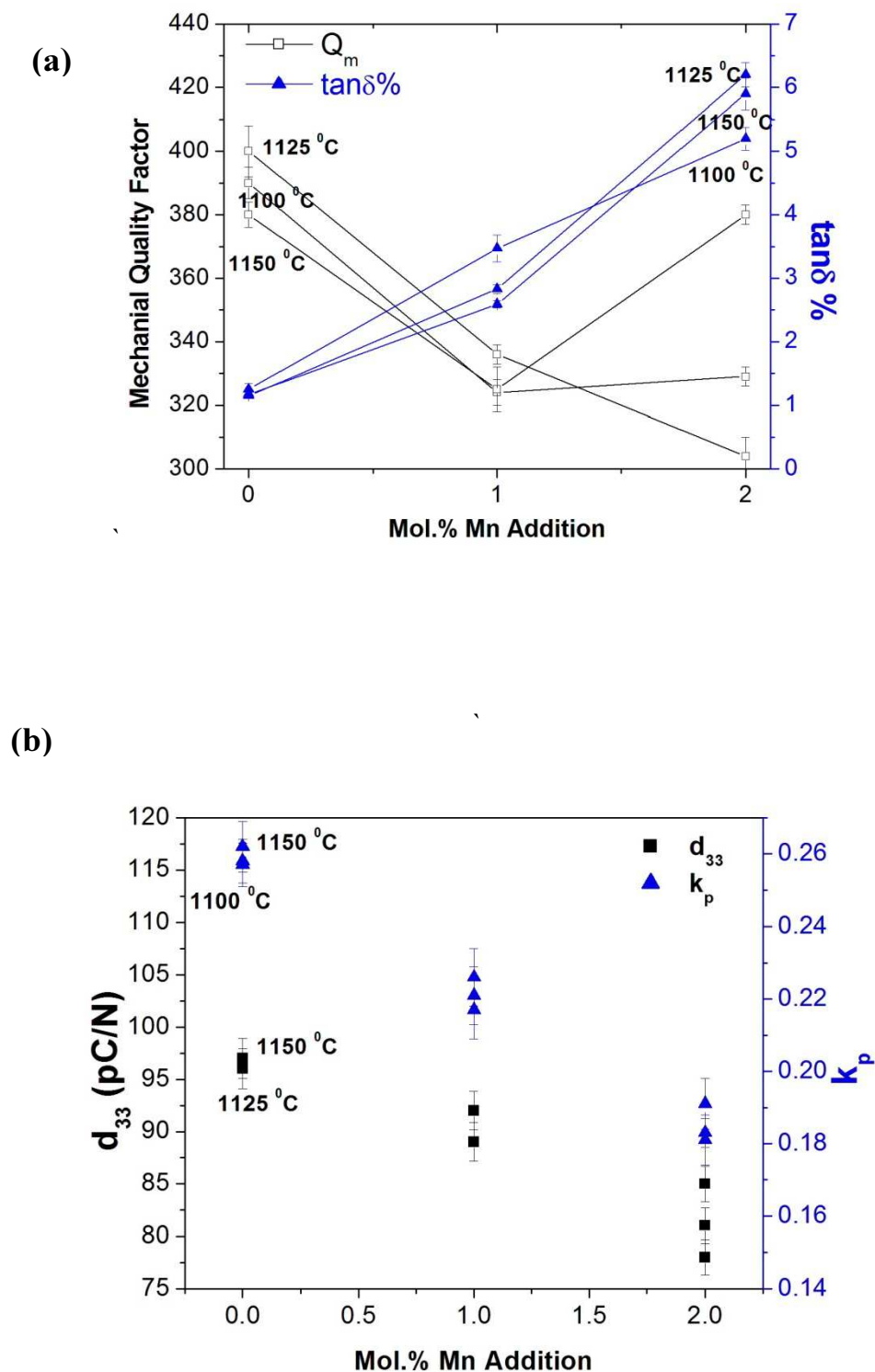


Fig. 4. 11. Effect of Mn-addition on properties of BNKLT88 ceramics sintered at different temperatures (a) mechanical quality factor and dielectric loss (b) piezoelectric charge coefficient and planar coupling coefficient. MnCO_3 was used as Mn source.

Table 4.1 provides the properties of 2% Mn-added ceramics ($\text{Bi}_{0.96}\text{Na}_{0.88}\text{K}_{0.08}\text{Ba}_{0.08}\text{TiO}_3 + x \text{ mol.\% Mn}$ ($x=0.02$) sintered at 1150, and 1100 °C in which MnO_2 was used as the source of Mn. Although, the mechanical quality factor of the ceramics sintered at 1100 °C is higher than that of MnCO_3 -added samples, the improvement is not considerable. In general, MnO_2 addition had a negligible effect on Q_m . Decreasing the sintering temperature from 1150 to 1100 °C, improved the dielectric and electromechanical properties due to the decelerated bismuth loss. These ceramics still suffer from a high dielectric loss (4.3-4.7 %) which is not acceptable for high power applications.

Table. 4. 1. Dielectric and electromechanical properties of Mn-added BNKLT88 ceramics sintered at different temperatures (MnO_2 was used as Mn source).

Sample	Density (g.cm^{-3})	d_{33} (pC.N ⁻¹)	ϵ_r	$\tan\delta\%$	k_p	k_t	Q_m
2% Mn- 1150 °C	5.82 ± 0.01	78 ± 1	408 ± 4	4.78 ± 0.26	0.181 ± 0.003	0.473 ± 0.008	398 ± 3
2% Mn 1100 °C	5.83 ± 0.02	81 ± 1	405 ± 6	4.34 ± 0.06	0.208 ± 0.001	0.477 ± 0.005	470 ± 4

In conclusion, regardless of the Mn source, Mn concentration or the sintering temperature, Mn-addition deteriorated the quality factor, piezoelectric and electromechanical properties of BNKLT88 ceramics.

4.3.2.2 *Mn-doped ceramics*

Table 4.2 lists the density and electromechanical properties of undoped and Mn-doped BNKLT88 ceramics sintered at different temperatures. Table 1 lists the density and electromechanical properties of undoped and Mn-doped BNKLT88 ceramics sintered at different temperatures. The electrical properties of these ceramics were very sensitive to the dopant concentration as well as the sintering temperature as provided in the table. A great enhancement in mechanical quality factor was achieved by optimization of the dopant level and the sintering temperature.

Table. 4. 2. The electromechanical properties of undoped and Mn-doped BNKLT88 ceramics.

% Mn	Sintering Temperature (°C)	Density (g.cm ⁻³)	d ₃₃ (pC.N ⁻¹)	$\epsilon_{33}^T/\epsilon_0$	Tan δ %	k _p	k _t	Planar Q _m	Thickness Q _m
0	1100	5.78	96	374	1.21	0.260	0.498	402	246
	1125	5.83	97	369	1.15	0.258	0.497	423	259
	1150	5.76	96	379	1.23	0.262	0.499	392	240
1	1100	5.76	89	363	1.48	0.244	0.491	666	282
	1125	5.74	92	354	1.42	0.237	0.479	683	307
	1150	5.71	93	358	1.63	0.231	0.488	618	295
1.4	1100	5.78	88	324	0.97	0.224	0.474	868	402
	1125	5.78	88	306	0.97	0.216	0.476	851	352
1.5	1075	5.83	88	340	1.56	0.235	0.494	904	391
	1100	5.88	85	308	0.89	0.218	0.487	974	437
	1125	5.77	86	327	1.06	0.216	0.483	847	395
	1150	5.72	86	330	1.17	0.212	0.481	801	353
1.6	1075	5.83	88	315	1.14	0.220	0.480	912	383
	1100	5.76	87	320	1.01	0.217	0.479	886	378
1.7	1075	5.92	88	320	1.36	0.221	0.469	935	406
	1100	5.81	87	319	1.10	0.211	0.457	906	387
2	1075	5.87	84	333	1.68	0.214	0.482	820	377
	1100	5.80	85	328	1.66	0.192	0.474	745	345
	1125	5.75	87	338	1.73	0.190	0.471	695	298
	1150	5.73	87	350	1.81	0.190	0.463	645	271
2.2	1075	5.84	84	297	1.71	0.184	0.470	603	302
	1100	5.82	83	307	1.78	0.179	0.459	569	279

* The standard deviation of density, d₃₃, ϵ_r , and tan δ is about ± 0.03 , ± 1 , ± 5 , and ± 0.03 , respectively

** The standard deviation of K_p and K_t is about ± 0.002 and ± 0.006 , respectively

*** The standard deviation of planar and thickness Q_m is about respectively 15 and 30, respectively

Figs. 4.12 (a)-(d) display the impedance-phase (Z - θ) spectra of different BNKLT ceramics around the resonance (f_r) and antiresonance (f_a) frequencies of the planar vibration mode. The MPB composition (BNKLT76) with the lowest Q_m exhibited a wide bandwidth in the vicinity of f_r and f_a for both impedance and phase angle spectra. In BNKLT88 ceramics, particularly upon Mn-doping, the bandwidth of the impedance and phase angle spectra is considerably decreased. As a result, the vibration energy is concentrated at the resonance and antiresonance frequencies leading to high mechanical quality factor (low mechanical loss).

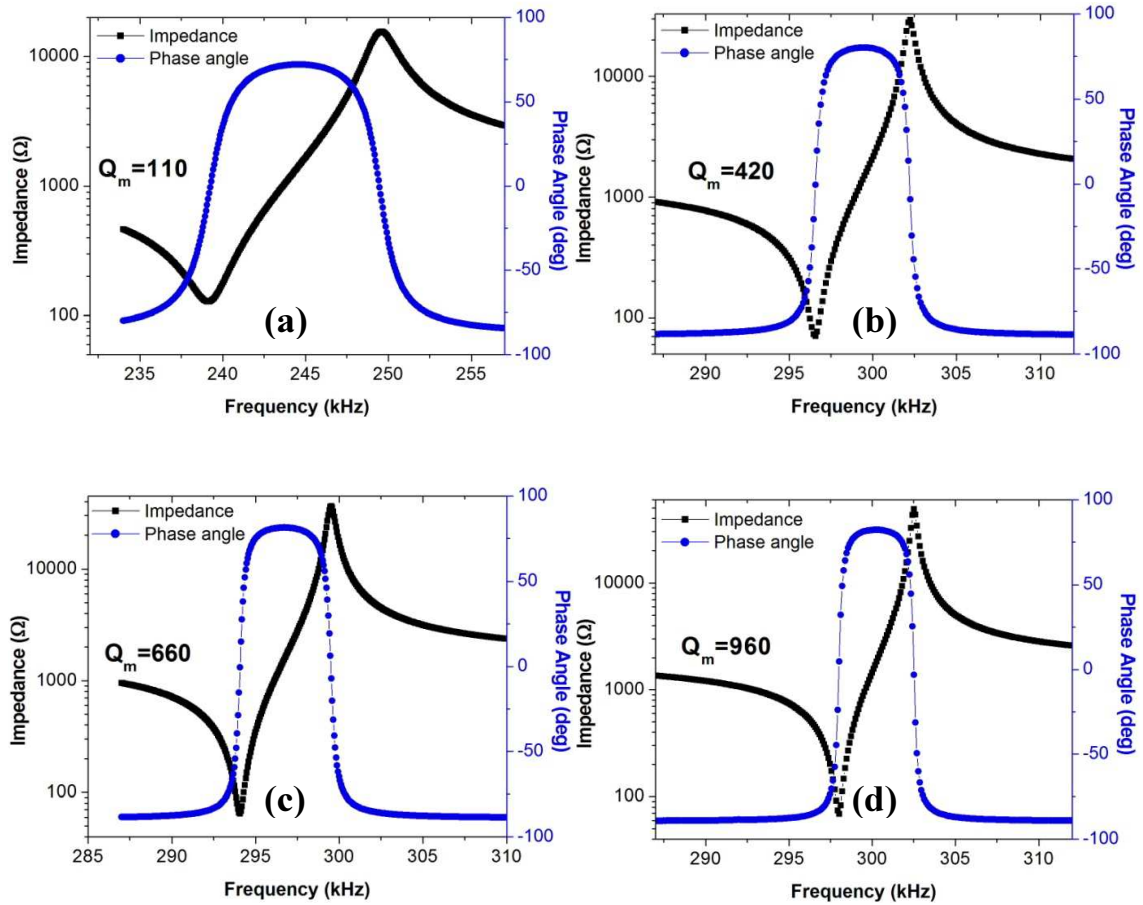


Fig. 4. 12. Impedance and phase angle spectra showing the resonance and antiresonance frequencies of planar mode in different ceramic sintered at 1100 °C: (a) BNKLT76 (b) undoped BNKLT88 (c) 1 mol.% Mn-doped BNKLT88 (d) 1.5 mol.% Mn-doped BNKLT88.

The effect of Mn-doping on the mechanical quality factor of BNKLT88 ceramics sintered at 1100 °C is illustrated in Fig. 4.13. The Q_m values measured by two different techniques (equivalent circuit and -3dB method from $Y-\theta$ spectra) are included in this graph. Both measurement methods yielded similar values ($\pm 5\%$). Increasing the Mn concentration up to 1.5 mol.% remarkably enhanced the planar and thickness Q_m . Further increase of the dopant concentration resulted in a reduction of the Q_m . The maximum planar and thickness Q_m (minimum elastic loss) were measured to be about 970 and 435, respectively. The mechanical quality factor of these ceramics was higher than Mn-doped KNN and BNKLT88 ceramics reported by Nagata et al (Q_m of 820 and 730, respectively) [20]. The planar quality factor in 1.4% and 1.625% Mn-doped samples was as high as 870 and 915. Other ceramics sintered at different temperatures showed a similar trend of variations of the Q_m with Mn concentration. Substitution of Ti with Mn is accompanied by formation of oxygen vacancies to maintain the charge neutrality. These oxygen vacancies form defect dipoles with acceptor cations (e.g. $V_O^{\bullet\bullet} - Mn_{Ti}''$) which are energetically favorable to be aligned in the direction of spontaneous polarization. Diploes form an internal bias field which stabilizes the domain configuration manifested as a horizontal offset in the P-E hysteresis loop [4, 8]. Defects can also diffuse into the domain walls, and result in domain wall pinning which leads to the enhancement of the Q_m , and decrease of dielectric, mechanical, and piezoelectric losses [5]. As can be observed in Fig. 4.14, the minimum dielectric loss ($\tan\delta \sim 0.9\%$) was also obtained at 1.5 mol.% Mn. Therefore, the optimum concentration of Mn dopant for achieving hard piezoceramics i.e. the minimum dielectric and mechanical losses was 1.5 mol.%. The dielectric constant for this composition (at 1 kHz) was about 310.

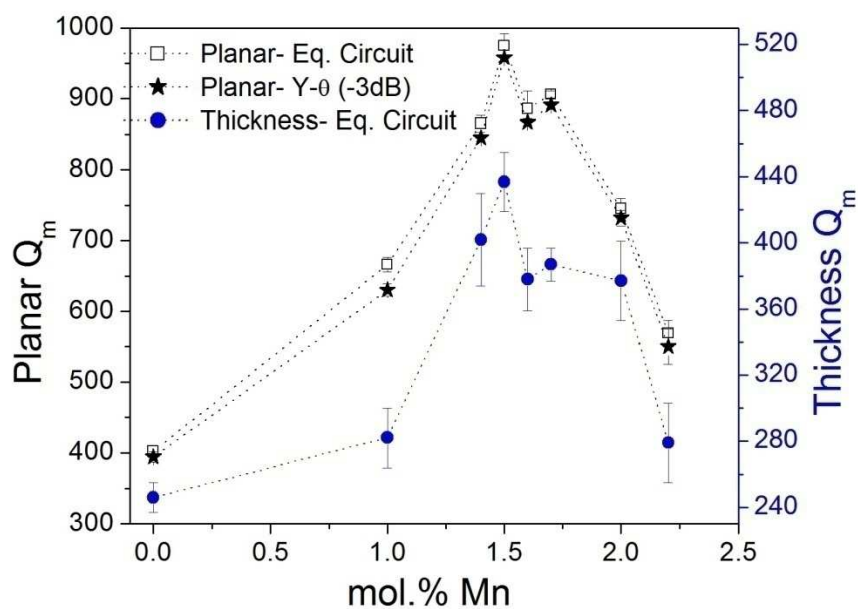


Fig. 4. 13. Effect of Mn-doping on the planar and thickness mechanical quality factors of BNKLT88 ceramics sintered at 1100 °C.

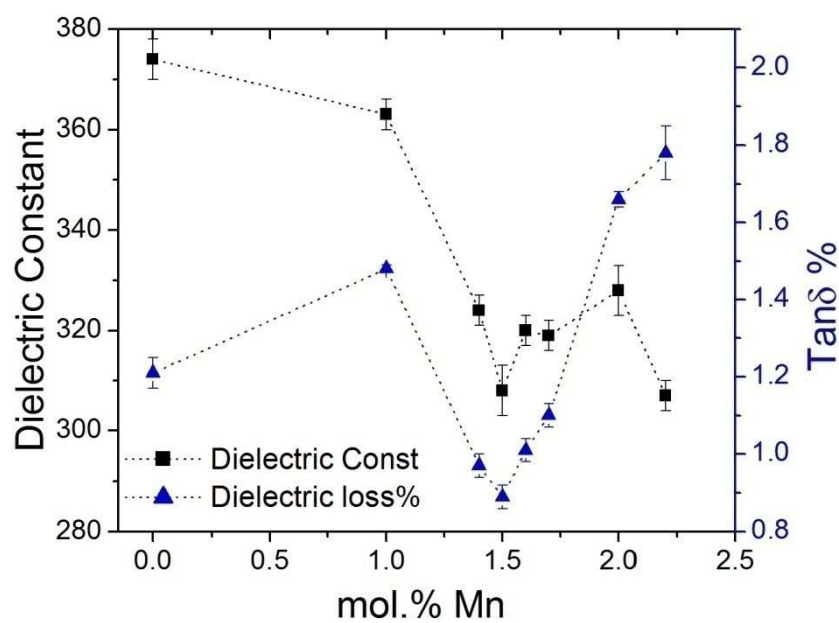


Fig. 4. 14. Effect of Mn-doping on dielectric properties of BNKLT88 ceramics sintered at 1100 °C.

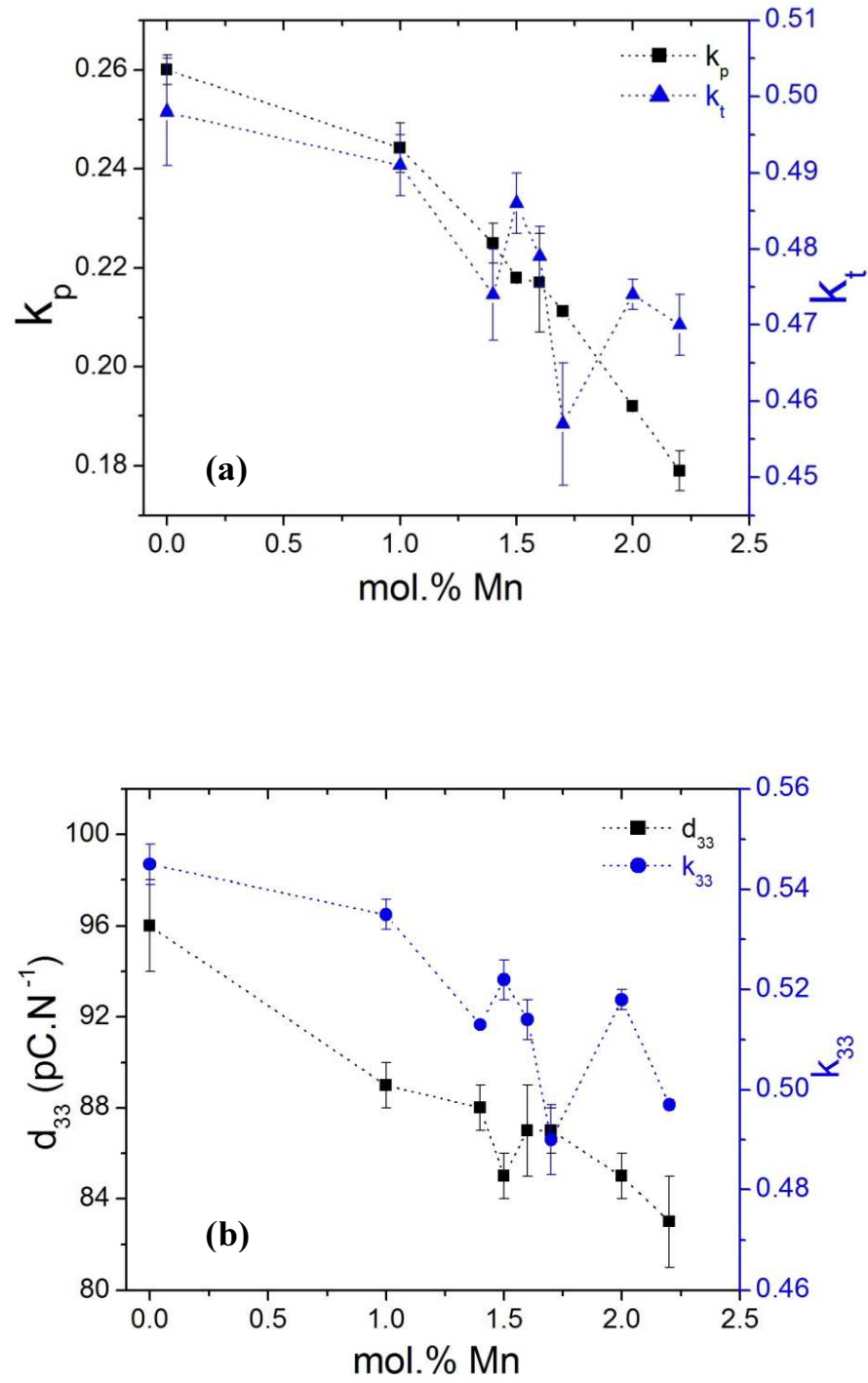


Fig. 4. 15. Effect of Mn-doping on (a) planar and thickness coupling coefficients (b) piezoelectric charge coefficient and longitudinal coupling coefficient of BNKLT88 ceramics sintered at 1100 °C.

As can be observed in Fig. 4.15 (a), Mn-doping decreased the planar and thickness coupling coefficient of BNKLT88 ceramics sintered at 1100 °C. The longitudinal piezoelectric and electromechanical coefficients were also reduced with increasing the concentration of the acceptor dopant (Fig. 4.15 (b)). The decrease in piezoactivity of the ceramics with Mn content originates from the domain wall pinning by oxygen vacancies as explained previously.

Fig. 4.16 shows the effect of sintering temperature on the density of 1.5 mol. % Mn ceramics. Other ceramics doped with different amounts of Mn, showed a similar dependency on the sintering temperature. The highest density was obtained at 1100 °C. With increasing the sintering temperature, the density was reduced due to the accelerated bismuth loss at higher temperatures. The bismuth loss at 1100 and 1150 °C was 0.5 and 0.7 wt.%, respectively. Accordingly, the highest Q_m was also achieved at 1100 °C which was the optimum sintering temperature for 1.5% Mn-doped ceramic. The reduced density and grain growth caused the Q_m to decrease at higher sintering temperatures than 1100 °C. As illustrated in Figs. 4.17 through 4.19, the mechanical quality factor as well as the dielectric and electromechanical properties of Mn-doped ceramics were very sensitive to slight variations of sintering temperature. Therefore, the processing condition of these ceramics including the temperature accuracy of the furnace should be carefully controlled in order to obtain enhanced properties. The optimum sintering temperature for 1% and 2% Mn-doped ceramics was 1125 and 1075 °C, respectively. The optimum sintering temperature of BNKLT88 ceramics was decreased by increasing the dopant concentration. Oxygen vacancies induced by acceptor dopants can accelerate the diffusion process at high temperatures and hence decrease the sintering temperature [5].

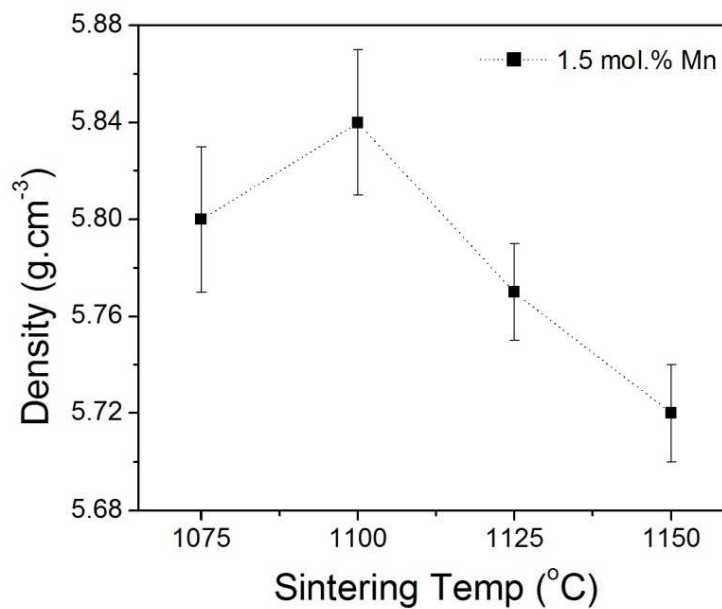


Fig. 4. 16. Effect of sintering temperature on density of 1.5 mol. % Mn-doped BNKLT88 ceramics.

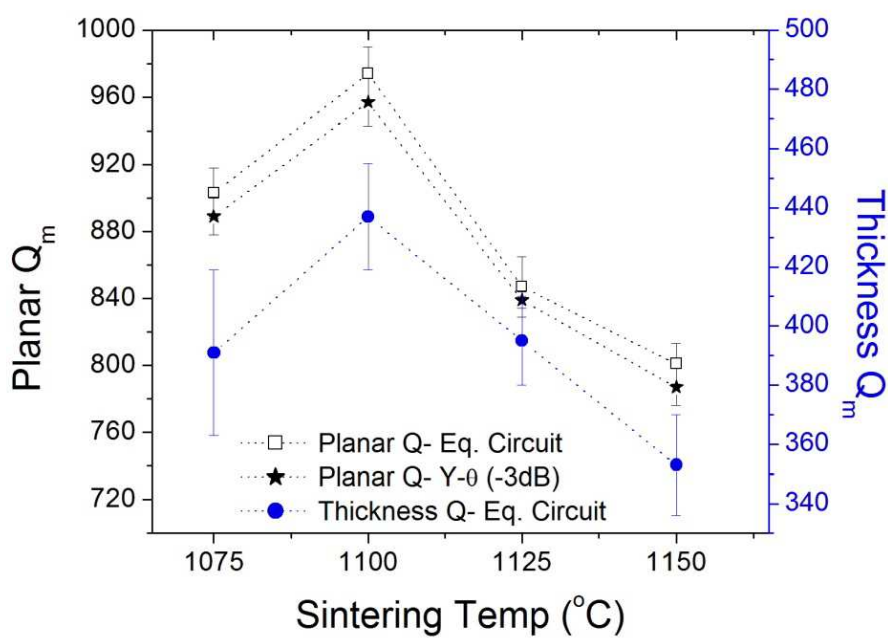


Fig. 4. 17. Effect of sintering temperature on planar and thickness mechanical quality factor of 1.5 mol. % Mn-doped BNKLT88 ceramics.

The influence of sintering temperature on the dielectric properties of Mn-doped ceramics is depicted in Fig. 4.18. As expected from variation trend of the density and Q_m with the sintering temperature, the lowest dielectric loss was obtained at 1100 °C. The dielectric constant also showed a minimum at this temperature. At higher temperatures, the properties degraded due to the reduction in density. The planar and thickness coupling coefficient also decreased with increasing the sintering temperature.

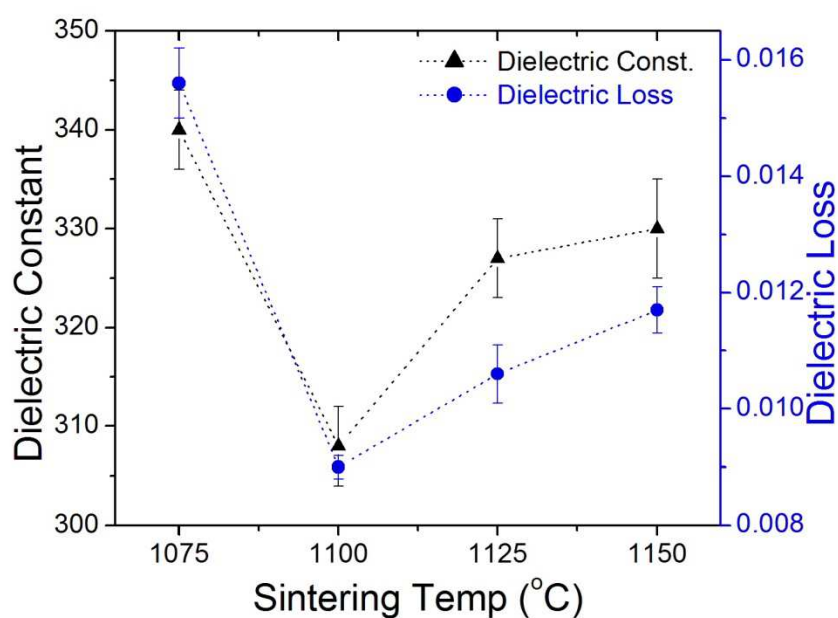


Fig. 4. 18. Effect of sintering temperature on the dielectric properties of 1.5 mol. % Mn-doped BNKLT88 ceramics.

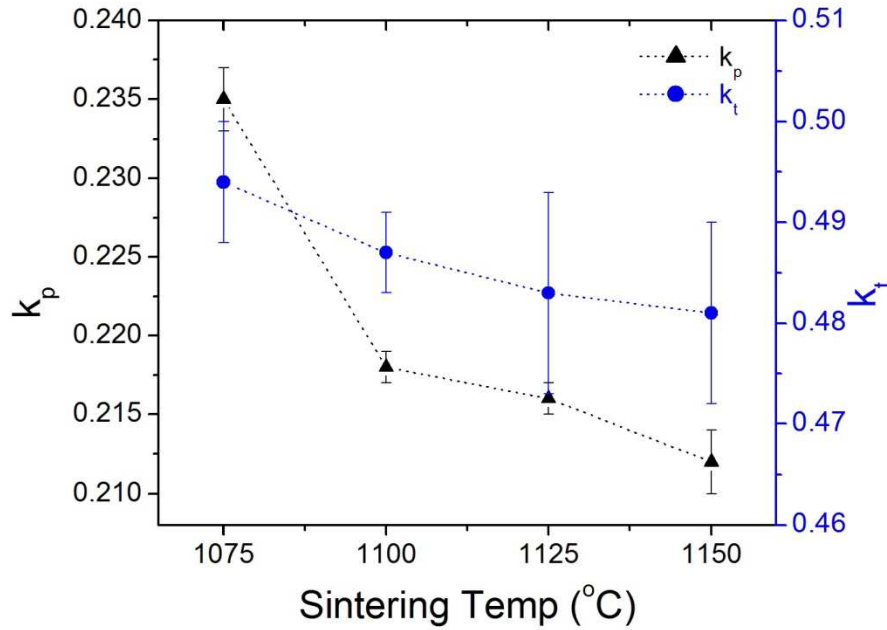


Fig. 4. 19. Effect of sintering temperature on the planar and thickness coupling coefficients of 1.5 mol. % Mn-doped BNKLT88 ceramics.

4.3.2.3 Fe-doped ceramics

All Fe-doped BNKLT88 ceramics were sintered at 1100 °C. Fig. 4.20 shows the effects of Fe-doping on planar and thickness Q_m of BNKLT88 ceramics. Variation of dielectric properties with Fe concentration is also depicted in Fig. 4.21. The highest planar and thickness Q_m (900 and 350, respectively) were obtained in 1.5 mol.% Fe-doped ceramics. This composition also showed the lowest dielectric loss ($\tan\delta \sim 0.90$) and dielectric constant ($\epsilon_r \sim 300$). Fe-doping decreased the d_{33} and k_p in a similar manner to Mn-doping. These properties in 1.5 mol.% Fe-doped samples were 81 pC.N⁻¹ and 0.20, respectively.

Fe-doped ceramics were subjected to a color change during the poling step. The color of the as-sintered ceramics was light yellow which turned into black after poling. Magnetite (FeO.Fe₂O₃) is extensively used as a black pigment in the dye industry. The

observed color change was possibly due to the valance change of Fe^{3+} cations under application of an electric field which also led into a local variation in concentration of oxygen vacancies. This electrocoloration effect which is an electric field induced valance change has been observed in other materials such as Fe-doped SrTiO_3 [31]. Compared to the Mn-doped ceramics, Fe-doped samples had a higher conductivity and needed to be poled at a lower temperature (85 °C).

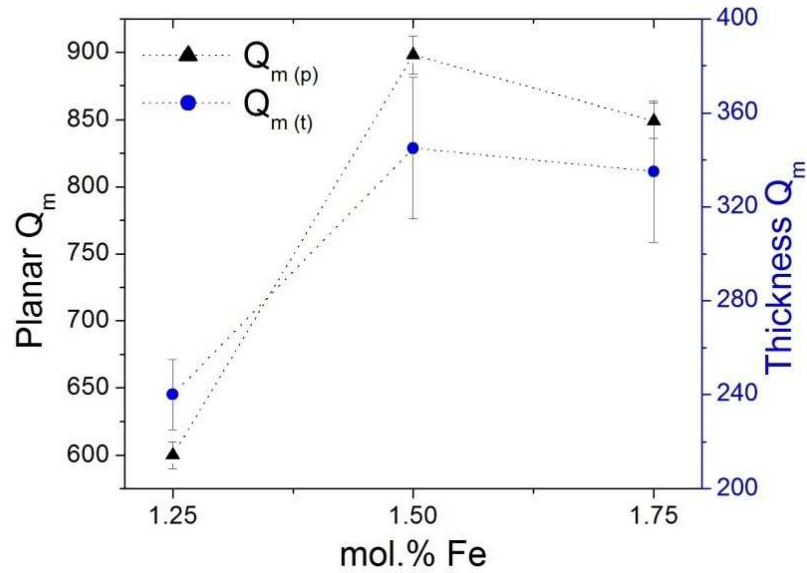


Fig. 4. 20. Effect of Fe-doping on the planar and thickness mechanical quality factor of BNKLT88 ceramics sintered at 1100 °C.

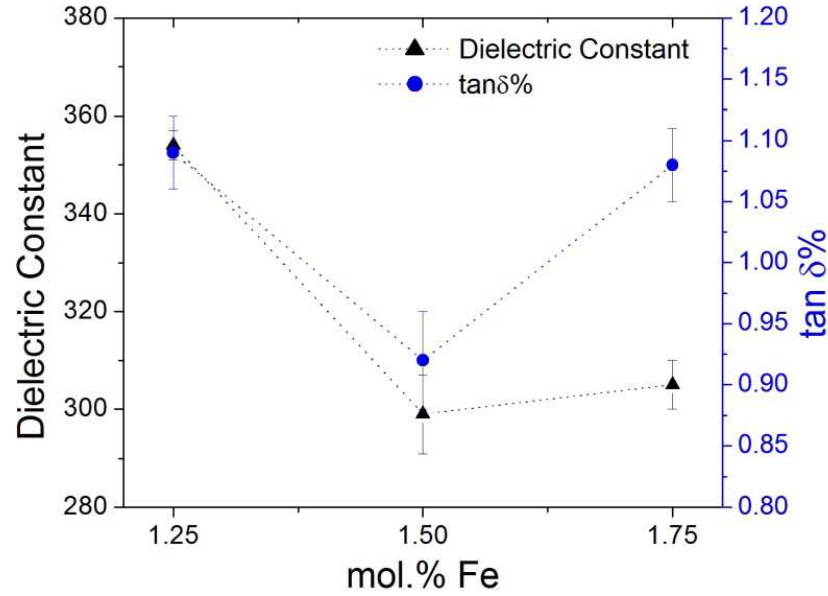


Fig. 4. 21. Effect of Fe-doping on dielectric properties of BNKLT88 ceramics sintered at 1100 °C.

Fig. 4.22 illustrates the P-E hysteresis loops of undoped, 1.5% Mn and 1.5 % Fe-doped BNKL88 ceramics aged for 48 hours at room temperature. Acceptor dopants had a negligible influence on the remnant or saturation polarizations, but increased the coercive field as well as the internal bias field (E_i). The internal bias is developed through diffusion of oxygen vacancies to the energetically favorable octahedral sites. Due to the off-center displacement of the B-site atoms in poled ferroelectrics, alignment of the defect dipoles (e.g. $V_{O}^{oo}-Mn_{Ti}''$) in the direction of the spontaneous polarization takes less energy than the opposite direction. The internal bias field plays a critical role in increasing the mechanical quality factor and stabilization of ferroelectric domains [4, 6]. The internal bias field in undoped, Fe-doped and Mn-doped BNKLT88 ceramics was measured to be 0.7, 2.5, and 3 kV.cm⁻¹, respectively.

Table 4.3 compares the properties of commercial hard PZTs (PZT4 and PZT8) and lead-free BNT-based ceramics developed in this research. The crucial material

properties for high power applications (Q_m , $\tan\delta$ and T_c) as well as k_t , in undoped and Mn-doped BNKLT88 ceramics are comparable to PZT4 and PZT8, respectively. Lead-based materials exhibit a considerably higher d_{33} , ϵ_r , and k_p . The main advantage of BNT-based ceramics is their high coercive field ($E_c \sim 5 \text{ kV}\cdot\text{mm}^{-1}$) compared to commercial PZT's ($E_c \sim 1.4\text{-}2 \text{ kV}\cdot\text{mm}^{-1}$) [2]. As presented in the next section, BNKLT88 ceramics will show superior performance at high vibration velocities due to their higher coercive field.

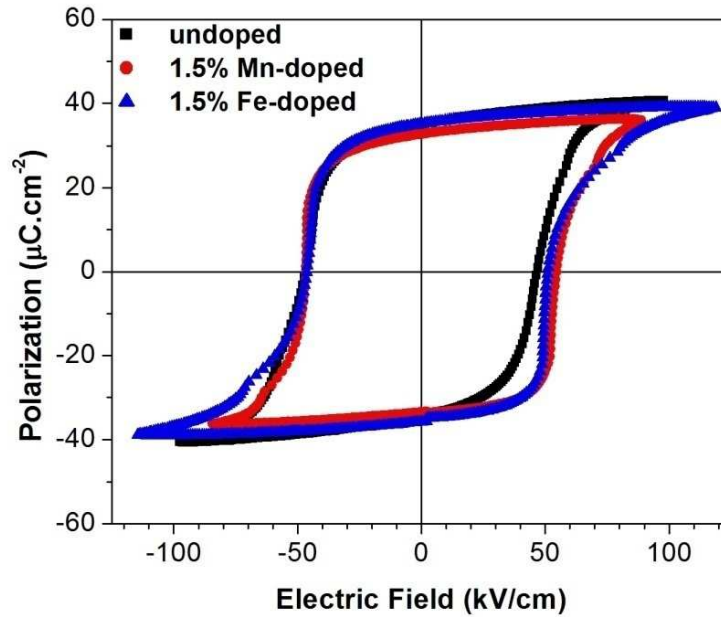


Fig. 4. 22. P-E hysteresis loops of undoped, 1.5% Mn and 1.5% Fe-doped BNKLT88 ceramics aged for 48 hours.

Table. 4. 3. Properties of commercial hard PZTs and lead-free BNT-based ceramics.

Property	PZT4	PZT8	BNKLT88	1.5Mn- BNKLT88	1.5Fe- BNKLT88
d_{33} (pC/N)	290	225	95	85	81
ε_{33}^T	1300	1000	380	310	300
Tan δ %	0.5	0.4	1.1	0.85	0.90
k_t %	51	48	49	48	46
k_p %	58-64	51-60	26	22	20
Q_m	500	1000	400	970	900
T_c (°C)	325	300	330	305	---
E_c (kV.cm ⁻¹)	14	20	47.2	52.2	51.7
E_i (kV.cm ⁻¹)~	3	3	0.7	3	2.5

4.3.3 High Drive Properties

The variation of impedance-frequency spectra with the vibration velocity in undoped BNKLT88 ceramics is illustrated in Fig 4.23. The resonance and antiresonance frequencies decreased with increasing the vibration velocity. At the same time, peak broadening (at f_r and f_a) happened as the vibration velocity is increased. Fig. 4.24 quantitatively shows the relative variations of the resonant frequency as a function of the vibration velocity in undoped and Mn-doped ceramics. As can be observed, the resonant frequency of all samples decreased with increasing the vibration velocity. This was due to the softening phenomenon arisen by evolution of domain walls at high electric fields. The same trend has been observed in other hard lead-free ceramics such as KNN and BNT [2,

32]. As depicted in Fig. 4.24, the rate of the frequency shift was suppressed by Mn-doping. Ceramics doped with 1.5 mol.% Mn showed the lowest rate of resonance and antiresonance frequency shift due to their more stable domain configuration. At a vibration velocity of 0.4 m.s^{-1} , the rate of frequency shift was decreased by 75% through Mn-doping.

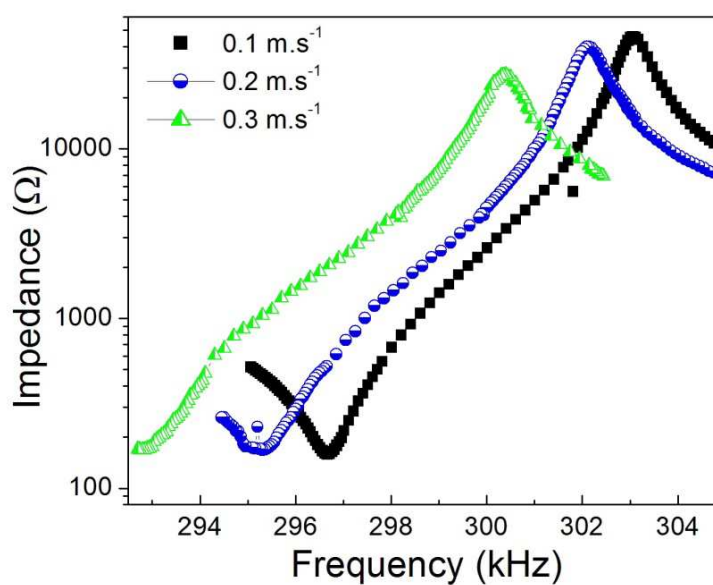


Fig. 4. 23. Variations of impedance spectra with the vibration velocity in undoped BNKLT88 ceramics.

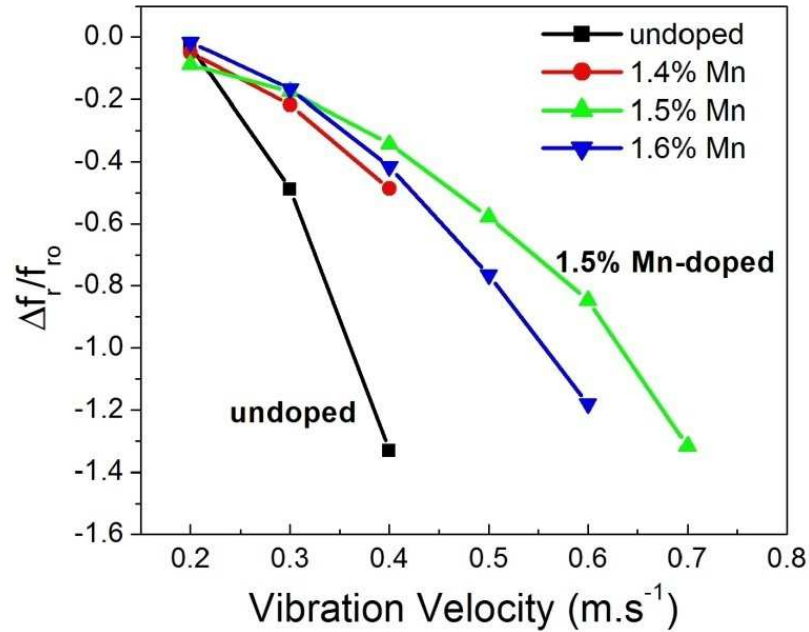


Fig. 4. 24. Relative variations of the resonance frequency with vibration velocity in undoped and Mn-doped BNKLT88 ceramics.

The heat generation in undoped and Mn-doped BNKLT88 ceramics was also measured as a function of vibration velocity and the results are depicted in Fig. 4.25. It is noticeable that Mn-doping effectively reduced the heat generation in BNKLT88 ceramics. The minimum temperature rise was observed in 1.5 mol.% Mn-doped sample. At a vibration velocity of 0.3 m.s⁻¹, the temperature rise in un-doped, 1.5% Mn-doped, and 1.625%Mn-doped samples were 26, 5, and 9 °C, respectively. The temperature rise in the MPB composition was measured at a vibration velocity of 0.1 m.s⁻¹ (not shown in the graph). As discussed in chapter 2, this is a soft ceramic (BNKLT76 composition) with a low Q_m of about 100. At 0.1 m.s⁻¹, this sample generated more heat (10 °C) compared to the hard ceramics and it was depoled at higher vibration velocities.

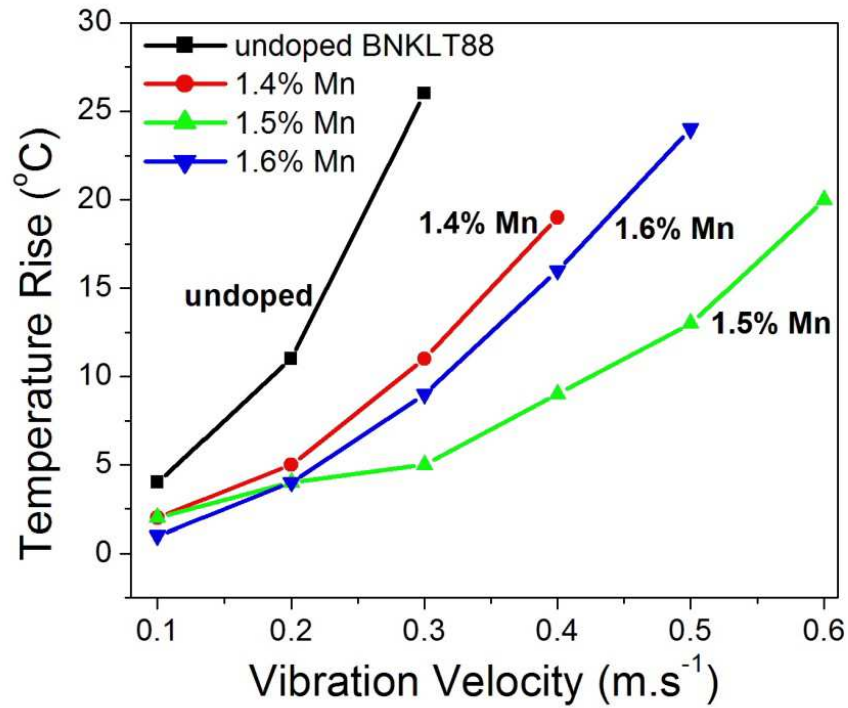


Fig. 4. 25. The heat generation under high drive condition in undoped and Mn-doped BNKLT88 ceramics.

Fig. 4.26 illustrates the mechanical quality factor of undoped and Mn-doped BNKLT88 ceramics versus the vibration velocity. The data for PZT4 and PZT8 ceramics are obtained from Ref [2].

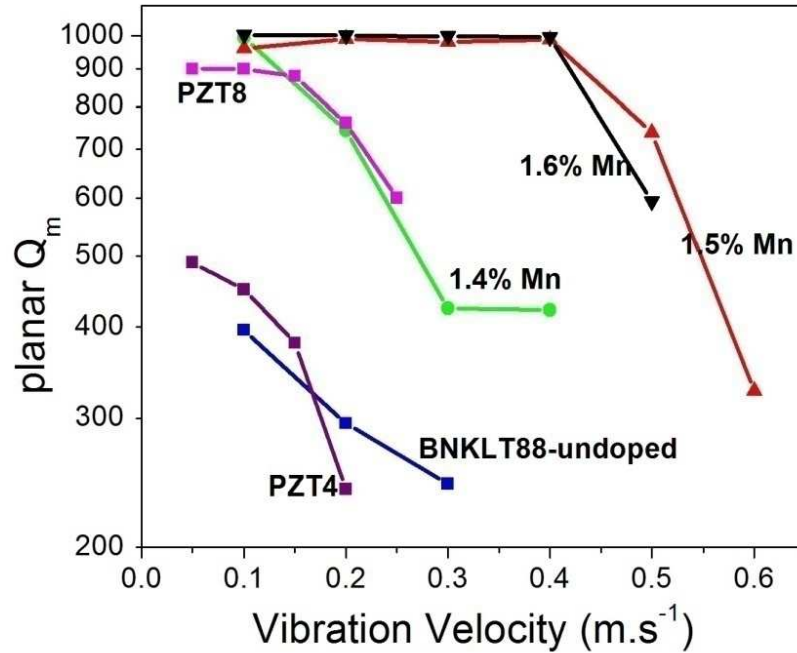


Fig. 4. 26. The mechanical quality factor of undoped and Mn-doped BNKLT88 ceramics versus the vibration velocity. The PZT4 and PZT8 data [2] are shown for a comparison.

The important feature in this figure is that the Q_m of Mn-doped samples remained almost constant up to vibration velocity of 0.4 m.s^{-1} . The Q_m values of 1.5% and 1.625% Mn-doped samples at a vibration velocity of 0.5 m.s^{-1} were 738 and 534, respectively. On the other hand, the Q_m of PZT8 ceramic sharply dropped at vibration velocities of higher than 0.2 m.s^{-1} . The PZT sample showed a Q_m of 595 at 0.25 m.s^{-1} . Similarly, the performance of the undoped BNKLT88 ceramics was greater than PZT4. Although the PZT4 sample possessed a higher Q_m at low vibration velocities (less than 0.15 m.s^{-1}), its Q_m decreased faster than that of BNKLT88. At a vibration velocity of 0.2 m.s^{-1} , the Q_m values of PZT4 and undoped BNKLT88 were 250 and 295, respectively.

The maximum vibration velocity is defined as the v_{rms} at a temperature rise of 20°C . The un-doped, 1.5% Mn-doped, and 1.625%Mn-doped BNKLT88 ceramics with a

disk-shape geometry showed a maximum vibration velocity of 0.28, 0.48, and 0.6 m.s^{-1} , respectively. The vibration velocity for rectangular-shape (31 resonance mode) hard PZTs falls in range of 0.3-0.5 m.s^{-1} . With considering the fact that the vibration velocity of rectangular samples is approximately 1.2-3 times that of disk-shape samples [33], the maximum vibration velocity in lead-free BNKLT88 ceramics is considerably higher than PZT4 and PZT8 ceramics. These materials also show better high power characteristics compared to the other hard lead-free ceramics such as Cu-doped $(\text{Na}_{0.5}\text{K}_{0.5})(\text{Nb}_{0.97}\text{Sb}_{0.03})\text{O}_3$, Co-doped BaTiO_3 and Co-doped 0.83BNT-0.084BKT-0.03BLT–0.056BT ceramics [2, 32].

Superior high power characteristics of BNT-based ceramics compared to PZTs, can be attributed to their higher coercive field [2]. The coercive field in hard PZTs falls in a range of 1.4-2 kV.mm^{-1} . However, in BNT-based ceramics the E_c is as high as 5 kV.mm^{-1} . Materials with a high coercive field have a more stable domain configuration and are more resistant to depoling under application of an electric field due to the difficulty of polarization reversal. A major part of the loss in ferroelectric ceramics is resulted by the domain wall motion. The reduced domain wall mobility in Mn-doped BNT-based ceramics, therefore, decreased the overall loss and heat generation under high drive conditions. On the contrary, the performance of hard PZTs is degraded at high electric fields because of the higher mechanical losses and heat generation. These results are in agreement with Co-doped and Mn-doped BNT ceramics reported by other researchers [2, 20].

Piezoelectric materials are usually designed to operate at the resonance frequencies. Recent results on lead-based ceramics have shown that the operation of

some piezoelectric devices at the antiresonance frequency can yield a higher efficiency. A low driving current along with a high driving voltage have been observed in transducers running at the antiresonance mode [13]. IEEE standards assume that the quality factors at the resonance and antiresonance frequencies have the same values. However, this assumption has not been confirmed experimentally. Figs. 4.27 (a)-(c) compare the resonance and antiresonance efficiencies of undoped, 1.5% and 1.6% Mn-doped BNKLT88 transducers. The mechanical quality factor and the corresponding temperature rise were measured as a function of the vibration velocity at both f_r and f_a (Q_A and Q_B , respectively). In undoped BNKLT88 ceramics, similar to PZTs [13], a higher efficiency was achieved at the antiresonance frequency compared to the resonance frequency ($Q_B > Q_A$ and $\Delta T_B < \Delta T_A$). On the contrary, Mn-doped transducers showed a higher efficiency at the resonance frequency (i.e. $Q_B \leq Q_A$ and $\Delta T_B \geq \Delta T_A$). The origins of the discrepancy between Q_A and Q_B are not clear yet. However, the phenomenological theories correlate the observed differences to the relative values of the dielectric, mechanical and piezoelectric losses. Different equations for longitudinal, thickness, shear and 31 vibration modes are driven which quantitatively express the difference between Q_A and Q_B . For 31-mode, for example, following equations have been developed [14]:

$$Q_{A,31} = \frac{1}{\tan \phi'_{11}} \quad (4.15a)$$

$$\frac{1}{Q_{B,31}} = \frac{1}{Q_{A,31}} - \frac{2}{1 + \left(\frac{1}{k_{31}} - k_{31}\right)^2 \Omega_{B,31}^2} (2 \tan \theta'_{31} - \tan \delta'_{33} - \tan \phi'_{11}) \quad (4.15b)$$

where $\tan\delta'$, $\tan\phi'$, and $\tan\theta'$ are intensive dielectric, mechanical, and piezoelectric loss factors, $\Omega_{B,31} = \frac{2\pi f_a L}{2\vartheta_{11}^E}$, and v_{11}^E is the sound velocity of the material in the direction of length under constant E.

With considering these equations, it is clear that $Q_B > Q_A$ if $2\tan\theta' > (\tan\phi' + \tan\delta')$ and $Q_B < Q_A$ if $2\tan\theta' < (\tan\phi' + \tan\delta')$. The piezoelectric loss is the factor that determines whether Q_B is larger than Q_A , though it was previously neglected by most researchers. Even in the datasheets provided by electroceramics manufacturers, the piezoelectric loss is not included. Recently, it has been confirmed that the magnitude of the piezoelectric loss is comparable to dielectric and mechanical losses [14]. There are various domain reversal possibilities in a crystal, which contribute to dielectric, mechanical and piezoelectric losses [6]. The dielectric loss is originated from the hysteresis during the 180° polarization reversal under an applied electric field. The extensive mechanical loss comes from reorientation of 90° domain walls under application of an external stress. The piezoelectric loss is believed to come from the 90° polarization reversal under application of an electric field [6]. It seems that the domain wall clamping effect of Mn as an acceptor dopant, effectively decreased the piezoelectric loss in a way that $2\tan\theta' < (\tan\phi' + \tan\delta')$ condition was met, and therefore, the efficiency of the transducer at the resonance frequency became higher than the antiresonance frequency.

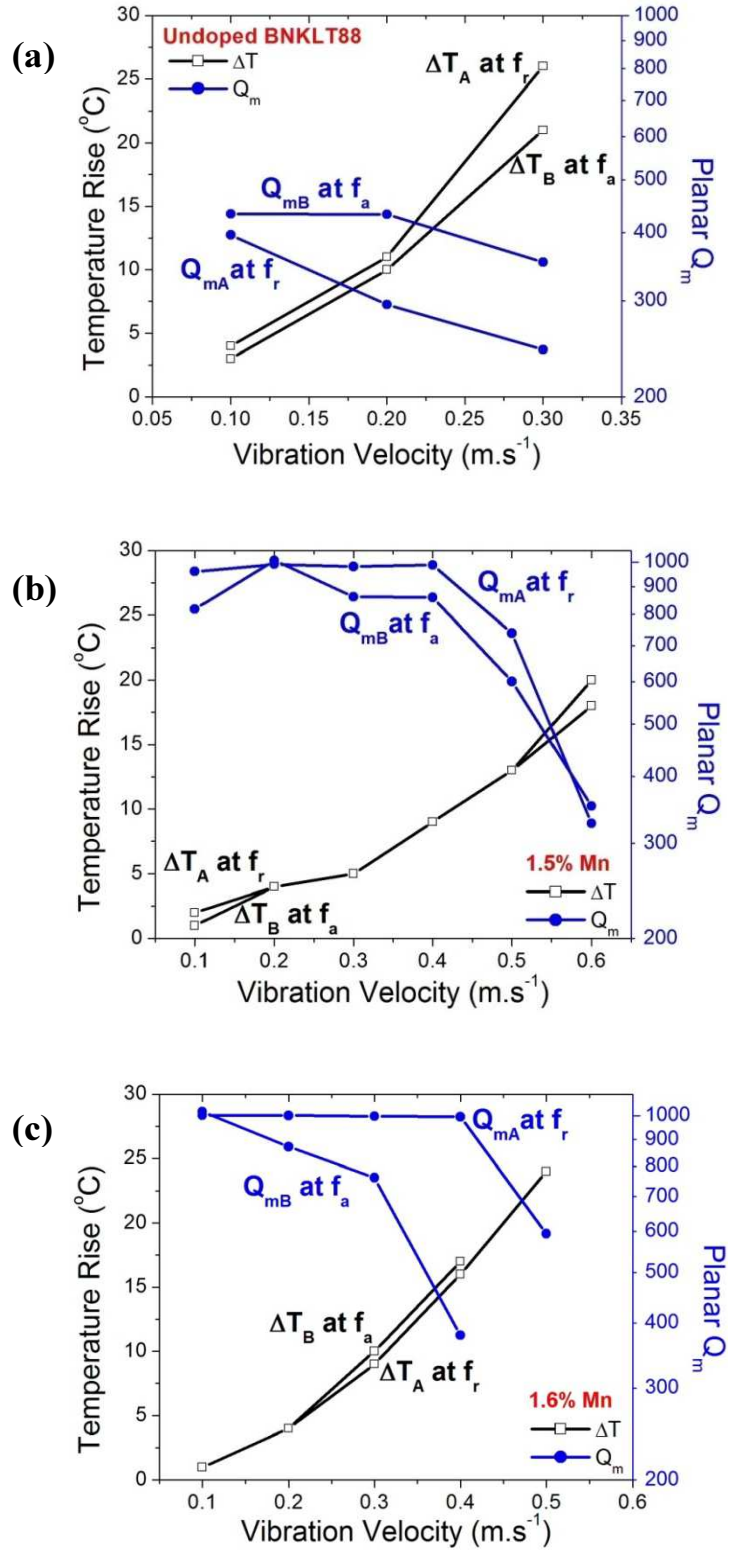


Fig. 4. 27. Effect of the vibration velocity on the temperature rise and mechanical quality factor measured at resonance and antiresonance frequencies in (a) undoped (b) 1.5% Mn-doped (c) 1.6% Mn-doped BNKLT88 ceramics.

Fig. 4.28 (a) demonstrates the controlled voltage and current in 1.5 mol.% Mn-doped BNKLT88 ceramics at different vibration velocities. As mentioned in the experimental procedures section, the current and voltage on the samples were automatically controlled by a Labview program in order to keep the vibration velocity constant. The lowest voltage and current were obtained at the resonance and antiresonance frequencies, respectively. Both the resonance and antiresonance frequencies generate large amplitude of mechanical displacement. The main difference between these two electromechanical resonances is the driving impedance/admittance [13]. While a low driving voltage and high driving current were required at the resonance frequency, the opposite was observed at the antiresonance frequency. With increasing the vibration velocity, the driving voltage and current increased as expected. The input driving power in the vicinity of fundamental resonances in undoped and Mn-doped ceramics is shown in Fig. 4.28(b). The minimum input powers in these graphs correspond to the resonance and antiresonance frequencies. At the resonance frequency under vibration velocities of 0.1 and 0.2 m.s⁻¹, the input power was decreased by about 70-75 % upon Mn-doping. In undoped ceramics, the input power at f_a was less than f_r which again confirmed the higher efficiency of the transducer at antiresonance frequency. On the other hand, in 1.5 mol.% Mn-doped ceramics, input power at the antiresonance frequency was higher or equal to that of resonance frequency which is agreement with the data shown in Fig. 4.27. Increasing the vibration velocity led to increasing the input power. It also resulted in shifting and broadening the fundamental peaks which was more discernible in undoped samples. This was caused by heat generation and decreasing the mechanical quality factor at high vibration velocities as discussed before.

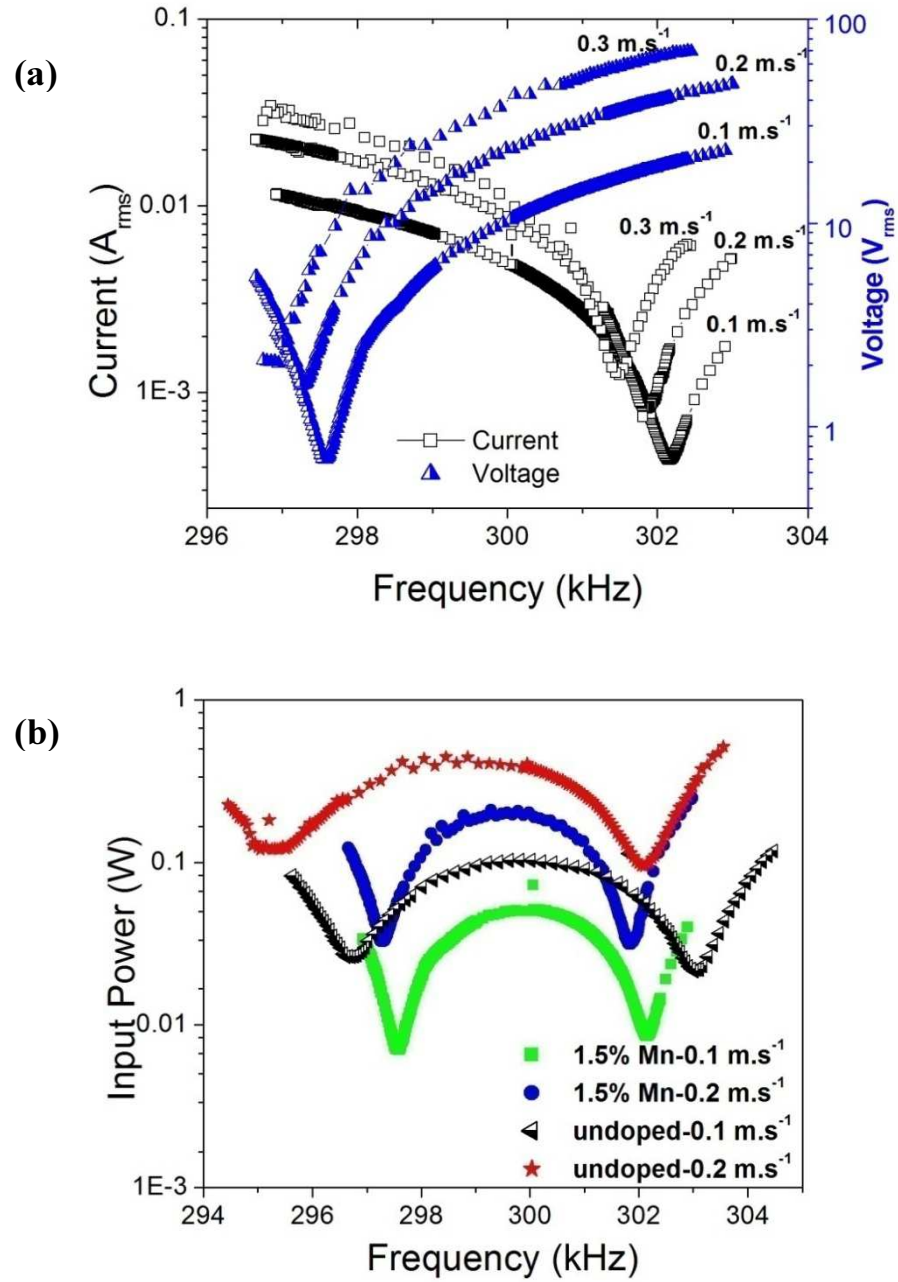


Fig. 4. 28. (a) Controlled voltage and current in 1.5 mol.% Mn-doped BNKLT88 ceramics at different vibration velocities (b) Input power across the resonance and antiresonance frequencies in undoped and 1.5 mol.% Mn-doped BNKLT88 ceramics.

4.4 Summary

In the ternary system of $x[\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3]-y[\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3]-(1-x-y)[\text{Bi}_{0.5}\text{Li}_{0.5}\text{TiO}_3]$, the highest mechanical quality factor ($Q_m \sim 420$) was obtained at a composition with x and y values of 0.88 and 0.08, respectively (at sintering temperature of 1125 °C). To further enhance the Q_m of these lead-free ceramics, the effects of acceptor dopants such as Mn and Fe were investigated. The processing and electromechanical properties of acceptor-doped $0.88[\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3]-0.08[\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3]-0.04[\text{Bi}_{0.5}\text{Li}_{0.5}\text{TiO}_3]$ (abbreviated to BNKLT88) ceramics prepared by mixed oxide route were comprehensively studied. Different amounts of Mn and Fe were added to the ceramics either in form of a dopant (B-site substitution) or an additive (added after calcination). The sintering temperature was optimized to obtain fully dense samples without formation of a liquid phase during sintering. Mn-addition did not exhibit any hardening effect and in fact led to a remarkable increase in the dielectric loss as well as a decrease in the Q_m . On the other hand, Mn and Fe-doping resulted in a considerable enhancement of Q_m . Acceptor dopants resulted in decreasing the planar coupling coefficient, dielectric constant, and dielectric loss due to the domain wall pinning effect of oxygen vacancies. The Q_m , d_{33} , k_p , ϵ_r and $\tan\delta$ values for 1.5 mol.% Mn-doped sample were 970, 87 pC.N⁻¹, 0.218, 310, and 0.009, respectively. Although it was more difficult to pole Fe-doped ceramics due to their higher conductivity compared to Mn-doped samples, a careful control of Fe-concentration and poling conditions yet yielded high values of mechanical quality factor. The Q_m , d_{33} , k_p , ϵ_r and $\tan\delta$ values for 1.5 mol.% Fe-doped sample were measured to be 900, 81 pC.N⁻¹, 0.198, 295, and 0.009, respectively. Acceptor dopants slightly decreased the optimum sintering temperature of BNKLT88 ceramics. The performance of Mn-

doped samples under high vibration velocity was evaluated by a high power measurement system. It was shown that Mn-doping effectively reduced the heat generation under high drive condition and resulted in a higher vibration velocity compared to the undoped samples. The BNKLT88 ceramics doped with 1.5 mol.% Mn exhibited the best high power performance with a maximum vibration velocity of 0.6 m.s^{-1} which was superior to PZT8 ceramics. High mechanical quality factor along with a high coercive field contributed to the enhanced high power performance of BNKLT88 ceramics. In most PZTs, antiresonance mode has a higher efficiency than resonance mode ($Q_B > Q_A$). Same behavior was observed in undoped BNKLT88 ceramics implying that $2\tan\theta' > (\tan\phi' + \tan\delta')$. In Mn-doped ceramics the efficiency at resonance mode was higher than antiresonance. This was attributed to the domain wall clamping effect of Mn which reduced the piezoelectric loss.

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5 Fabrication and Evaluation of a Single Element $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based Ultrasonic Transducer

Abstract

This chapter discusses the fabrication and characterization of a single element high frequency ultrasonic transducer with a lead-free piezoelectric element. $[0.88(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)-0.08(\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3)-0.04(\text{Bi}_{0.5}\text{Li}_{0.5}\text{TiO}_3)]$ composition was chosen as the active element of the transducer. As presented in chapters 3 and 4, this relatively hard piezoelectric composition exhibited a thickness coupling coefficient k_t of 0.49, and a dielectric constant of 380 (at 1 kHz). A low dielectric constant is desired for high frequency single element transducers to enlarge the aperture size and improve the resolution. To make the transducer, a 109 μm thick ceramic was sandwiched between an epoxy-tungsten backing layer and a silver epoxy matching layer. An epoxy lens was also incorporated into the transducer's design to focus the ultrasound beam and improve the lateral resolution. The pulse-echo response of the transducer was also simulated by the KLM model. The focused transducer with a center frequency of 22.9 MHz demonstrated a -6dB bandwidth of 55% and an insertion loss of -32 dB, while the -20dB pulsed length was measured to be 150 ns. It was shown that the transducer was able to produce clear images of a phantom made of 30 μm copper wires. For a comparison, a 20 MHz lead-based transducer with a PZT4 (hard PZT) active element was also modeled by the KLM method. The results indicated that the fabricated transducer with a lateral resolution of 260 μm and a relatively high depolarization temperature could be considered as a candidate for replacement of lead-based materials in ultrasonic transducer applications.

5.1 Introduction

High frequency ultrasound, in range of 20-200 MHz, has been extensively studied in high resolution diagnostic imaging of fine tissues such as skin, [1-4] gastrointestinal tract, [5] the arterial walls, [6] eye, [4, 7] blood vessels, [4] Fallopian tubes and endometrial texture [8, 9] and so forth. Selection of piezoelectric materials as the active element of transducers has a significant influence on the performance of high frequency ultrasonic transducers. Due to their high electromechanical properties, lead-based materials, such as PbTiO_3 (PT), $\text{Pb}_x(\text{Zr,Ti})_{1-x}\text{O}_3$ (PZT), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT) and $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PIN-PMN-PT), [10-16] have been commercially used for fabrication of transducers. However, the toxicity of lead has raised global efforts to find lead-free materials as alternative compositions. Although the electromechanical properties of lead-free materials are yet inferior to their lead-based counterparts, several studies have shown that lead-free compositions such as $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT), LiNbO_3 and $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) can be successfully employed for making ultrasonic transducers for a wide range of frequencies and applications. [15, 17-30]

The objective of the work presented in this chapter was to fabricate and evaluate the performance of a 20 MHz single element ultrasonic transducer using a lead-free composition. The dielectric and piezoelectric properties of the BNKLT ceramics were presented in Table 3.2, chapter 3. As mentioned in that chapter, the BNKLT76 and BNKLT68 ceramics exhibited the highest electromechanical properties and dielectric constant among the studied compositions. However, the comparison of the piezoelectric data provided in Table 3.2 reveals that BNKLT88 possesses the highest value of k_t to k_p

ratio which can improve the performance of the transducer by suppressing the effect of planar vibration. Additionally, BNKLT88 composition has a low value of clamped dielectric constant ($\epsilon_{33}^s/\epsilon_0=275$). To have an efficient electrical impedance matching, transducers need to be designed to operate at an electrical impedance of 50 Ω . Since the electrical impedance holds an inverse relation with the dielectric constant, a larger radiating area (aperture) can be obtained in high frequency single element transducers made by materials with a low dielectric constant. This consequently results in a better lateral resolution and electrical impedance matching. In addition, BNKLT88 has a higher depolarization temperature and lower dielectric loss compared to other investigated compositions [31]. A higher Q_m of this material compared to other low Q_m compositions such as MPB is expected to yield a transducer with a narrower bandwidth which is not desirable for medical imaging applications. However, due to the low dielectric loss of BNKLT88 composition, a transducer with a lower insertion loss is anticipated. Thus, the BNKLT88 ceramic with compromised properties was selected as the active element for the fabrication of a 20 MHz single element transducer.

5.2 Experimental Procedure

5.2.1 Fabrication of Ultrasonic Transducers

0.88BNT-0.08BKT-0.04BLT (BNKLT88) ceramic was prepared via conventional mixed oxide route. Appropriate molar ratios of the raw materials containing oxide and carbonate powders Bi_2O_3 (Alfa Aesar, 99%), Na_2CO_3 (Alfa Aesar, 99.997%), K_2CO_3 (Alfa Aesar, 99.997%), Li_2CO_3 (Sigma-Aldrich, 99.99%), and TiO_2 (Sigma-Aldrich, 99.9%) were mixed in acetone and zirconia media for 12 hours, then dried and calcined

at 800 °C for 3 hours. The calcined powders were ball milled again for 24 hours. After drying, 8 wt.% polyvinyl alcohol (PVA) binder solution was added to the dried powders. Samples of 14.6 mm in diameter and 1.2 mm in height were uniaxially pressed at 120 MPa and sintered at 1150 °C for 2 hours. After sintering, the ceramic was lapped down and then coated with 150 nm thick Au using the gold-sputtering technique. The ceramic was then poled in a silicon oil bath at 70-100 °C under an applied electric field of 40-50 kV.cm⁻¹ for 15 minutes.

Fig. 5.1 illustrates the schematic structure of the transducer with an acoustic lens attached. As shown, the BNKLT88 ceramic is sandwiched between the backing and matching layers. In order to obtain a resonance frequency of about 20 MHz, the ceramic element was lapped down to a thickness of 109±1 µm (The desired thickness according to the simulation was 115 µm. However due to the limitations of manual polishing, the obtained thickness was slightly lower than 115 µm). The gold electrode with diameter of 2.4 mm and 150 nm thickness was sputtered on one side of the ceramic to act as the bottom electrode. Then, a 200 µm diameter copper wire was attached to the bottom electrode using silver epoxy. The thickness of backing layer was 1.3 mm to provide ~30dB round trip acoustic attenuation around 20 MHz. The backing layer was made of a mixture of 30 wt.% tungsten powder (Aldrich, 99.99%) homogeneously dispersed in STYCAST-1265 epoxy and cured at 65 °C for 4 hours. The sample was then placed inside a brass tube and the gaps were filled with EPOTEK-301 epoxy. The epoxy was cured at room temperature for 24 hours. The physical and acoustic properties of the active and passive layers are presented in Table 5.1.

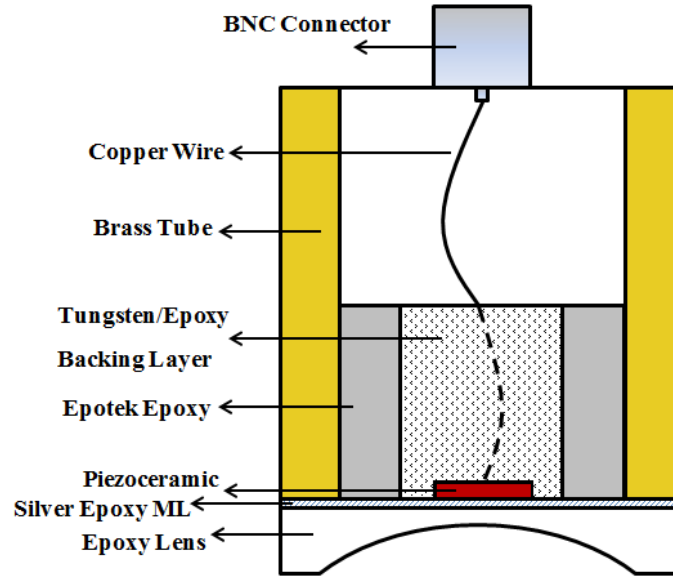


Fig. 5. 1. Schematic structure of the ultrasonic transducer with a single matching layer and lens.
(The picture is not drawn to scale).

Table 5. 1. The physical and acoustic properties of the transducer's components.

Material	Density (g.cm ⁻³)	Sound Velocity (m.s ⁻¹)	Thickness (μm)	Acoustic Impedance (MRayl)	Attenuation@ (dB.cm ⁻¹ .MHz ⁻¹)
Backing Layer	6.65	1574	1300	10.5	29.5
Matching Layer	4.00	1850	15 - 20	7.4	5.5
Active Element	5.84	5458	109	31.9	-

To decrease the reflection coefficient of acoustic wave at the ceramic-medium interface, the front side of the transducer was covered with silver epoxy (DuPont 4922N) serving both as the matching layer and as top electrode connecting the ceramic to the brass tube. In general, the thickness of matching layer needs to be equal to $\lambda/4$ (where λ is the wavelength of acoustic wave in the matching layer) to achieve maximum transmission of acoustic wave into the medium. Considering $Z_{Ceramic}=31.9$ MRayls and $Z_{water}=1.5$ MRayls, the desired acoustic impedance of matching layer (Z_M) falls in a range of 5.2-6.9 MRayls using the following equations: [14, 32]

$$Z_M = \sqrt{Z_{water} \cdot Z_{Ceramic}} \quad (5.1a)$$

$$Z_M = \sqrt[3]{2Z_{water}^2 \cdot Z_{ceramic}} \quad (5.1b)$$

For a double matching layer design, the appropriate acoustic impedances for the first and second layers can be calculated through following equations, yielding values of 2.3 and 8.6 MRayls, respectively.

$$Z_{M1} = Z_{water}^{3/7} \cdot Z_{Ceramic}^{4/7} \quad (5.2a)$$

$$Z_{M2} = Z_{water}^{6/7} \cdot Z_{Ceramic}^{1/7} \quad (5.2b)$$

In this study, the addition of an EPOTEK-301 epoxy lens onto the front side was preferred over the press focusing procedure due to the ease of fabrication process, avoiding any damage to the piezoceramic, and potentially achieving larger bandwidth. [33] As shown in Fig. 5.2, the transducer was mounted facing up in a holder and then the epoxy was molded atop using a steel ball bearing. The steel ball was first covered with a layer of paraffin film (Parafilm) and connected to a holder which was attached to an X-Y-Z stage. A drop of epoxy was placed on the front face of the transducer and the ball was lowered to a distance of 30 μm above the ceramic to create $\sim\lambda/4$ thick epoxy at the lens apex. When the lens thickness right above the ceramic edge is less than $0.1R$ (where R is the radius of curvature of the lens) and the F-number is higher than 2.5, the focal length (F) of the transducer can be calculated by the following equation: [34]

$$F \approx R \left[1 - \frac{C_2}{C_1} \right]^{-1} \quad (5.3)$$

where R is the radius of curvature of the lens (4.85 mm for this work), C_1 is the sound velocity in the lens (2640 m.s^{-1}), and C_2 is the sound velocity in water (1480 m.s^{-1}).

According to this equation, the focal length of the transducer is estimated to be around 11 mm.

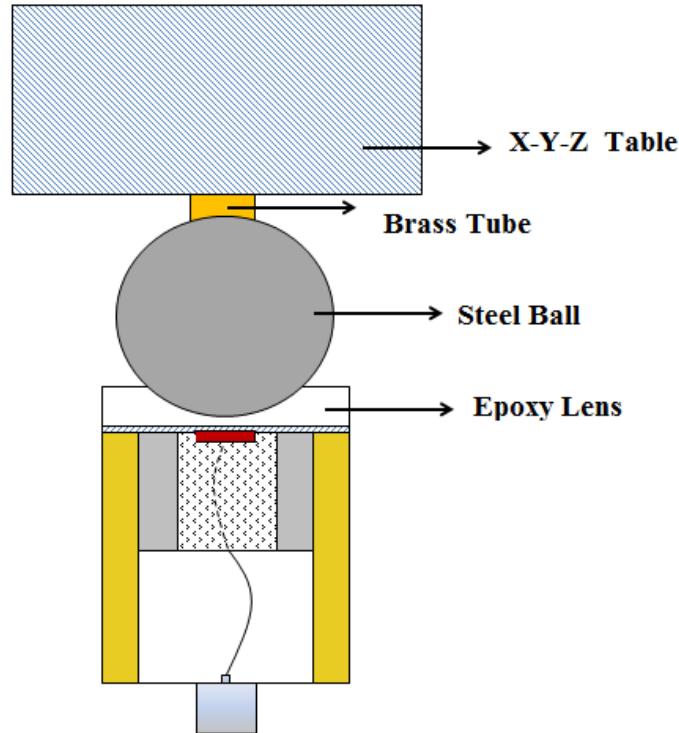


Fig. 5. 2. Schematic illustration of the lens forming technique on front face of the transducer.
(The picture is not drawn to scale).

5.2.2 Characterization of the Transducer

The pulse-echo responses of the transducer were evaluated using a conventional pulse-echo method in water at room temperature. As shown in schematically in Fig. 5.3, the transducer was mounted in a water tank in front of a 20 mm thick stainless steel plate (as the target) and then connected to a variable attenuator and the pulser/receiver (Model 5800PR; Panametrics, Waltham, MA). The measurement for the unfocused transducer was carried out at a transducer to target distance of 22 mm corresponding to the transducer acoustic focal point (transition point from near field to far field) calculated by:

$$N = \frac{a^2}{\lambda} = a^2 \cdot \frac{f_c}{C} \quad (5.4)$$

where a is the radius of the transducer, C is the sound velocity, and λ is the wavelength corresponding to the transducer center frequency (f_c). In the case of lens-focused transducer, the stainless steel target was placed at the geometric focal point. The transducer was aligned in respect to the target by maximizing the echo signal amplitude. Attention was paid to avoid formation of air bubbles on the surface of the transducer or the target. Table 5.2 represents the transmission and receiving parameters set on the pulser. The lateral resolution and depth of field were measured by collecting echo amplitudes when the transducer was laterally or axially scanned over a fine object (e.g. a 150 μm glass fiber or a 30 μm copper wire). The transducer position was controlled by a micrometer attached to the X-Y-Z table. Similar technique was utilized for imaging studies. To create images of the wire phantom, one wire was located at the focal point of the transducer while four other wires located at different planes under and above the focal point. An step size of 10 μm was set for the data acquisition. The time domain signals were processed by a program written in Matlab software to display images in a 30 dB dynamic range.

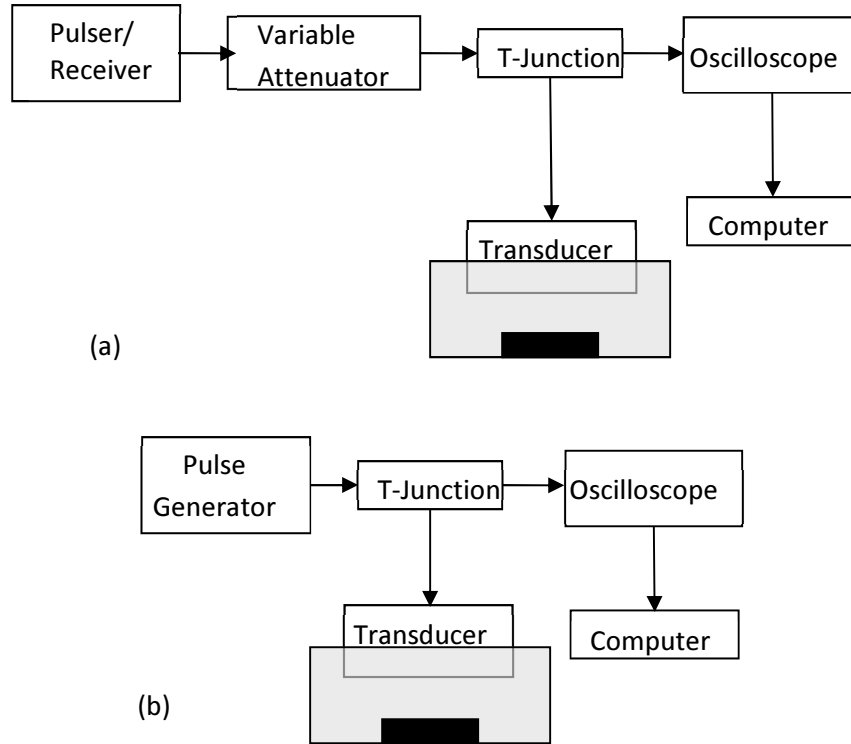


Fig. 5. 3. Schematics of the experimental set-up for (a) shock excitation and (b) burst excitation.

Table 5. 2. Parameters set on the pulser/receiver during measurements.

Transmit	Receive
Mode: THRU	HP Filter: 1 KHz
Frequency: 1 KHz	LP Filter: 30 MHz
Energy: 12.5 μ J	Output Attenuation: 9.8 dB
Damping: 50 Ω	Input Attenuation: 0 dB
	Gain: 40 dB

Shock excitation of the transducer at 50 Ω damping was implemented with an output voltage of 3 V, employing a variable attenuator. The echo waveform was recorded by a 500 MHz digital oscilloscope (LeCroy 9354TM; Chestnut Ridge, NY) set to 50 Ω coupling. The frequency spectrum of the transducer echo response was obtained using the built-in Fast Fourier Transform (FFT) function of the oscilloscope. The bandwidth of the

transducer was calculated from the center frequency (f_c), low and high frequencies (f_L and f_H , respectively) at -6dB points of the frequency response spectrum.

Insertion loss (IL) which is defined as the ratio of the output power (P_o) to input power (P_i) can be calculated by having the ratio of the received echo voltage to the pulse excitation voltage: [19]

$$IL = 10 \log \left(\frac{P_o}{P_i} \right) = 20 \log \left(\frac{V_o}{V_i} \right) \quad (5.5)$$

The value of V_i was read on the oscilloscope while the function generator was terminated by a 50 Ω load connected to the oscilloscope. The V_o was the peak-to-peak amplitude of the echo response reflected from a steel target located at the focal point of the transducers.

The transducer acoustic performance was also predicted using the one-dimensional KLM model. The model included 109 μm thick ceramic, 1.3 mm thick tungsten-STYCAST epoxy as backing material, and 15-20 μm thick silver paint matching layer. For the focused transducer, an EPOTEK-301 lens was included in the model.

The KLM model (after R. Krimholtz, D. A. Leedom, G. L. Matthaei) is the most widely used technique to simulate the performance of ultrasound transducers. In comparison to other models introduced by Mason or Redwood, the KLM model provides an easier approach for optimization of the transducer performance [35]. The electrical equivalent circuit in this model contains a 3-port network representing the transducer elements as shown in Fig. 5.4. There are two acoustic ports with transmission lines of two quarter wave representing the backing and front layers as well as an electrical port representing the piezoelectric element. The acoustic and electrical ports are separated by

a transformer with an electromechanical conversion coefficient of Φ which is a function of the thickness coupling coefficient of the piezoelectric material.

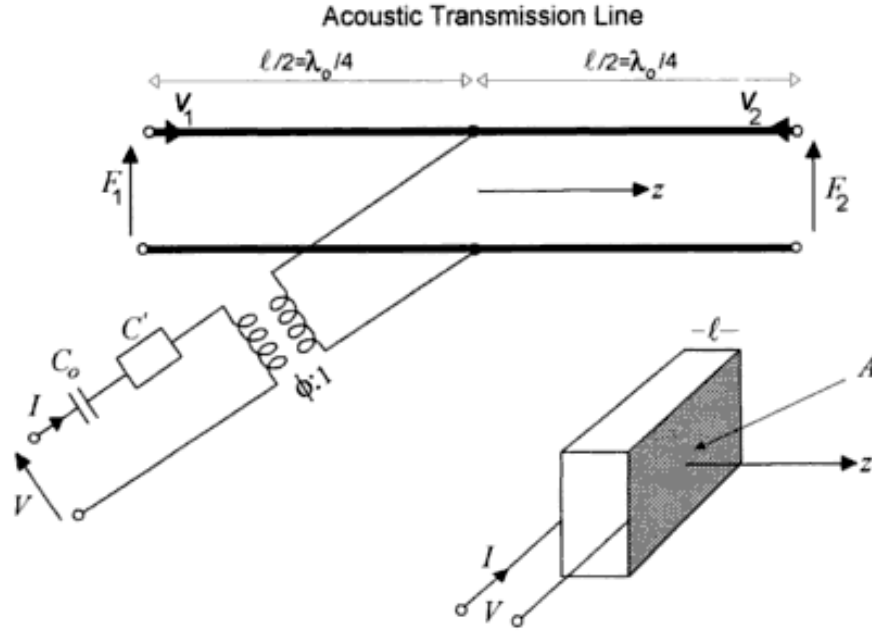


Fig. 5. 4. The KLM model of an ultrasound transducer. Distance l is the thickness of the transducer, and A is the transducer surface area [35].

On electrical side of the circuit, the voltage (V) is proportional to the current (I) via electrical impedance (Z): $V=ZI$. Similarly on the acoustic sides, there is a linear relationship between force (F) and velocity (v): $F=Z_o v$ (Where Z_o is the acoustic impedance of the material). The acoustic and electrical impedances are related to each other through the following equation: $Z_o=Z \cdot \Phi^2$. The capacitor C' of the electrical port has an impedance whose reactance is zero at the antiresonance frequency. The behavior of a transducer is simulated by considering fundamental equations such as:

$$C_o = \epsilon_{33}^s \cdot \frac{A}{l} \quad (5.6a)$$

$$\phi = k_t \sqrt{\frac{\pi}{\omega_o Z_a C_o}} \cdot \frac{\sin c(\frac{\pi \omega}{2\omega_o})}{\pi \omega / 2\omega_o} \quad (5.6b)$$

$$Z_a = A Z_o = \rho A v = A \sqrt{c^D \rho} \quad (5.6c)$$

$$\omega_o = \frac{\pi v}{l} = \frac{\pi}{l} \sqrt{\frac{c^D}{\rho}} \quad (5.6d)$$

Where C_o is the capacitance, ω_o is the antiresonance angular frequency, v is the sound velocity, Z_o is the acoustic impedance, and ϵ_{33}^s is the high frequency permittivity (constant stress condition).

5.3 Results and Discussion

5.3.1 Unfocused Transducer

Fig. 5.5 shows the impedance and phase angle of the BNKLT88 transducer without matching layer. It should be mentioned that the ceramic was re-poled after polishing and attachment of backing and matching layers to eliminate the effect of partial depoling that may happen during polishing step. The values of electrical impedance and phase angle at the resonant frequency of 22.8 MHz, are 30.3 Ω and -58 degree, respectively.

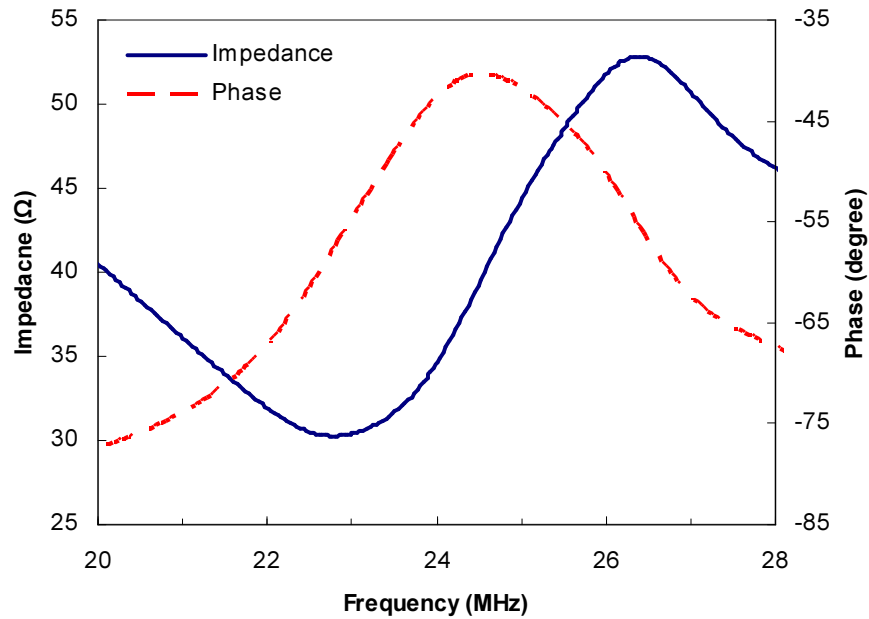


Fig. 5. 5. The electrical impedance magnitude and phase of the transducer without matching layer measured in air.

Figs. 5.6 and 5.7 show the pulse-echo response of the unfocused transducer without and with a matching layer, respectively. When no matching layer was applied, a 150 nm thick gold was sputtered on the front face of the transducer. The transducer with no matching layer showed a narrow bandwidth (25.83%) and a long pulse length (310 ns) which deteriorates the resolution. The transducer with matching layer exhibited a wider bandwidth with a center frequency of 22.3 MHz. The -6dB bandwidth of the transducer increased from 25.83% to 61.36% with addition of a single matching layer. Matching layer also improved the echo response of the traducer with shortening the pulse length from 310 to 130 nanoseconds at -20dB. The pulse-echo response predicted by the KLM model is also included in Figs. 5.7 (a) and (b) for comparison with the experimental data. Table 5.3 presents the experimental and modeled acoustic characteristics of unfocused transducer. There is a good agreement between the experimental result and KLM model.

The value of two-way insertion loss of the un-focused transducer was calculated to be -28.6 dB. This is the corrected value of insertion loss after compensation for the effects of attenuation in water ($2.2 \times 10^{-4} \text{ dB} \cdot \text{mm}^{-1} \cdot \text{MHz}^{-2}$) as well as the transmission into the steel plate ($Z_{\text{steel}} = 46 \text{ MRayls}$, and $Z_{\text{water}} = 1.5 \text{ MRayls}$).

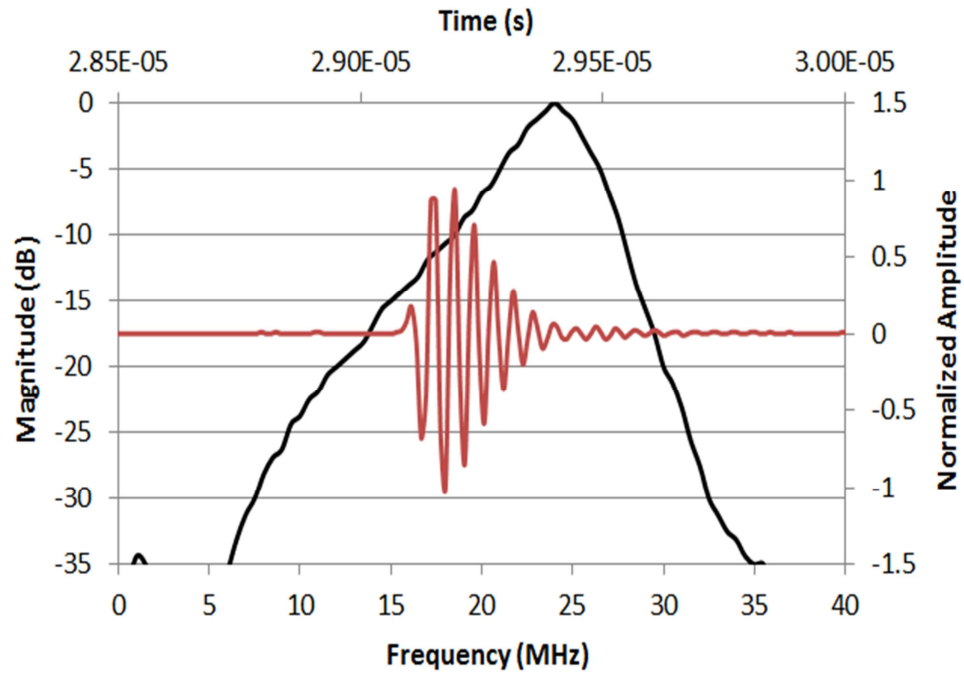


Fig. 5. 6. Time domain and frequency domain of the unfocused transducer without matching layer.

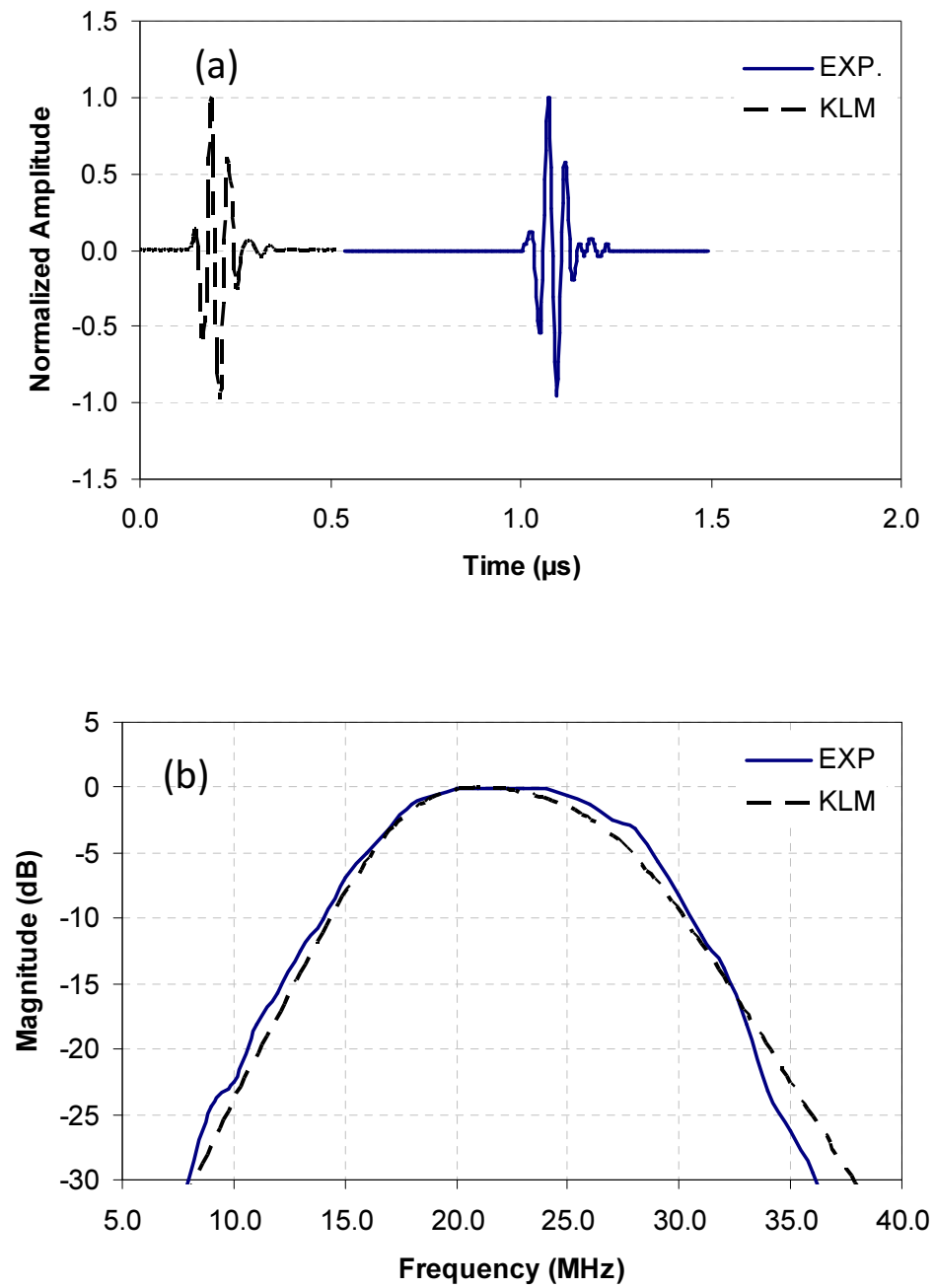


Fig. 5. 7. (a) Time domain and (d) frequency domain of the unfocused transducer with single matching layer. The KLM results have also been shown for comparison.

Table 5. 3. The measured and KLM-calculated parameters of the unfocused transducer with and without matching layer.

Parameter	Shock excited		KLM
	Without ML	With ML	
f_L	20.63	15.45	15.90
f_H	26.75	29.12	28.35
f_C	23.69	22.29	22.13
-6dB BW%	25.83	61.36	56.27
-20dB Pulse length	310	130	132
Insertion loss (dB)	-----	-28.6	-33.4

The deviation of the center frequency from 20 MHz is due to the lower thickness of the polished ceramic (109 μm) than the desired thickness (115 μm) as well as inaccuracy in the thickness of matching layer and the lens. Particularly at high frequencies, the pulse-echo response is very sensitive to the variations of the matching layer thickness. Figs 5.8. (a)-(c) show the KLM models of BNKLT88 transducers with various matching layer (silver-epoxy) thicknesses. The ceramic thickness and electrode radius in this model were 115 μm and 1.25 mm, respectively. The corresponding quarter wavelength thickness for the silver epoxy matching layer was 23 μm . As demonstrated in this Fig 5.8. and summarized in table 5.4, ± 5 μm variation in thickness of the matching layer shifted the center frequency by ± 1 MHz. As the matching layer thickness increases, the center frequency decreases and the -6dB bandwidth increases at the expense of a higher insertion loss and less sensitivity. Based on the KLM models, the thickness of the matching layer in the fabricated transducer was estimated to be about 15 μm .

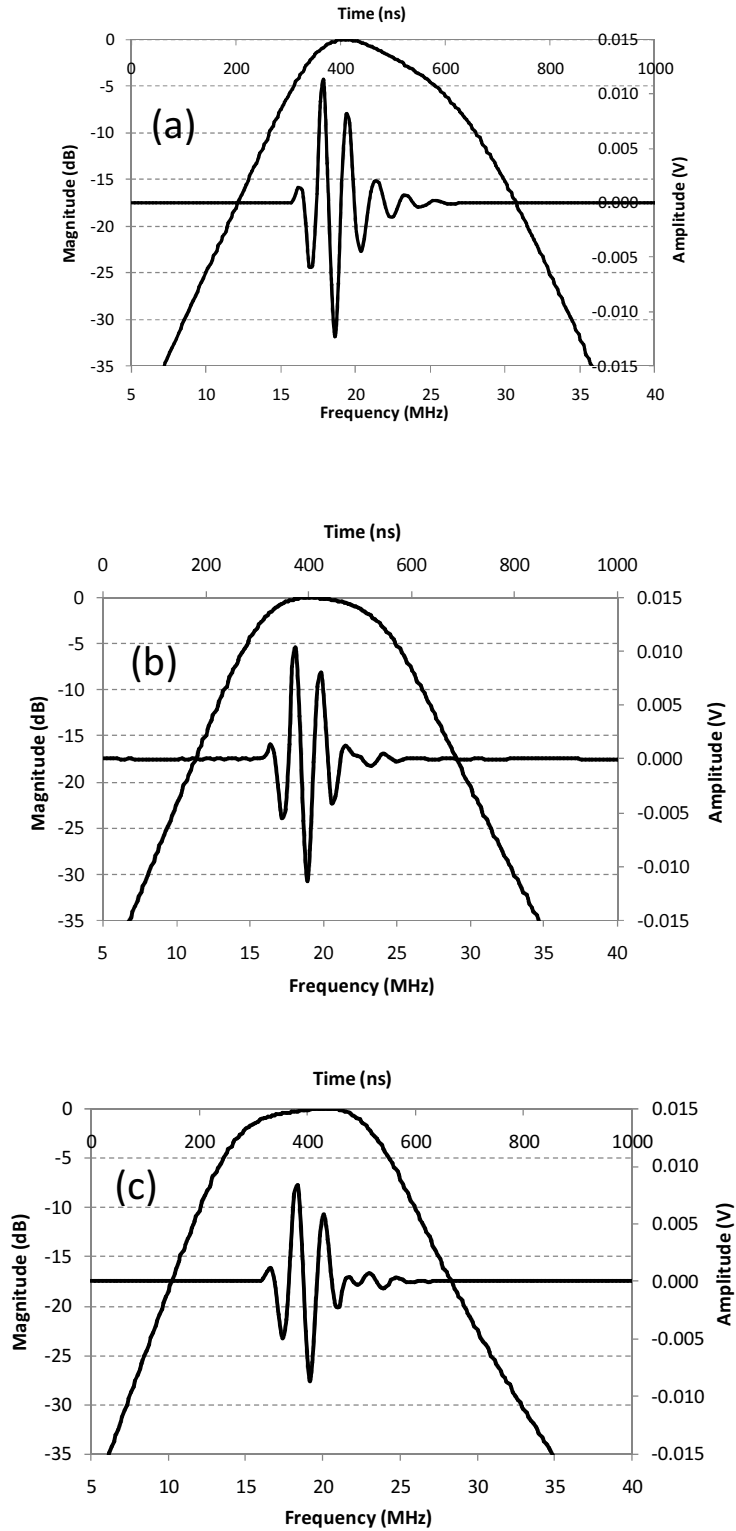


Fig. 5. 8. The KLM models showing the influence of the matching layer thickness on the pulse-echo response of BNKLT88 ultrasonic transducer. (a) 18 μm , (b) 23 μm , and (c) 28 μm .

Table 5. 4. Effect of the matching layer thickness on the properties of a BNKLT88 ultrasonic transducer simulated by the KLM model.

ML Thickness	18 μm	23 μm	28 μm
f_c	20.9	20	19
-6dB BW%	49.8	54.2	59.1
Insertion loss (dB)	-32.4	-33.3	-35.4

Fig. 5.9 shows the lateral response of the unfocused transducer acquired by scanning across a 150 μm glass fiber. The lateral resolution at -6dB is 740 μm . Theoretical value of lateral resolution (R_{lat}) calculated from eq. (5.7) is about 610 μm .

$$R_{lat} = \frac{\lambda.F}{2a} = \lambda.F^\# \quad (5.7)$$

where the F is the natural focal length and $2a$ is the diameter of transducer. Since the accuracy of the lateral resolution predicted by this equation is about 20%, the value measured is in agreement with the calculated one.

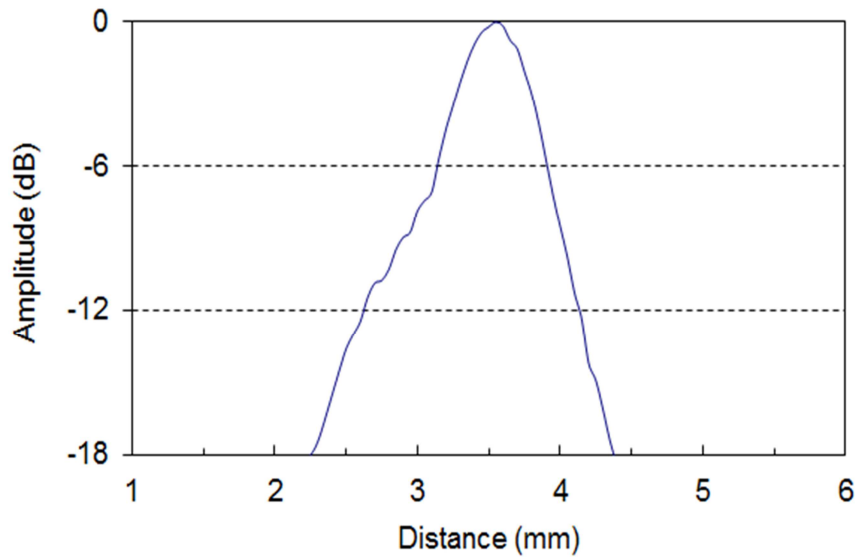


Fig. 5. 9. Lateral line spread response for the unfocused transducer obtained by scanning the transducer across a 150 μm glass fiber.

Fig. 5.10 illustrates an image of a wire phantom consisting of five nickel wires with $240\text{ }\mu\text{m}$ diameter. The lateral and axial spacing of wires are 10 mm and 5 mm , respectively. The image of wire located at the focal point (corresponding to $Z=23\text{ mm}$ in the figure) has a higher contrast and is sharper than the images of other wires positioned out of the focal point. With moving away from the focal point, the resolution of the images decreases and the lines become wider and less intense due to the increase of the beam width out of focal zone.

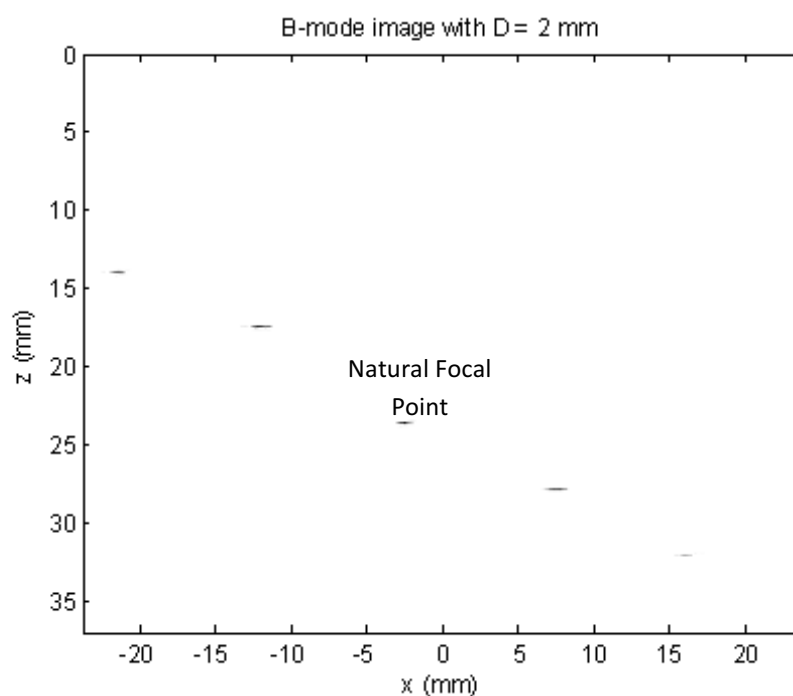


Fig. 5. 10. Image of wire phantom made of five $240\text{ }\mu\text{m}$ nickel wires. Image was obtained by unfocused transducer at a dynamic range of 30 dB .

5.3.2 Focused Transducer

Fig. 5.11 shows the pulse-echo waveform and frequency spectrum of the focused transducer under shock excitation. The center frequency and -6dB bandwidth were calculated to be 22.9 MHz and 55 % respectively, while the -20dB pulse length is 150 nanoseconds. The narrowing of the bandwidth compared to the unfocused transducer can be attributed to non-uniform thickness of the Epotek lens. The KLM model of lens focused transducer is also included in Fig. 5.11. As shown, there is a good agreement between the experimental result and KLM model.

The focal length of the transducer was measured to be about 10.9 mm which was very close to the expected value of 11 mm, calculated from eq. (5.3). Table 5.5 summarizes the properties of the lens-focused transducer.

Fig. 5.12 (a) depicts the lateral resolution of the transducer obtained by measuring the peak-to-peak amplitude of pulse-echo response from a copper wire (30 μm in diameter). Based on the data obtained, the -6dB lateral resolution is about 260 μm . This value was measured to be around 740 μm for unfocused transducer. The addition of lens, therefore, improved the lateral resolution by 65 percent. Using the equations (5.7) and (5.8) [4], the theoretical values of axial and lateral resolutions of the focused transducer (R_{ax} and R_{lat}), were also calculated to be 62 μm and 280 μm , respectively. The results are in agreement with the measured values.

$$R_{ax} = \frac{C}{2\Delta f} \quad (5.8)$$

Where C and Δf are the sound velocity and frequency width ($f_{\text{high}} - f_{\text{low}}$), respectively

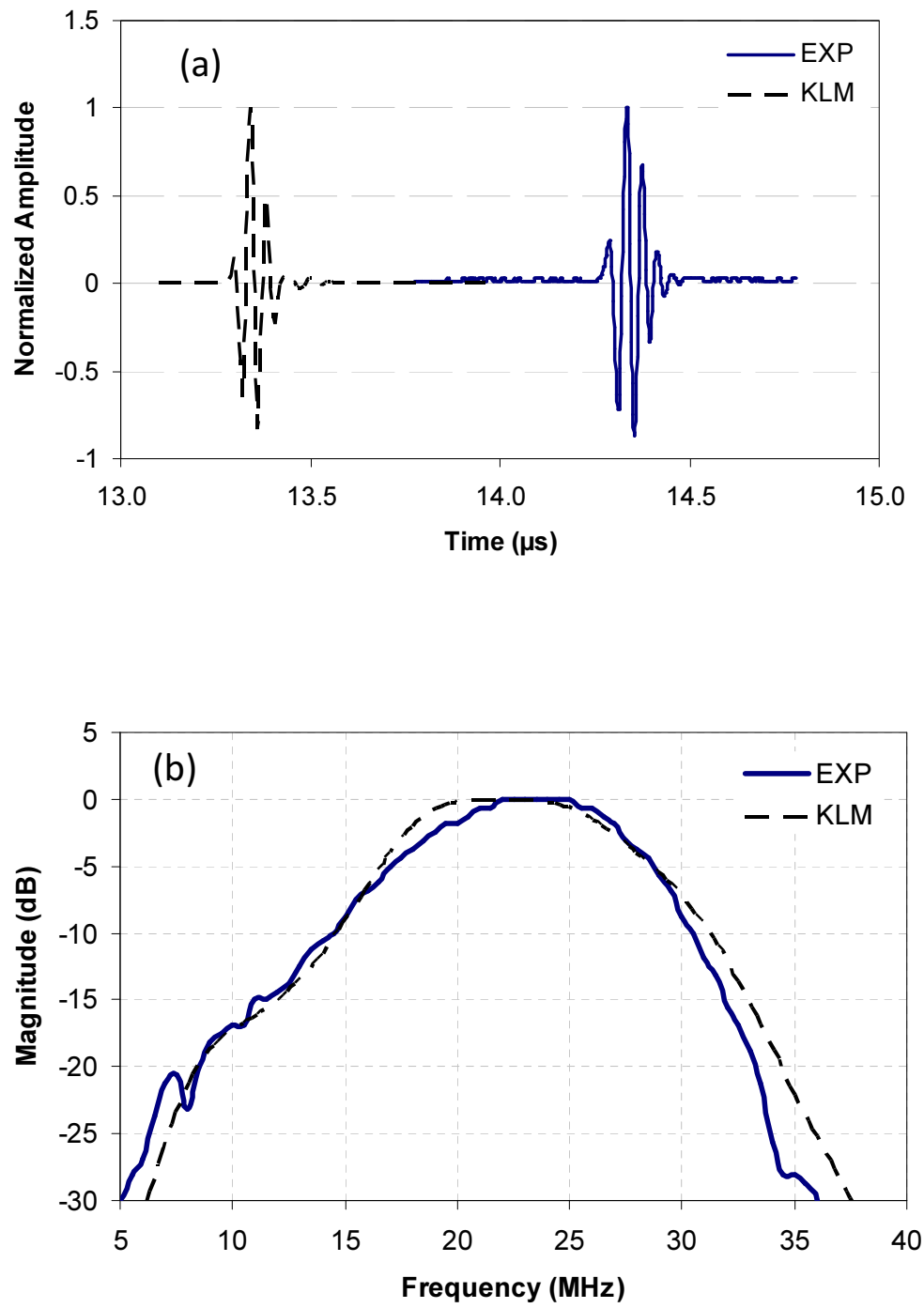
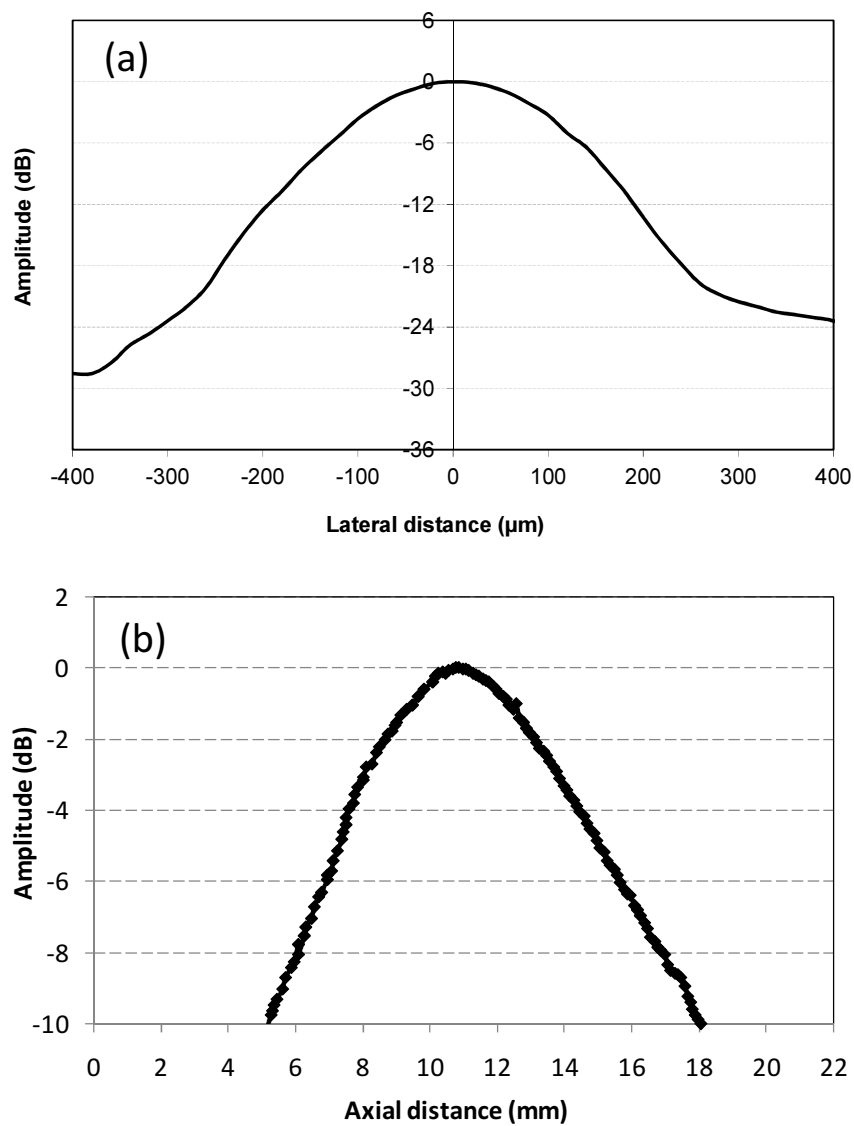


Fig. 5. 11. Shock excited (a) time and (b) frequency domains of the lens-focused transducer.

Table 5. 5. The measured acoustic properties of the focused transducer.

Parameter	Shock excited	KLM	Burst excited (mono-cycle)
f_L	16.6	16.3	16.6
f_H	29.2	29.2	29.8
f_C	22.9	22.7	23.2
-6dB BW%	55.0	56.7	56.9
Insertion Loss (dB)	----	-34.8	-32.1

Fig. 5. 12. (a) Lateral line spread response for the focused transducer obtained by scanning the transducer across a 30 μm copper wire (b) Axial beam profile of the focused-transducer.

The axial beam profile of the transducer is shown in Fig. 5.12 (b). The maximum amplitude occurs at an axial distance of 11 mm corresponding to the focal length of the transducer and the -6dB depth of field (DOF) is 8.6 mm. The following equation can be used to estimate the theoretical value of DOF of a transducer:

$$\text{DOF} = 7 \lambda (F^\#)^2 \quad (5.9)$$

With plugging the λ and $F^\#$ values into this equation, the DOF was calculated to be 8.9 mm.

The imaging capability of the transducer was examined by scanning a wire phantom made of five copper wires (30 μm in diameter) as well as a diced ceramic (600 μm ceramic width). The phantoms used as the imaging targets are shown in Figs. 5.13 (a)-(b). The produced images are shown in Fig 5.13 (c)-(d), respectively. The image of wire located at the focal point has a higher contrast and is sharper than the images of other wires positioned out of the focal point. With moving away from the focal point, the resolution of the images decreased and the lines became wider and less intense due to the increase of the beam width out of focal zone.

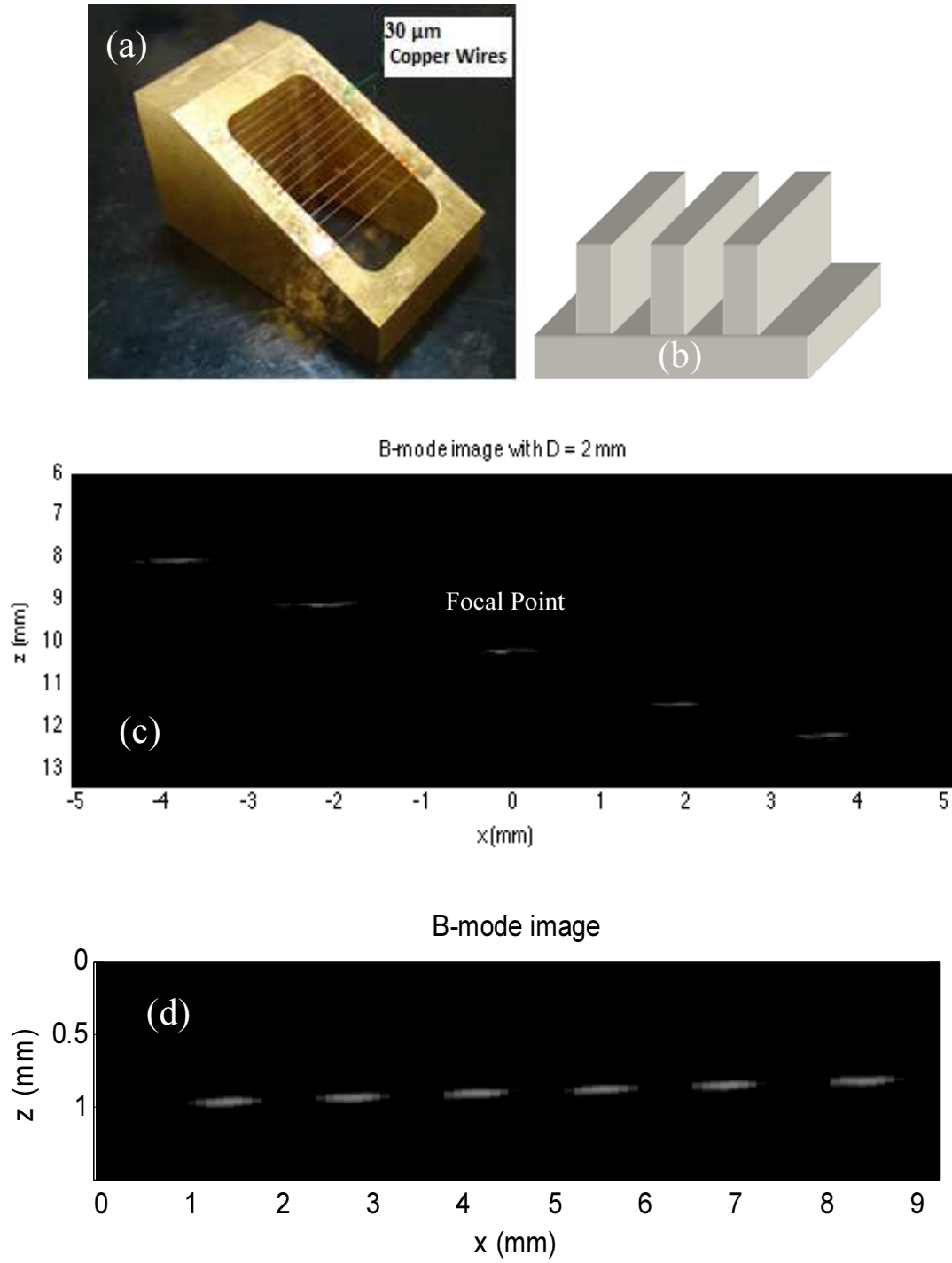


Fig. 5. 13. (a) A wire phantom of 30 μm copper wires (b) schematic of a 2-2 diced ceramic. The images of (c) wire phantom (d) diced ceramic produced by the focused transducer.

To compare the pulse-echo response of the BNKLT88 transducer with a lead-based material, a 20 MHz PZT4 transducer was designed by the KLM model. A PZT4 ceramic with the properties shown in table 5.6 was chosen as the active element of the transducer. The same backing and matching layers were included into the design. The ceramic thickness, aperture radius, and matching layer thickness were 102 μm , 0.685 mm, and 23 μm , respectively. For the focused transducer, an epoxy lens with a thickness of 33 μm was added as the second matching layer. The simulated time and frequency domains of these transducers are depicted in Fig 5.14 and the transducers properties are summarized in table 5.7. Compared to the BNT-based transducer, the PZT4 showed a narrower bandwidth and a lower insertion loss due to the higher mechanical quality factor and lower dielectric loss. It is also notable that the higher dielectric constant of PZT4 compared to the BNKLT88 composition, resulted in a smaller aperture size in the PZT transducer. According to the eq. (5.7), it is expected that the lateral resolution of the PZT4 transducer is inferior to that of BNT-based transducer.

Table 5. 6. Acoustic and electrical properties of PZT4 ceramic used in modeling of a 20 MHz ultrasonic transducer. The properties are obtained from Ref [36]. Properties of BNKLT88 ceramics are also shown for comparison.

Material	Density (g.cm^{-3})	Sound Velocity (m.s^{-1})	Thickness (μm)	Acoustic Impedance (MRayl)	ϵ_{33}^s	k_t	Q_m	$\tan\delta\%$
PZT4	7.50	4600	102	34.5	638	0.51	500	0.5
BNKLT88	5.84	5458	109	31.9	275	0.499	400	1.1

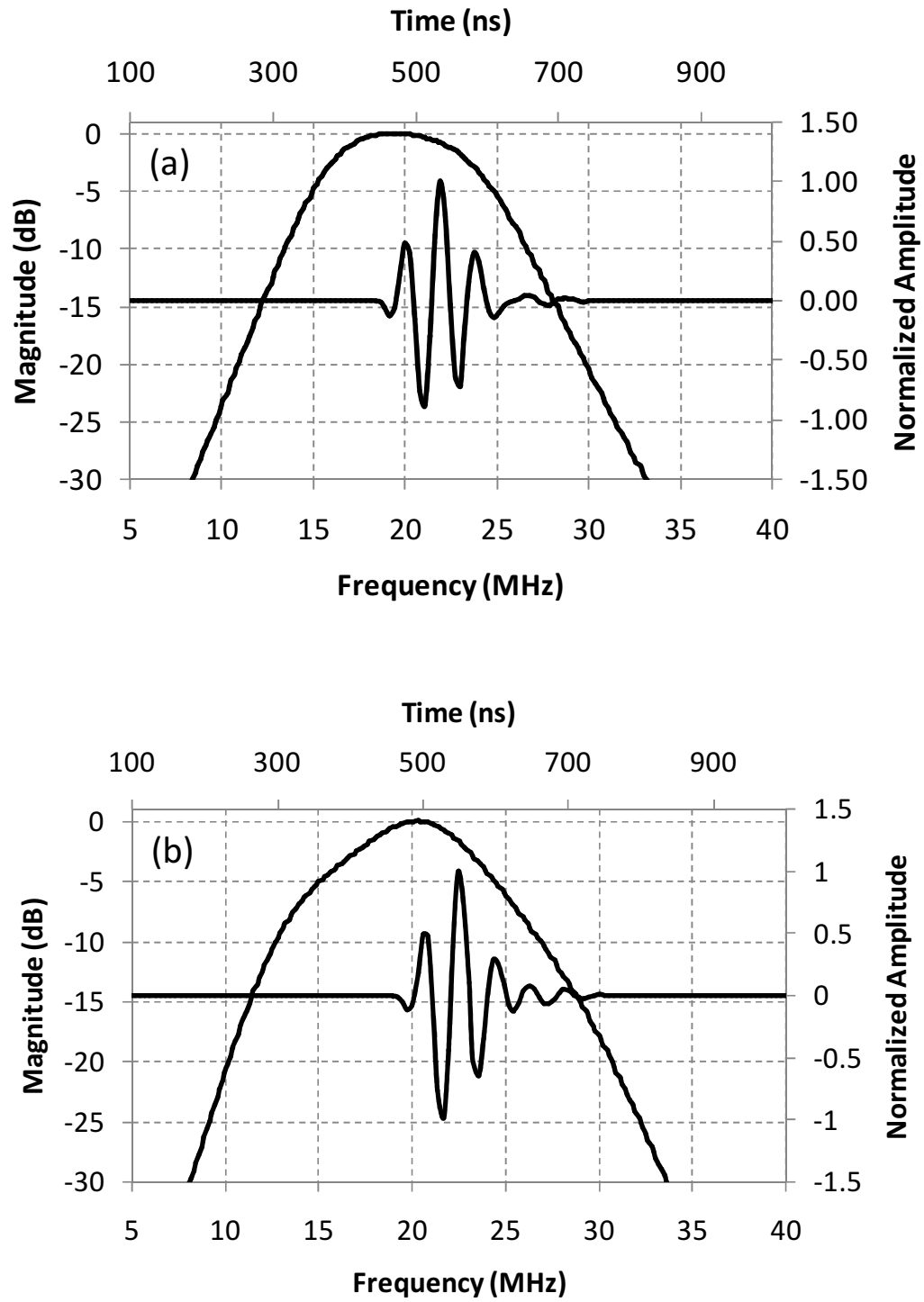


Fig. 5. 14. The KLM simulation of 20 MHz transducers with a PZT4 ceramic as the active layer (a) with a single matching layer (Silver-Epoxy) (b) with ML and epoxy lens attached.

Table 5. 7. The acoustic properties of 20MHz PZT4 transducers simulated by the KLM model.

Parameter	Single ML	With Lens
f_L	14.7	14.5
f_H	25.3	24.9
f_C	20.0	19.7
-6dB BW%	53.0	52.8
Insertion Loss (dB)	-30.0	-28.4

5.4 Summary

Table 5.8 compares the characteristic of several lead-free transducers reported by different researchers. The values of the bandwidth and insertion loss of these transducers fall in the range of 45-72% and 13-32 (-dB), respectively. The bandwidth and insertion loss values of the BNKLT88 transducer fabricated in this work is similar to those of other lead-free compositions such as KNN and LiNbO₃ based materials. As shown in the simulations, the performance of the BNT-based transducer was also comparable to PZT4. In addition, it is benefited of having a high depolarization temperature and less heat generation.

Table 5. 8. A comparison of acoustic performance of lead-free transducers.

Transducer Active Element	f_c (MHz)	-6dB BW%	Insertion Loss (-dB)
Unfocused BNKLT88 (This work)	22.3	61	28.6
focused BNKLT88 (This work)	22.9	55	32.1
Unfocused KNN-LT-LS [18]	26.3	71.8	21
Focused LiNbO ₃ [33]	22-23	60-72	13.4-19.5
Unfocused (Ba _{0.95} Sr _{0.05})(Zr _{0.05} Ti _{0.95})O ₃ [37]	42.2	76.4	26
Unfocused KNN-LT [38]	40	45	18
Unfocused 0.95BNT-0.05BT Crystal [39]	25.39	46.16	31.9

In summary, BNKLT88 composition with a relatively high k_t to k_p ratio and a low dielectric constant could be considered as a suitable candidate for fabrication of a high frequency single element ultrasonic transducer. Unfocused and lens-focused transducers were fabricated using BNKLT88 ceramics as an active element. The piezoceramic with a thickness of 109 μm was sandwiched between a mixture of epoxy-tungsten powder (as a backing layer) and a 15 μm silver epoxy (as a matching layer). The transducer with no

matching layer showed a narrow bandwidth (25.83%) and a long pulse length (310 ns). The -6dB bandwidth of the unfocused transducer increased from 25.83% to 61.36% with addition of a single matching layer. Matching layer also improved the echo response of the traducer with shortening the pulse length from 310 to 130 nanoseconds at -20dB. In the focused transducer, an acoustic lens made of EPOTEK-301 epoxy was attached to the transducer to improve its lateral resolution. The acoustic characterization of the focused transducer demonstrated that at a center frequency of 23 MHz, the -6dB bandwidth and insertion loss were 55% and -32.1 dB, respectively. A phantom made of copper wires (30 μm in diameter) was utilized to investigate the imaging capability of the transducer. An image of the wire phantom was successfully produced by the fabricated transducer with a lateral resolution of 260 μm .

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6 Ferroelectric and Dielectric Properties of BNT-BKT-BT Thin Films by Pulsed Laser Deposition

Abstract

The effect of deposition parameters on the microstructure, crystallinity, and ferroelectric properties of $0.88(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $0.08(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ - 0.04BaTiO_3 thin films with MPB composition grown on SrRuO_3 coated SrTiO_3 substrates by pulsed laser deposition was investigated. The parameters studied were the laser repetition rate, substrate temperature, oxygen pressure, and laser energy. It was found that the films prepared at 800°C , 10 Hz, 400 mtorr and 1.2 J.cm^{-2} exhibited the highest ferroelectric properties. The measured remnant polarization, dielectric constant (at 1 kHz), and coercive field of the film deposited under optimized condition were about $30\text{ }\mu\text{C.cm}^{-2}$, 645, and 85 kV.cm^{-1} , respectively. Increasing the oxygen pressure during deposition from 200 mtorr to 400 mtorr improved the crystallinity, microstructure, dielectric constant and polarization of the films. The leakage current and dielectric loss were suppressed at 400 mtorr due to the less concentration of oxygen vacancies and disappearing pinholes and surface undulations. Thin films with off-MPB composition $0.94(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $0.04(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ - 0.02BaTiO_3 on the rhombohedral side of the phase diagram were also deposited by the PLD technique. Compared to the MPB films, the off-MPB composition exhibited lower polarization, lower dielectric constant, a lower leakage current and a higher coercive field.

6.1 Introduction

Several deposition techniques such as sol-gel, [1-4] chemical solution deposition (CSD), [5, 6] metalorganic solution deposition (MOSD), [7-9] and pulsed laser deposition (PLD) [10-16] have been employed to prepare BNT-based thin films. The PLD is a popular technique due to its simplicity of operation, capability to deposit complex oxides even containing light elements, and of forming epitaxial as well as multilayer thin films [17-20]. However, high quality thin films with enhanced electrical properties can only be achieved if the deposition parameters are optimized. These include the substrate temperature, oxygen partial pressure, laser energy density and repetition rate, the target-substrate distance, and cooling regime [21-28].

In this chapter, the processing-property relationship in 0.88BNT-0.08BKT-0.04BT (BNKBT88) thin films with MPB composition deposited by the PLD technique is reported. The effect of processing parameters such as the oxygen pressure and laser repetition rate on the evolution of phase, microstructure, ferroelectric and dielectric properties were extensively studied. In addition, 0.94BNT-0.04BKT-0.02BT (BNKBT94) thin films (with off-MPB composition and a rhombohedral symmetry in the ceramic form) were prepared to compare their electrical properties with the MPB composition.

6.2 Experimental Procedure

6.2.1 Thin Film Deposition

Dense ceramic targets with desired compositions (BNKTBT88 and BNKTBT94) were prepared by the method described in chapter 3. The diameter and thickness of the targets before sintering were about 38 mm and 8 mm, respectively. Targets were attached to the target carousel by a silver paste (Silver paste plus, SPI Supplies, PA) and dried for 15 minutes by a heat gun. After installing the targets, the chamber was evacuated down to 8×10^{-6} Torr, and then baked out at 850 °C for 3 hour.

The bottom electrode and thin films were deposited by pulsed laser deposition (PLD) technique with a KrF excimer laser of 248 nm wavelength (Coherent, Compex 205, Germany). A commercial SrRuO₃ (SRO) target (Purity 99.9+%, Super Conductor Materials Inc, NY) was employed to deposit a bottom electrode on a (001)-SrTiO₃ (STO) substrate (MTI Corporation, CA) with dimensions of 10×10×0.5 mm³. The SRO bottom electrode was deposited at substrate temperature of 800 °C, oxygen pressure of 150 mtorr, laser repetition rate of 5 Hz, and laser energy of 200 mJ. Following the deposition, the SRO was annealed in 1 atm oxygen pressure at 650 °C for 1 hour and then cooled down to room temperature. Thin films were deposited on a SRO coated (001)-STO substrates at 800 °C. Oxygen background pressure was changed in the range of 200-500 mTorr. The laser beam energy was kept at a constant value of 170 mJ (corresponding to an energy density to 1.2 J.cm⁻²). The laser repetition rate was varied from 2 to 10 Hz. The target-substrate distance was adapted to be 6 cm. After the deposition, films were cooled down under 1 atm oxygen pressure in the PLD chamber. The details of standard operation procedure for depositing thin films with the PLD system are as the following:

I. Preparation of the instruments

1. Laser, chiller, and the two mechanical pumps were first turned on and warmed up for a few minutes. The mechanical pumps were turned on one at a time to prevent the current overflow and fuse break. The chiller was kept on when the turbo pump are running and the water pressure must not exceed 25 psi. If the laser is running at low energies (~ 200 mJ), the water chiller can be turned off to let the laser working temperature go up to some degrees higher than the room temperature. This can stabilize the laser beam energy while running at low voltages.
2. Heater flange was removed by removing the bolts and manually increasing the oxygen pressure inside the chamber to push the flange outward.

II. Substrate preparation and installation

3. Three small beakers and a pair of tweezers were cleaned using acetone and methanol.
4. STO substrates were removed from packaging using Teflon tweezers and placed in acetone for 1-2 minutes. The substrate was rinsed in acetone and methanol and then soaked in methanol.
5. While the substrate was soaked in methanol, the chamber is vented with oxygen through the backfill valve with the shutter closed on the substrate heater before removing the heater flange from the chamber. Heater was then removed and immediately replaced with the blank flange.
6. The substrate was then rinsed with methanol, then de-ionized water and dried clean with compressed air/nitrogen.

7. Silver paint (Leitsilber 200 Conductive Silver Paint, Ted Pella, CA) was applied as a small drop on the heater block. Substrate was placed carefully on the drop of paint and allowed to flow to the edges.

8. Silver paint was dried by turning on the heater and running to 125 °C, which could be part of the heating up procedure to the final deposition temperature. The heater was on hold at 125 °C, while the heater flange was placed back into the chamber.

III. Base Pressure Pump-down

9. The right angle valve to pump #2 was opened (roughing pump directly connected to chamber) to begin the pump-down sequence and shutter was raised.

10. The heater was started again to run to deposition temperature while the roughing pump was evacuating the chamber.

11. At approximately 50 mTorr, oxygen was bled into the system to flush out contaminants. This was repeated several times to ensure a better and faster pump-down.

12. The right angle valve to pump #1 was then opened to rough out the turbo-pump while the heater was reaching the desired temperature.

13. Once the pressure on Convectron gauge was below 20 mTorr, the turbo-pump is started.

14. The right angle valve to pump #2 was closed, and the gate valve was opened to switch to the high vacuum turbo-pump.

15. The system was then allowed to pump-down for 1.5 hours at minimum, or until the pressure was in the range: $5-8 \times 10^{-6}$ Torr.

IV. Oxygen Pre-anneal

16. The switch on the MKS oxygen controller was turned to AUTO and the gate valve was immediately closed. The right angle valve to pump #2 was then turned two turns using the screw on the handle to judge to stabilize at the desired pressure. The turbo-pump was shut off and the right angle valve to pump #1 was closed to isolate the turbo. Turbo-pump was vented by attaching the plastic tube to nitrogen cylinder to let the nitrogen into the turbo-pump for 10 seconds.

17. The pressure on MKS controller was readjusted to the desired value, and the substrate was allowed to equilibrate and burn off organic residue for 30 minutes before film deposition.

V. Film Deposition

18. The laser was first started to allow the pulse energy to stabilize. Using the laser power meter in front of the beam, the power output was then measured for a 40 second trend to ensure the stability of the output.

19. Lens assembly and laser port were uncovered and the shutter on the heater was closed. Target was selected and target rotation was started.

20. The beam stop was then opened to begin the film deposition for the predetermined time.

21. After deposition for the desired time, the laser was stopped using first the beam stop and then the keypad to stop the deposition.

22. The right angle valve to pump #2 was closed, the switch on the MKS controller was turned to CLOSE, and target rotation was stopped.

VI. Post-deposition anneal

23. The heater was shut off the heater or allowed to continue with the cool down/annealing program.

24. The chamber was filled the chamber with 1 atm oxygen at the start of the annealing segment.

25. After the annealing procedure heater was automatically switched off and reset.

VII. Cooling and Shut-down

26. All equipments were shut down if not continuing with another film/layer (Convectron and turbo-pump). Films were grown by this technique, with variation in deposition time to control film thickness.

6.2.2 Microstructural and Chemical Characterization of Thin Films

High resolution X-ray diffraction (XRD, Philips, X'Pert, PW 3040, Cu K α) was utilized for phase analysis and determination of the growth orientation. Cu source was used for the x-ray incident beam in conjunction with an asymmetric monochromator optics consisted of single crystal germanium in asymmetric configuration. The asymmetric monochromator results in a beam of 17 arc seconds angular divergence, but still allow for a reasonable intensity through [29]. To increase the intensity of the diffraction peaks and decrease the error pertaining to the x-ray beam/sample misalignment, thin films were aligned in respect to the incident beam. To investigate the epitaxy of the grown films, a 360° ϕ -scan was carried out while 2 θ angle was fixed at the angle corresponding to (011) plane. While θ -2 θ scan reflects the out-of-plane orientation of the films, ϕ -scan provides

information about the in-plane orientation. In polycrystalline films, multiple in-plane orientations are detected. However, epitaxial films should exhibit a single orientation.

Field emission scanning electron microscopy (FESEM-Zeiss, Sigma) was utilized for microstructural characterization. The samples were cut in half after the deposition and the fresh cross section was used for cross sectional SEM images. No coating was applied to the surface of samples. However, to diminish the charging effect, the FESEM was operated at 3 kV instead of the standard operating voltage (5 kV). The thickness of the films was estimated using the software provided by Sigma.

The chemical compositions profiles of the films were examined by Rutherford backscattering spectroscopy (RBS) with a 2 MeV He^+ probe. The RBS provides useful information about the concentration and depth distribution of elements and thickness of thin films. This technique employs the elastic collision between high kinetic energy particles from the incident beam (He^+ ion source) and stationary particles (atoms) located in the sample. Elastic in this context means that no energy is either lost or gained during the collision. High energetic ions, therefore, can penetrate few microns below the surface of the sample before they elastically scattered off an atom. These backscattered particles which escape the sample are detected and analyzed based on their energy. The elements contained by a sample can be determined from the positions of peaks in the energy spectrum. The composition of the films was then quantitatively analyzed by the SIMNRA 6.0 software package without using any standard sample.

6.2.3 Electrical Characterization of Thin Films

To evaluate the electrical properties of thin films, 50 nm thick Au top electrodes (200 μm in diameter) were deposited by DC sputtering (Kurt J Lesker, CA) and using a metallic mask. The dielectric properties were measured using an impedance analyzer (LCR meter-HP4194A) at room temperature. The capacitance (C_p) and dielectric loss were measured in frequency range of 1 kHz to 1 MHz at an oscillation level of 500 mV. Dielectric constant (ϵ_r) was calculated based on the following equation:

$$\epsilon_r = \frac{C_p \cdot t}{A \cdot \epsilon_0}$$

Where t is the thickness of the film and A is the electrode area.

Ferroelectric properties of thin films were measured by an RT66A ferroelectric test system (Radiant Technologies Inc., NM) controlled by Vision software. The P-E hysteresis loops were measured at a pulse width of 1 ms (1 kHz frequency) using a triangular wave signal. Leakage current (I-V curve) of the films was also measured by a Precision LC (Radiant Technologies Inc., NM) equipment.

6.3 Results and Discussion

Fig. 6.1 (a) shows the effects of repetition rate (2, 5, and 10 Hz) on the ferroelectric properties of BNKTBT88 thin films. Other deposition parameters were fixed at 800 $^{\circ}\text{C}$, 170 mJ, and 400 mtorr. A high remnant polarization $P_r \sim 30 \mu\text{C} \cdot \text{cm}^{-2}$ was obtained for the film deposited at 10 Hz. The high P_r of this film can be credited to its dense microstructure and lower concentration of point defect as will be discussed later. Figs. 6.1 (b)-(d) display the surface morphologies of thin films deposited at various repetition rates. While the film deposited at 10 Hz had a uniform microstructure without obvious

porosities, the other films exhibited island-type structure with $\langle 001 \rangle$ -oriented blocks and pyramids on the surface along with microporosities dispersed on the surface. Porosities are known to increase the leakage current and deteriorate the ferroelectric properties of thin films.

Fig. 6.2 (a) depicts the hysteresis loops of thin films deposited at different oxygen pressures (200, 300, 400, and 500 mtorr). Other deposition parameters were kept at constant values of 800 °C, 170 mJ, and 10 Hz. The saturated polarization as well as the remnant polarization increased with increasing the background oxygen pressure up to 400 mtorr. Similar results have been achieved for KNN-based thin films deposited by the PLD [21]. It has been previously reported that the oxygen pressure has an important role in controlling the stoichiometry, growth orientation, microstructure and electrical properties of ferroelectric thin films made by PLD [27, 28, 30-34].

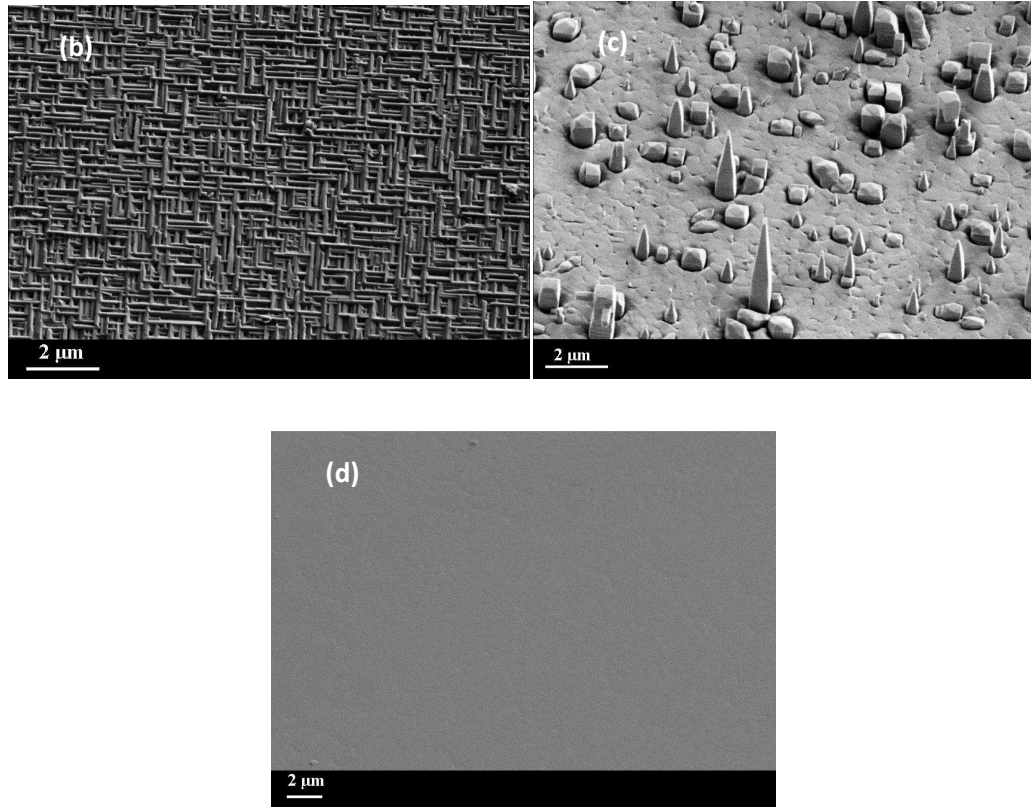
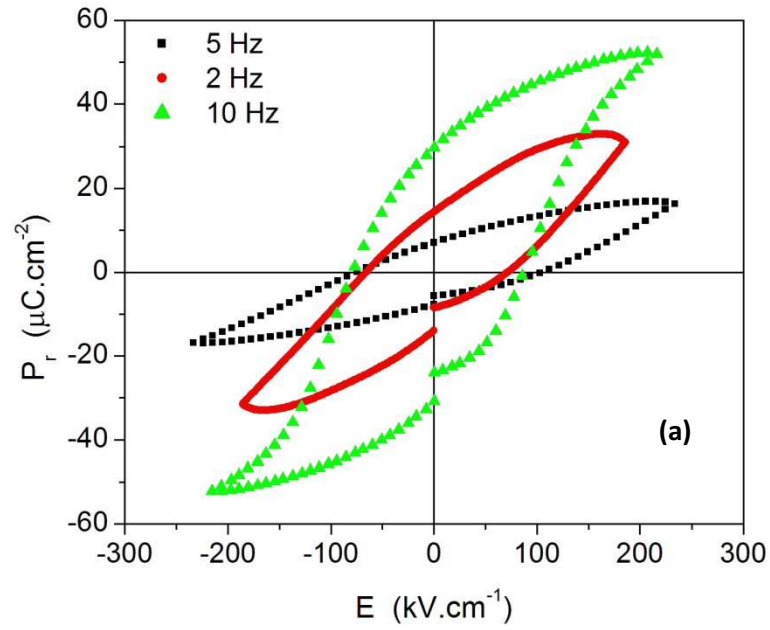


Fig. 6. 1. (a) P-E hysteresis loops of the films deposited at different repetition rates (b) FESEM micrographs showing the top surfaces of the films deposited at (b) 2 Hz (c) 5 Hz (d) 10 Hz.

The effect of oxygen pressure can be explained by considering some phenomena which simultaneously occur when a ceramic target is radiated by a laser beam. A portion of the kinetic energy of species in the plasma plume is lost as a result of the elastic collision with oxygen molecules. The energy loss is obviously more pronounced at higher oxygen pressures. This is accompanied by the contraction of plasma plume which affects the deposition rate as well as the microstructure of the film particularly at low deposition temperatures. The results showed that the deposition rate diminished from 6.1 to 4.3 nm.min⁻¹ as the background pressure increased from 200 mtorr to 500 mtorr. For this reason, the deposition time was accordingly altered so that all thin films had the same thickness of about 500 nm for electrical characterization. Since the films were thick enough to contain misfit dislocations at the film-substrate interface, they could be considered as strain-relieved films [35]. As a result, the influence of mismatch strain on the lattice parameter and electrical properties could be neglected. FESEM micrographs in Figs. 6.2 (b)-(e) illustrate the surface morphologies of films deposited at different background oxygen pressures. The films deposited at 200 and 300 mtorr consisted of truncated pyramids and cone/rod-shaped features aligned in <001> crystallographic orientation. These surface anomalies became indiscernible in the samples deposited at 400 mtorr and then reappeared in form of surface modulation and micro-pinholes at 500 mtorr pressure.

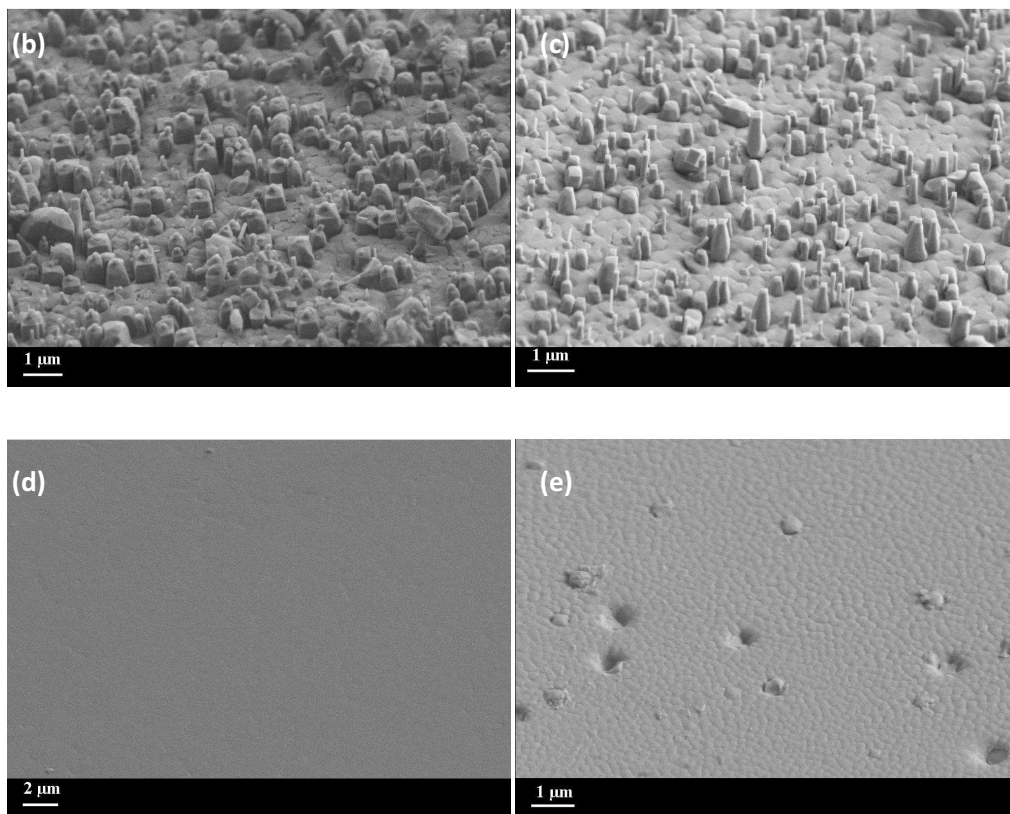
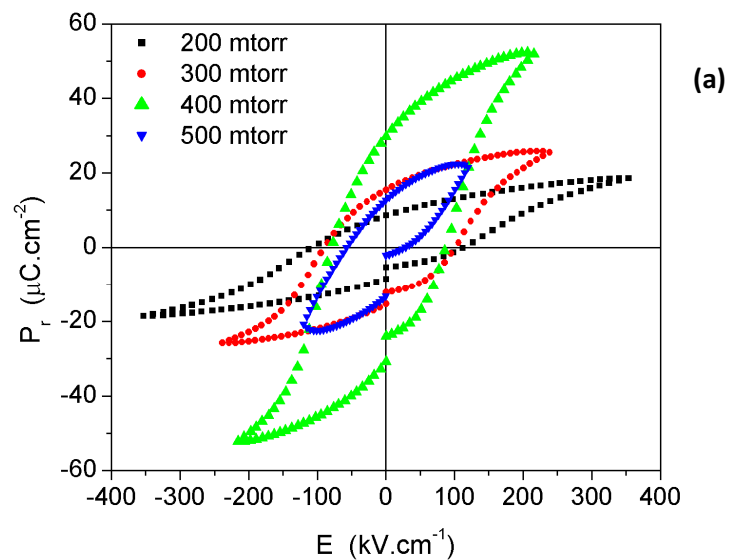


Fig. 6. 2. a) P-E hysteresis loops of the films deposited at various oxygen pressures. FESEM micrographs of the top surfaces of thin films deposited at (b) 200 mtorr (c) 300 mtorr (d) 400 mtorr (e) 500 mtorr. Other deposition parameters are: 170 mJ, 10 Hz, 800 °C.

Fig. 6.3 (a) shows the X-ray diffraction pattern of BNKTBT88 thin film deposited at 400 mtorr showing that the film is highly oriented in the <001> direction and there is no evidence of secondary phase formation or any reflection from other crystallographic planes. To confirm the fact that the film was grown epitaxially, the phi-scan of the <011> pole of the film is depicted in the inset in Fig. 6.3 (a). Four peaks 90 degrees apart illustrate the epitaxial growth of the thin film with a cube-on-cube <001> crystallographic relation between the film and the substrate. Fig. 6.3 (b) shows the (002) peaks of XRD patterns of thin films prepared at different oxygen pressures. As shown, the (002) peaks became more intensified as the oxygen pressures increased up to 400 mtorr, indicating of improved crystallinity at higher pressure. This was also confirmed by measuring the FWHM of the rocking curve of (002) reflections obtained by ω -scan. The FWHM value decreased from 0.16° to 0.08° by varying the oxygen pressure from 200 mtorr to 400 mtorr. A similar trend has also been reported for PZT [31] and KNN-based [21] thin films deposited by the PLD technique. At the same time, 2θ position of (002) peaks slightly shifted to lower angles with decreasing the background pressure. This was attributed to the enlargement of lattice parameters and the expansion of unit cell. This could be ascribed to the deviation from stoichiometric composition and the presence of oxygen vacancies ($V_O^{\bullet\bullet}$) at lower deposition pressures [33, 36, 37]. If a thermodynamic equilibrium between the film and the deposition ambient is maintained, according to eq.

$$O_O(s) = \frac{1}{2} O_2(g) + V_O^{\bullet\bullet} + 2e^-,$$

at low oxygen pressures, oxygen atoms (O_O) may leave the unit cell in form of gas ($O_2(g)$). This results to creation of ionized oxygen vacancies and free electrons (e^-). Therefore, with decreasing the oxygen pressure, formation of oxygen

vacancies is facilitated and chemical composition of the films is deviated from stoichiometry.

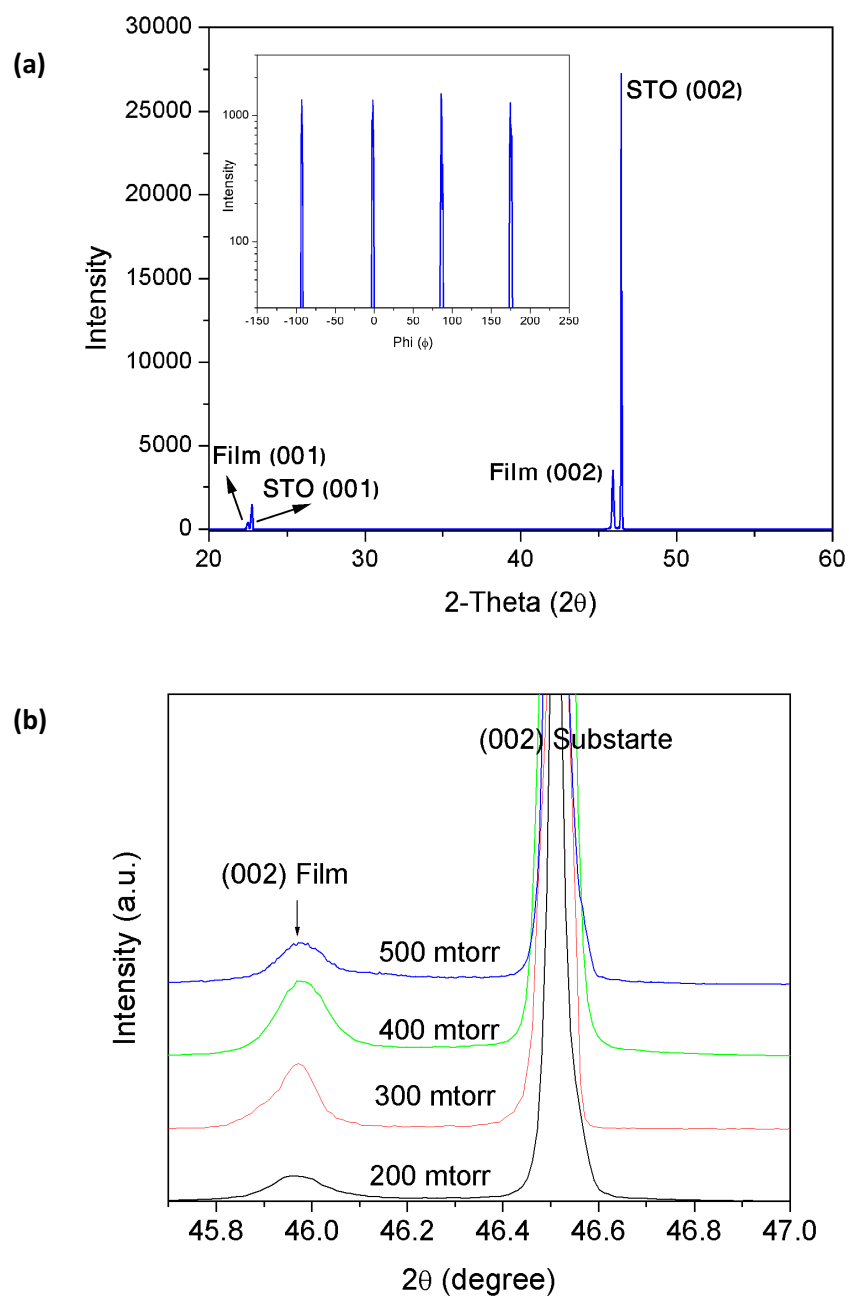


Fig. 6. 3. The X-ray diffraction pattern of BNKTBT88 film deposited at 400 mtorr. Inset shows the (011) phi-scan of the film (b) (002) peak of XRD patterns for thin films deposited at different oxygen pressures.

The loss of every oxygen atom from the lattice leaves two electrons behind. Some of these electrons can be absorbed by Ti^{+4} ions to convert to Ti^{+3} ions. [37] The reduction of Ti^{+4} ions is accompanied by an increase in ionic radius and hence the expansion of unit cell. The enlargement of the lattice parameters can be also expressed through electrostatic repulsive forces between positively charged oxygen vacancies and cations located at the A-site and B-site positions in the perovskite structure. Therefore, it is expected that at lower oxygen pressures, the film composition deviates from stoichiometric composition due to the incorporation of oxygen vacancies into its lattice. In lead-free compositions such as BNT and KNN-based materials, this behavior is even more complicated. The presence of light elements such as K, and Na, beside a volatile element such as Bi, makes the material processing more challenging. Volatilization of A-site elements and deviation from stoichiometry are major issue in deposition of these films. Thermodynamically, a higher oxygen pressure is desirable to suppress the loss of A-site elements. The equilibrium constant of the volatilization reaction $[M_2O(s) = \frac{1}{2}O_2(g) + 2M(g)]$ is fixed at a constant temperature. With the increasing the oxygen pressure, the above reaction proceeds in the reverse direction, giving rise to a decrease in the concentration of cation vacancies [31]. However, as mentioned earlier, kinetics also plays a significant role on the chemical composition and microstructure of the film. The plasma plume consists of high energy ions and low energy neutrals. The momentum loss of these species when collide with oxygen molecules is more pronounced for light cations such as Na^+ and K^+ . At low oxygen pressures, these light elements undergo thermalization while heavier elements can continue their path towards the substrate. This phenomenon prevents achieving stoichiometric films. As the pressure increases, heavier elements also

experience thermalization which consequently increases the probability of obtaining stoichiometric composition by balancing the flow of particles towards the substrate. This phenomenon is called discriminated thermalization [21, 32]. Thus, the optimization of oxygen pressure is one of the most important parameters in obtaining films with stoichiometric composition and minimum concentration of lattice defects. The lattice defects, in turn, decrease the extrinsic contribution of domain walls motion by pinning them. As shown in Fig. 6.2 (a), the coercive field of thin films decreased from 112 to 85 kV.cm^{-1} with increasing the oxygen pressure from 200 mtorr to 400 mtorr. The lower value of coercive field is an indication of lower concentration of point defects in the sample prepared at 400 mtorr. If the oxygen pressure during deposition is very high (such as 500 mtorr in this paper), the particles lose a major portion of their kinetic energy and there will not be an appropriate flux of particles towards substrate. In this case, the chemical composition, microstructure and surface roughness of a deposited film is deteriorated. This consequently results in poor ferroelectric properties (low remnant and saturation polarization) as can be seen in Fig. 6.2 (a).

Figs. 6.4 (a)-(d) illustrate the chemical composition profiles of thin films deposited at different oxygen pressures. These RBS data demonstrate that the film deposited at 10Hz and 400 mtorr has the least deviation from the stoichiometric composition. Quantitative RBS analysis is a challenging task for these films since they contain both heavy and light elements. As shown in Fig. 6.4, negligible contributions of Na and K atoms to the total intensity of spectra may result in a considerable error in quantitative measurements of these light elements. However, the quantity of heavy elements such as Bi, Ti, and Ba can be accurately calculated. Using the RBS technique, therefore, the compositions of such

BNT thin films can be relatively compared. Table 6.1 summarizes the quantitative analysis of the RBS data shown in Fig. 6.4. The compositions of thin films prepared at 400 mtorr and 300 mtorr are close to the stoichiometric composition. Decreasing the oxygen pressure down to 200 mtorr or increasing the oxygen pressure up to 500 mtorr intensifies the volatilization of bismuth and consequently oxygen deficiency. These lead to extensive non-uniformity of the composition-depth profiles shown in Figs. 6.4 (a),(d). Fig. 6.5 shows the current density of thin films as a function of applied electric field at different oxygen pressures. The leakage current was suppressed by increasing the oxygen pressure up to 400 mtorr and then increased again at 500 mtorr. These variations in the leakage current can be explained by the effects of oxygen pressure on the microstructure, chemical composition and the concentration of the positive and negative charge carriers (electrons, electron holes, and oxygen vacancies) as mentioned earlier. High leakage current in BNT films gives rise to an unsaturated hysteresis loop and thus a low remnant polarization value [38]. The enhanced ferroelectric properties of the film deposited at 400 mtorr are strongly correlated with its lower leakage current caused by a reduction in the concentration of point defects.

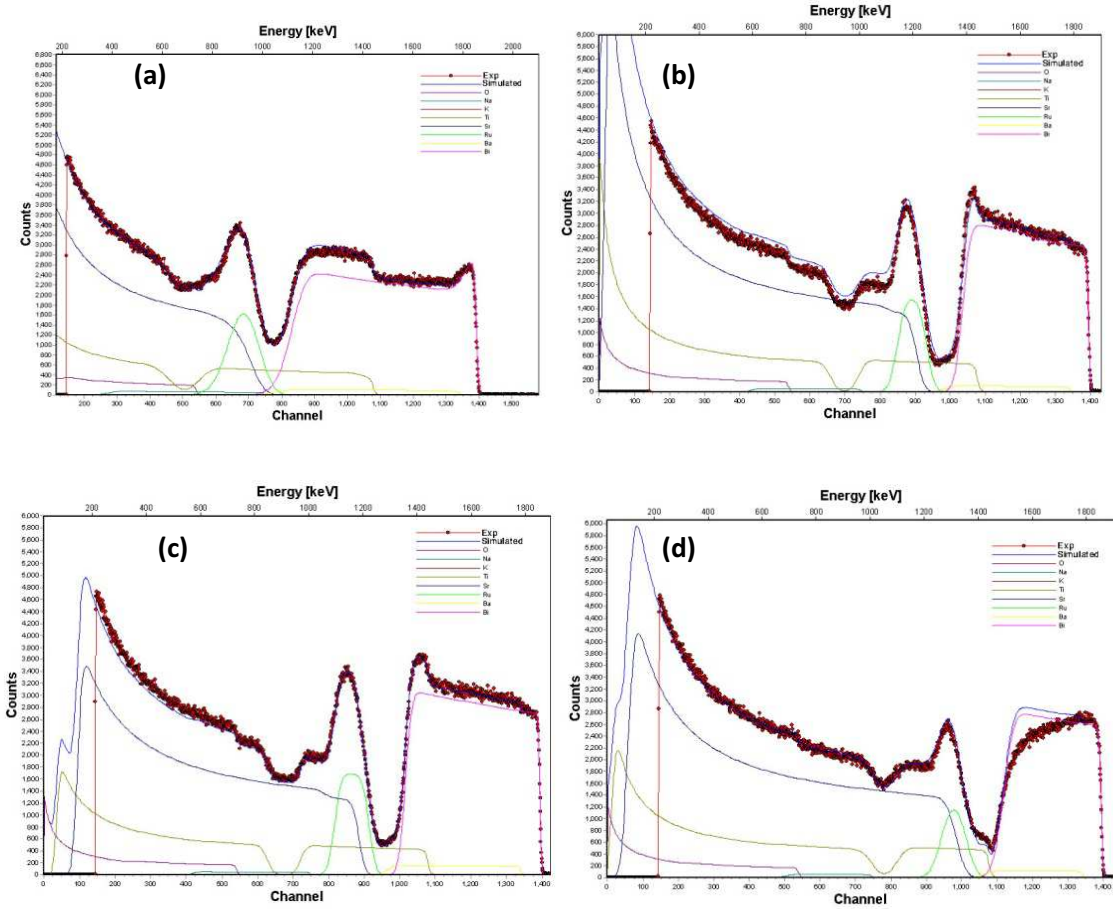


Fig. 6. 4. RBS composition profile of BNKTBT88 thin films deposited at 10 Hz under different oxygen pressure: (a) 200 mtorr (b) 300 mtorr (c) 400 mtorr (d) 500 mtorr.

Table 6. 1. Quantitative analysis of RBS data shown in Fig. 6.4. It is assumed that total concentration of Na and K elements is the same as stoichiometric composition.

Element	Stoichiometry	200mtorr	300mtorr	400mtorr	500mtorr
Bi	0.096	0.084	0.0863	0.0970	0.0858
Ti	0.2	0.223	0.217	0.208	0.2202
Ba	0.008	0.006	0.007	0.011	0.0085
O	0.6	0.591	0.5937	0.5990	0.5895

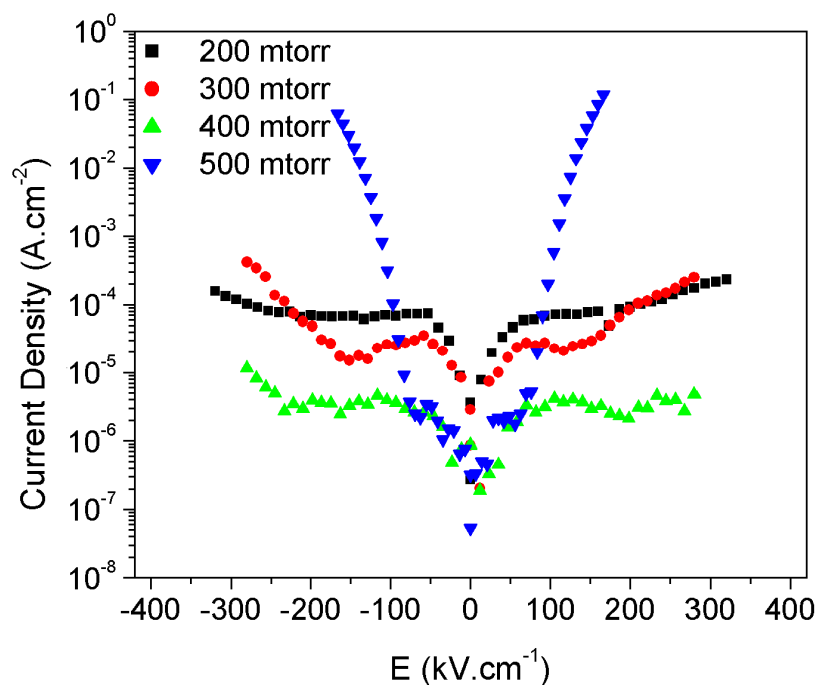


Fig. 6. 5. The leakage current behavior of BNKTB88 thin films deposited at different oxygen pressures.

The effect of oxygen pressure on dielectric properties of films is depicted in Fig. 6.6 which resembles of polarization behavior with oxygen pressure. The film prepared at 400 mtorr had the highest dielectric constant (K). The K value at 1 kHz increased from 330 to 645 when the oxygen pressure increased from 200 mtorr to 400 mtorr. The enhancement of the dielectric constant with oxygen pressure has also been observed for other ferroelectric thin films prepared by the PLD method [21, 33]. A higher dielectric loss along with a sharp decrease in K value was observed in the film deposited at 200 and 500 mtorr. This dielectric constant relaxation at low frequencies is a characteristic of films containing space charges created as a result of oxygen and A-site deficiency. This is in agreement with high value of leakage current presented in Fig. 6.5. The leakage current mechanisms in these thin films have been studied and presented in chapter 7.

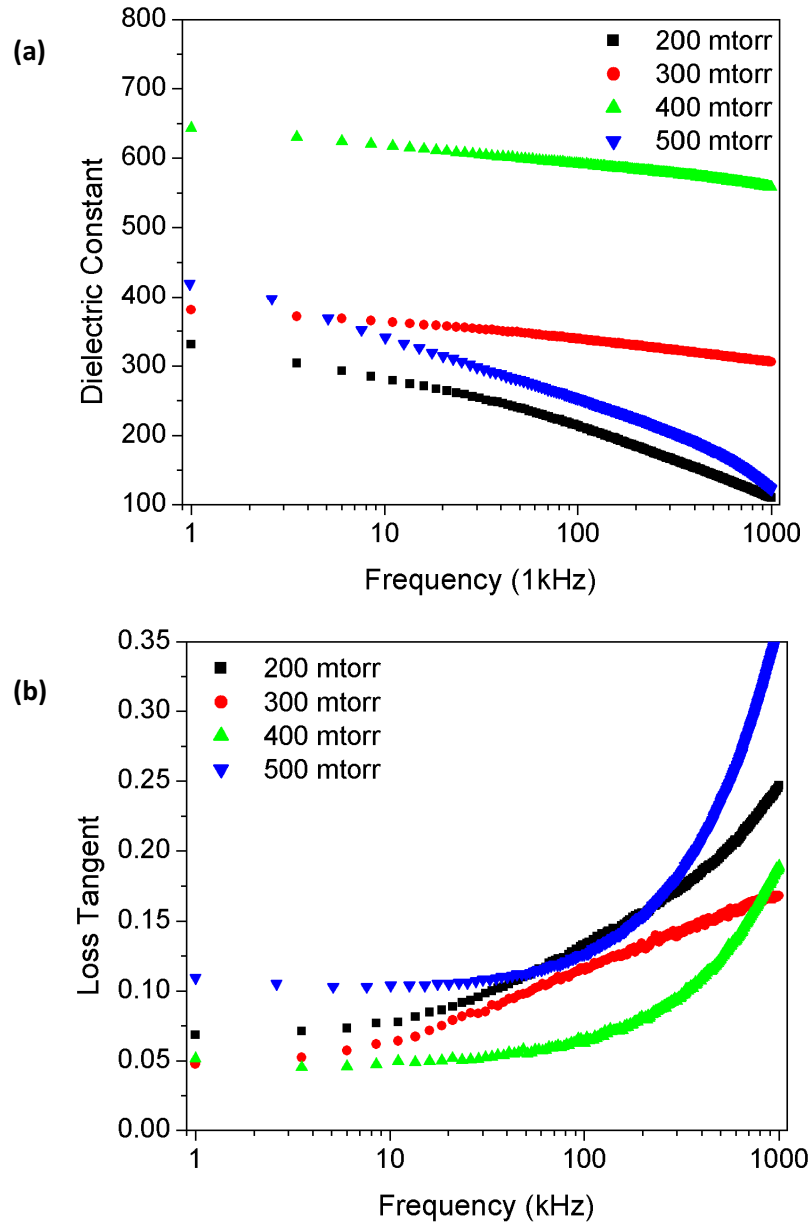


Fig. 6. 6. The effect of oxygen pressure on (a) dielectric constant (b) dielectric loss of BNKTBT88 thin films.

The P-E hysteresis loop of the BNKTBT94 film (rhombohedral composition) is shown in Fig. 6.7. The saturation polarization, remnant polarization and coercive field values are $46.8 \mu\text{C.cm}^{-2}$, $16.6 \mu\text{C.cm}^{-2}$ and 147.5 kV.cm^{-1} , respectively. The remnant polarization of

the film retains 46% of the bulk value and the coercive field is 114% larger compared to the ceramic. The higher concentration of lattice defects in thin films can effectively pin some of the domain walls and increase the coercive field in comparison to bulk ceramics. Particularly in BNT based thin films processed at high temperatures, due to the high volatility of A-site elements, oxygen vacancies form to compensate for Na and Bi vacancies and maintain the charge neutrality. These oxygen vacancies increase the coercive field by hindering the domain wall motion. The substrate constraint also plays an important role in clamping the non-180° ferroelectric domains and increasing the coercive field. In comparison BNKBT88 composition, the BNKBT94 film exhibited a lower remnant polarization and higher coercive field. Fig. 6.8 shows the leakage current of the BNKBT94 and BNKBT88 thin films deposited at 4Hz and 200 mtorr. The current density of BNKBT94 film rapidly increases with the applied voltage and then plateaus at a value of about $1.1 \times 10^{-5} \text{ A.cm}^{-2}$, where the applied field is in the range of 136 kV.cm^{-1} to 310 kV.cm^{-1} . Upon further application of the electric field, the current density increases monolithically and, finally, the leakage current at 628 kV.cm^{-1} was measured to be about $5 \times 10^{-3} \text{ A.cm}^{-2}$. The I-V curve of the BNKBT88 thin film (with MPB composition) deposited under the same conditions has also been incorporated in Fig. 6.8. As can be observed, the leakage current of the present film is suppressed by more than 4 orders of magnitude at 250 kV.cm^{-1} , compared to the thin film with MPB composition

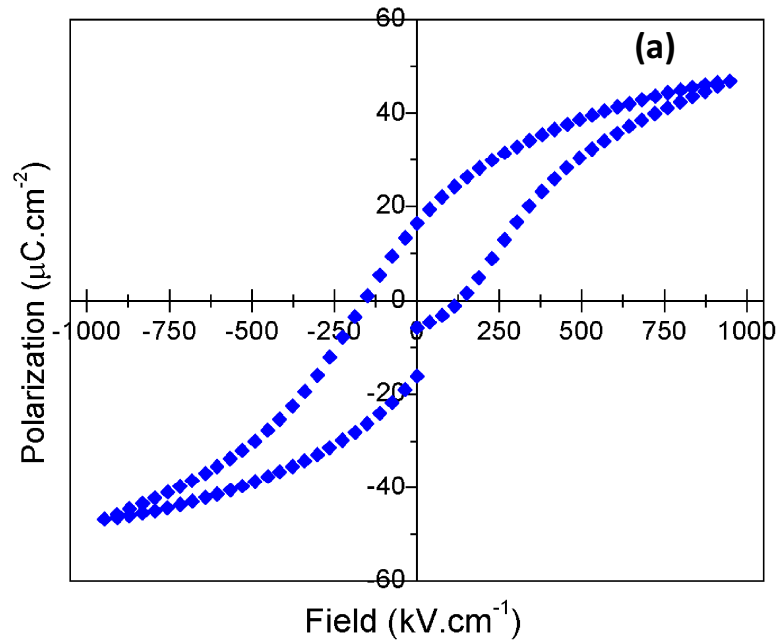


Fig. 6. 7. Polarization-electric field hysteresis loop of BNKTBt94 thin film

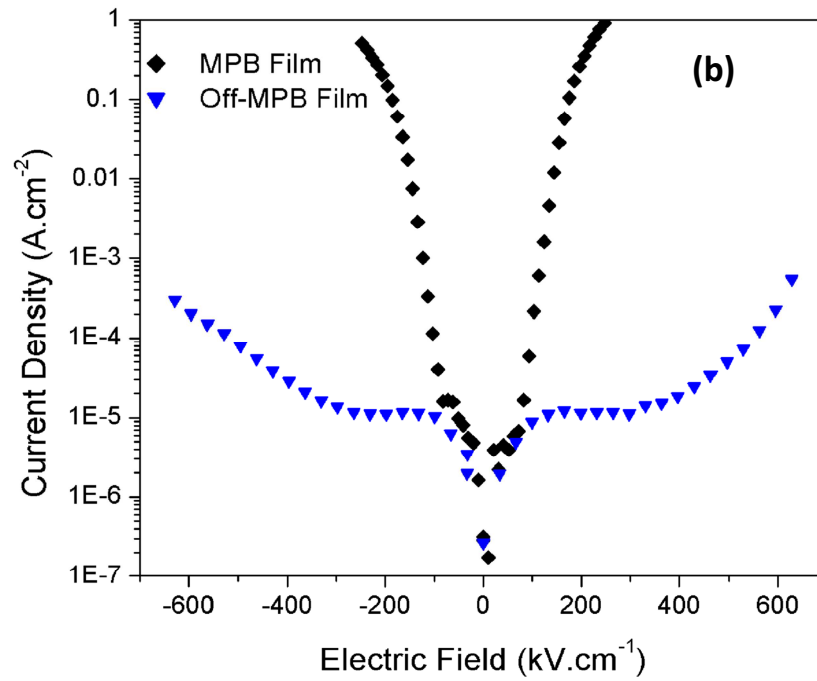


Fig. 6. 8. The leakage current density of BNKTBt94 (off-MPB) and BNKTBt88 (MPB) thin films deposited at 4 Hz and 200 mtorr.

The parameters that may affect the leakage current are microstructure, chemical composition, charge carrier's mobility and concentration, internal lattice stress and band gap energy. Controlling of the leakage current by modification of the microstructure and surface roughness [20-23], or changing the predominant conduction mechanisms through the variation of chemical composition (doping) for dielectric films with different compositions have also been addressed by other researchers [24-26]. To exemplify, the Schottky barrier height in SrTiO₃ thin films increases with decreasing the surface roughness which improves the insulative properties of the films [21]. The 0.94BNT-0.04BKT-0.02BT film can be considered a moderate insulator film in comparison to other BNT films available in the literature. To exemplify, 0.94BNT-0.06BT films on LaNiO₃/Al₂O₃/Si and Pt/Si substrates exhibit a leakage current of 9×10^{-4} A.cm⁻² and 2×10^{-4} A.cm⁻² at 300 kV.cm⁻¹ [10, 15]. BNT films on Pt/Ti/SiO₂/Si substrates processed by RF magnetron sputtering and sol-gel techniques also show a current density of 1.7×10^{-5} A.cm⁻² and 6×10^{-5} A.cm⁻² at 100 kV.cm⁻¹ [6,16,17]. It has been reported that the high leakage current of BNT thin films prevents obtaining saturated hysteresis loops which results in films with low remnant polarizations [3,11,16,18,19], but the film presented in this paper shows a well-saturated hysteresis loop along with a relatively low conductivity. While a low breakdown voltage has been reported to be one of the main challenges in BNT-based thin films [18], the results of this chapter showed that off-MPB film could tolerate applied voltages of higher than 35 V (corresponding to 1.1 MV.cm⁻¹). Considering its high breakdown voltage and fairly high coercive field along with a low leakage current, this BNT-based film can be introduced as a suitable lead-free candidate for high power applications.

6.4 Summary

The effects of deposition parameters including the laser repetition rate and oxygen pressure during deposition on the microstructure and properties of BNKTBT88 thin films (MPB composition) have been studied. The films were deposited on SRO coated STO substrates by the PLD technique. The results indicated that high quality films with a smooth surface, uniform thickness and optimum ferroelectric properties could be grown under optimized processing condition. The optimum deposition parameters were found to be 10 Hz repetition rate, substrate temperature of 800 °C, oxygen pressure of 400 mtorr, and laser energy of 170 mJ. Under such a condition, the film exhibited a saturated polarization hysteresis loop with a remnant polarization of 30 $\mu\text{C.cm}^{-2}$ and coercive field of 85 kV.cm^{-1} . The dielectric constant and loss tangent at 1 kHz were measured to be 645 and 0.052, respectively. It was observed that variations in ferroelectric properties and leakage current of the films had one to one correlation with the crystallinity, microstructure and chemical composition of the films.

Thin films with composition of BNKTBT94 (rhombohedral side of the phase diagram) were also deposited by the PLD technique. These films with a thickness of about 400 nm demonstrated a saturated hysteresis loop with remnant polarization of 16.6 $\mu\text{C.cm}^{-2}$ and a high coercive field of 147.5 kV.cm^{-1} . The leakage current of the film was measured to be $1.1 \times 10^{-5} \text{ A.cm}^{-2}$ at 310 kV.cm^{-1} . Compared to the BNKTBT88 film, the BNKTBT94 composition exhibited lower polarization, lower dielectric constant, a lower leakage current and a higher coercive field.

The results showed that the optimization of the processing parameters effectively enhanced the electrical properties of lead-free BNT-based thin films. These materials can be promising alternative for lead-based thin film in different applications.

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7 Leakage Current Mechanisms in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based Thin Films

Abstract

This chapter discusses the electrical conduction mechanisms in 0.88 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -0.08 $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ -0.04 BaTiO_3 thin films (MPB composition) in the temperature range of 200-350 K. As explained in earlier chapters, the film was deposited on a <001>- oriented $\text{SrRuO}_3/\text{SrTiO}_3$ substrate by pulsed laser deposition technique. At all measurement temperatures, the leakage current behavior of the film matched well with the Lampert's triangle bounded by three straight lines of different slopes. The relative location of the triangle sides varied with temperature due to its effect on the density of charge carriers and un-filled traps. At low electric fields, the ohmic conduction governed the leakage mechanism. The calculated activation energy of the trap is 0.19 eV implying the presence of shallow traps in the film. With increasing the applied field, an abrupt increase in the leakage current was observed. This was attributed to a trap-filling process by the injected carries. At sufficiently high electric fields, the leakage current obeyed the Child's trap-free square law and the space charge limited current was the dominant mechanism.

7.1 Introduction

Due to their remarkable ferroelectric properties, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT)-based thin films have attracted a notable interest as possible alternative to their lead-based counterparts in applications such as microelectromechanical systems (MEMS), ferroelectric random access memories (FERAM), and capacitors [1-7]. Reliable performance of these devices depends on leakage current value of the ferroelectric material. In general, lead-free materials suffer from high values of leakage current which hinders their widespread usage in such devices [3,4,7]. Understanding the underlying mechanisms of charge carrier transportation in these thin films may provide a means to suppress the leakage current to the values demanded for devices.

The leakage current behavior in some of lead-free thin films such as $(\text{K},\text{Na})_{0.5}\text{NbO}_3$ (KNN) [11-14] and BiFeO_3 (BFO)-based [15-19] compositions has been extensively investigated. On the other hand, published literatures pertaining to BNT-based systems have mainly focused on the ferroelectric and piezoelectric properties of these thin films. Only a limited number of studies have just discussed the AC and DC electrical conductivities of BNT-based thin films at room temperature [20-23].

The specific aim of this work is to study the mechanisms of leakage current in thin films with the morphotropic phase boundary (MPB) composition of $0.88 \text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - 0.08 \text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 - 0.04 \text{BaTiO}_3$ (0.88BNT-0.08BKT-0.04BT). While exhibiting a remarkable remnant polarization (P_r) of $30 \mu\text{C}\cdot\text{cm}^{-2}$, this composition suffers from high leakage current even at low electric fields.^{1,2} To explore the leakage mechanisms, the current density of the film was measured in a temperature range of 200-350 K and electric fields of 0-230 $\text{kV}\cdot\text{cm}^{-1}$. The data obtained were analyzed according to

the ohmic, space charge limited current, trap-filled-limit, Poole-Frenkel, and Schottky models.

7.1.1 Electrical conduction mechanisms in ferroelectric thin films

In ferroelectric ceramics the leakage current is usually negligible, and only the current due to the polarization reversal and pyroelectricity is of a great importance. However, in ferroelectric thin films the contribution of the leakage current under application of an external electric field can be so large that can mask the ferroelectricity and change the P-E hysteresis characteristics of the films. Understanding the conduction mechanisms can help in finding solutions to suppress the leakage current. The conduction mechanisms responsible for leakage current in thin films fall into two general categories:

- 1) Bulk limited mechanisms: in these mechanisms the charge carrier transportation is contorted through the bulk of the materials. Several subcategories such as ohmic conduction, space charge limited current (SCLC), Poole-Frenkel emission from deep traps and electron hopping can be mentioned as the most important mechanisms in this group.

- 2) Interface limited mechanisms: In this category, the charge carrier transportation is limited by interfacial properties of the film such as the potential barrier at the electrode interface. Fowler-Nordheim tunneling, and thermionic emission also known as Schottky emission are some of the mechanisms belonging to this category. Simultaneous occurrence of different conduction mechanisms in a film complicates the analysis and interpretation of the obtained data. In most cases, however, within a limited range of

applied electric field, one of the mechanisms is dominating the others. Furthermore, since conduction mechanisms have different dependencies on the variations of the temperature and film thickness, measurement of I-V curves at various temperatures and thicknesses would be beneficial in determining the underlying leakage mechanisms. Direct tunneling is also possible to happen in very thin films. Quantitative explanation of some of these mechanisms is provided in the results and discussion section.

7.2 Experimental Procedure

The pulsed laser deposition (PLD) technique was utilized to deposit <001>-oriented epitaxial 0.88BNT-0.08BKT-0.04BT (BNKBT88) thin films with MPB composition on SrRuO₃ coated SrTiO₃ substrates at 800 °C with a KrF laser energy density, repetition rate, and oxygen pressure of 1.2 J.cm⁻², 2 Hz, and 400 mtorr, respectively. The thickness of the films was about 400 nm. Au top electrodes of 200 μm in diameter and 50 nm in thickness were then sputtered on the film for electrical characterization. For leakage current (J-E curve) measurement versus temperature, the sample was fixed on the stage using thermal conductive glue. Then, two probes were connected to the top and bottom electrodes. After evacuating the sealed chamber, liquid nitrogen was purged to cool down the sample. The temperature of the stage was then increased by a heater block. After assuring of temperature stability, the I-V data were then collected in a temperature range of 200-350 K by an Agilent HP4140b semiconductor parameter analyzer.

7.3 Results and Discussion

Fig. 7.1 shows the current density of the thin film as a function of applied electric field at different temperatures. As shown, the leakage current increases by raising the temperature. The J-E curve demonstrates an asymmetric behavior under the application of positive and negative bias voltage. This can be attributed to different work function values of the SRO and Au as well as adhesion quality of the interface between the film and either electrode [15,22,24,25]. Hereafter, for the analysis of leakage current mechanism, we only concentrate on the portion of the J-E curve where a positive voltage is applied to the bottom electrode.

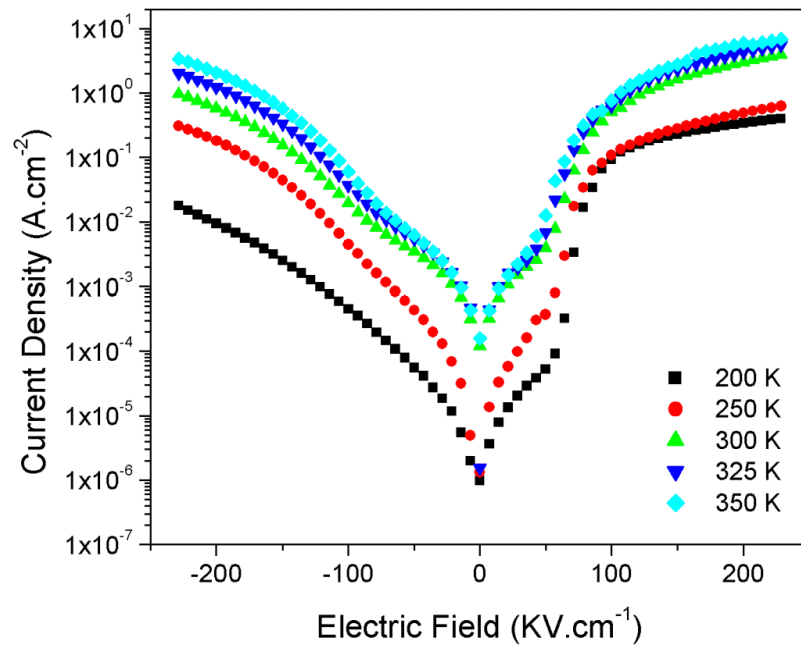


Fig. 7. 1. The current density-electric field (J-E) characteristic of the BNT thin film under positive and negative biases in the temperature range of 200-350 K.

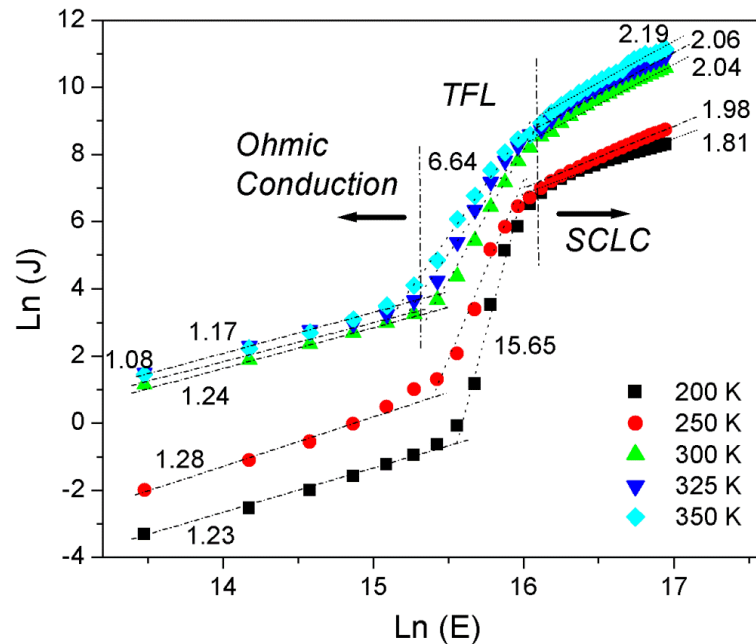


Fig. 7. 2. Re-plot of the leakage current curves at different temperatures on a logarithmic scale.

To probe the electrical conductivity mechanisms of the film, the J-E curve is re-plotted on a logarithmic scale as illustrated in Fig. 7.2. At all temperatures, the curves exhibit three distinct regions whose slopes follow different conduction mechanisms. The values of the slopes obtained through linear fitting are shown on the plot. At low electric fields ($<40 \text{ kV.cm}^{-1}$), the calculated slope values are around unity implying that the ohmic conduction is the dominant leakage mechanism. This is in agreement with previously reported findings on the leakage current behavior of lead-free thin films where the ohmic conduction is responsible for electrical charge transport at low voltages [12,14,15,21,22]. In the ohmic region, when the electrodes are well adhered to the film and form an ohmic contact with infinite supply of charge carriers, the current density can be expressed by [26]:

$$J = n\mu E \quad (7.1)$$

where μ is the charge carrier mobility and e in the unit charge. In this equation, the total density of free-electrons (n) can be replaced by the thermal equilibrium electron density (n_o) because the density of injected electrons (n_e) at low electric fields is negligible.

In Fig. 7.2, it can also be observed that as the applied voltage increases, the current density sharply ascends to high values and then the slope declines equating to a value of ≈ 2 . In the temperature range measured, this regime appears to be governed by the Space-Charge-Limited Current (SCLC) that holds a linear relationship between $\text{Log } J$ and $\text{Log } E$ with a slope value equal to two [26-28]:

$$J = \frac{9}{8} \mu \varepsilon \theta \frac{V^2}{L^3} \quad (7.2)$$

where V is the applied voltage, ε is the permittivity, θ is the ratio of free to total carrier density, and L is the thickness of the film. The SCLC has also been recognized as the principal conductivity mechanism in room temperature in 0.94BNT-0.06BT thin films when the LaNiO₃ bottom electrode is biased at a positive voltage [21].

Some other leakage current mechanisms including bulk-controlled Poole-Frenkel (PF) and interface-controlled Schottky mechanisms have also been suggested as fundamental conduction mechanisms in ferroelectric thin films [12,14,15,19,29]. PF mechanism, quantitatively expressed in eq. (3), describes the field assisted thermal emission of charge carriers from traps under high electric fields.^{28,30,31}

$$J = J_o \exp\left(\frac{\beta_{PF} E^{0.5} - \Phi_{PF}}{k_B T}\right), \quad (7.3)$$

$$\beta_{PF} = \sqrt{\frac{e^3}{\pi \varepsilon_o \varepsilon_r}},$$

$$J_o = \sigma_o E$$

where β_{PF} is the Poole-Frenkel coefficient, ϵ_r is the dielectric constant in the optical frequency range, Φ_{PF} is the trap level, k_B is the Boltzmann's constant, T is absolute temperature, and σ_o is a constant. If electrical conductivity ($\sigma=J/E$) is plotted versus $E^{0.5}$ on a logarithmic scale, the dielectric constant of a material can be calculated from the slope of the fitted line. The dielectric constant at optical frequencies is equal to the square of its refractive index ($\epsilon_r=n^2$) [32]. The value of refractive index reported for BNT-based thin films [33,34] is in the range of 2.1-2.5 yielding a relative permittivity value falling in the range of 4.4-6.25. The slope of the fitted line (given in Table 7.1) can be obtained by calculating β_{PF} and using eq. 3. If the PF mechanism dominates the leakage current, the experimental and calculated values of slopes at different temperatures should be identical. To investigate the possibility of PF mechanism in the film, $\ln(\sigma)$ is plotted versus $E^{0.5}$ in Fig. 7.3 (a). There is a substantial discrepancy between the slope values shown on the graph and the calculated ones presented in Table 7.1. The PF mechanism, therefore, cannot be considered as an active mechanism of electrical conduction in this thin film.

Table 7. 1. Calculated slopes ($\beta/k_B T$) assuming that Poole-Frenkel and Schottky mechanisms (Eqs. 7.3 and 7.4) were governing leakage behavior. Calculation is done with two different values of refractive index for BNT-based thin films found in literature.^{33,34}

Temperature (K)		200	250	300	325	350
Calculated Poole-Frenkel slope (10^{-4})	n=2.1	20.97	16.77	13.98	12.90	10.19
	n=2.5	17.61	14.08	11.74	10.84	10.06
Calculated Schottky slope (10^{-4})	n=2.1	10.48	8.38	6.99	6.45	5.99
	n=2.5	8.80	7.04	5.87	5.42	5.03

The current density for the Schottky emission can be estimated by [28,30,31]:

$$J = AT^2 \exp\left(\frac{\beta_s E^{0.5} - \Phi_s}{k_B T}\right), \quad (7.4)$$

$$\beta_s = \sqrt{\frac{e^3}{4\pi\epsilon_o\epsilon_r}}$$

where β_s is the Schottky coefficient, A is a constant, and Φ_s is the barrier height in the interface. Schottky emission is similar to thermionic emission of from a metal surface to the vacuum. The carriers are emitted from electrode interface into the conduction band of the material and the energy barrier is lowered by a $\beta_s.E^{0.5}$ factor.

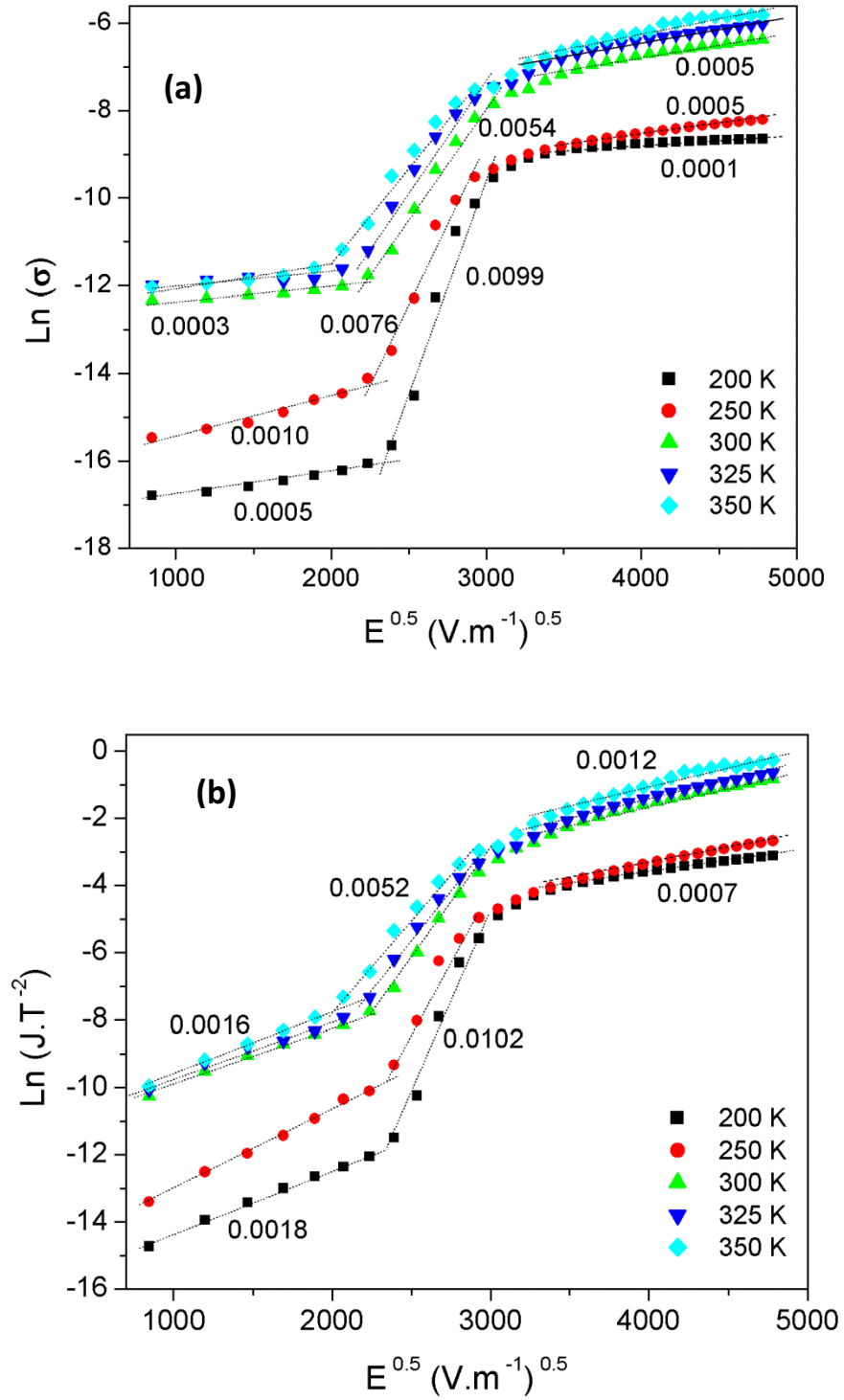


Fig. 7. 3. Analysis of the leakage current curves at different temperatures to investigate the possibility of (a) Poole-Frenkel and (b) Schottky mechanisms. The slope values are depicted on the plots.

With the same line of reasoning discussed above, the $\ln(J.T^2)$ versus $E^{0.5}$ will show a linear trend if Schottky mechanism exists. The calculated slopes listed in Table 7.1 are compared with those obtained from the graphs in Fig. 7.3 (b). Due to the discrepancy between the calculated and experimental results, the possibility of existence of Schottky mechanism is also ruled out. The predominant leakage mechanism in BNKTBT88 thin film at high electric fields is, therefore, the SCLC mechanism as pointed out earlier.

According to the argument above, then, the leakage current behavior of the thin film studied in this article can be explained by Lampert's theory [26]. Provided that a constant mobility is maintained during single carrier injection to the insulator, the J - E (or I - V) curve on the logarithmic scale is bounded by three distinct lines which form a triangle called the Lampert's triangle.

Fig. 7.4 depicts this triangle for the data collected at 300 K. The sides of the triangle are defined according to the Ohm's law (at low E) and Child's trap-free square law, also known as Mott and Gurney's law (SCLC at high E). The third side of the triangle is a vertical or a very steep line called trap-field-limit (TFL). The relative location of these boundaries and their intersections depend on numerous factors, such as the equilibrium density of free-carriers, the density and the levels of traps, the dielectric constant of the material, the device size, and the measurement condition, particularly the temperature.

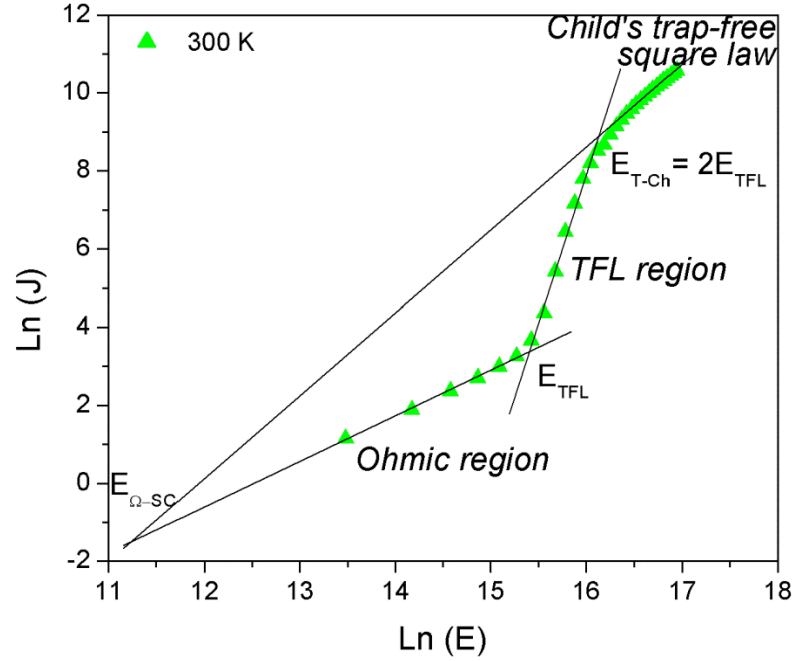


Fig. 7. 4. Details of Ln J-Ln E graph showing the Lampert's triangle measured at 300 K.

As mentioned above, the transition from ohmic to SCLC mechanism is accompanied by a sudden increase in the leakage current at intermediate voltages where the slope values are calculated to be as high as 6.6 to 15.6. Similar behavior has also been reported for <111>-oriented BNT thin films on platinized silicon substrates when the bottom electrode is positively biased²². This phenomenon can be elucidated by the trap filled limit (TFL) theory. As the electric field increases, traps are filled with charge carriers causing the Fermi level and therefore the leakage current to increase. The threshold voltage for filling up the traps is called TFL voltage [20,26,27,35], which can be estimated according to the eq. (5):

$$V_{TFL} = \frac{e n_{t0} L^2}{2 \epsilon_0 \epsilon_r} \quad (7.5)$$

where n_{t0} is the un-filled equilibrium trap density.

Fig. 7.5 (a) depicts the threshold voltage at the onset of TFL region (V_{TFL}) versus temperature. As demonstrated, the V_{TFL} declines as the temperature rises. This can be attributed to the increase of dielectric constant and the decrease of the un-filled trap density in proportion to the rise in temperature.³⁶ In other words, higher temperature thermally activates the charge carriers and thus reduces the required voltage to fill the traps. Therefore, the transition to the SCLC regime occurs at lower voltages. This result is consistent with data reported by other researchers [15,37,38].

In addition, as can be noticed in Fig. 7.2, the increase in temperature reduces the slope of the TFL region (a_{TFL}) and this agrees with the Lampert's model [26]:

$$a_{TFL} = \frac{d \ln I}{d \ln V} = \frac{n_{io}}{n_o} \quad (7.6)$$

where “ n_o ” exponentially increases with temperature according to the eq. (7): [35]

$$n_o = N_c \exp\left(-\frac{E_f - E_c}{k_B T}\right), \quad (7.7)$$

where N_c , E_f , and E_c are the effective density of states function, Fermi level, and conduction band level, respectively.

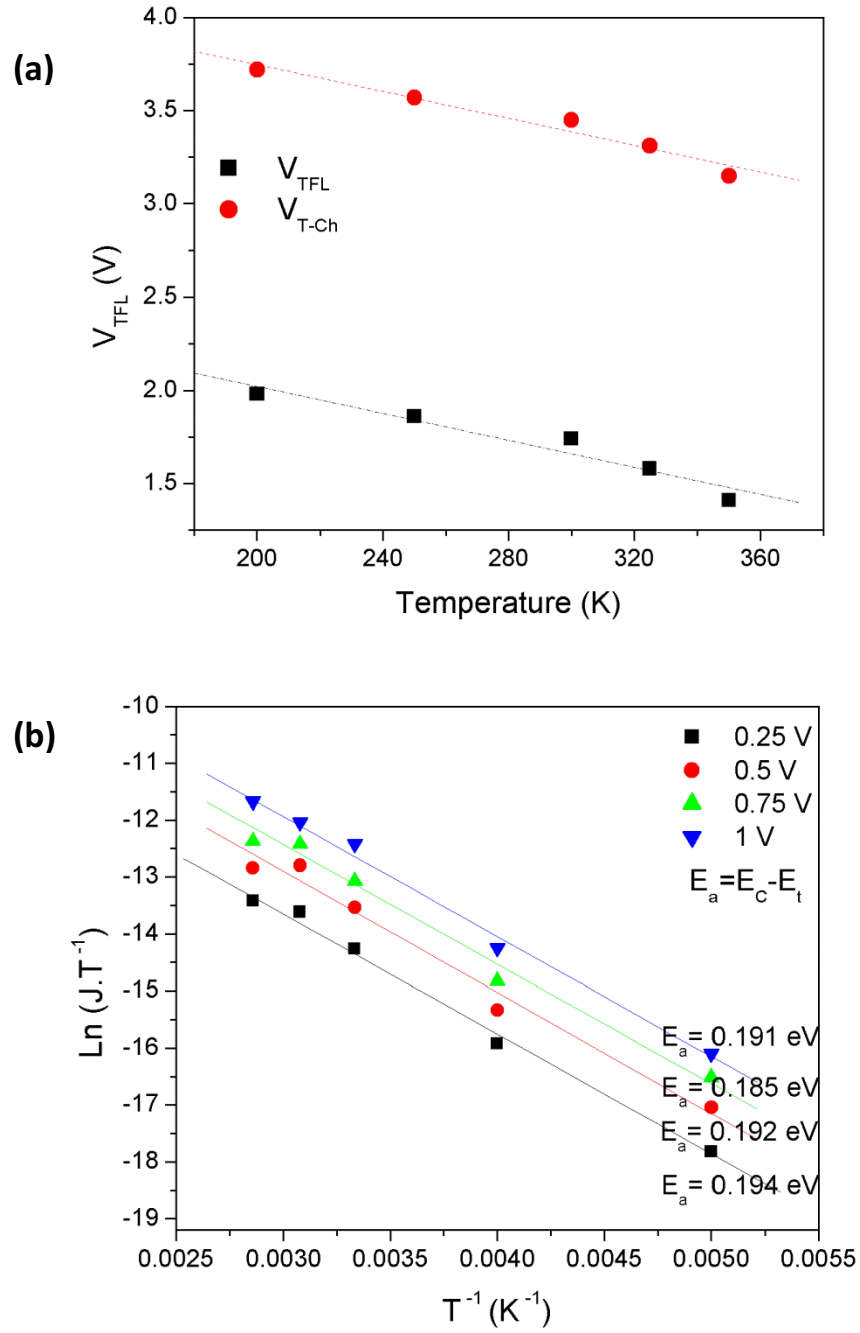


Fig. 7. 5. (a) The temperature-dependence of the threshold voltage for onset of TFL (V_{TFL}) and trap-free space charge (V_{T-Ch}) regions (b) calculation of trap energy level at different voltages.

Once all traps are filled, more injected carriers contribute to the conduction process. This creates a large concentration of space charges in the insulator, resulting in the SCLC behavior. When the electric field is sufficiently high, the density of injected electrons is much higher than the thermal equilibrium electron density. A criterion for the onset of SCLC regime is to extrapolate the trap-free line to lower voltages until it intersects with the ohmic curve resulting in:

$$V_{\Omega-SC} = \frac{8}{9} n_o \frac{eL^2}{\theta \epsilon_o \epsilon_r} \quad (7.8)$$

Table 7.2 summarizes the electrical properties of the thin film compared with some other films found in the literature. The calculation method has been described in refs [37,39]. The activation energy, which is the difference between the energy of the conduction band edge and the trap ($E_a = E_c - E_t$), can be calculated from the slope of the $\ln(J.T^{-1})$ versus T^{-1} plot [39] as shown in Fig. 7.5 (b). This value for the BNT-based thin film studied in this work is about 0.19 eV indicating that the film contains shallow traps located close to the conduction band edge. Shallow traps with activation energy of 0.08 eV have also been reported for BNT thin films deposited by magnetron sputtering.²⁰ In that case, the conductivity was attributed to the weakly localized electrons induced by formation of oxygen vacancies in the lattice. In comparison to other thin films presented in Table 7.2, the BNT-based thin film exhibits a high value of mobility ($5.82 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), which results in a high leakage current. This value is close to the electronic mobility reported for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thin films [29].

Table 7. 2. Electrical properties of 0.88BNT-0.08BKT-0.04BT thin film compared with Dy₂O₃ and LaAlO₃ metal-oxide-semiconductor (MOS) capacitors.

Thin film	V _{TFL}	μ	n _{to}	n _o	θ	μ _{eff} ^a = μ.θ	E _c -E _t	N _c
	(V)	(cm ² .V ⁻¹ .s ⁻¹)	(cm ⁻³)	(cm ⁻³)		(cm ² .V ⁻¹ .s ⁻¹)	(eV)	(cm ⁻³)
This work	1.7	5.82x10 ⁻³	6.97x10 ¹⁵	5.73x10 ¹³	0.037	2.15x10 ⁻⁴	0.19	8.95x10 ¹⁷
Dy ₂ O ₃ ^b	1.3	1.2x10 ⁻⁶	1.53x10 ¹⁹	9.68x10 ¹⁷	0.2	2.4x10 ⁻⁷	0.20	4.53x10 ²¹
LaAlO ₃ ^c	0.76	4.0x10 ⁻¹⁰	1.x10 ¹⁹	8.7x10 ¹⁶	0.03	1.2x10 ⁻¹¹	0.36	1.2x10 ²³

^a Ref⁴⁰

^b Ref³⁷

^c Ref³⁹

As shown in this work, insulator thin films may have various charge traps. At low voltages, the equilibrium number of un-filled traps (n_{to}) is much higher than that of electrons (n_o). Therefore, all injected carriers can be easily trapped. Further increase of voltage causes the number of injected electrons to approach the trap density at the TFL voltage. Consequently, the injected charges are transported to the conduction band leading to a sharp increase in the current density. Assuming that the capacitance of material is maintained at a constant value, the conductivity curve follows the trap-free square law at a voltage of $V_{T-Ch}=2V_{TFL}$ where $n_e \approx n_{to}$ [26,35]. As shown in Fig. 7.5 (a), the ratio of the V_{T-Ch} to V_{TFL} in different temperatures is close to 2, again confirming the validity of the application of the Lampert's model to the film.

7.4 Summary

The temperature dependence of electrical conductivity in $0.88 \text{ Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.08 \text{ Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3\text{-}0.04 \text{ BaTiO}_3$ (MPB composition) thin films deposited by pulsed laser deposition on $\langle 001 \rangle$ -oriented SRO/STO substrates was assessed. I-V curves were measured in a temperature range of 200-350 K under vacuum. With comparison of the calculated and experimental data, conduction mechanisms such as Fowler-Nordheim, Schottky, and Poole-Frenkel were excluded from possible mechanisms operating in these films. It was found that at low electric fields, where the concentration of injected carriers is less than the equilibrium concentration of free carriers, the ohmic conduction governs the leakage current. As the applied electric field increases, the leakage current abruptly rises due to filling the shallow traps by injected carriers at the trap-filling-limit (TFL) voltage. At higher electric fields, as a result of increasing the density of injected carriers, the leakage current follows the Child's trap-free square law where the space-charge limited current overrides other conductivity mechanisms. The leakage current behavior of thin films in the studied range of temperature (200-350 K) matched with the Lampert's triangle.

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8 Dielectric and ferroelectric Properties of Mn-doped BNT-BKT-BLT Thin Films

Abstract

$\text{Bi}_{0.5}(\text{Na}_{0.76}\text{K}_{0.2}\text{Li}_{0.04})_{0.5}\text{TiO}_3$ (MPB composition) and $\text{Bi}_{0.5}(\text{Na}_{0.88}\text{K}_{0.08}\text{Li}_{0.04})_{0.5}\text{TiO}_3$ (off-MPB composition; rhombohedral side) thin films were deposited on SrRuO_3 coated (001)- SrTiO_3 substrates by pulsed laser deposition. The effects of oxygen pressure and Mn-doping on the ferroelectric and dielectric properties, and microstructure of films were investigated. With increasing the oxygen pressure from 200 to 400 mtorr, the leakage current density at 200 kV.cm^{-1} increased from 1.5×10^{-4} to $5 \times 10^{-3} \text{ A.cm}^{-2}$. Upon Mn-doping, the leakage current was suppressed by more than two orders of magnitude and the polarization was considerably enhanced. The remnant polarization and dielectric constant (at 10 kHz) of 2 mol.% Mn-doped film with MPB composition deposited at 400 mtorr were measured to be 23 $\mu\text{C.cm}^{-2}$ and 660, respectively. The XPS results showed coexistence of Mn^{2+} , Mn^{3+} , and Mn^{4+} in doped-films. Oxidation of Mn^{2+} to higher valence states by absorbing holes along with occupation of A-site vacancies were suggested as possible reasons for a reduced leakage current and dielectric loss in Mn-doped films. BNKLT88 thin films with off-MPB composition showed a lower polarization and permittivity compared to the MPB composition. However, the insulative properties of off-MPB composition were superior to MPB films.

8.1 Introduction

Lead-free ferroelectric thin films have attracted a lot of attention during past few years. However, compared to their lead-based counterparts they suffer from inferior insulating properties. This is one of the main drawbacks facing the development of lead-free thin films for practical applications such as capacitors and memories in which low values of leakage current and dielectric loss are demanded. Recently, it has been demonstrated that the leakage current of lead-free films such as $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) [1-3], $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) [4-6], BaTiO_3 (BTO) [7], NaNbO_3 (NN) [8-10], and BiFeO_3 (BFO) [11] can be reduced by manganese doping. A literature survey, however, shows that there is controversy in the published results on the effects of Mn on leakage current and dielectric properties. Some researchers have reported that Mn-doping deteriorates the electrical properties of lead-free thin films and crystals [12-16]. Kawae et al [11] indicated that formation of deep traps by Mn-doping decreased the leakage current of BFO thin films. Chung et al [15], on the contrary, showed that Mn doping increased the leakage current and dielectric loss due the creation of oxygen vacancies. While Mn-doping in KNN-based thin films remarkably enhanced the remnant polarization and suppressed the leakage current [1,3,17], it did not enhance the ferroelectric properties of KNN thick films [18]. The formation of oxygen vacancies acting as trapping centers in Mn-doped BTO thin films increased the dielectric loss at low frequencies [7]. On the other hand, Chu et al demonstrated that the dielectric loss was decreased considerably with Mn doping [19]. A high concentration of Mn also deteriorates the electrical properties by formation of secondary phases [1,20]. Differences in deposition techniques, microstructure, crystallographic orientation, compositional homogeneity and defects may

be responsible for the variation of results in the published literature. Thus, more research is still needed to be implemented to clarify the effects of Mn-doping in lead-free materials.

Mn basically acts as an acceptor dopant replacing Ti^{4+} or Fe^{3+} in the perovskite structure and creates doubly ionized oxygen vacancies [14,21]. It is believed that the fluctuation of Mn valence states is the key factor for decreasing the leakage current [9,22]. On the other hand, the processing parameters, particularly the oxygen pressure affect the concentration of intrinsic oxygen vacancies, electronic defects, and the Mn oxidation state. Therefore, PO_2 during the growth, cooling or post-annealing treatment is one of the most critical factors with which the effect of Mn-doping is correlated [22]. In this chapter, the influence of 2 mol.% Mn-doping and oxygen pressure on the electrical properties of BNKLT76 and BNKLT88 thin films deposited by PLD is presented. As mentioned previously, the BNKLT76 composition is a morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases which exhibits relatively high values of piezoelectric charge coefficient ($d_{33} \sim 174 \text{ pC.N}^{-1}$), planar coupling coefficient ($k_p \sim 0.36$), and thickness coupling coefficient ($k_t \sim 0.52$) in the bulk form [23,24]. A ferroelectric to antiferroelectric phase transition determines the depolarization temperature of this composition which is reported to occur at about 170°C [24]. Despite comprehensive studies on ceramics with the MPB and off-MPB compositions, there are no reports on the ferroelectric and dielectric properties of the BNKLT76 and BNKLT88 thin films. This chapter summarizes the results pertaining to the processing-property relationship in undoped and Mn-doped BNT-BKT-BLT (BNKLT) thin films. As presented in chapters 3 and 4, this ternary system in the ceramic form, exhibited wide

range of electrical properties depending on the chemical composition and the processing conditions.

8.2 Experimental Procedure

Undoped and 2 mol.% Mn-doped films (~500 nm thick) with target composition of $\text{Bi}_{0.5}(\text{Na}_{0.76}\text{K}_{0.2}\text{Li}_{0.04})_{0.5}\text{TiO}_3$ (BNKLT76) and $\text{Bi}_{0.5}(\text{Na}_{0.8}\text{K}_{0.08}\text{Li}_{0.04})_{0.5}\text{TiO}_3$ (BNKLT88) were deposited on SrRuO_3 coated (001)- SrTiO_3 substrates by the PLD technique. (001)-oriented films were grown at a substrate temperature of 800 °C, laser repetition rate of 10 Hz, laser energy density of 1.2 J.cm^{-2} and different oxygen pressures (150 to 400 mtorr). Following the deposition, films were cooled down inside the PLD chamber at 1 atm oxygen pressure. The thickness of the films was measure to be about 450-550 nm. The microstructural and electrical characterizations were carried out as previously mentioned in chapter 6.

The oxidation state of the elements such as Ti and Mn was studied by X-ray photoelectron spectroscopy (XPS, Al K_{α} , K-Alpha, Thermoscientific). XPS is a method for characterizing the top few atomic layers at the surface of a solid. XPS can not only give the elemental composition of a surface but can provide insights into the chemical bonding at the surface. X-ray photon incident on a sample can ionize an atom producing an ejected free electron. The kinetic energy K of the photoelectron depends on the energy of the photon $h\nu$, as expressed by the Einstein photoelectric relation $K=h\nu-\text{BE}$, where BE is the binding energy of the electron to the atom concerned. This relation is the basis of XPS. Since $h\nu$ is known, a measure of K determines BE. The value of BE is

specific to the atom concerned; measurement of BE serves as a fingerprint to identify the atom. XPS can be used to detect all elements except hydrogen and helium. The qualitative and quantitative chemical state analysis capabilities, combined with extreme surface sensitivity have made XPS the most broadly applicable surface analysis technique today. XPS is a quantitative technique. The intensities of photoelectron peaks are directly proportional to the number of atoms present. Therefore, using elemental sensitivity factors, peak intensities can be converted to atomic concentrations with a relative error of $\sim 10\%$. The exact binding energy of core electrons is determined by the local chemical environment, permitting the identification of nearest neighbor bonding or oxidation states.

8.3 Results and Discussion

8.3.1 Undoped Thin films

Figs. 8.1 (a)-(b) show the effect of oxygen pressure on the P-E hysteresis loops and current densities of undoped BNKLT76 (MPB composition) films. With increasing the oxygen pressure from 200 to 300 mtorr, the remnant polarization drops from 11.5 to $9.4 \mu\text{C}\cdot\text{cm}^{-2}$. With further increase of the background pressure to 400 mtorr, the P_r was enhanced to $19.3 \mu\text{C}\cdot\text{cm}^{-2}$. Fig. 8.1 (b) shows the J-E curves of BNKLT76 thin films deposited at various oxygen pressures. The leakage current increased by more than one order of magnitude as the oxygen pressure changed from 200 to 400 mtorr. In BNKTBT thin films (chapter 6) it was found that the leakage current initially decreased with increasing the oxygen pressure and then increased again. However, In BNKLT thin film

the leakage current increased with increasing the background pressure. (BNKLT76 thin films prepared at 200 and 300 mtorr almost show the same leakage current). A higher leakage current in the film deposited at 400 mtorr may originate from deviation of chemical composition from stoichiometry, increased electron-hole concentration, and a thinner film thickness. Similar results were reported on KNN-based thin films deposited at different oxygen pressures [25].

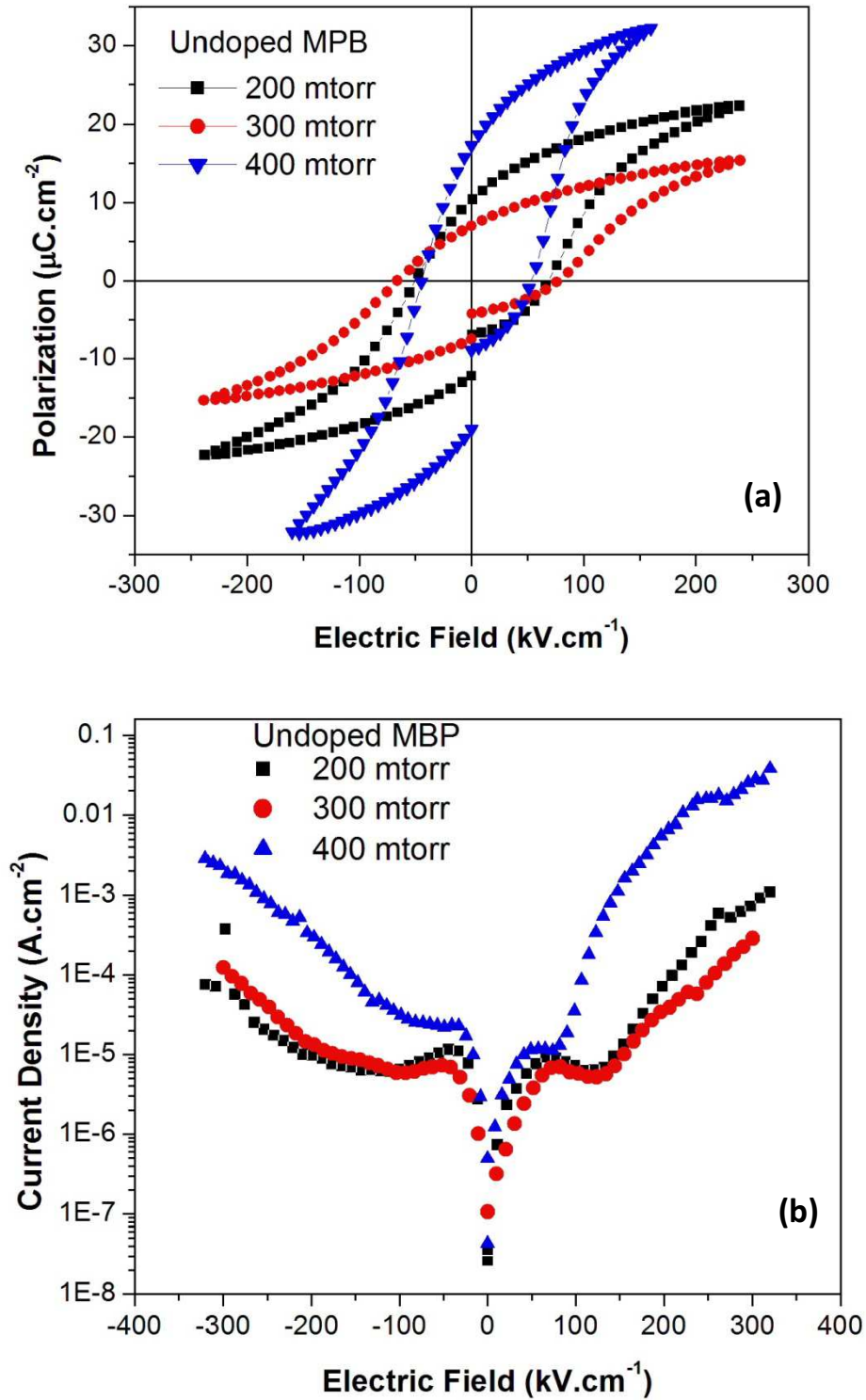


Fig. 8. 1. Effect of oxygen pressure on the (a) P-E hysteresis loop (b) leakage current density of undoped BNKLT76 thin films.

Figs. 8.2 (a)-(c) show the effect of oxygen pressure on microstructure of undoped BNKLT76 thin films. At low oxygen pressures, rods of rectangular cross section oriented out-of-plane were observed. With increasing the oxygen pressure, the size and number of these rods were reduced. This can be attributed to the decreased kinetic energy of ablated species as the background pressure increased. At 400 mtorr, these surface features were disappeared and a nearly smooth surface was obtained.

8.3.2 Mn-doped Thin films

Figs. 8.3 (a)-(b) display the effect of oxygen pressure on the P-E hysteresis loops and leakage current densities of Mn-doped BNKLT76 films. Similar to undoped films, the highest P_s were obtained at 400 mtorr. The Mn-doped BNKLT76 film grown at 200 mtorr with a P_r of $20 \mu\text{C.cm}^{-2}$ exhibited a compromise between the polarization and leakage current. The influence of oxygen pressure on Mn-doped samples was analogous to undoped films, i.e. the leakage current increased with increasing the background pressure. However, the leakage current values were lower than undoped composition. The current densities at 300 kV.cm^{-1} were measured to be 1.5×10^{-2} and $2 \times 10^{-4} \text{ A.cm}^{-2}$ at 150 mtorr and 450 mtorr, respectively.

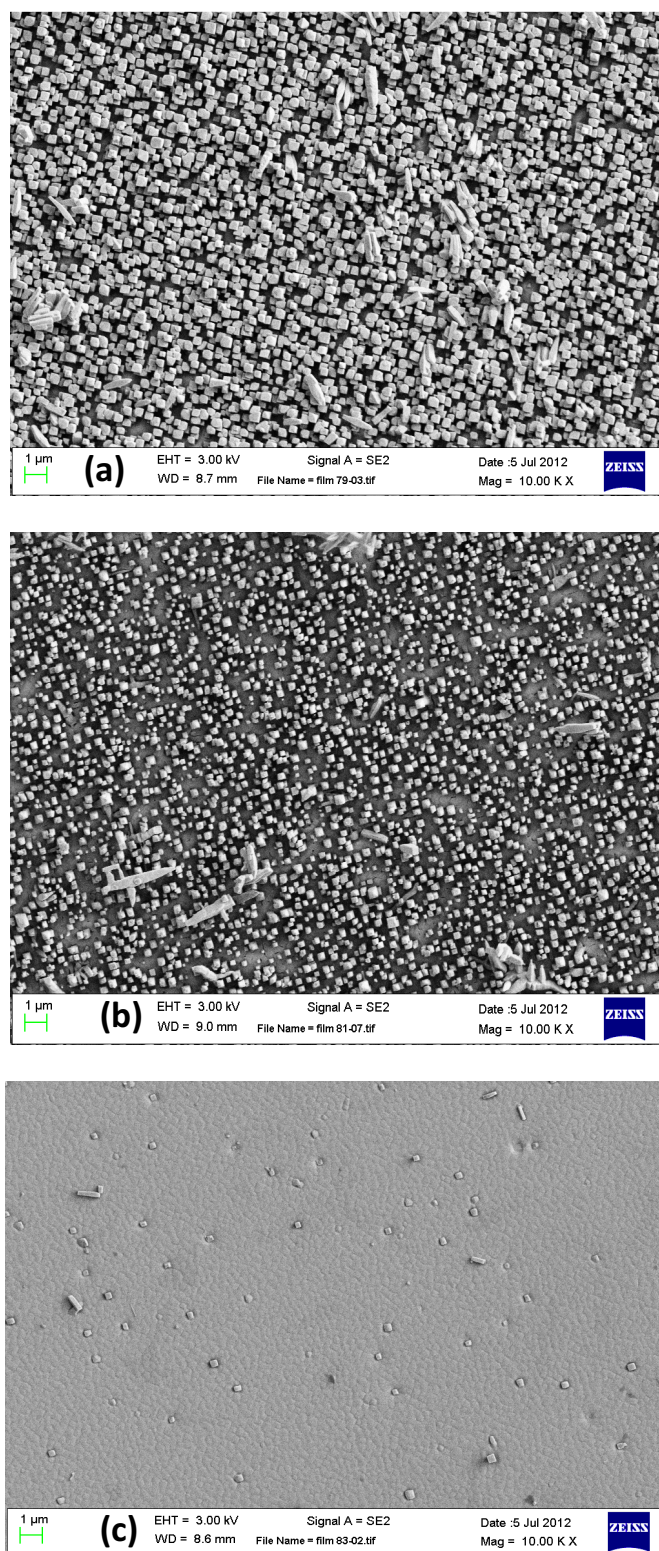


Fig. 8. 2. Microstructure of undoped BNKLT76 thin films deposited at (a) 200 mtorr, (b) 300 mtorr, and (c) 400 mtorr.

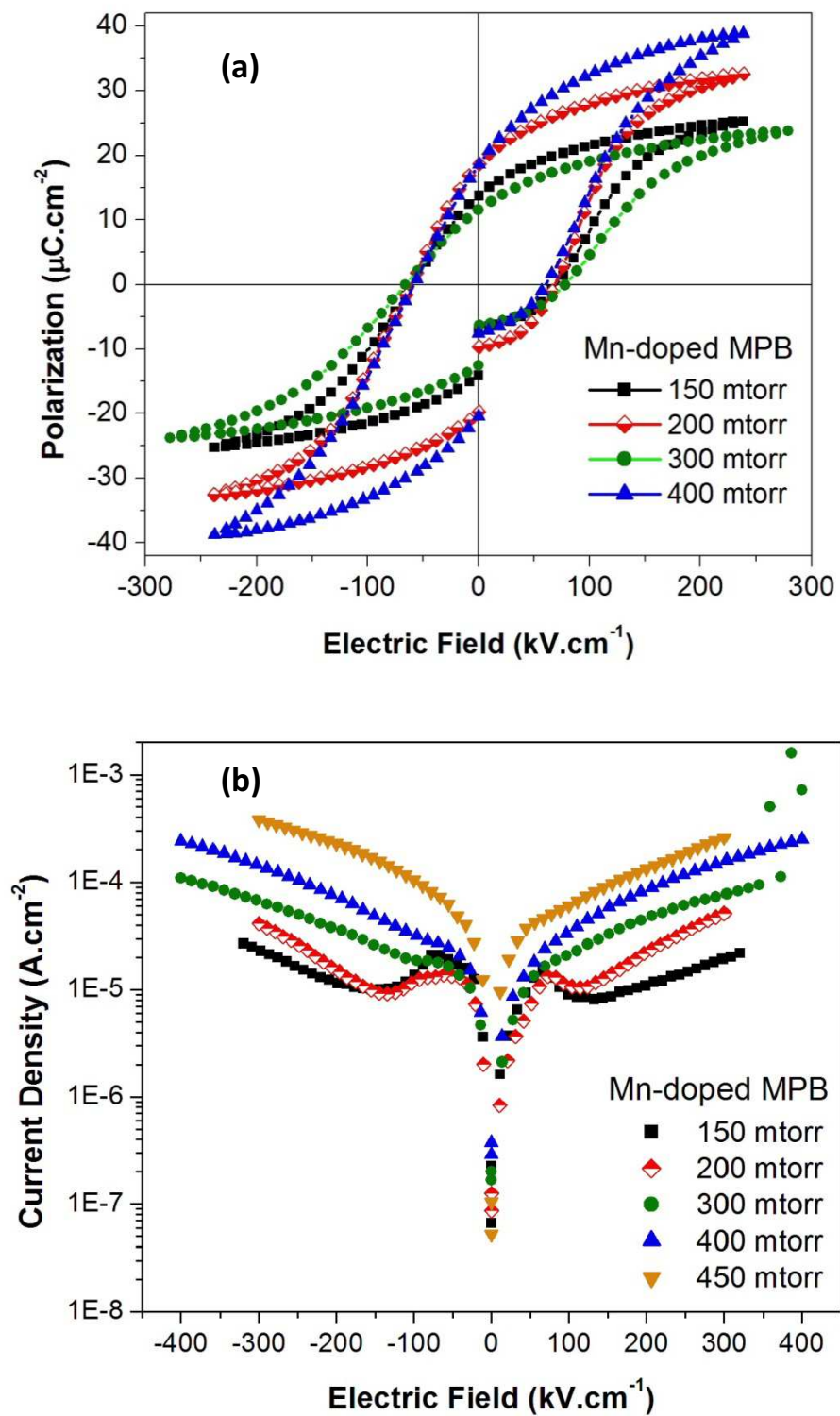


Fig. 8. 3. Effect of oxygen background pressure on (a) current density (b) P-E hysteresis loops of 2 mol.% Mn-doped BNKLT76 (MPB) thin films.

Figs. 8.4 (a)-(c). demonstrate the FESEM microstructures of Mn-doped BNKLT76 films deposited at 150, 300, and 400 mtorr. The rod-shape features which were observed in undoped films at low oxygen pressures did not exist in Mn-doped samples. At 150 mtorr, the film contained oriented cubes and pyramids on the surface. With increasing the oxygen pressure to 300 mtorr, the surface undulations became finer and flatter and their morphology changed to a polygonal shape. At a higher background pressure (450 mtorr), the population of these surface features was remarkably diminished although several particles with a relatively large size of $\sim 1 \mu\text{m}$ appeared on the surface. A similar trend was observed in the microstructure of undoped films deposited at different oxygen pressures as pointed out earlier.

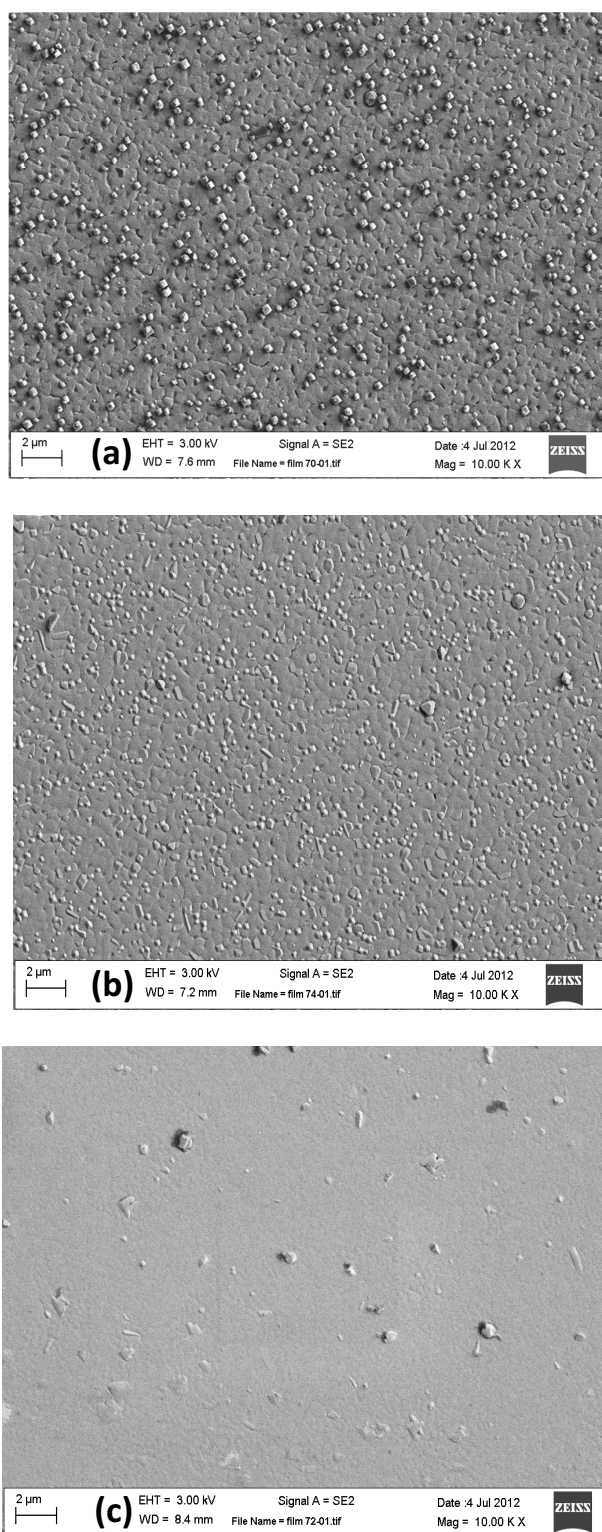


Fig. 8. 4. Microstructures of 2 mol.% Mn-doped BNKLT76 thin films deposited at different oxygen pressures. (a) 150 mtorr, (b) 300 mtorr, and (c) 400 mtorr.

The variations of relative permittivity and dielectric loss in Mn-doped BNKLT76 films with oxygen pressure are depicted in Fig. 8.5. Increasing the oxygen pressure from 150 to 450 mtorr, enhanced the relative permittivity at 10 kHz from 458 to 670. However, due to the high concentration of space charges and charge carriers (mainly electron-holes) in the films prepared at 400 and 450 mtorr, the dielectric constant abruptly decreased at higher frequencies. The dielectric relaxation in these films was accompanied by a steep rise in dielectric loss at high frequencies (see Fig. 8.5 (b)).

Fig. 8.6 compares the leakage current of Mn-doped and undoped BNKLT76 films deposited at 200 and 400 mtorr. Increasing the oxygen pressure from 200 to 400 mtorr in undoped films increased the leakage current density at 200 kV.cm⁻¹ from 1.5×10^{-4} to 5×10^{-3} A.cm⁻². It can be observed that the Mn-doping remarkably decreased the leakage current of both films deposited at different oxygen pressures. The leakage current density of the doped film prepared at 200 mtorr remained below 2×10^{-5} A.cm⁻² even at high electric fields which was significantly lower than other undoped BNT-based thin films with MPB composition [26, 27]. The effect of Mn-doping was particularly more pronounced in the film deposited at 400 mtorr in which the leakage current density at 300 kV.cm⁻¹ was decreased by more than two orders of magnitude. The reduction in leakage current is also in agreement with 0.5 mol% Mn doped BNT-BT thin films prepared by the PLD [5]. Wu et al reported that addition of 2 mol.% Mn in BNT thin films prepared by sol-gel, did not considerably decrease the leakage current, while increasing the concentration of Mn up to 6 mol.% suppressed the leakage current by one order of magnitude [20].

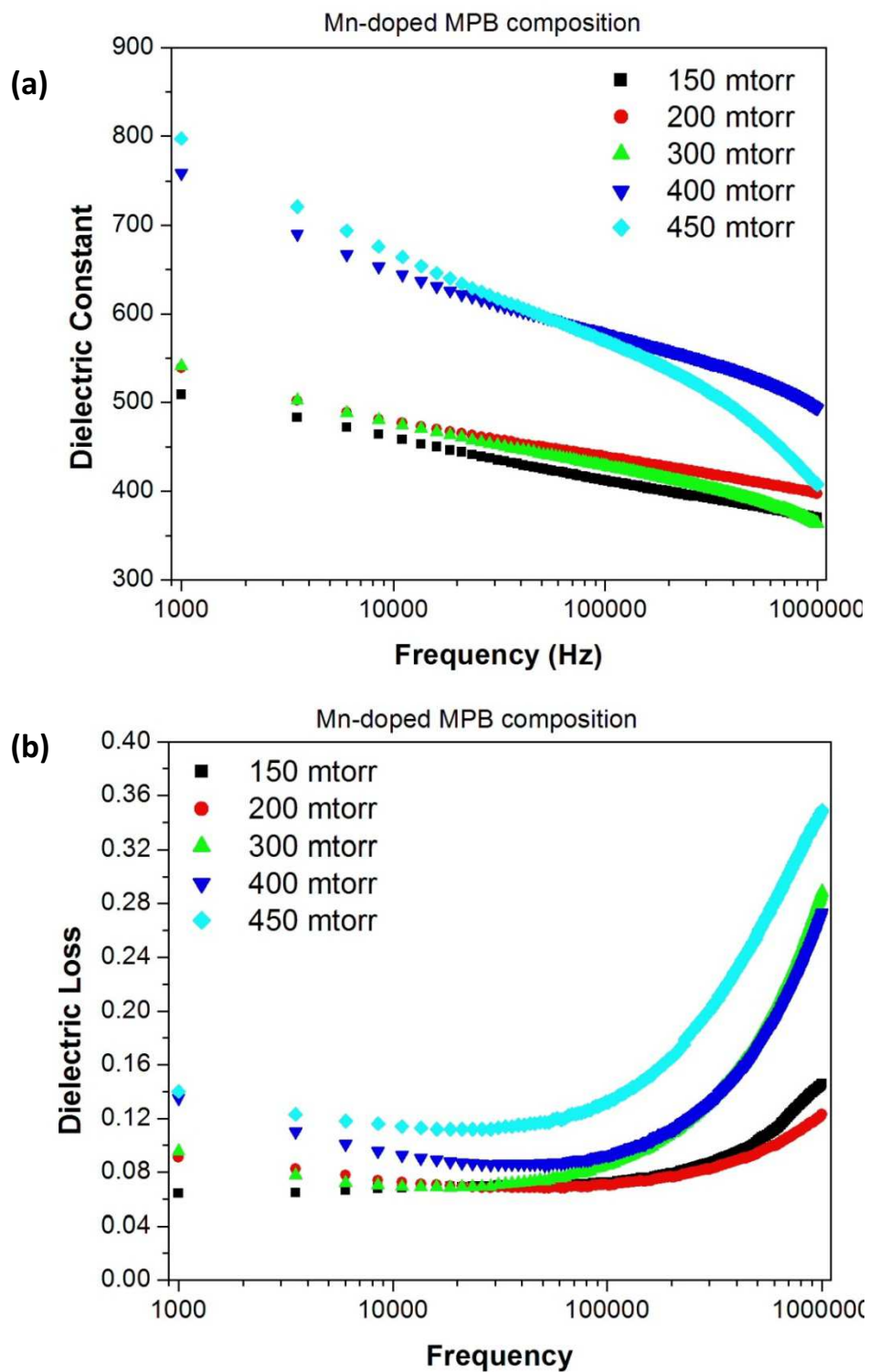


Fig. 8. 5. Influence of oxygen pressure on dielectric properties of Mn-doped BNKLT76 thin films
(a) dielectric constant (b) dielectric loss.

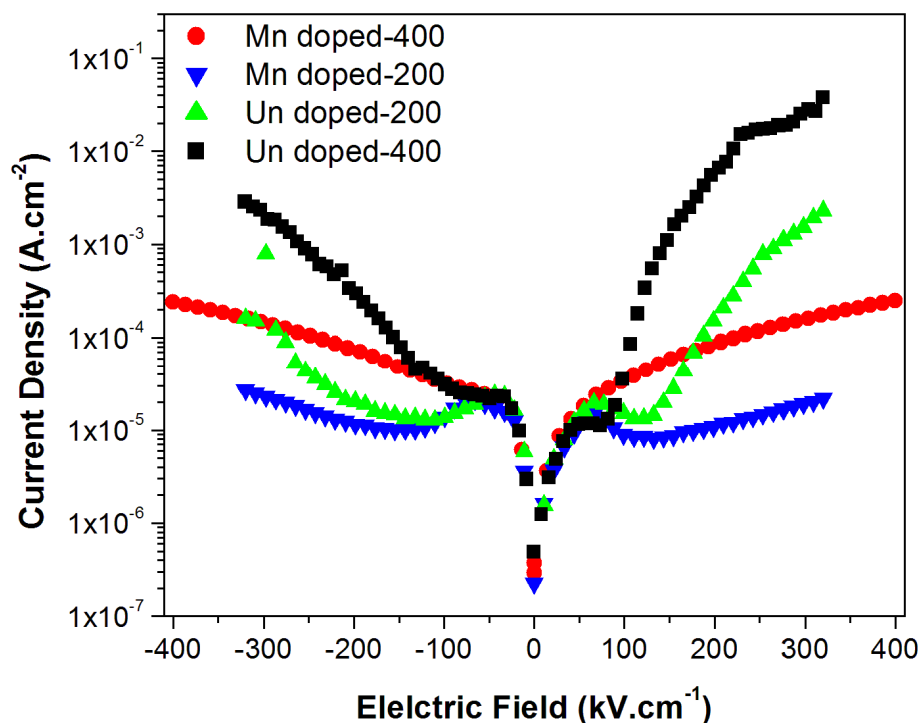


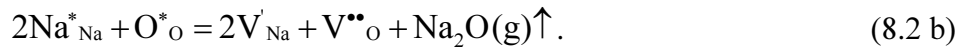
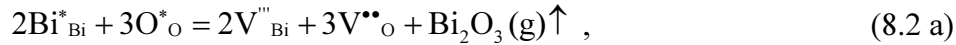
Fig. 8. 6. The leakage current density of Mn-doped and undoped BNKLT76 films grown at 200 and 400 mtorr.

Due to the fact that Mn is a multivalent element, it might be incorporated into the lattice under different valences such as Mn^{2+} ($r \sim 0.67 \text{ \AA}$ low spin, $r \sim 0.83 \text{ \AA}$ high spin), Mn^{3+} ($r \sim 0.58 \text{ \AA}$ low spin, $r \sim 0.64 \text{ \AA}$ high spin), and Mn^{4+} ($r \sim 0.53 \text{ \AA}$). Considering the ionic radii of different cations in the host lattice [Ti^{4+} ($r \sim 0.61 \text{ \AA}$), Bi^{3+} ($r \sim 1.03 \text{ \AA}$), Na^{+} ($r \sim 1.02 \text{ \AA}$), K^{+} ($r \sim 1.38 \text{ \AA}$), and Li^{+} ($r \sim 0.74 \text{ \AA}$)], Mn is expected to occupy the Ti cations located at the B-site. Therefore, Mn-doping is accompanied by formation of extrinsic oxygen vacancies to maintain the charge neutrality:



where Mn'_{Ti} and Mn''_{Ti} represents Mn^{3+} and Mn^{2+} at the Ti site respectively, and $V^{\bullet\bullet}_O$ denotes an oxygen vacancy.

In addition, the volatilization of A-site elements during the high temperature processing results in formation of intrinsic oxygen vacancies [9, 10, 28, 29] to compensate for the negatively charged A-site vacancies:



Intrinsic and extrinsic oxygen vacancies can act as charge carries leading to an increase in the leakage current particularly at temperatures higher than room temperature [12, 28, 29]. They can also function as bridging connectors between B-site cations facilitating the electron hopping phenomenon which is a known source of electrical conduction in ferroelectric thin films with the perovskite structure [20]. The results obtained in this research as well as several other works confirm that Mn-doping improves the insulating properties of perovskite thin films. It is believed that the oxygen vacancies have negligible contribution to the leakage current of thin films at room temperature. Furthermore, possible formation of the defect complexes such as $[Mn'_{Ti}-V_O^{\bullet\bullet}]'$ and $[Mn''_{Ti}-V_O^{\bullet\bullet}]$ [2, 30, 31], decreases the concentration of free oxygen vacancies. However, it is possible that oxygen vacancies indirectly increase the leakage current through formation of holes ($h^\bullet$). Exposure of oxygen vacancies to an oxygen environment (during the deposition, cooling or annealing steps) creates $h^\bullet$ leading to a p-type conduction behavior:



These holes have higher mobility than oxygen vacancies and particularly deteriorate the insulating properties at room temperature [29]. As shown in Fig. 8.6, leakage current of undoped and Mn-doped BNT-based thin films increased with oxygen pressure. According to eq. 8.3, a higher oxygen pressure increases the concentration of holes which in turn increases the leakage current of the films. In addition, the oxygen pressure during the deposition of thin films with PLD process, affects the stoichiometry of the films. On the one hand, increasing the oxygen pressure may thermodynamically hinder the volatilization of A-site elements by decreasing the equilibrium constant of the oxide dissociation. On the other hand, the kinetic energy of the species flying from the plasma plume towards the substrate decreases as the oxygen pressure increases. This momentum change which is more significant for lighter elements along with a contraction in the plume size, may lead to the deposition of films with non-uniform chemical composition. The electrical properties of thin films, therefore, are a complex function of the oxygen pressure [32] which affects the chemical composition of the films as well as the defect structure.

The oxidation states of Mn and Ti were explored by XPS and the representative spectra are depicted in Fig. 8.7 (a)-(b). Fig. 8.7 (a) shows the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ XPS spectra in Mn-doped film deposited at 400 mtorr. The peak observed at a binding energy of 641.2 eV corresponds to the divalent manganese cation. Since the Mn peaks of different oxidation states are located very close to each other, it is difficult to indicate the exact position for each valence state. However, the peak broadening of Mn $2p_{3/2}$ orbit at a binding energy of about 645 eV reveals the coexistence of Mn²⁺ with higher valence cations (Mn³⁺ and Mn⁴⁺) which is similar to Mn-doped BFO thin films and KNN crystals

[22, 31]. Using the peak fitting analysis the ratio of Mn^{2+} to Mn^{3+} and Mn^{4+} was calculated to be about 3:1. The XPS spectrum of the doped film grown at 200 mtorr (not shown here) also exhibited existence of mixed valence states for Mn. It is suggested that Mn divalent cations incorporated at the B-site can absorb electron-holes [9, 10, 28]. As a result, Mn^{2+} is oxidized to Mn^{+3} or Mn^{+4} according to the following equations:



Manganese in BNT-based thin films, therefore, reduces the leakage current by limiting the contribution of the holes. This is consistent with the results of other Mn-doped thin films [5, 7, 9, 10, 20]. According to Fig. 8.6, the leakage current suppression was more pronounced in the film deposited at 400 mtorr probably due to the fact that this film contained higher concentration of holes compared to the sample prepared at 200 mtorr.

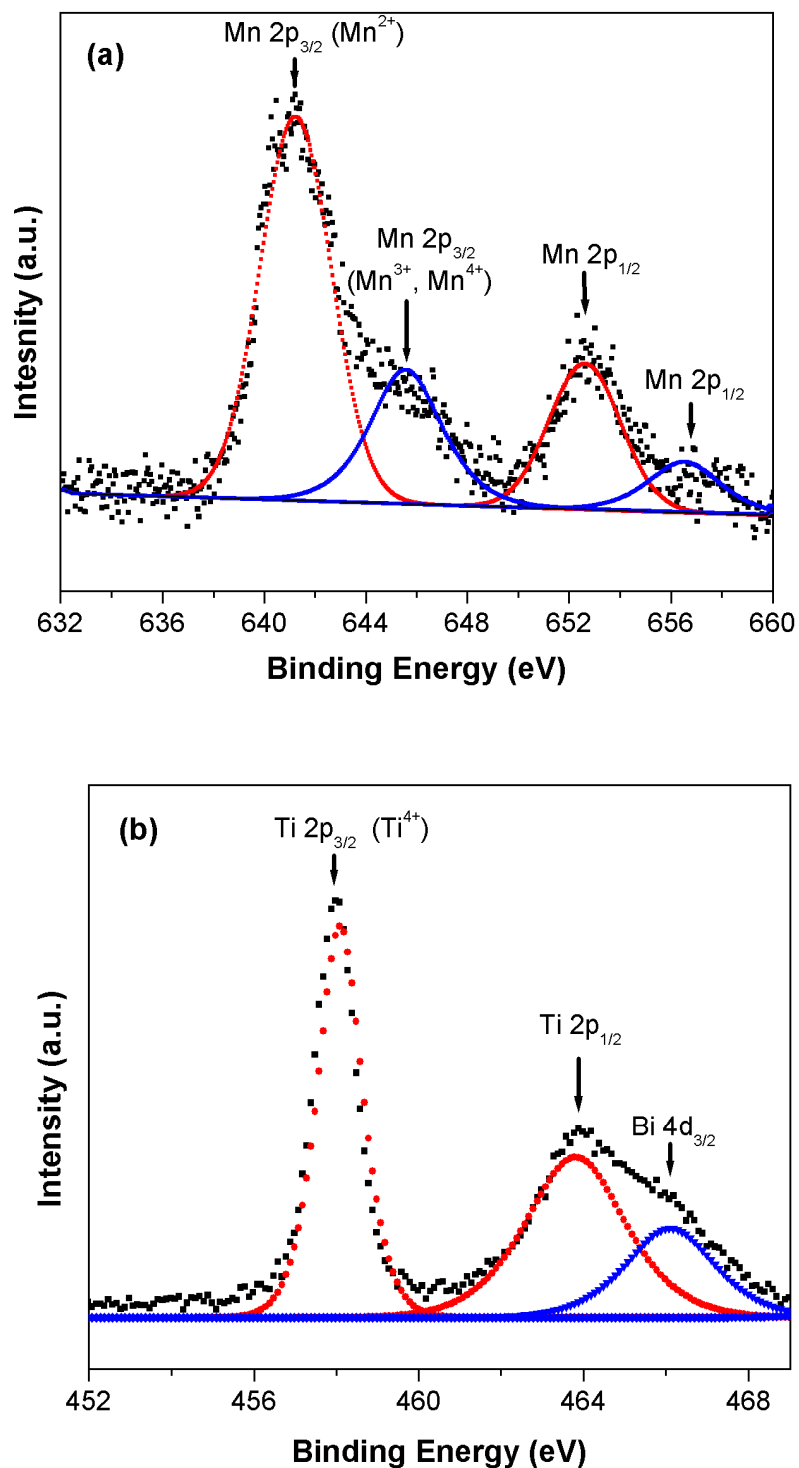


Fig. 8. 7. (a) Mn 2p XPS spectrum of Mn-doped BNKLT76 film prepared at 400 mtorr (b) Ti 2p XPS spectrum of undoped BNKLT76 film deposited at 200 mtorr.

Although it is more probable that Mn ions replace the B-site of ABO_3 Perovskite structure [9, 20, 21, 28-30, 33], the possibility of the A-site occupation by Mn cannot be excluded [5, 34-36]. Since the ionic radii of Mn^{2+} and Mn^{3+} ions are also close to those of Bi^{3+} , Na^+ , K^+ , and Li^+ , manganese can fill A-site vacancies created as a result of A-site volatilization. Therefore, it decreases the concentration of vacancies and hence declines the leakage current which is supported by the obtained data. It is shown that Mn addition improves the resistivity of BNT crystals probably with the same proposed mechanism [36]. Simultaneous occupation of the A- and B-sites by Mn which induces both hard and soft characteristics has been reported for other materials such as KNN thin films [3]. As mentioned previously, one of the other origins of electrical conduction and dielectric loss in thin films and ceramics with the perovskite structure is the electron hopping through B-site cations of different valences such as Ti^{4+} and Ti^{3+} [20, 37, 38]. In BNT-based thin films deposited by sol-gel technique, Mn doping decreased the leakage current by preventing the reduction of Ti^{4+} to Ti^{3+} [20, 37]. Fig. 8.7 (b) illustrates the Ti 2p XPS spectrum for undoped sample deposited at 200 mtorr showing that Ti exists in form of Ti^{4+} ($2p_{3/2}$ peak appearing at 457.5 eV). The same valence state of Ti was also found in the films deposited at 400 mtorr. Since there was no indication of Ti^{3+} existence in undoped films, the electron hopping could not be considered as a dominant mechanism of electrical conduction in these thin films.

Fig. 8.8 shows the polarization-electric field (P-E) hysteresis loops for undoped and Mn-doped BNKLT76 films. It was found that manganese doping remarkably enhanced the ferroelectric polarization of the samples which was in agreement with other reports [5, 20, 39, 40].

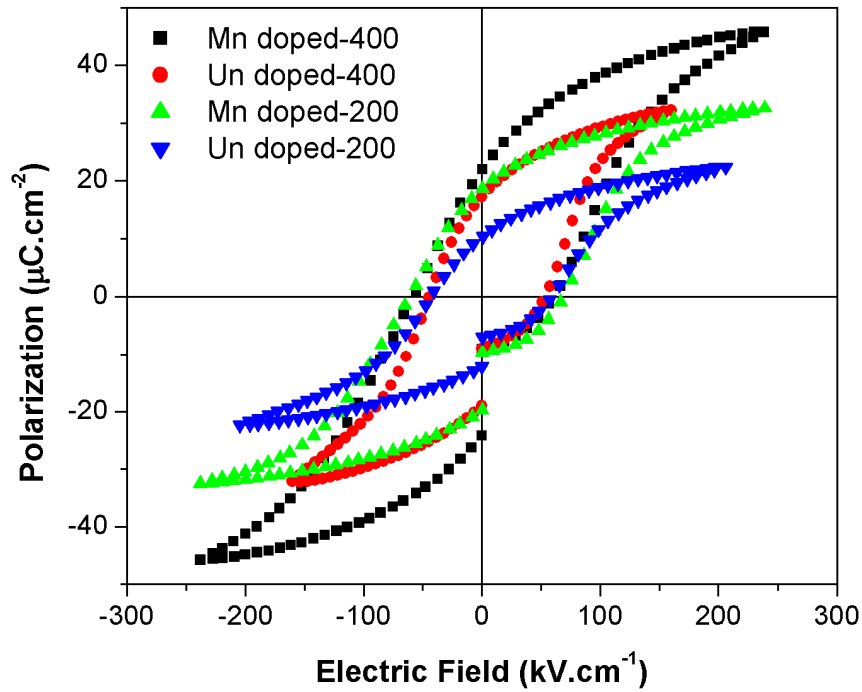


Fig. 8. 8. P-E hysteresis loops of Mn-doped and undoped BNKLT76 thin films deposited at 200 and 400 mtorr measured at 1 kHz.

The remnant polarization (P_r) and saturation polarization (P_s) also increased with increasing the oxygen pressure. The P_r in undoped films increased from 10.3 to 17.3 $\mu\text{C.cm}^{-2}$ as the oxygen pressure changed from 200 to 400 mtorr. After Mn-addition, the P_r of the BNKLT76 films prepared at 200 and 400 mtorr was enhanced by 80 and 35 percent, respectively. The highest P_r (23 $\mu\text{C.cm}^{-2}$) is achieved for Mn-doped sample deposited at 400 mtorr. The enhancement of the remnant polarization by Mn-doping can be explained through distortion of TiO_6 octahedra [41-43] and the increased tetragonality [5, 31] upon replacement of the B-site with Mn. Manganese substitution may increase the dipole size by lengthening the off-center displacement in the perovskite structure, and hence the polarization is improved. In BNT single crystals, the Mn doping results in an

in-phase octahedral tilting [44] and it increases the ordering of polar nano-regions [35, 44] which in turn enhances the ferroelectric and dielectric properties and decreases the leakage current and dielectric loss [36, 45]. The reduced leakage current also played a role in the enhancement of polarization by increasing the effective applied electric field. Mn-doping was found to increase the coercive field of thin films which is a common effect of B-site acceptor substitution and is also observed in Mn-doped KNN-based thin films [3]. The pinning of the domain walls by oxygen vacancies and the alignment of defect dipoles in the direction of the applied electric field caused an increase in the coercive field in Mn-doped thin films.

The dielectric constant and dielectric loss of the BNKLT76 films were measured as a function of frequency as depicted in Fig. 8.9. The dielectric properties showed a relaxation type behavior as the loss tangent monolithically increased and relative permittivity decreased with frequency. Increasing the oxygen pressure increased the dielectric loss and the permittivity which was in agreement with the leakage current data. The dielectric constant of undoped BNKLT76 films at 10 KHz enhanced from 470 to 690 by increasing the oxygen pressure from 200 to 400 mtorr. It was noticeable that the dielectric loss was effectively decreased by Mn-doping. Similar to the leakage current behavior, the influence of Mn doping in improvement of the dielectric loss was more noticeable for the film deposited at 400 mtorr. The dielectric loss at 10 kHz for samples deposited at 200 and 400 mtorr decreased from 0.09 to 0.07 and 0.14 to 0.10 respectively, through Mn doping. Despite decreasing the loss tangent, Mn doping did not degrade the dielectric constant as illustrated in Fig. 8.9. The dielectric constant of Mn-doped BNKLT76 film was close to that of the undoped film deposited at 200 mtorr while the

dielectric constant of the 400 mtorr film just decreased by less than 8 percent after Mn doping. A decrease in dielectric loss and relative permittivity with Mn addition has also been observed in BNT-BKT thick films [6]. Improvement in dielectric properties can be attributed to the effects of Mn on the concentration of defects, lattice distortion, and formation of defect-complexes [2] as discussed previously.

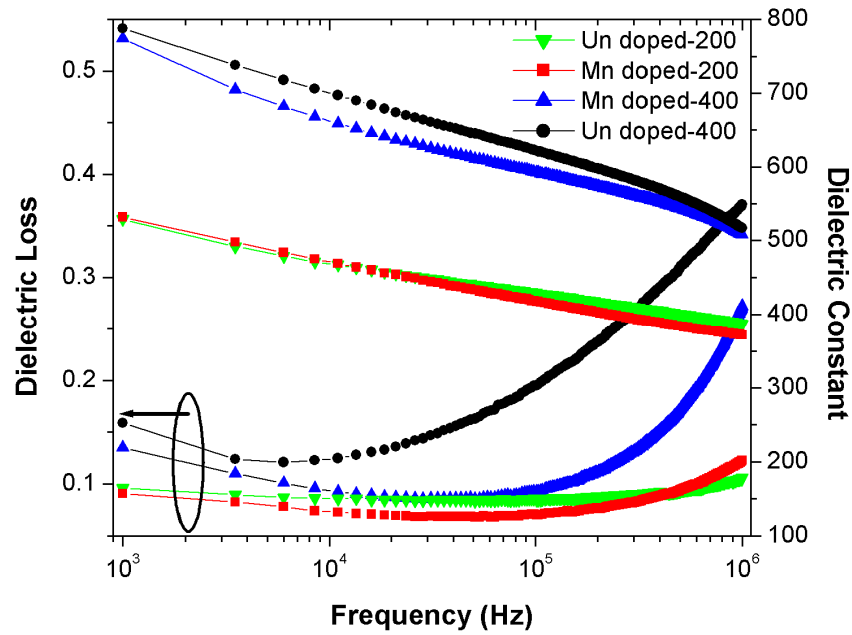


Fig. 8. 9. Dielectric constant and dielectric loss as a function of frequency for Mn-doped and undoped films grown at 200 and 400 mtorr.

8.3.3 BNKLT76 versus BNKLT88 Thin Films

Figs. 8.10 (a)-(b) and Fig. 8.11 compare the P-E hysteresis loops, leakage current, and dielectric properties of undoped BNKLT76 (MPB composition) and BNKLT88 (Rhombohedral side) thin films deposited at 400 mtorr. The BNKLT88 thin film showed a lower remnant and saturated polarizations and a higher coercive field in comparison to the BNKLT76 composition. The P_r values for BNKLT88 and BNKLT76 films were 12.2

and $19.3 \mu\text{C}.\text{cm}^{-2}$, respectively. The coercive fields of these films were measured to be 82 and $53 \text{ kV}.\text{cm}^{-1}$, respectively. In addition, the leakage current density of BNKLT88 film under high electric fields was one order of magnitude less than the MPB composition. As can be observed in Fig. 8.11, the dielectric loss and relative permittivity in BNKLT76 films were higher than BNKLT88. The dielectric constant relaxation with increasing frequency is more obvious in MPB composition. Similarly, this film also shows a higher rate of increase in dielectric loss with frequency. The relative permittivity at 1 kHz for BNKLT76 and BNKLT88 films were 770 and 440, respectively.

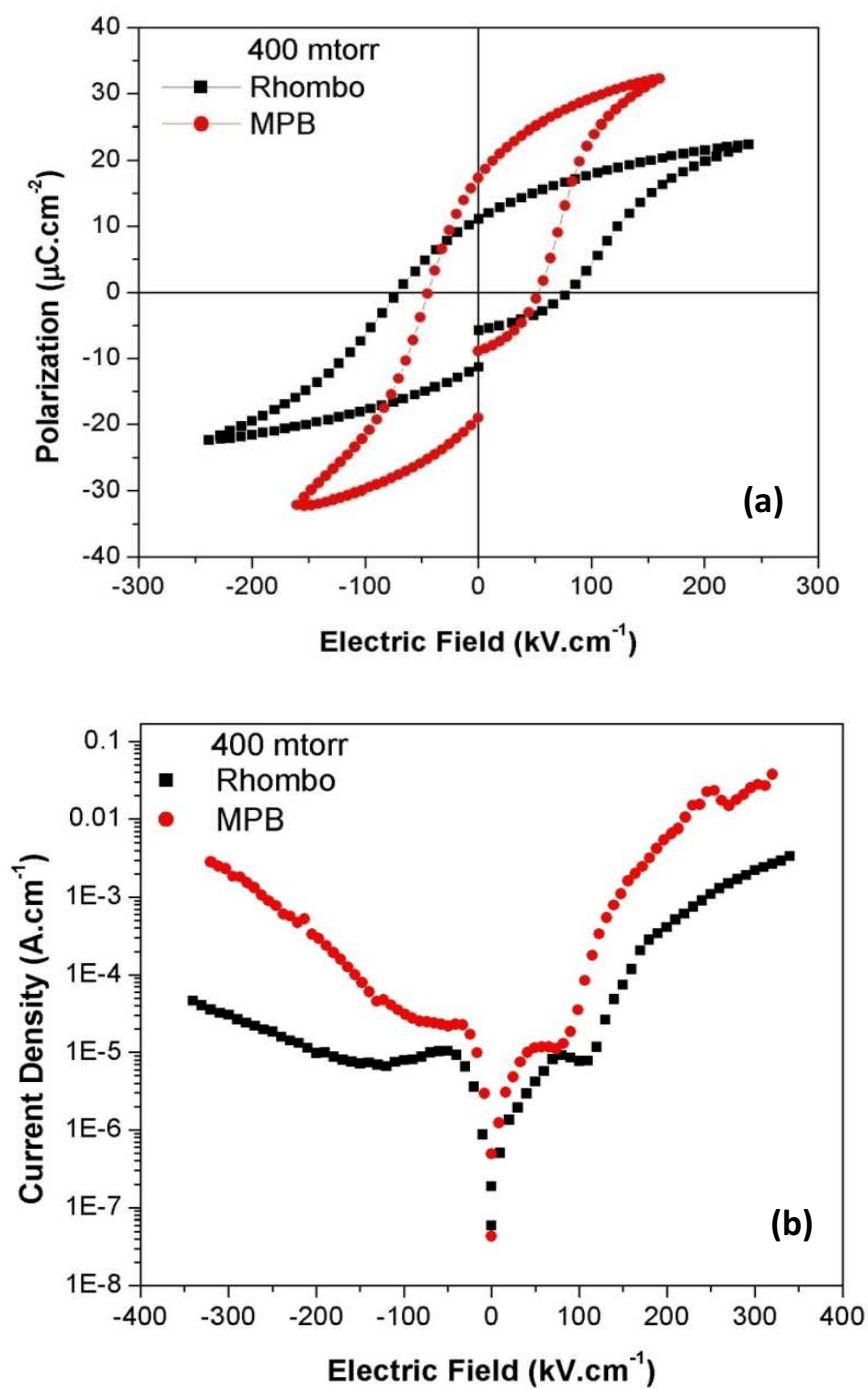


Fig. 8. 10. Comparison of undoped BNKLT76 (MPB) and BNKLT88 (Rhombohedral) thin films deposited at 400 mtorr. (a) P-E hysteresis loops (b) Current density.

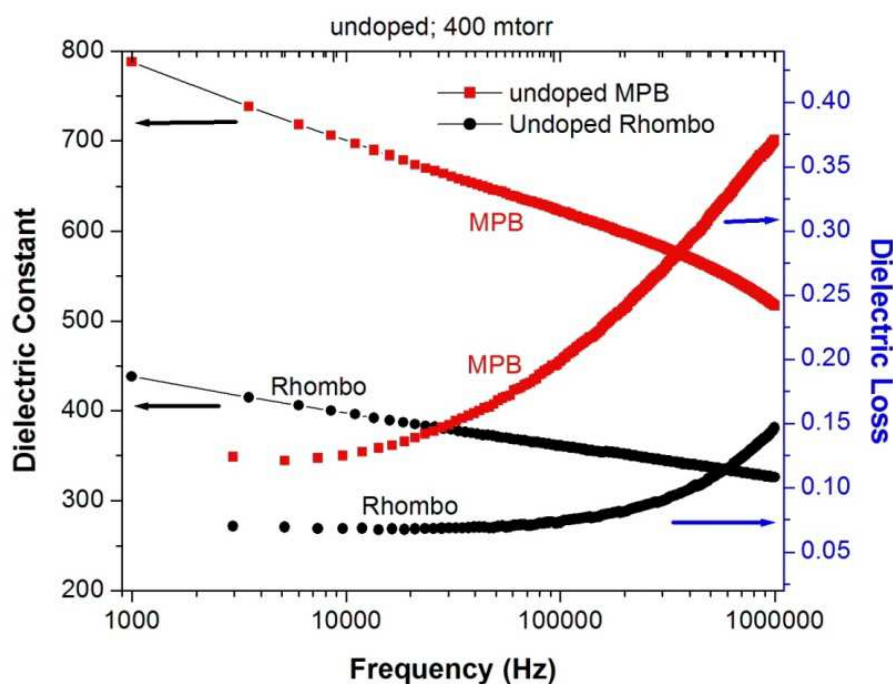


Fig. 8. 11. Dielectric properties of undoped BNKLT76 (MPB) and BNKLT88 (Rhombohedral) thin films deposited at 400 mtorr.

Figs. 8.12 (a)-(b) and 7.13 compare the P-E hysteresis loops, current densities and dielectric properties of Mn-doped BNKLT76 and BNKLT88 films grown at 200 mtorr. The Mn-doped BNKLT76 composition exhibited a higher polarization, dielectric constant and dielectric loss than BNKLT88 composition which was in agreement with the data achieved in undoped thin films. As observed in Fig. 8.12 (b), the leakage current values of Mn-doped MPB and rhombohedral sides are very close to each other even at high electric fields. The relative permittivity and dielectric loss of Mn-doped BNKLT76 and BNKLT88 films at 10 kHz were 480, 6.5% and 385, 4.5%, respectively. It is noticeable that the dielectric loss of Mn-doped BNKLT88 film remained under 5% up to 100 kHz.

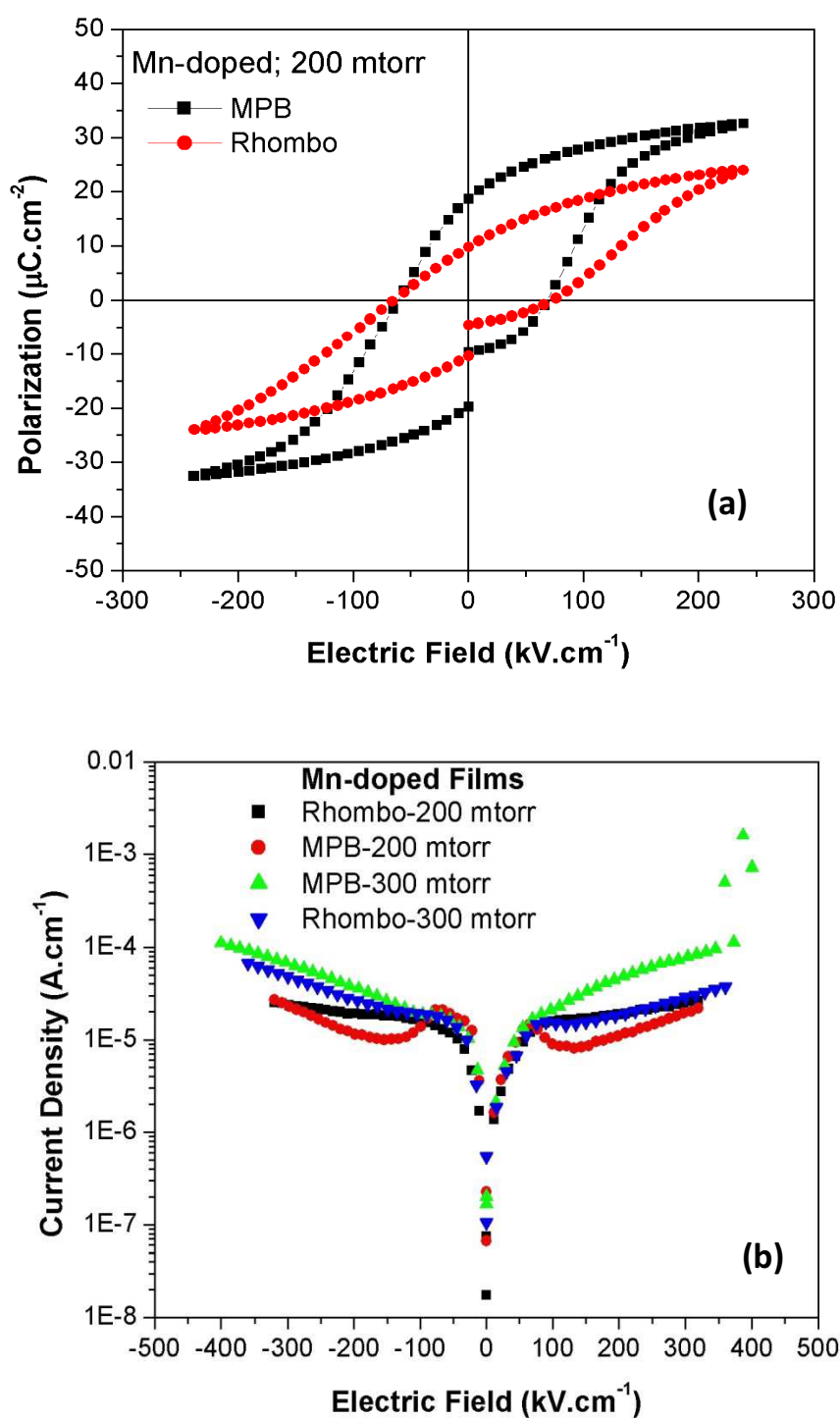


Fig. 8. 12. (a) P-E hysteresis loops of 2 mol.% Mn-doped BNKLT76 (MPB) and BNKLT88 (Rhombohedral) films deposited at 200 mtorr. (b) Current density of the films prepared at 200 and 300 mtorr.

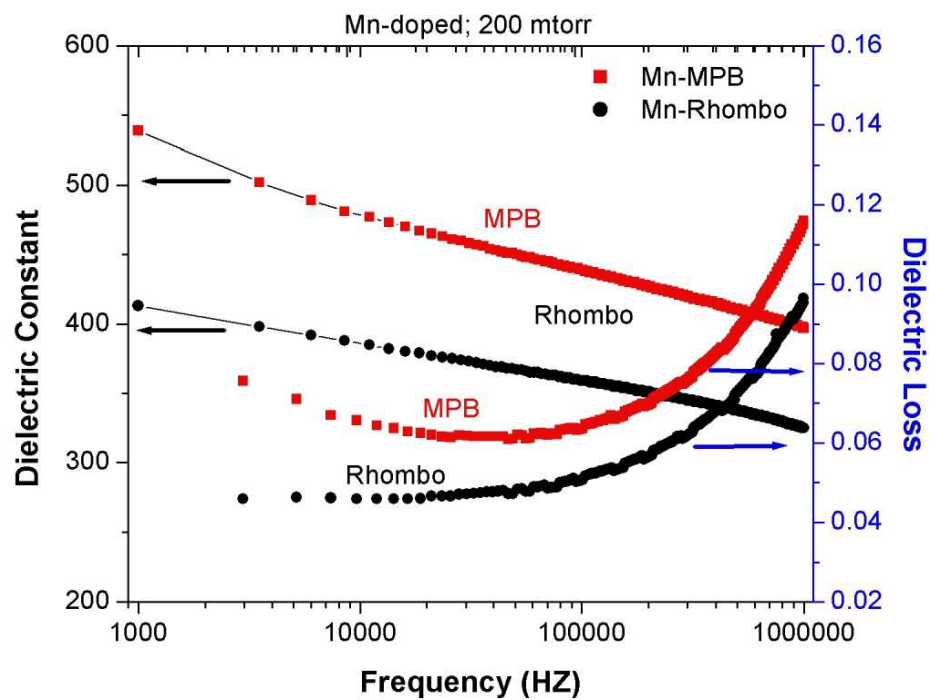


Fig. 8. 13. Dielectric properties of 2 mol.% Mn-doped BNKLT76 (MPB) and BNKLT88 (Rhomboidal) films deposited at 200 mtorr.

8.4 Summary

Dielectric and ferroelectric properties of undoped and 2 mol.% Mn doped BNKLT76 (MPB composition) and BNKLT88 (off-MPB composition on the rhombohedral side) thin films deposited by the PLD technique were evaluated. Increasing the oxygen pressure from 200 to 400 mtorr, increased the remnant polarization and dielectric constant. The leakage current and dielectric loss were also increased at higher pressures. The gas molecules present in the oxygen atmosphere can be absorbed by oxygen vacancies in the unit cell. This results in formation of electron-holes which have a major contribution in the leakage current of ferroelectric thin films leading to p-type conductivity. Mn-doping effectively suppressed the leakage current and dielectric loss of BNT-based thin films. It was suggested that Mn substitutes both the A- and B-sites of the perovskite structure and enhanced the ferroelectric polarization of the films by the distortion of the TiO_6 octahedron and compensating for the charge carriers. Mn divalent cations can annihilate the generated holes via oxidation to higher valence states which is confirmed by the XPS results. Due to the similarity of the ionic radii of Mn^{2+} and Mn^{3+} cations with A-site elements, it is possible that Mn occupies the A-site vacancies. This is another reason for the reduced leakage current observed in Mn-doped films. Despite decreasing the loss tangent, Mn did not degrade the dielectric constant of the films. Undoped BNKLT88 films showed higher coercive field, lower polarization and permittivity, and better insulating properties (low dielectric loss and leakage current density) in comparison to the BNKLT76 films. The same trend was observed in Mn-doped films; however, Mn-doping decreased the difference between the dielectric loss and leakage current of MPB and off-MPB thin films. Mn-doped BNKLT76 film

deposited at 400 mtorr possessed the highest ferroelectric properties. The remnant polarization and dielectric constant (at 10 kHz) of this film were measured to be 23 $\mu\text{C}\cdot\text{cm}^{-2}$ and 660, respectively. Mn-doped BNKLT76 thin films with a relatively high remnant polarization and dielectric constant can be considered as potential candidates for replacement of lead-based ferroelectric counterparts.

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9 Summary and Conclusions

In this study, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT)-based ceramics, thin films, ultrasonic and high power transducers were developed. Significant conclusions were drawn from the experiments carried out in each category:

A) BNT-based ceramics:

Solid solutions of BNT with other lead-free piezoceramics such as $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BKT), $\text{Bi}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ (BLT), and BaTiO_3 (BT) were prepared by mixed oxide route and conventional sintering. Six compositions containing different amounts of BKT, BLT, and BT in ternary systems of BNT-BKT-BT and BNT-BKT-BLT were studied. The studied compositions were:

- (1) 0.88 BNT- 0.08 BKT- 0.04 BT
- (2) 0.94 BNT- 0.04 BKT- 0.02 BT
- (3) 0.78 BNT- 0.15 BKT- 0.07 BT
- (4) 0.76 BNT- 0.20 BKT- 0.04 BLT
- (5) 0.88 BNT- 0.08 BKT- 0.04 BLT
- (6) 0.68 BNT- 0.28 BKT- 0.04 BLT

Raw materials including carbonates and oxides were mixed and then calcined at 800 °C for 3 hours. Green pellets were pressed at 150 MPa, and then sintered at 1100-1150 °C for 2 hours. It was concluded that:

1- 0.88BNT-0.08BKT-0.04BT (abbreviated to BNKLT88) and 0.076BNT-0.20BKT-0.04BLT (BNKLT76) ceramics with morphotropic phase boundary (MPB) compositions exhibited soft piezoelectric characteristics with a relatively high values of piezoelectric coefficient (d_{33} ~170-175 pC.N⁻¹), dielectric constant (850-950), and planar coupling coefficient (k_p ~0.32-0.37). However, these compositions suffered from a high dielectric loss ($\tan\delta$ ~2.2-3.1%) as well as a low mechanical quality factor (Q_m ~100-130).

2- The rhombohedral side of Li-substituted ceramics with composition of 0.88BNT-0.08BKT-0.04BLT (BNKLT88) showed hard piezoelectric characteristics, i.e. high mechanical quality factor (Q_m ~420), low dielectric loss ($\tan\delta$ ~1.2%), and high depolarization temperature (T_d ~220 °C). These values were comparable to commercial hard PZT4 with a Q_m ~500. BNKLT88 composition also showed higher coercive field (E_c ~47 kV.cm⁻¹) and lower polarization compared to the MPB composition (BNKLT76). The remnant polarization for rhombohedral and MPB compositions were 35 and 41 μ C.cm⁻², respectively. The coercive field for BNKLT76 composition was 27 kV.cm⁻¹.

B) Acceptor-doped BNT-based ceramics:

An attempt was made to enhance the mechanical quality factor of BNT-based ceramics up to the value reported for hard PZT8 ceramics (Q_m ~1000). Acceptor dopants (Mn²⁺ and Fe³⁺) were doped in the B-site of the perovskite structure. Different concentration of Mn (0.01, 0.014, 0.015, 0.016, 0.0175, 0.02, and 0.022) and Fe (0.0125, 0.015, 0.0175) were doped into BNKLT88 ceramic. Samples were sintered at different

temperatures (1075-1150 °C) to achieve the highest density and mechanical quality factor (Q_m). It was found that:

1- Mn or Fe-doping resulted in a considerable enhancement of planar and thickness Q_m of BNKLT ceramics. The highest Q_m and lowest dielectric loss in both Mn and Fe doped ceramics were obtained at 1.5 mol.% dopant concentration. In Mn-doped ceramics sintered at 1100 °C, a planar Q_m of about 970 and $\tan\delta$ of 0.88% were obtained. In Fe-doped ceramics, planar Q_m as high as 900 was achieved.

2- Acceptor dopants create oxygen vacancies to maintain the charge neutrality. Oxygen vacancies decreased the mechanical, dielectric and piezoelectric losses through their domain wall pinning effect. The piezoelectric and coupling coefficient of ceramics also decreased with increasing the Mn concentration. It was found that, acceptor dopants increased the coercive field and internal bias field of BNKLT88 ceramics.

3- The optimum sintering temperature for 1.5 mol.% Mn-doped BNKLT88 ceramics was 1100 °C. At higher temperatures, the density of ceramics decreased due to the bismuth volatilization. It was also found that the optimum sintering temperature in these materials decreased with increasing the dopant concentration.

C) High power transducers based on hard-BNT ceramics:

High power characteristics of undoped, and Mn-doped (1.4%, 1.5%, and 1.6 mol.%) transducers under a constant vibration velocity mode were studied. The following conclusions were drawn:

1- Mn-doping remarkably improved the high power properties of BNT-based transducers. The heat generation and resonance frequency shift were significantly reduced upon Mn-doping. The maximum vibration velocity of sample was also enhanced in Mn-doped samples.

2- 1.5 mol.% Mn-doped BNKLT88 transducers, showed the maximum vibration velocity (0.6 m.s^{-1}), minimum heat generation, minimum input power, and the best efficiency among the studied compositions.

3- Undoped BNKLT transducers showed a better efficiency (higher mechanical quality factor and less heat generation) at the resonance frequency than the antiresonance frequency. An opposite case was observed in Mn-doped transducers. Decreasing the piezoelectric loss by Mn-doping was suggested as a possible reason for the observed discrepancy between the resonance and antiresonance modes.

4- The main difference between resonance and antiresonance frequencies was the driving impedance/admittance. While a low driving voltage and high driving current were required at the resonance frequency, the opposite was observed at the antiresonance frequency.

5- The input power required to run the transducer was decreased by Mn-doping and increased by increasing the vibration velocities. The minimum input powers were observed at resonance and antiresonance frequencies because of the large displacement of the transducer at these fundamental frequencies.

6- Due to the combined effects of high mechanical quality factor and high coercive field, the performance of hard-BNT transducers were superior to commercial hard PZTs (PZT4 and PZT8). A more stable domain configuration in hard lead-free

BNT-based ceramics compared to PZT, resulted in higher mechanical quality factor under high drive condition.

D) BNT-based ultrasonic transducers:

High frequency single element ultrasonic transducers were designed and fabricated based on lead-free BNKLT88 composition. This composition with a relatively high k_t to k_p ratio and a low dielectric constant ($\epsilon_r=380$) could be considered as a promising material for fabrication of a high frequency single element ultrasonic transducers. It was revealed that:

- 1- The -6dB bandwidth of the transducer increased from 25.83% to 61.36% with addition of a single matching layer.
- 2- The lateral resolution of the transducer was improved from 740 to 260 μm by addition of an epoxy lens.
- 3- The lens-focused transducer with and focal point of 11 mm and a center frequency of 23 MHz, exhibited a -6dB bandwidth and insertion loss of 55% and -32.1 dB, respectively.
- 4- Image of a wire phantom made of copper wires (30 μm in diameter) was produced by the lens-focused transducer.
- 5- The pulse-echo response of a 20 MHz PZT4 transducer was simulated by the KLM model. The simulated transducer showed similar acoustic characteristics compared to the lead-free BNKLT88 transducer.

E) BNT-based thin films:

BNT-based thin films with four different compositions in BNT-BKT-BT as well as BNT-BKT-BLT systems were deposited on (001)-oriented $\text{SrRuO}_3/\text{SrTiO}_3$ substrates by pulsed laser deposition technique. The studied compositions were:

0.88BNT-0.08BKT-0.04BT (BNKBT88)

0.94BNT-0.04BKT-0.02BT (BNKBT94)

0.076BNT-0.20BKT-0.04BLT (BNKLT76)

0.88BNT-0.08BKT-0.04BLT (BNKLT88)

The effects of deposition parameters such as the laser repetition rate and background oxygen pressure on the microstructure, chemical composition, and electrical properties of thin films were investigated. The leakage current mechanisms at different temperatures were also studied. The results of this study can be briefly summarized as follows:

1- The BNKBT88 films with MPB composition prepared at 800 °C, 10 Hz, 400 mtorr and 1.2 J.cm^{-2} exhibited the highest ferroelectric properties. The measured remnant polarization, dielectric constant (at 1 kHz), and coercive field of the film deposited under optimized condition were about $30 \text{ } \mu\text{C.cm}^{-2}$, 645, and 85 kV.cm^{-1} , respectively. The chemical composition analysis by RBS technique showed that the film deposited with mentioned parameters had the minimum deviation from stoichiometry.

2- Compared to the MPB thin films, off-MPB compositions (on the rhombohedral side) showed lower polarization, lower permittivity, lower dielectric loss and lower leakage current.

3- In BNKLT76 thin films with MPB composition, increasing the oxygen pressure from 200 to 400 mtorr, increased the leakage current density at 200 kV.cm⁻¹ from 1.5×10^{-4} to 5×10^{-3} A.cm⁻².

4- Mn-doping decreased the leakage current (by more than two orders of magnitude) and dielectric loss of BNT-based thin films. The polarization was also considerably enhanced by Mn-doping. The remnant polarization and dielectric constant (at 10 kHz) of 2 mol.% Mn-doped BNKLT76 films deposited at 400 mtorr were measured to be 23 μ C.cm⁻² and 660, respectively.

5- The XPS results showed coexistence of Mn²⁺, Mn³⁺, and Mn⁴⁺ in doped-films. Oxidation of Mn²⁺ to higher valence states by absorbing holes along with occupation of A-site vacancies were suggested as possible reasons for a reduced leakage current and dielectric loss in Mn-doped films.

6- The leakage current density of MPB thin films (BNKLT88) in a temperature range of 200-350 K, matched with the Lampert's triangle. At low electric fields the ohmic conduction was the dominant leakage mechanism. As the applied electric field increased, the leakage current abruptly increased due to filling the shallow traps by injected carriers at the trap-filling-limit (TFL) voltage. At higher electric fields, the leakage current followed the Child's trap-free square law where the space-charge limited current overweighed other conductivity mechanisms.

On the basis of the obtained results in this study, it can be concluded that lead-free BNT-based compositions with comparable electromechanical and ferroelectric properties to their lead-based counterparts are potential candidate for fabrication of various piezoelectric devices in the future.

10 Suggestions for Future Work

The development of lead-free piezoelectric devices based on ceramics or thin films is at its preliminary stage. Since the performance of such devices is strongly correlated with electromechanical and ferroelectric properties of the materials, comprehensive studies need to be carried out to obtain a deeper understating of lead-free materials. In this chapter, few suggestions are made to carry out further research on BNT-based ceramics, thin films and devices, as continuation of the results presented in this dissertation:

- One of the interesting applications for BNT-based thick films is ultra-high frequency transducers such as intravascular transducers. The first requirement for fabrication of these transducers is to develop the knowledge and technology of deposition of BNT-based thick films. Since the pulsed laser deposition is not recommended for deposition of thick films, other methods such as sol-gel or tape casting can be investigated to deposit BNT-based thick films. A comprehensive processing-property relationship needs to be implemented in this area before it will be possible to fabricate ultra-high frequency transducers.
- High intensity focused ultrasound (HIFU) are used for therapeutic purposes such as treatment of tumors. To obtain a high energy beam with a low bandwidth, piezoelectrics with high mechanical quality factor must be integrated into the transducer. Mn-doped BNKLT88 ceramics developed in this study can be used as the basis for fabrication of HIFU at different frequencies.

- Lead-based piezoelectric transformers have been commercially produced for years. The results of this study revealed that Mn-doped BNT ceramics possessed superior high power performance compared to PZT4 and PZT8. Therefore, it will be interesting to employ Mn-doped BNT-ceramics in fabrication of high power devices such as transformers, ultrasonic cleaners, and motors.
- One of the main drawbacks of making different devices such as Field-effect transistor based on BNT-based thin films is the high leakage current and dielectric loss of these films. The results of this study showed that leakage current can be reduced by Mn-doping and decreasing the oxygen pressure. In other ferroelectric thin films, using an appropriate buffer layer has been suggested for suppression of the leakage current. Combined effects of processing parameters, dopants and buffer layer on the leakage current behavior of BNT-based thin films needs to be studied to obtain better understanding of insulative properties of these films. Particularly, deposition of these films on Pt/Si substrates is extremely challenging due to the film-substrate reaction. Besides using a buffer layer, decreasing the deposition temperature can hinder the film-substrate reaction. However, the film crystallinity will be adversely affected at low deposition temperatures. Rapid annealing techniques such as laser annealing can be employed to crystallize the films deposited at low temperatures. The processing condition including the deposition and annealing parameters should be optimized to achieve a low value of leakage current. Addition of excess bismuth to compensate for the Bi loss during the processing is also expected to decrease the leakage current. A

comprehensive research is suggested to be carried out to study all these different factors.

- The electrical properties of ferroelectric thin films are a function of the films thickness. The thickness of the films affects the strain at the film-substrate interface. In most cases, the leakage current also increases with decreasing the film thickness. Depending on the growth mechanisms, the films thickness can even affect the chemical composition. It is worthy to study the electrical properties and growth mechanism of BNT-based thin films as a function of the thickness.

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