

Electromechanical strain and bipolar fatigue in $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-(Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\text{-(Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ ceramics

Nitish Kumar^{a)} and David P. Cann

Materials Science, School of Mechanical, Industrial, and Manufacturing Engineering,
Oregon State University, Corvallis, Oregon 97331, USA

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Lead-free ceramics of composition $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-(Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\text{-(Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ were prepared using solid state synthesis techniques. The dielectric spectra showed a T_{max} of more than 320 °C for all compositions, and the transitions became increasingly diffuse as the $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ content increased. A lower temperature transition, indicating a transformation from an ergodic to a non-ergodic relaxor state, was also seen for all compositions, and this transition temperature decreased as the mole fraction of $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ increased. The composition with 1% $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ showed characteristic ferroelectric-like polarization and strain hysteresis. However, compositions with increased $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ content became increasingly ergodic at room temperature with pinched polarization loops and no negative strain. Among these compositions, the magnitude of d_{33}^* increased with $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ content, and the composition with 10% $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ exhibited a d_{33}^* of 422 pm/V. Fatigue measurements were conducted on all compositions and while the 1% $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ composition exhibited a measurable, but small loss in maximum strain after a million cycles; all the other compositions from 2.5% to 10% $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ were essentially fatigue-free. Lastly, optical and alternating current impedance measurements were employed to identify intrinsic conduction as the dominant conduction mechanism. These compositions were also highly insulating with high resistivities ($\sim 10^7 \Omega\text{-cm}$) at high temperatures (440 °C). © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4817524>]

INTRODUCTION

$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT)-based piezoceramics currently dominate the industry however the search for an appropriate lead-free replacement due to environmental concerns continues.¹ Developing a material that could serve as a drop-in replacement for PZT is a significant technical challenge. A different approach aims at developing Pb-free alternative materials targeted at specific applications. There have been a number of promising developments in the last decade. For example, textured (K,Na)NbO₃ (KNN) based compositions were shown to have excellent piezoelectric properties.² In addition, various binary and ternary systems based on $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BNT), $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ (BKT), BaTiO_3 (BT), and KNN have been widely investigated and have shown promising piezoelectric properties compared to Pb-based compositions.^{3–17}

In particular, the BNT-based systems have been extensively studied since its discovery by Smolenskii *et al.*¹⁸ Under an applied electric field, BNT-based compositions undergo a phase transformation to a polar ferroelectric phase where domains become stable. This is considered to play an important role in high strain exhibited in compositions based on BNT.^{3,5,6,8–13} Jo *et al.* recently proposed that all BNT-based compositions could be classified into two kinds of relaxors: non-ergodic and ergodic.¹⁹ While the former transforms irreversibly to a ferroelectric state, the latter

undergoes a reversible transformation on application of an electric field. The reversible phase transformation for these ergodic relaxors is indicated by the absence of a remnant strain in these compositions. As a result, all of the induced strain can be used for actuator applications and consequently these compositions feature large high-field piezoelectric coefficients. A second peculiar phenomenon observed with BNT-based systems is a transition from an ergodic to a non-ergodic state at approximately 100–200 °C.^{6–8,10,12–14,17} Above this transition temperature, the polarization loops are pinched and electromechanical strain data shows no negative values which is characteristic of a reversible field-induced phase transformation.

Fatigue properties are important for the long-term reliability of these systems. In PZT, a severe degradation in the maximum strain and polarization has been observed beyond 10^5 cycles at field levels close to twice the coercive field E_c .²⁰ In BNT-based compositions, it has been shown that the degradation in properties due to fatigue is not as severe and asymmetric as in PZT.^{3,21,22} In fact, in many systems fatigue is absent especially in compositions which are ergodic at room temperature.^{3,22} It is expected that the reversible field-induced phase transformation might be responsible for absence of fatigue.²² This study will demonstrate the basic piezoelectric properties and fatigue behavior of $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-BKT-BNT}$ piezoelectric ceramics with the aim of identifying the fatigue mechanism. While most piezoelectric actuator devices are activated in unipolar mode, all of the fatigue studies in this work were conducted under bipolar driving fields. The primary reason for this is that it has been shown that bipolar operating fields have

^{a)}Author to whom correspondence should be addressed. E-mail address: nitishkumar.iitk@gmail.com. Tel.: 541-908-5018. Fax: 541-737-2600

a more severe impact on the electromechanical strain and thus the differences between the behavior of different compositions will be more pronounced.

EXPERIMENTAL

Ceramics of the composition $x\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ -0.4BKT-(0.6-x)BNT ($0.01 \leq x \leq 0.1$) were prepared via conventional solid state processing. For convenience, henceforth, a composition designated as X-Y-Z would represent X% $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (BMT), Y% BKT, and Z% BNT. The precursor powders used were Bi_2O_3 (>99.9%), MgCO_3 (>99%), TiO_2 (>99.9%), K_2CO_3 (>99%), and Na_2CO_3 (>99.5%). The mixed powders were ground using a vibratory mill for 6 h using ethanol as a medium and then dried overnight in an oven ($\sim 80^\circ\text{C}$). All the compositions were calcined between 950°C and 1050°C for 6 h and then milled and dried again. Green pellets in the shape of thin discs were made by cold-pressing uniaxially at a pressure of 150 MPa and then sintered on a bed of calcined powder in a closed alumina crucible at 1100°C - 1125°C for 3–4 h. All the sintered pellets were polished to around 0.8 mm thickness. X-ray diffraction (Bruker AXS D8 Discover, Madison, WI, USA) was used for phase and crystal structure determination. Prior to any electrical measurements, silver electrodes were applied on both sides of the pellets and then fired at 700°C for 30 min. The pellets were placed in a high temperature measurement cell (NorECs AS ProbostatTM, Oslo, Norway) and temperature dependent dielectric properties were measured using an LCR meter (Agilent 4284A, Santa Clara, CA, USA). An impedance analyzer (Solartron SI1260A equipped with Solartron 1296A dielectric interface, Farnborough, UK) was used to measure the impedance in the frequency range of 1 Hz to 1 MHz. The SMarT impedance measurement software program was used to collect the data. Polarization hysteresis was measured at room temperature and 1 Hz (using Radiant Technologies RT66A, Albuquerque, New Mexico). Strain measurements were conducted at 0.1 Hz in conjunction with an interferometric sensor (MTI Instruments 2100 Fotonic Sensor, Albany, New York). Fatigue tests were conducted on unpoled samples by applying a bipolar triangular waveform at 10 Hz with a peak field of 50 kV/cm. The optical measurements were carried out on the sintered pellets over the wavelength range of 200–1100 nm at room temperature using an Ocean Optics HR4000 UV-Vis Spectrometer (Ocean Optics, Dunedin, FL) with a balanced deuterium/tungsten halogen source.

RESULTS AND DISCUSSION

All compositions in this study exhibited a single perovskite phase within the limits of the x-ray diffraction instrument used. The {200} reflections showed splitting that is characteristic of tetragonal symmetry and as is evident from the Fig. 1, the splitting diminished as the BMT content increased. The radial shrinkages after sintering for all compositions were typically greater than 13% with high sintered densities.

Figure 2 shows the evolution of dielectric properties with composition. The dielectric loss ($\tan \delta$) for all compositions at 1 kHz remained below 5% up to 400°C . As is typical of

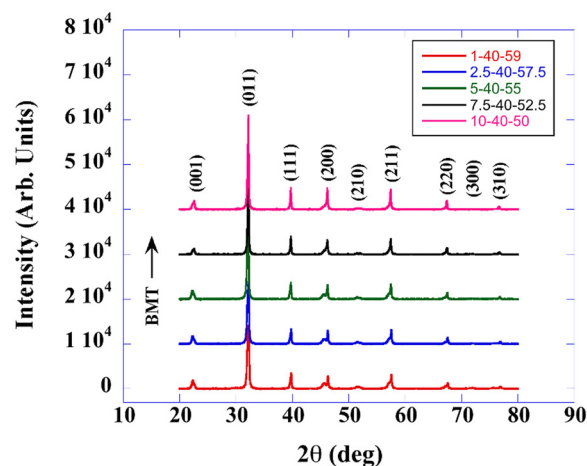


FIG. 1. XRD data for the indicated compositions where X-Y-Z corresponds to the BMT-BKT-BNT mole fractions, respectively.

BNT-based systems, the temperature at which the relative permittivity was maximum (T_{\max}) ranged between 320°C and 350°C for all compositions. As shown in the data, the transitions became increasingly diffuse as the BMT content increased. In a similar system, this dielectric maximum corresponded to the gradual disappearance of local tetragonal distortions.⁶ Also typical of BNT-based systems, a low temperature transition can be seen, which is linked to the transition from a high temperature ergodic state to a non-ergodic relaxor state.¹⁹ This transition shifted to lower temperatures as the BMT content increased, indicating that the ergodic nature of these compositions increased with the addition of BMT.

The polarization hysteresis data for the 1% BMT composition exhibited characteristics approaching normal ferroelectric behavior (Fig. 3(a)) including a remanent polarization and negative strain indicative of domain switching, typical of non-ergodic relaxors. However, as the BMT content increased, the polarization loops became increasingly pinched with a decreasing remanent polarization and the maximum polarization decreased with an increase in BMT content as well. The strain data for the 1-40-59 composition showed a typical butterfly shape, which is again characteristic of ferroelectricity, induced irreversibly in non-ergodic relaxors on application of electric field. However, consistent with polarization data, the negative strains vanished as the BMT content increased indicating that there was no domain switching for these compositions. Among the compositions which exhibited no domain switching, the maximum strain increased as the BMT content increased, with the 10-40-50 composition showing a highest effective piezoelectric coefficient (d_{33}^*) of 422 pm/V. The low remanent polarization and negligible remanent strain for higher BMT compositions is indicative of a non-polar phase at zero electric field, which is consistent with the dielectric data.

Figure 4 shows the effects of fatigue on the polarization for various compositions. The fatigue tests were conducted by applying a bipolar triangular waveform with a peak field of 50 kV/cm at 10 Hz. It is clear that there was no significant change in the polarization after 10^6 cycles as is seen in the case of PZT.²⁰ A closer examination revealed that the

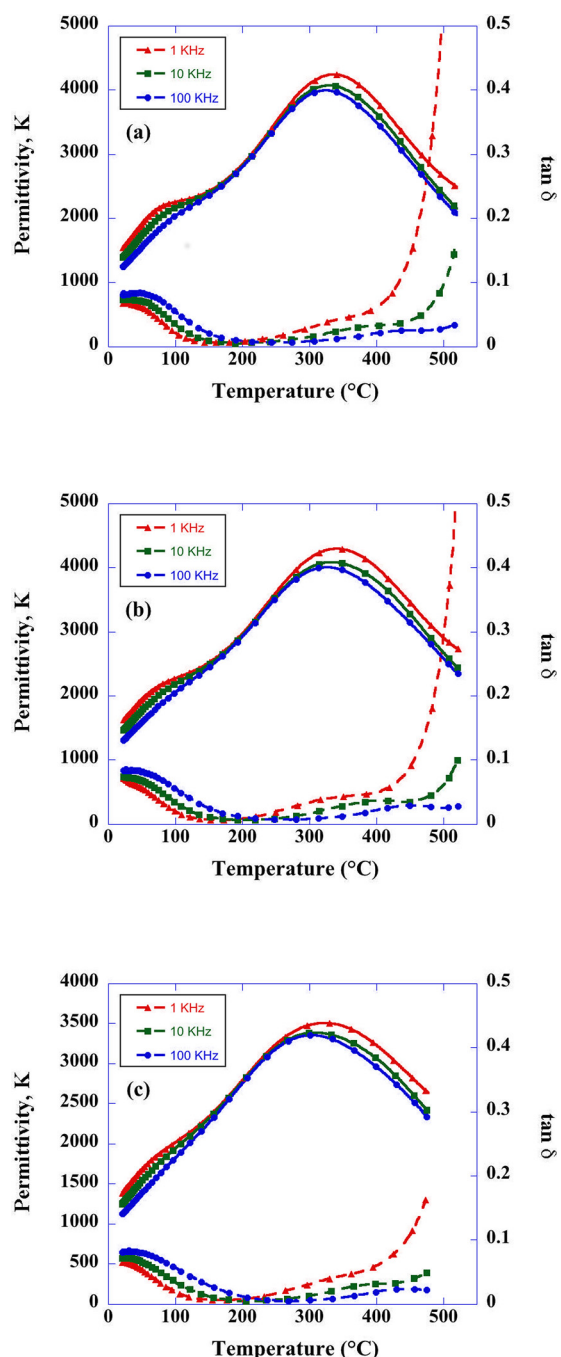


FIG. 2. Temperature dependence of dielectric constant (solid lines) and dielectric loss (dashed lines) for (a) 1-40-59, (b) 5-40-55, and (c) 10-40-50 compositions.

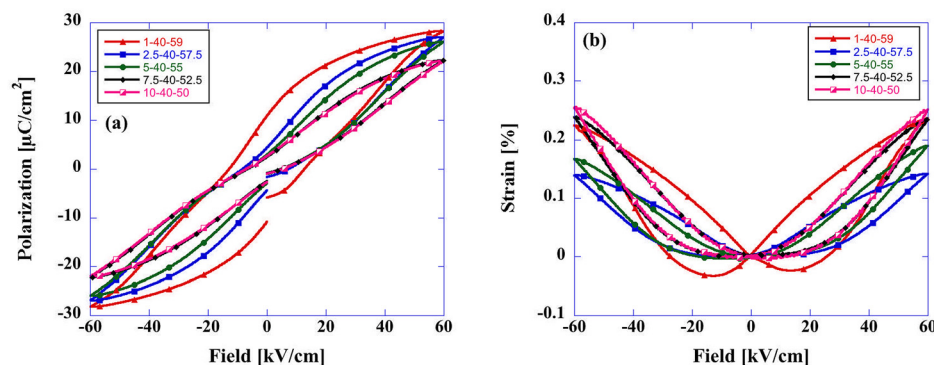


FIG. 3. (a) Room temperature polarization at 1 Hz and (b) electromechanical strain at 0.1 Hz for various compositions tested at 60 kV/cm.

coercive field decreased by 2%–15% over the various compositions. This is in contrast to the behavior shown by PZT where coercive field typically increases after many cycles; it is, however, consistent with the behavior shown in the composition $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3-(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BZT-BKT-BNT).^{3,23} In addition, the maximum polarization increased by a small amount of 2%–6% after 10^6 cycles, similar to observations in BZT-BKT-BNT, but again different from PZT which shows a decrease of more than 50% after a similar number of cycles.²⁰

The magnitude of the degradation in the electromechanical strain data strongly depended on the BMT content (Fig. 5). In particular, composition that exhibited clear evidence of domain switching (i.e., 1-40-59) experienced a $\sim 40\%$ decrease in maximum strain. It is also important to note that the magnitude of the degradation was largely symmetric. This is in contrast to observations during bipolar fatigue studies of PZT where the degradation of the strain can be severely asymmetric. In one study, the maximum strain decreased by $\sim 90\%$ along one field direction and $\sim 58\%$ for the opposite polarity.²⁰ For the other compositions, the degradation of strain was minimal. For the 10-40-50 composition, for an applied field of 50 kV/cm, the degradation of strain was only 0.9%. The maximum strain for the 2.5-40-57.5 composition, in fact, increased by approximately 10% after 10^6 cycles. Overall, it can be summarized that the composition range from 2.5% to 10% BMT were essentially fatigue free.

The results from ac impedance are shown in Fig. 6. The resistivities of these compositions were $\sim 10^7 \Omega\text{-cm}$ at 440°C , which is at least two orders of magnitude higher than PZT.²⁴ The activation energies for conduction, calculated from Arrhenius plot, were between 1.4 eV and 1.7 eV. Diffuse reflectance measurements were carried out following the method of related work using Kubelka-Munk²⁵ and Tauc equations^{26,27} to plot Fig. 7. The optical band gap can be calculated to values between 3 eV and 3.1 eV. The high resistivities measured in these compositions and that the activation energies for conduction that are nearly half of the optical band gap suggest that intrinsic conduction is the dominant transport mechanism in these compositions. Other titanate perovskites often exhibit activation energies close to 1 eV due to ionization of oxygen vacancies.²⁸ In PZT, the fatigue behavior is strongly influenced by the presence of these oxygen vacancies and the domain wall mobility is severely affected by defect agglomerates.²⁹ The predominance of

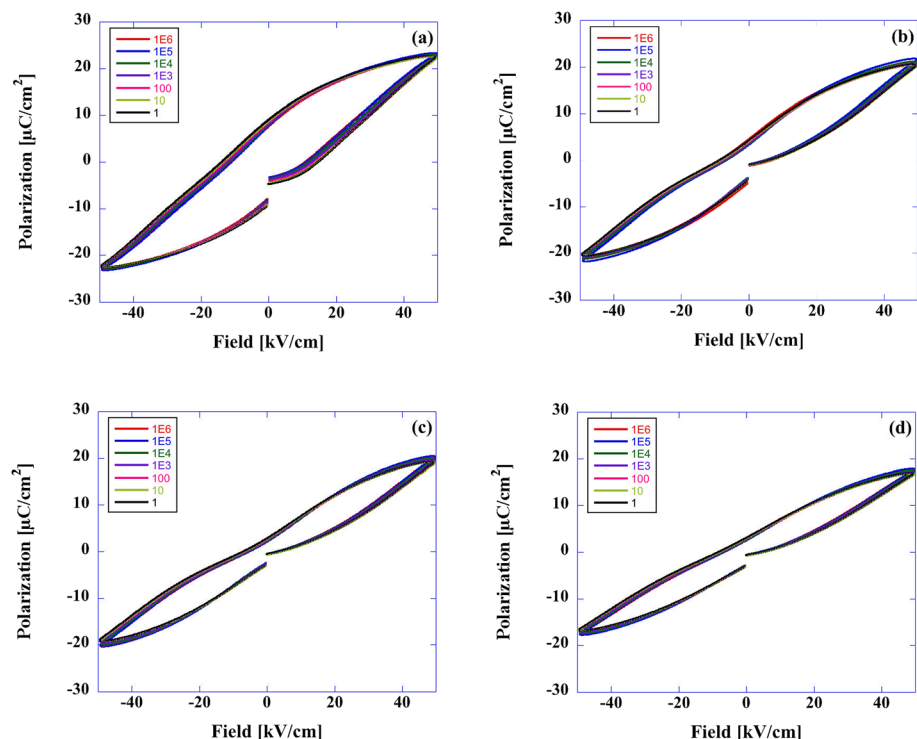


FIG. 4. Effect of fatigue on room temperature polarization (at 10 Hz) for (a) 1-40-59, (b) 2.5-40-57.5, (c) 5-40-55, and (d) 10-40-50 compositions tested at 50 kV/cm and 10 Hz up to a million cycles.

oxygen vacancies in PZT is also supported by the activation energy of conduction close to 1 eV for PZT.²⁴

To this point, the amount of literature available on piezoelectric fatigue of bismuth-based perovskites is scarce and almost all of the studies are on BNT-based systems.^{3,21,22,30,31} Luo *et al.* studied the fatigue behavior of BNT-BaTiO₃-K_{1/2}Na_{1/2}NbO₃ (BNT-BT-KNN) and found that KNN destabilized ferroelectric long range order in the system which had an obvious effect on fatigue, analogous to

BMT in this study.²² They attributed the observed fatigue in low KNN composition to domain wall pinning and formation of microcracks and to the repeated field induced phase transition in the high KNN composition. A major distinction from this study was that the ergodic composition (higher KNN) was not fatigue free. A bipolar fatigue study on binary BNT-BT compositions revealed significant degradation in material properties including a decrease in the maximum polarization by more than 33% and a decrease in the maximum

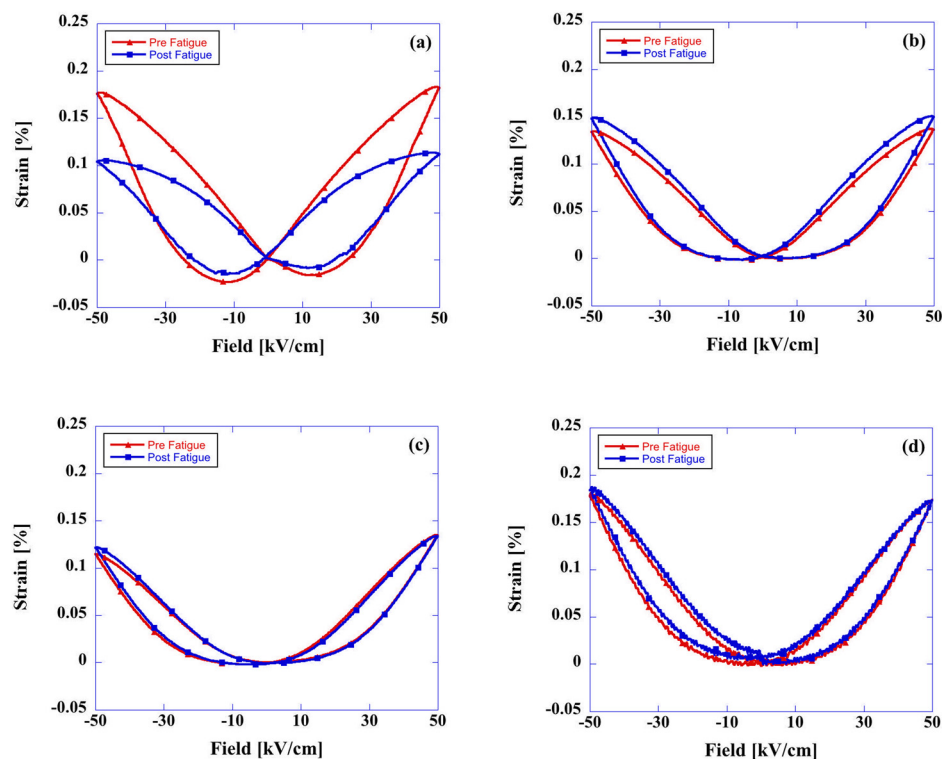


FIG. 5. Effect of fatigue on room temperature electromechanical strain (at 0.1 Hz) for (a) 1-40-59, (b) 2.5-40-57.5, (c) 5-40-55, and (d) 10-40-50 compositions tested at 50 kV/cm and 10 Hz up to a million cycles.

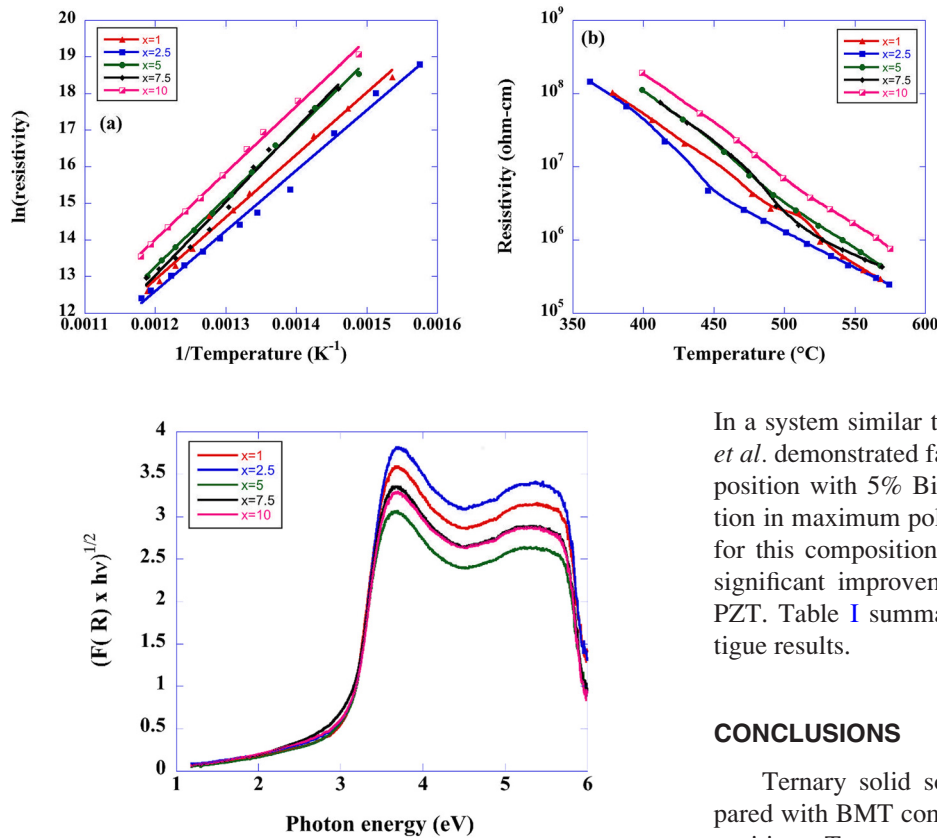


FIG. 7. Tauc plot, where $F(R)$ is the ratio of effective absorption and scattering coefficients and $h\nu$ is photon energy for various compositions.²⁵

strain by 60% after one million cycles.²¹ Ehmke *et al.* showed that addition of 1% CuO improved the fatigue property of BNT-BT.³⁰ In a different study, fatigue in BNT-BT was proposed to be a two-stage mechanism, including a transformation to a ferroelectric structure from a relaxor state followed by cyclic domain wall pinning and fragmentation.³¹

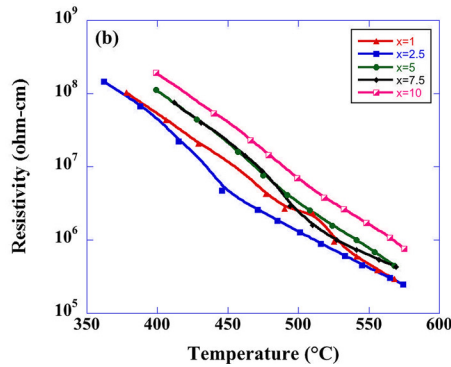
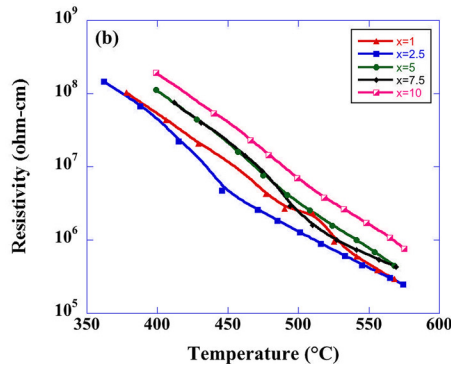


FIG. 6. (a) Arrhenius plot, $\ln(\text{resistivity})$ with inverse temperature and (b) variation of resistivity with temperature.



In a system similar to this study, BZT-BKT-BNT, Patterson *et al.* demonstrated fatigue-free behavior for an ergodic composition with 5% $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$.³ There was no degradation in maximum polarization or strain after a million cycles for this composition. All these materials, however, show a significant improvement in fatigue resistance compared to PZT. Table I summarizes the compositions studied and fatigue results.

CONCLUSIONS

Ternary solid solutions of BMT-BKT-BNT were prepared with BMT concentrations up to 10 mol%. For all compositions, T_{max} remained above 320 °C and a typical ergodic to non-ergodic relaxor transition was also evident near 200 °C. The polarization and strain loops for the 1-40-59 composition exhibited characteristics consistent with ferroelectric behavior. However, with the addition of BMT, the dielectric behavior became more diffuse and the polarization hysteresis became increasingly pinched without any measurable negative strain. All the compositions were evaluated under 50 kV/cm bipolar cycling and exhibited fatigue behavior significantly better than PZT. For all compositions, the

TABLE I. Table summarizing the bipolar fatigue results of various bismuth-based compositions available in the literature. The values represent the change in material properties due to fatigue with respect to their original values. “+” sign indicates increase and “−” sign a decrease in that property after fatigue. Data in asterisk (*) are approximate values extrapolated from plots wherever direct values were not available in the literature.

Composition	Number of fatigue cycles	Driving field level (kV/cm)	Change in remnant polarization (P_r)	Change in maximum polarization (P_{max})	Change in coercive field (E_c)	Change in high field piezoelectric constant (d_{33}^*)	References
BNT-BT-KNN (93-6-1)	10^6	60 ($3E_c$)	−37%*	−36%*	+100%	−50%*	22
BNT-BT-KNN (91-6-3)	10^6	60 ($4E_c$ *)	+66%*	−14%*	+50%*	−7%	22
BNT-BT (94-6)	10^6	60 ($2E_c$)	−50%	−51%*	+22%	−60%	21
BNT-BT +1% Cu (94-6)	100	60 ($2E_c$)	+0%	+0%*	+0%*	+0%*	30
BZT-BKT-BNT (2.5-40-57.5)	10^6	50 ($2E_c$)	−5.1%	+1.4%	−20%	−13%	3
BZT-BKT-BNT (5-40-55)	10^6	50 ($5E_c$)	−7%	+6.8%	−20%	+4%	3
BMT-BKT-BNT (1-40-59)	10^6	50 ($\sim 3.5E_c$)	−14.9%	+1.9%	−24.6%	−39%	The present work
BMT-BKT-BNT (2.5-40-57.5 to 10-40-50)	10^6	50 ($5E_c$ to $7E_c$)	−0.7% to −20%	+2% to +8%	−2% to −13%	+0% to +10%	The present work

maximum polarization was largely unaffected by fatigue cycling up to at least a million cycles. In addition, there was minimal effect of fatigue on the maximum electromechanical strain for compositions with 2.5% BMT to 10% BMT. Transport measurements in these compositions showed the presence of high resistivities (e.g., 10 M Ω -cm at 440 °C) and activation energies equal to half of the measured optical band gap. It is proposed that the lower defect concentrations and the nature of the relaxor-ferroelectric transition in these compositions are responsible for the fatigue resistance.

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