

Electric-field-induced volume change and room temperature phase stability of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -x mol. % BaTiO_3 piezoceramics

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Electric-field-induced volume change and room temperature phase stability of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_{3-x}$ mol. % BaTiO_3 piezoceramics

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Phase stability of $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_{3-x}$ BaTiO_3 ($0 \leq x \leq 0.15$) under electric field was investigated by measuring volume changes during a bipolar poling cycle. The unique nature of field-dependent phase stability with three distinctive regions is revealed by comparative studies using commercial soft PZT and relaxor PLZT. For $x \leq 0.06$ and $x \geq 0.13$, similarly with PZT and PLZT, the axial strain expands with the contracting radial strain, but the former results in a remanent volume demonstrating an electric-field-induced phase transition. For $0.08 \leq x \leq 0.12$, this field-induced phase transition is distinguished by negligible radial contractions implying polarization rotation. A “poling-induced” morphotropic phase boundary forms at $x = 0.07$. © 2011 American Institute of Physics. [doi:10.1063/1.3615675]

Since the $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_{3-x}$ BaTiO_3 (BNT-100xBT) solid solution system on BNT-rich side was reported 20 years ago,¹ the phase stability and its correlation to functional properties have been of interest. A phase diagram proposed in the report states that a morphotropic phase boundary (MPB) between rhombohedral BNT and tetragonal BT is located at 6–7 mol. % BT content where the electro-mechanical properties are notably enhanced similarly as in the classical PZT ceramics. However, the advantage in the properties due to the formation of this MPB is significantly attenuated by the loss of temperature stability, because the so-called depolarization temperature (T_d) inherent to BNT-0BT decreases rapidly down to as low as 100 °C around the MPB, which rules the materials out of numerous practically important applications. It follows that not much attention had been paid to BNT-100xBT, but directed mostly to exploring other BNT-based systems possibly with a higher T_d and better piezoelectric properties.^{2,3}

Recently, attention has been redrawn to the BNT-100xBT system, because several counterintuitive and intriguing aspects of the system were revealed by structural studies via x-ray diffraction (XRD). Ranjan and Dviwedi⁴ reported that the crystal structure of a series of compositions from BNT-6BT to BNT-10BT is nothing but cubic. Independently, Zhang *et al.*⁵ also proposed that BNT-6BT has no visible deviation from a cubic symmetry within the resolution limit of the XRD apparatus used. A clue to making this seemingly contradicting aspect comprehensible was given by Daniels *et al.*,⁶ who showed by an *in situ* XRD technique on a compositionally-graded specimen, that the initial structure of nominally BNT-7BT was indeed cubic but transformed into a tetragonal symmetry on the application of electric field. A follow-up systematic investigation on compositionally-homogeneous samples further showed that an XRD profile featuring an MPB from the structural point of view occurs unexpectedly at BNT-11BT. Also, a range of compositions from BNT-6BT to BNT-10BT undergo a phase transi-

tion from pseudocubic to a mixture of rhombohedral and tetragonal phases.⁷ Neutron diffraction study on BNT-6BT (Ref. 8) further identified an electric-field-induced structural transition that is accompanied by the change in the oxygen octahedral tilting system.

Although more than five phase diagrams for BNT-100xBT have been proposed for the time being,^{9–13} many issues still remain uncertain. This implies that the phase diagram of BNT-100xBT could be too complicated to be understood by the application of usual characterization techniques. In fact, recent structural studies questioned even the previously designated rhombohedral symmetry for BNT-0BT, proposing a monoclinic symmetry alternatively.^{14,15} The uncertainties in the structure and phase identity of BNT-100xBT in the literature appear largely due to the limited spatial resolution of the diffraction-based techniques. Specifically saying, many structural investigations may have neglected the fact that BNT-100xBT exhibits a dielectric relaxation, the origin of which could be assigned to the presence of polar nano-regions (PNRs).^{16–18} Note that the structural uncertainty has been a long-standing controversial issue even in the classical relaxor materials.

Phase transitions involving crystallographic symmetry changes are commonly expected to result in density change. In this case, they can be effectively evaluated by measuring volume change during electrical cycling.^{19,20} In this letter, therefore, we present the compositional dependence of electric-field-induced volume change during electrical poling to give a clue to the existing controversies over the phase stability of the BNT-100xBT system.

Disc-shaped samples of BNT-100xBT ($0 \leq x \leq 0.15$) were prepared by a mixed oxide route, following the procedure reported elsewhere.⁷ Ferroelectric $\text{Pb}_{0.99}(\text{Zr}_{0.45}\text{Ti}_{0.47}\text{Sb}_{0.67}\text{Ni}_{0.33})_{0.08}\text{O}_3$ (soft PZT, PIC151, Lederhose, Germany) and hot-pressed relaxor $(\text{Pb}_{0.92}\text{La}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ (relaxor PLZT, Boston Applied Technology, MA) ceramics were purchased from commercial suppliers as reference materials. Prior to strain measurements, ground and polished disc-shaped samples were thermally annealed at 400 °C for 30 min. To estimate electric-field-induced volume

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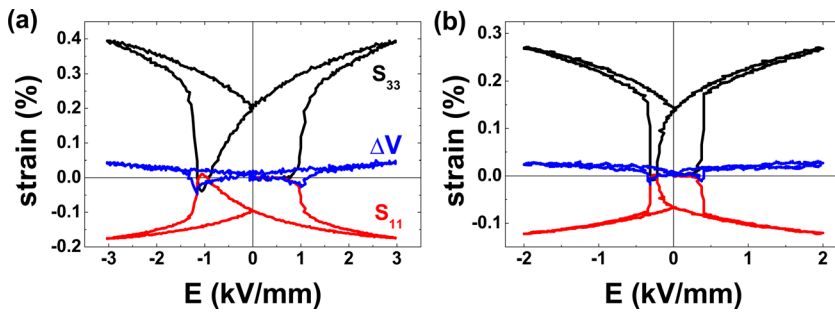


FIG. 1. (Color online) Axial and radial strains measured simultaneously during bipolar poling cycle on commercial (a) soft PZT and (b) relaxor PLZT 8/65/35.

changes, electric-field-induced strain changes were measured parallel and perpendicular to the field direction simultaneously. The details of the measurement technique were described elsewhere.^{19,20}

Figure 1(a) displays electric-field-induced strains as well as the corresponding volume change of commercial soft PZT. The radial strain, measured along the perpendicular direction to the electric field, is mirror-imaged to the axial strain with the scale of about a half. The volume change (ΔV) during the cycle is estimated by $\Delta V \approx S_{33} + 2S_{11}$. Except for the anomalies at critical fields such as the poling and the coercive field, ΔV increases linearly with electric field, which indicates that the hydrostatic piezoelectric coefficient (d_h) of this material also increases with electric field,²¹ since domain switching can be assumed isometric.

The same set of data for relaxor PLZT is given in Fig. 1(b). Note that the currently investigated PLZT is a relaxor converting into a ferroelectric phase after electrical poling treatment.²² The measured strain hystereses and volume change appear related to that of the soft PZT ceramic with no indication of additional features due to the relaxor characters of PLZT. A nearly constant volume change during electrical cycling implies that d_h may be independent of electric field, and the field-induced strain is mostly due to isometric domain reorientation. It is noted that there is no remanent volume after the transition from relaxor to ferroelectric, which suggests that this transition involves no crystallographic symmetry change, and thus, the macroscopically

observed ferroelectric order results from a coalescence of PNRs into macroscopic ferroelectric domains of the same symmetry.

The electric-field-induced strain and volume changes for all compositions of BNT-100xBT investigated are presented in Fig. 2. Three distinctive regions are denoted in terms of the shape of hysteresis curves as well as the changes in the remanent volume (V_{rem}). For $0 \leq x \leq 0.06$ (region I), the shape profile of axial and radial strains is mirror-imaged with a different scale similarly observed in the soft PZT and relaxor PLZT. However, two distinctive features are denoted. One is the presence of V_{rem} that decreases monotonously with increasing BT content, and the other the positive minimum strain level measured on the negative side of the bipolar strain curve, which will be termed as “irrecoverable” strain (S_{irr}). The former reveals that the phase transition during electric field application is accompanied by the change in the molar volume of the phase, i.e., different packing density at the unit cell level. The latter indicates that this transition irreversibly leads to a ferroelectric state with the introduction of ferroelectric domains that actually switch during cycling. Note that even BNT-0BT, commonly considered as a single rhombohedral or monoclinic phase, shows a remanent volume and positive S_{irr} , demonstrating that it undergoes an electric-field-induced phase transition (EFIPT). Based on the observed dielectric relaxation in unpoled samples,²³ it was suggested that this phase transition should be a relaxor-to-ferroelectric transition, involving a coalescence of PNRs into

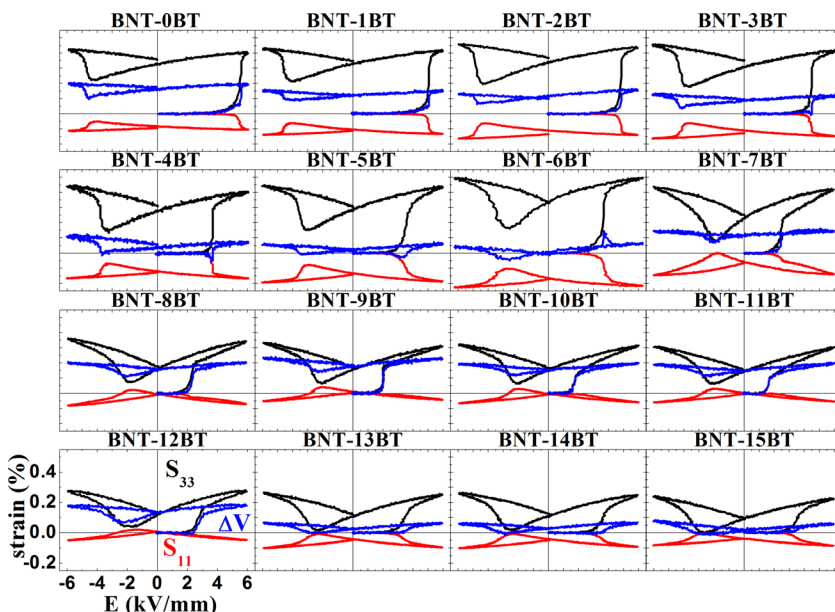


FIG. 2. (Color online) Electric-field-induced strain and volume changes of BNT-100xBT ($0 \leq x \leq 0.15$) during a bipolar poling cycle.

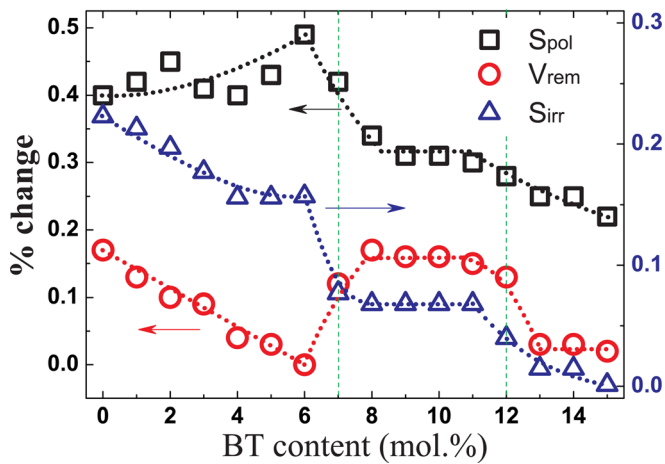


FIG. 3. (Color online) Summary of the key parameters derived from Fig. 2. S_{pol} , V_{rem} , and S_{irr} denote the poling strain, the remanent volume, and the irrecoverable strain, respectively.

macroscopic ferroelectric domains as in the case of PLZT, but distinguished by a concurrent symmetry change.

The second region where $0.08 \leq x \leq 0.12$ (region II) is featured by a significant asymmetry between the axial and radial strains with BNT-7BT having an intermediate feature between region I and region II. It is interesting to see that the change along the radial direction below poling field is so suppressed, until the phase transition is completed, and that the remanent volume (V_{rem}) is almost equal to the remanent strain (S_{rem}) along the field direction and S_{11} becomes even positive during the cycle. This implies that the EFIPT occurs concurrently along all directions regardless of the field direction, which is consistent with the previous *in situ* XRD results that showed the development of tetragonal symmetry via polarization rotation.⁷ Finally, the field-induced changes are analogous to those in usual ferroelectric materials with a minimal V_{rem} and S_{irr} for $0.13 \leq x \leq 0.15$ (region III).

Three parameters, the poling strain (S_{pol}), S_{irr} , and V_{rem} are summarized as a function of composition in Fig. 3. The region I is featured by an increase in S_{pol} and decrease in both S_{irr} and V_{rem} , which implies that the difference in the molar volume between the symmetries before and after poling becomes smaller with increasing x . On the other hand, the region II exhibits little compositional dependence of all three parameters, while all parameters decrease simultaneously in the region III. It is noted that the $S_{\text{pol}} - S_{\text{irr}}$ is maximal in BNT-7BT, which explains the peak in electro-mechanical properties at the composition.⁷

EFIPT was demonstrated via *in situ* volume change measurement in BNT-100 x BT for $0 \leq x \leq 0.12$. Next to V_{rem} , a newly-introduced parameter, S_{irr} was utilized to identify EFIPT. All EFIPT were identified irreversible with creating ferroelectric domains. It was shown that the enhanced electromechanical properties at BNT-7BT are due to an “electric-field-induced MPB” between the phases of different symmetries, resulting from the irreversible EFIPT. The exact structural identity and nature of the phase transition observed in region I still need further investigations.

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