Bipolar piezoelectric fatigue of Bi(Zn0.5Ti0.5)O3-(Bi0.5K0.5)TiO3-(Bi0.5Na0.5)TiO3 Pb-free ceramics

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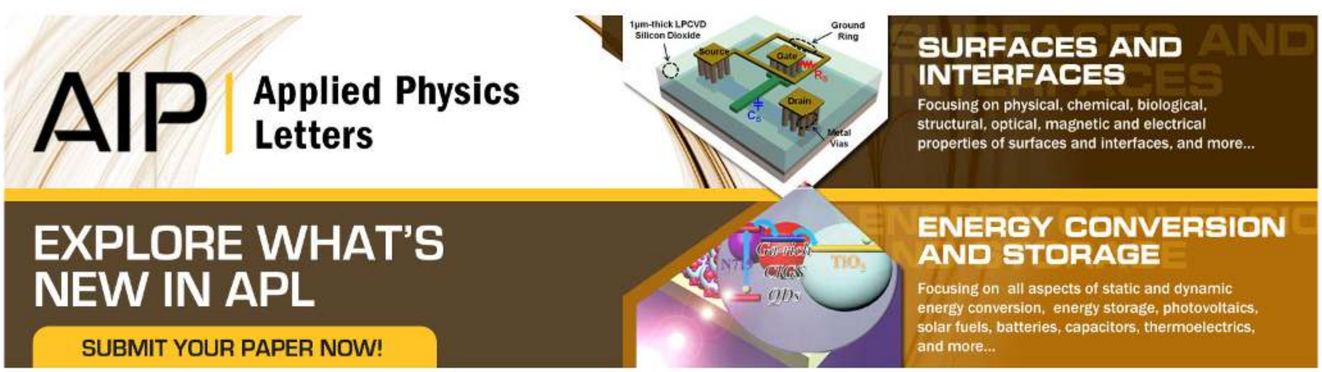

Bipolar piezoelectric fatigue of $Bi(Zn_{0.5}Ti_{0.5})O_3$-$(Bi_{0.5}K_{0.5})TiO_3$-$(Bi_{0.5}Na_{0.5})TiO_3$ Pb-free ceramics

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The piezoelectric fatigue behavior of Pb-free ceramics based on solid solutions of $Bi(Zn_{0.5}Ti_{0.5})O_3$-$(Bi_{0.5}K_{0.5})TiO_3$-$(Bi_{0.5}Na_{0.5})TiO_3$ was characterized at 50 kV/cm after 10^6 bipolar cycles. Ferroelectric compositions containing 2.5% $Bi(Zn_{0.5}Ti_{0.5})O_3$ exhibited only minor losses in maximum strain (~10%). In compositions with 5% $Bi(Zn_{0.5}Ti_{0.5})O_3$ that exhibit large electric field-induced strains, the electromechanical strain actually increased 4%, exhibiting essentially fatigue free behavior. This finding demonstrates that these materials have excellent potential for demanding high cycle applications such as microelectromechanical systems actuators. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4738770]

The search for lead-free alternatives to lead-zirconate titanate (PZT) continues to gain more attention as companies endeavor to reduce the impact of Pb-containing materials on the environment. Compounds such as $(Bi_{0.5}K_{0.5})TiO_3$ (BKT) and $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT), and their solid solutions with $BaTiO_3$ (BT) or $KNaNbO_3$ (KNN) and other tetragonal perovskites exhibit promising piezoelectric properties[1–10] and are considered as possible candidates to replace Pb-based materials.[9,11,12] One promising system achieves a large normal ferroelectric response, BNT-BT, through a mechanism tied to phase coexistence and an enhanced capacity for domain texturing associated with relaxor behavior similar to La-modified PZT.[13,14] In the closely related ternary system (BNT-BT-KNN), an anomalous large electromechanical strain approaching 0.4% develops in association with a phase transition from pseudocubic to tetragonal symmetry.[15–17]

Another common method has been forming solid solutions of BNT–BKT with end members that are unstable in ambient processing conditions, such as $Bi(Mg_{0.5}Ti_{0.5})O_3$ or $Bi(Ni_{0.5}Ti_{0.5})O_3$.[18] Previously, it was shown that when BNT-BKT is combined with increasing concentrations of $Bi(Zn_{0.5}Ti_{0.5})O_3$ (BZT), a transition from normal ferroelectric behavior to a material with large electric field induced strains was observed.[19,20] The higher BZT containing compositions are characterized by large hysteretic strains (>0.3%) with no negative strains that might indicate domain switching. Polarization hysteresis measurements show pinched loops with low or negligible remanent polarizations that yield relatively small low field d_{33} values. The Bi-based systems, generally, have shown complex poling behavior and it has been difficult to achieve repeatable low-field, piezoelectric coefficients (d_{33}).

In addition to the environmental concerns driving this work, PZT is also known to exhibit poor piezoelectric fatigue properties with relatively severe degradation in strain behavior after only a few millions of cycles of applied field.[21–26] In bipolar fatigue studies for PZT, the permanent effects are tied to reduction in strain and switchable polarization simultaneously, implying a reduction of the mobility of domain walls. Significant fatigue was found begin in the range of 2.5×10^5 and 3×10^5 cycles of applied fields at twice the coercive field level.[1,23,27] A clear asymmetry of the degradation of the maximum strain on positive versus negative applied voltage was observed as another important component of the fatigue effect. Due to the dominating presence of oxygen vacancies in perovskite ferroelectrics, a defect agglomeration model was proposed to explain the pinning of domain walls and the induced polarization offset necessary to explain both fatigue effects seen in PZT.[23,27]

It should be noted completely electrostrictive rhombohedral phases of lanthanum doped PZT behavior were shown to be fatigue free up to 10^6 cycles.[23,24] More recently, morphotropic phase boundary (MPB) compositions of 94BNT-6BT have been investigated for piezoelectric fatigue at twice the coercive field ($2E_C$) for 10^6 cycles. In this case, fatigue in the bipolar case was highly accelerated and largely developed within the first 100-1000 cycles. After 1000 cycles, the polarization dropped by 47.4% of the initial value and E_C began to increase.[28] However, for most Pb-free ceramics, very little fatigue data are available. The total decrease in strain (~36%) was not nearly as large or asymmetric as for PZT.[28] The addition of CuO acted to stabilize the rhombohedral phase into a tetragonal phase and improved the fatigue characteristics without negatively impacting the piezoelectric response.[29]

Ceramics of xBZT–0.4BKT–(0.6-x)BNT were produced via conventional solid state synthesis, for x = 0.025 and 0.05. Starting powders of (Bi_2O_3, TiO_2, ZnO, $NaCO_3$, and KCO_3) with >99.9% purity were milled for six hours using high-energy vibratory milling. Calcinations were performed in covered crucibles at 900–950 °C for 6 h followed by a second six hour vibratory milling step.

The milled, calcined powders were mixed with 3 wt. % solution of Paraloid (PL) binder and uniaxially pressed into 12.8 mm pellets at a pressure of 150 MPa. Sintering was performed at 1050 or 1100 °C for 4 h. Prior to electrical measurements, samples were polished to sub-millimeter thickness and high-temperature silver paste (Heraeus C1000) was fired on both sides in air at 650 °C for 30 min. Hysteresis measurements were made using a sawyer-tower circuit-based Radiant

Technology Premier II ferroelectric test system utilizing Vision software. Strain hysteresis measurements were taken in conjunction with an MTI Instruments 2100 Fotonic Sensor. The fatigue testing was performed on unpoled samples by applying a 10 Hz bipolar triangular waveform at 50 kV/cm on both the 0.025 and 0.05 BZT samples. Additional testing was performed on 0.05BZT at $2E_C$ (20 kV/cm). The fatigue tests performed in this study were carried out under bipolar conditions because it has been shown in the literature that bipolar cycling results in more severe degradation of the polarization and electromechanical strain compared to unipolar cycling.[23]

These tests were chosen to highlight any differences in fatigue behavior across the transition in behavior from "normal" ferroelectric response at 2.5%BZT, to the high electromechanical strain response of 5% BZT. The two different polarization and strain hysteresis behaviors for these compositions are demonstrated in Figures 1(a) and 1(b), respectively. In this work, only the bipolar fatigue characteristics of these two compositions were analyzed. The 2.5% BZT was tested at a field level of 50 kV/cm which amounts to approximately $2E_C$. These testing conditions are equivalent to fatigue tests carried out on PZT which allows for a basic comparison.[21] The 5% BZT composition was tested at two different field levels, 20 kV/cm and 50 kV/cm. Since this material exhibits unconventional hysteresis behavior as shown in Fig. 1, these two field levels were chosen to provide different modes of comparison. The 20 kV/cm test is nominally equivalent to $2E_C$, though admittedly it is not fully accurate to define a coercive field in this way as it does not represent full switching in a conventional sense. Additionally, the fatigue test was carried out at 50 kV/cm so that a direct comparison could be made to previous work. All three fatigue tests were carried out on three identical specimens and the results for each testing condition were very similar in each case. The data traces included in the figures correspond to a representative sample and the numerical data in this letter represent the average of all tests at a given condition.

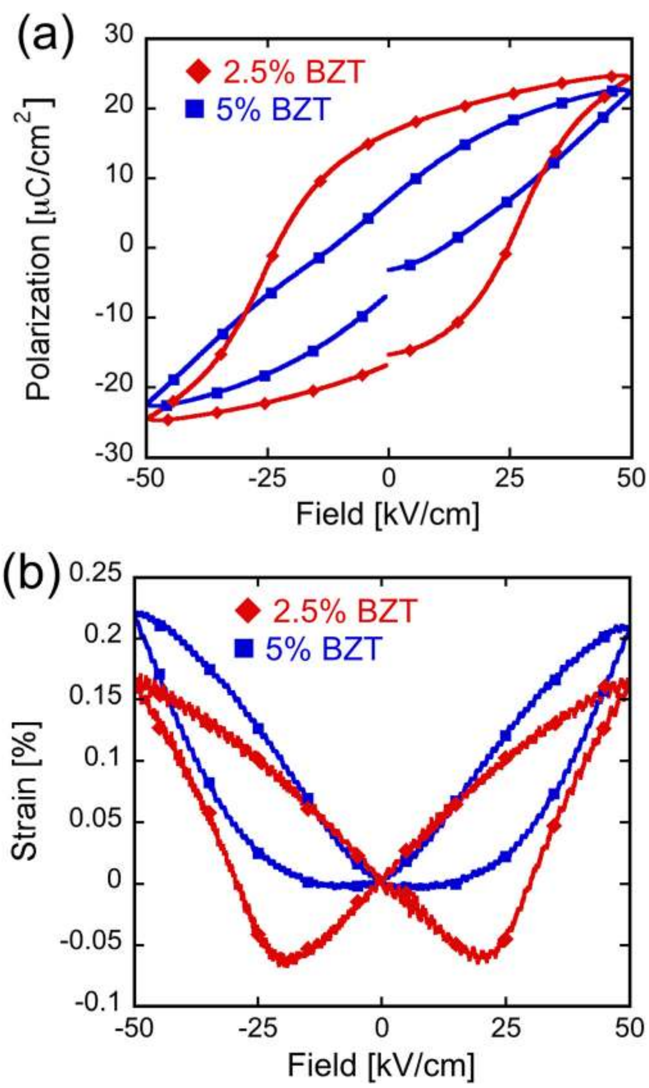

FIG. 1. (a) Polarization and (b) strain behaviors of 2.5%BZT and 5%BZT showing typical ferroelectric loops that transition to a pinched, high electromechanical strain behavior with increased BZT content

$2E_C$ of 2.5%BZT (50 kV/cm): Changes in the polarization and electromechanical strain behavior of a 2.5% BZT composition before and after 10^6 bipolar cycles at 50 kV/cm are shown in Fig. 2. Following the completion of one million cycles of fatigue at 50 kV/cm, clear trends can be observed in the polarization hysteresis data. The coercive field was seen to decrease from approximately 25 to 20 kV/cm, a decrease of approximately 20%. Following an initial decrease in maximum polarization likely tied to stabilization of the domain structure, only a small increase in polarization of $\sim 0.3\,\mu C/cm^2$ was measured over an initial value of $24.3\,\mu C/cm^2$. This amounts to a small 0.9% increase from the initial cycle to the 10^6 cycle. In the case of the remanent polarization (P_r), the opposite effect was observed with a slightly larger decrease of 4.6% in the average sample. The electromechanical strain data showed relatively small, but consistent decreases of approximately 10% in the maximum strain for both positive and negative applied fields. A similar loss in the negative strain was also observed. The symmetry of the strain hysteresis was maintained upon completion of the fatigue cycling.

$5E_C$ of 5%BZT (50 kV/cm): In Fig. 3, the change in the polarization and electromechanical strain behavior of a 5% BZT composition before and after 10^6 bipolar cycles was obtained at 50 kV/cm is shown. In the data taken at a field of 50 kV/cm, similar to the 2.5% BZT composition, the E_C values steadily decreased by 20%. This was accompanied by an increase in the maximum polarization of approximately 5.7%. The remanent polarization in these samples decreased by an average of 8.5%. These changes in the polarization, while larger in both cases were not reflected by a correspondingly larger change in strain behavior. These results deviated sharply in comparison to that of the normal ferroelectric strain behavior observed for 2.5%BZT samples, with a minor increase in the maximum electromechanical strain of approximately 4%. It is also important to note that the strain loops maintained a high degree of symmetry after 10^6 cycles. No change in the amount of negative strain was observed for these samples.

$2E_C$ of 5%BZT (20 kV/cm): For 5% BZT samples tested at the lower field of 20 kV/cm similar, trends were for the most part observed. The value of E_C decreased by approximately 20% after 10^6 cycles. However, P_{MAX} increased by a slightly larger amount (∼14%). The largest change in behavior was

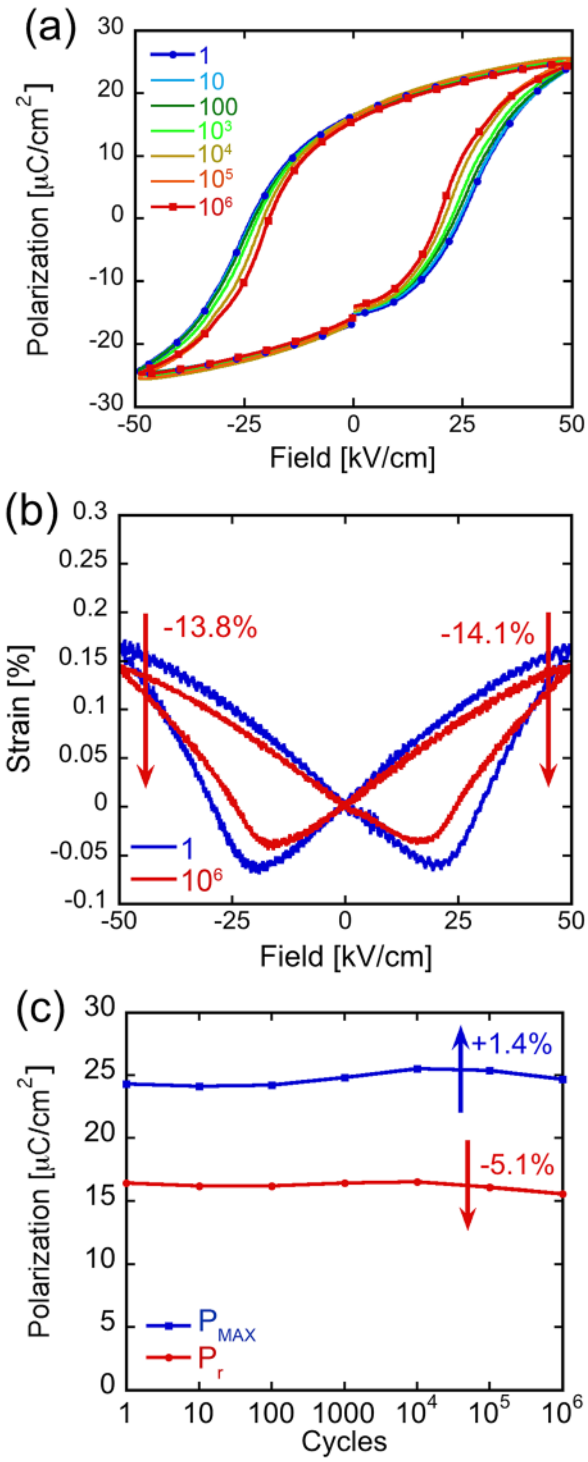

FIG. 2. Fatigue results for a typical 2.5%BZT sample tested at 50 kV/cm and 10 Hz for (a) polarization hysteresis, (b) strain hysteresis, and (c) change in polarization values with increasing number of cycles completed.

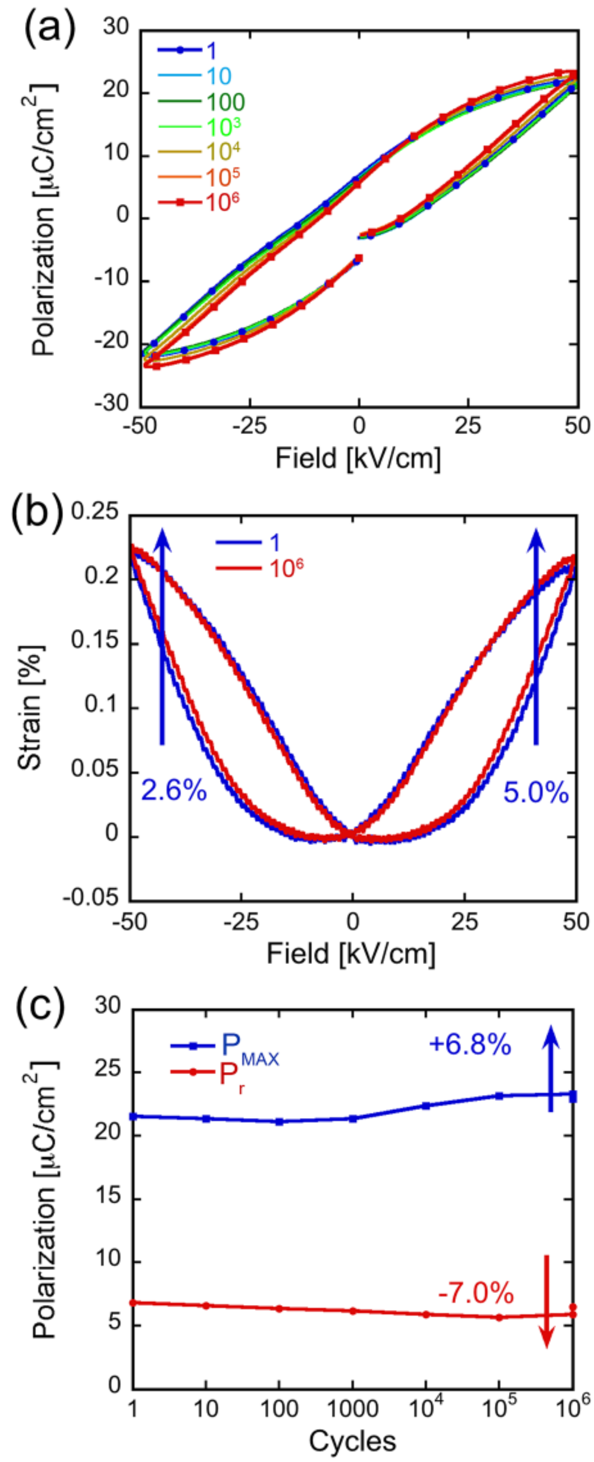

FIG. 3. Fatigue results for a typical 5%BZT tested at 50 kV/cm and 10 Hz for (a) polarization hysteresis, (b) strain hysteresis, and (c) change in polarization values with increasing number of cycles completed.

seen for any of the conditions tested in the case of remanent polarization. The P_r values of the samples were found to actually increase by ∼20% rather than show the minor decreases seen in the other tests for both 2.5% and 5% BZT. The strain hysteresis was measured at both 20 kV/cm and 60 kV/cm before and after the 10^6 cycle fatigue test. Since the strain at 20 kV/cm resulted in strain levels that were insufficiently high compared to error limits of the probe utilized, the strain measurements at 60 kV/cm were needed to make a valid comparison. The data showed similar strain behavior to the data taken at 50 kV/cm with a minor increase in the maximum strain of 6% compared to the initial value. The general symmetry of the strain loop was also maintained in these samples. Overall, the electromechanical strain behavior of the 5%BZT samples was shown to be essentially free of fatigue out to 10^6 cycles independent of the cycling voltage used.

In fatigue tests of PZT-based materials, commonly an offset field is developed and increases drastically due to segregation of point defects.[23,27] In the data in this study, only a small offset in coercive field was observed. Offsets on the order of ~0.50 kV/cm were recorded for the 5%BZT composition and an offset of 1.3 kV/cm for the 2.5%BZT composition when tested at 50 kV/cm. The offset in E_C of both positive and negative applied fields remained similar throughout the fatigue testing, which decreased to nearly zero after 10^6 cycles for samples tested at 50 kV/cm.

The performance of these materials represents a significant improvement on the fatigue data on PZT. The 5% BZT compositions showed no loss in electromechanical strain and the 2.5% showed a small decrease in the maximum strain values of approximately 10%. This decrease, however, is quite minimal when compared to the reduced strain and significant hysteresis asymmetry seen in previously published work on PZT. Two different mechanisms describe the loss in polarization of up to ~50% of the initial value when cycled at $2E_C$ (~20 kV/cm).[21,27] In electrostrictive PZT compositions, discolored regions appear after 3×10^5 cycles due to microcracking damage in the ceramic localized near the electrodes, which act to screen the rest of the bulk of the sample.[21] Importantly, no such discoloration was observed in either the 2.5% BZT or 5%BZT compositions in this study. The other fatigue mechanism is tied to the formation of defect agglomerates which is responsible for a ~50% reduction in polarization after 3×10^6 cycles.[27] For PZT (Ref. 27) and in BNT-BT,[29] the coercive field increases as the fatigue mechanism progresses, which is the opposite of the behavior observed in the BZT-BKT-BNT system in this work. Although the fatigue in the 2.5%BZT case is much reduced compared to PZT, it may be possible to further enhance the stability with small CuO additions, as was recently demonstrated for the BNT-BT system.[29,30]

The explanation for the excellent fatigue characteristics in these BZT solid solutions is likely attributable to a lower concentration of intrinsic defects. In PZT-based materials, sintering temperatures in the range of 1200 to 1350 °C are known to introduce numerous point defects such as oxygen vacancies and Pb vacancies. The BZT-based materials in this study have significantly lower sintering temperatures between 1050 and 1100 °C which would likely result in a significantly lower defect density. A set of experiments linking the fatigue characteristics to defect concentrations is currently underway.

This study has demonstrated that ceramics based on the solid solution of BZT-BNT-BKT exhibited essentially fatigue-free behavior compared to PZT-based materials. Compositions with 2.5% BZT show well saturated hysteresis loops similar to conventional ferroelectric materials, and after 10^6 bipolar cycles at 50 kV/cm the material experienced only a 10% loss in electromechanical strain. The P_{MAX} was increased by 0.9%, while P_r decreased by 4.6%. Compositions with 5% BZT exhibited large, hysteretic field-induced strains, and after 10^6 bipolar cycles at 50 kV/cm the electromechanical strain actually increased 4%. The P_{MAX} and P_r showed similar trends to the 2.5% BZT case, but changed by slightly larger amounts of +5.7% and −8.5%, respectively. In all of the samples tested at both 20 and 50 kV/cm, the coercive field decreased by 20%. Based on these results, these Pb-free materials have great potential for use in piezoelectric applications requiring a large number of bipolar cycles such as MEMS devices and piezotransformers.

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