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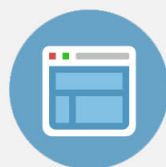
Enhanced piezoelectricity and nature of electric-field induced structural phase transformation in textured lead-free piezoelectric Na$_{0.5}$Bi$_{0.5}$TiO$_3$-BaTiO$_3$ ceramics

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This letter provides a comparative description of the properties of textured and randomly oriented poly-crystalline lead-free piezoelectric 0.93(Na$_{0.5}$Bi$_{0.5}$TiO$_3$)-0.07BaTiO$_3$ (NBT-BT) ceramics. A high longitudinal piezoelectric constant of (d_{33}) $\sim$ 322 pC/N was obtained in (001)$_{PC}$ textured NBT-7BT ceramics, which is almost $\sim$2$\times$ times the d_{33} coefficient reported for randomly oriented ceramics of the same composition. *In situ* neutron diffraction experiments revealed that characteristically different structural responses are induced in textured and randomly oriented NBT-BT ceramics upon application of electric fields (E), which are likely related to the varying coherence lengths of polar nanoregions and internal stresses induced by domain switching. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4709404]

Structural transformations in functional materials under external stimuli are known to impart exotic responses and play an important role towards controlling material properties.[1] Such behaviors find applications in many devices such as sensors and actuators.[2] Relaxor-based piezoelectric single crystals have been widely investigated with regard to electric (E)-field-induced phase transitions that result in large strains.[3] To exemplify, synchrotron x-ray diffraction studies by Noheda *et al.*[4] and neutron diffraction studies of Ohwada *et al.*[5] on 92% Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-8% PbTiO$_3$ (PZN-8%PT) show that under the application of electric (E) fields, the crystal goes through an irreversible rhombohedral-to-monoclinic A-type-to-monoclinic C-type (R-M$_A$-M$_C$) transformation sequence. In this case, it was proposed that the ferroelectric polarization initially moves on the R-T (tetragonal) path but then changes irreversibly to the (orthorhombic) O-T path, finally settling on a ground state with M$_C$ symmetry. Furthermore, it was proposed from the optical measurements that in the M$_C$ state the polarization vector rotates within the *ac* plane under the application of an electric field.[6] It was hypothesized that the rotation of the polarization vector causes a large coupling between the polarization and electric field, thereby resulting in a giant piezoresponse.[6]

Recently, due to environmental concerns, lead-free piezoelectric materials have gained tremendous importance.[7] However, the properties of lead-free piezoelectric materials are far inferior to those of lead-based systems.[8] Out of the various possibilities, lead-free (Na$_{0.5}$Bi$_{0.5}$TiO$_3$)-BaTiO$_3$ (NBT-BT) system has emerged as a potential candidate to replace lead-based piezoelectric systems.[9–11] The phase transformation behavior of NBT and its solid solutions with BT as a function of E-field has been investigated recently in many studies. Different variants of phase diagrams for NBT-BT have been proposed that consists of ferroelectric rhombohedral and tetragonal phases as end components and an antiferroelectric or ferrielectric orthorhombic components as an intermediate phase.[12–16] Coexistence of rhombohedral and tetragonal phases has been observed over a broad range of temperatures and E-fields. While the orthorhombic phase is proposed to have an antiferroelectric (AFE) characteristic,[17,18] recent studies instead describe it as a relaxor phase with polar nanoregions.[19,20] The high piezoelectric response and E-field induced strain in NBT based systems has been attributed to structural phase transitions under the application of E-field.[21–23] Similar to NBT-BT systems, NBT-KBT (Ref. 24), and NBT-BT-KNN (Ref. 16) systems were also found to depict structural phase transformations under E-field. Recently, the time dependent nature of these types of structural phase transitions under external E-field has also been reported.[24]

Building upon these prior studies, we report the E-field induced structural changes in randomly oriented and (001)$_{PC}$ textured polycrystalline ceramic specimens of NBT-7BT. It should be noted here that very few researchers[25] have been successful in growing the (001)$_{PC}$ textured NBT-BT ceramics. We found that the randomly oriented and textured specimens of the same composition show drastically different piezoelectric responses as well as different polarization-electric field (P-E) hysteresis and phase transformation behaviors under applied E-fields. Specifically, the textured specimens show pinched P-E hysteresis loop at room temperature in contrast to normal ferroelectric P-E loops observed for randomly oriented specimens. In the past, the origin of pinched loop has been associated with various factors including the presence of AFE phase, acceptor doping, aging effect, internal-bias, and the presence of polar nanoregions.[15] In this study, examination of *in situ* bulk neutron diffraction patterns revealed that the pseudo-cubic nature of the bulk lattice was maintained in the textured specimen subsequent to the application of E-field.

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In contrast, significant distortions in diffraction peak profiles were observed in the randomly oriented specimen, indicating coexistence of phases with rhombohedral and tetragonal symmetries. Although the $(001)_{PC}$ textured specimen exhibits no electric-field-induced phase transformation, it shows a much higher d_{33} ($\sim$320 pC/N) than that of the randomly oriented specimen ($\sim$160 pC/N). Based on these observations, we assert that structural instability, at least on a bulk scale, is not a necessary prerequisite to obtain large piezoelectric properties in NBT-BT ceramics. We propose that the enhanced piezoelectric behavior of the $(001)_{PC}$ textured specimen[26] is partially due to its domain engineered state as well as preservation of the "relaxor" nature due to the existing polar nanoregion.

Synthesis of randomly oriented polycrystalline ceramics of NBT-BT was performed using conventional solid state reaction method. For texturing, NBT-platelets were aligned in the powder matrix of NBT-BT using the tape casting technique followed by lamination and binder burnout. All the specimens were sintered in air at 1150–1200 °C. The degree of $(001)_{PC}$ texture, as calculated by the Lotgering factor method,[27] was found to be $\sim$92%. Both textured and randomly oriented specimens were found to have a similar composition within 1.0 at. %, as confirmed by elemental analysis using Energy-dispersive x-ray spectroscopy (EDS). For electrical measurements, silver electrodes were fired on the flat faces of the specimens. The specimens were poled along the thickness, and the macroscopic piezoelectric properties were measured using the Berlincourt method along the same direction, which was the $(001)_{PC}$ oriented direction of the textured NBT-BT specimen. The *P-E* hysteresis measurements were performed using a Precision II ferroelectric testing system. Incremental electric fields were applied to the randomly oriented and $(001)_{PC}$ textured samples in steps of 0.5 kV/mm to a maximum of 1.5 kV/mm. The randomly oriented polycrystalline sample was 5 mm × 5 mm × 2.4 mm in dimensions, and the electric field was applied across the 2.4 mm thickness. The textured sample was 5 mm × 5 mm × 2.3 mm in dimensions, and the electric field was applied across the 2.3 mm thickness. Neutron diffraction patterns, parallel and perpendicular to the direction of the applied electric field, were collected *in situ* at the VULCAN beamline of the Spallation Neutron Source at the Oak Ridge National Laboratory [Ref. 28]. The experimental setup is schematically illustrated in Figure 1. The incident neutron beam was 3.0 mm in width for both the samples.

Figures 2(a) and 2(b) depict the *P-E* hysteresis loops under cyclic electric fields for the randomly oriented and the $(001)_{PC}$ textured polycrystalline specimens. The remnant and maximum polarizations attained by the application of external field was found to be similar in both the cases. The coercive field (E_C) of the randomly oriented specimen was higher than that of the textured specimen (Fig. 3). The textured specimen was also found to exhibit a pinched hysteresis loop at RT. The remnant polarization ($2P_r$) and its first derivative as a function of applied electric field are depicted in Figs. 2(c) and 2(d) for the randomly oriented and textured specimens, respectively. It can be seen from these plots that the rate of increase in P_r with respect to increase in applied electric field amplitude is small in the case of the randomly
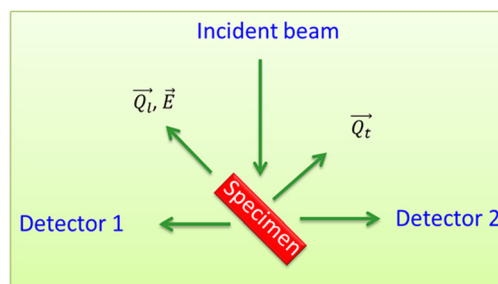

FIG. 1. Schematic of *in situ* neutron diffraction experiment at VULCAN. Detector 1 measures diffracted neutrons with momentum transfer along $\vec{Q}_l$ parallel to the direction of applied electric field $\vec{E}$. Detector 2 measures diffracted neutrons with momentum transfer along $\vec{Q}_t$ transverse to the direction of applied electric field $\vec{E}$.

oriented specimen. However, in the case of the textured specimen, there is a clear jump in the value of P_r above the coercive field regime followed by a plateau. This sudden increase in remnant polarization and a sharp peak in the dP/dE vs. E plot for the textured specimen depict a coherent nature of the domain switching in this sample.

Figures 2(e) and 2(f) depict the temperature dependence of relative permittivity at various frequencies for the randomly oriented and the textured polycrystalline ceramics in their unpoled states. The small anomaly observed at low temperatures is related to the depoling temperature (T_d) in NBT-BT. The value of T_d was found to be $\sim$90 and $\sim$130 °C for the textured specimen and the randomly oriented ceramics, respectively. At higher temperatures, a broad peak depicting the diffused nature of phase transition (DPT) could be observed for both the specimens. The shifting of T_m (temperature corresponding to the maximum relative permittivity) with a change in the frequency of applied electric field depicts the relaxor nature of this material and can be attributed to the presence of polar nanoregions (PNRs).

Figure 4(a) shows the changes in the $(200)_{PC}$ diffraction peak profile of the randomly oriented polycrystalline specimen as a function of applied electric field amplitude. Results are shown only for fields of 1 kV/mm and higher to clarify the differences in the diffraction profiles. A clear distortion of the $(200)_{PC}$ peak parallel to the direction of the applied electric field was observed for a field amplitude of 1.5 kV/mm. A similar distortion of the $(200)_{PC}$ diffraction peak profile was also observed along the direction transverse to the direction of the applied *E*-field, as shown in Fig. 4(b). The $(111)_{PC}$ diffraction peak shows gradual appearance of a shoulder with increasing amplitude of applied E-field, for directions both parallel and transverse to the *E*-field, as shown in Figs. 4(c) and 4(d), respectively. The *in situ* bulk diffraction patterns reveal the development of structural distortions within the pseudocubic phase of the randomly oriented specimen upon application of an *E*-field. Subsequent distortions in both $(200)_{PC}$ and $(111)_{PC}$ diffraction peaks with increasing *E*-fields could be attributed to further changes in the volume fractions of coexisting phases with tetragonal and rhombohedral symmetries as well as changes in the volume fractions of non-180° ferroelectric domains of the two coexisting phases. This result is consistent with previous reports on bulk diffraction measurements showing
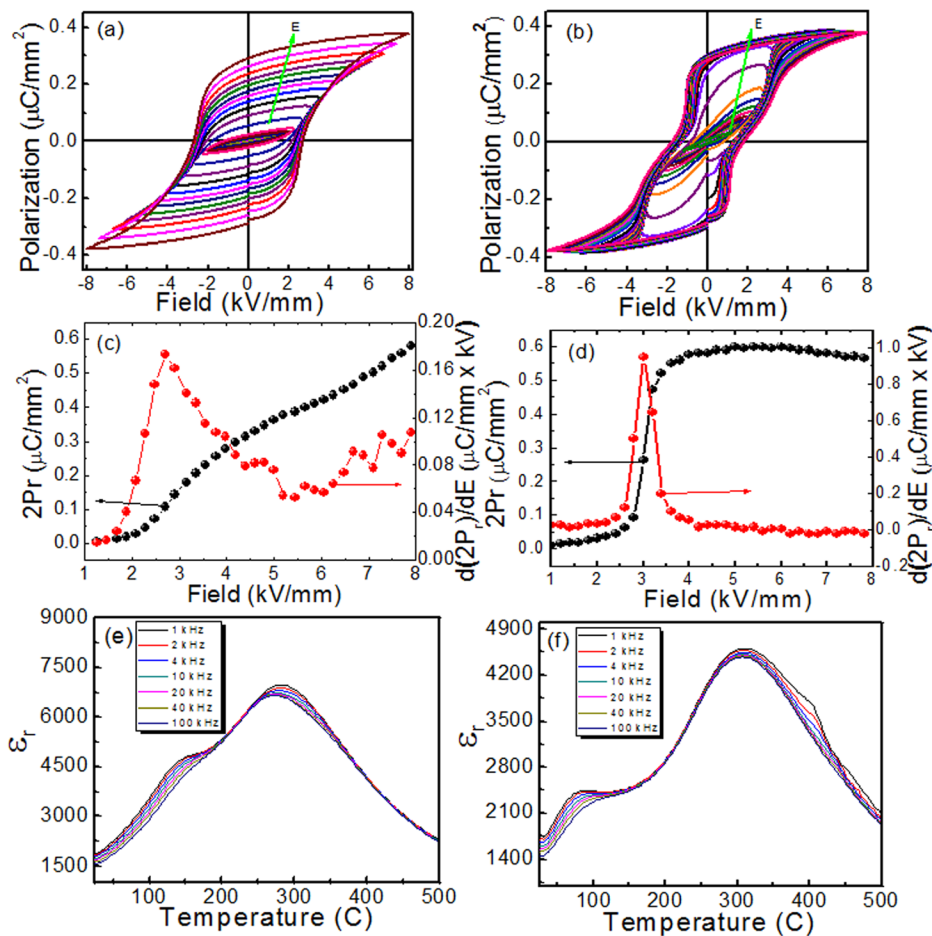
FIG. 2. PE hysteresis loops at 1 Hz for NBTBT polycrystalline ceramics (a) randomly oriented (b) textured. The field dependence of $2P_r$ and its derivative with respect to applied electric field for (c) randomly oriented (d) textured. The sharp peak in the dP_r/dE plots of textured specimen indicates coherent switching of the specimen. Temperature dependence of relative permittivity for (e) randomly oriented, (f) textured polycrystalline NBT-BT ceramics.

E-field-induced phase transformations in NBT-BT ceramics near the MPB [Ref. 16].

In contrast to the behavior observed for the randomly oriented specimen, no evidence of E-field-induced phase transformation was evident in the $(001)_{PC}$ textured specimen from the *in situ* neutron diffraction patterns collected at different electric field amplitudes, as shown in Fig. 5. Remarkably, the $(200)_{PC}$ peak profile shows no significant distortion for field amplitudes up to 1.5 kV/mm, as shown in Figs. 5(a) and 5(b). The $(111)_{PC}$ peak profile for the textured sample measured along the direction of the applied electric field also shows no structural distortions. In the transverse direction,
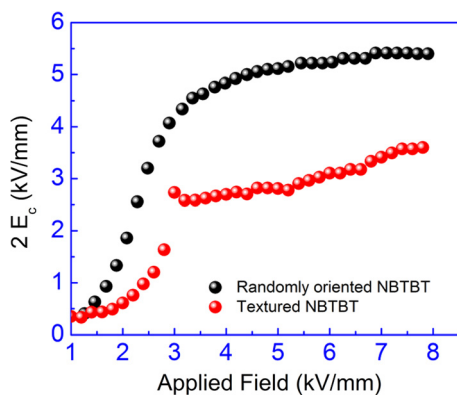

FIG. 3. Comparative plots of coercive fields (E_c) versus applied electric field (E) for textured and randomly oriented polycrystalline NBT-BT ceramics.

the intensity of $(111)_{PC}$ peak was much lower to draw any significant conclusion and therefore is not shown here. These results clearly reveal that phase instability under the application of electric fields does not play a significant role towards enhanced piezoelectric properties of the $(001)_{PC}$ textured NBT-BT ceramics. It is pointed out here that creation of phase instabilities is often considered as a guiding principle for the enhancement of dielectric and piezoelectric properties of ferroelectric materials.[29,30] It is therefore interesting that the randomly oriented NBT-BT ceramics that exhibit electric-field-induced phase transformation have a lower d_{33} coefficient as compared to the $(001)_{PC}$ textured ceramics of the same composition which exhibits no such phase transition. Next, we explore the possible causes for a difference in the E-field induced phase transformation behavior of the randomly oriented and the $(001)_{PC}$ textured NBT-7BT ceramics.

Recently, we have shown that although Rietveld refinement of bulk neutron diffraction pattern of NBT-7BT indicates a rhombohedral R3c symmetry, the structure is monoclinic at a local scale [unpublished]. The local symmetry of the PNRs can arise from localized displacements of Bi^{3+}, Ba^{2+}, and Na^+ away from the $[111]_R$ (R stands for rhombohedral phase) direction towards $[100]_T$ (T stands for tetragonal phase). Since the coherence length of such displacements is of the order of several nanometers, the local displacements towards $[100]_T$ are compensated over larger length scales, and the bulk structure appears almost pseudocubic with slight rhombohedral distortion. It was proposed
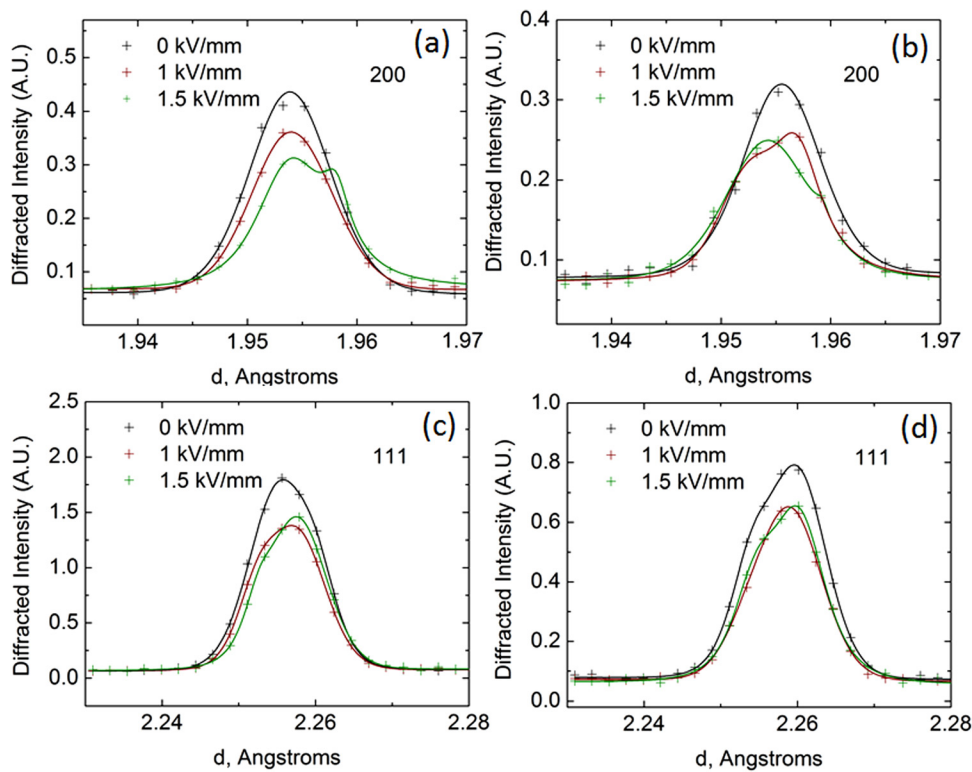
FIG. 4. Changes in the $(200)_{PC}$ diffraction peak profile for the randomly oriented polycrystalline specimen, (a) parallel, and (b) transverse, to the direction of the applied electric field. Figures (c) and (d) show changes in the $(111)_{PC}$ diffraction peak profile for the same specimen, parallel, and transverse to the applied electric field direction, respectively.

earlier that the observed electric field induced phase transformation behavior in NBT-BT is a consequence of relaxor-to-ferroelectric transformation brought about by changes in the coherence length of the PNRs [Ref. 19]. The difference in the observed phase transformation behaviors of the randomly oriented and the textured specimens can be proposed as a consequence of the evolution of coherence length of the PNRs within these two specimens, as explained below. While the $(001)_{PC}$ textured specimen essentially retains a relaxor character with shorter coherence length even after the application of electric fields, such is not the case for the randomly oriented specimen. This hypothesis is consistent with the observed pinched *P-E* loops and a smaller E_c for the $(001)_{PC}$ textured specimens, both of which are characteristic of a relaxor-like behavior. On the contrary, the randomly oriented specimen shows normal ferroelectric P-E loops and therefore does not exhibit a predominant relaxor behavior.

Another possible explanation for the difference in E-field induced phase transformation behavior could be due to internal stresses generated during domain switching. In
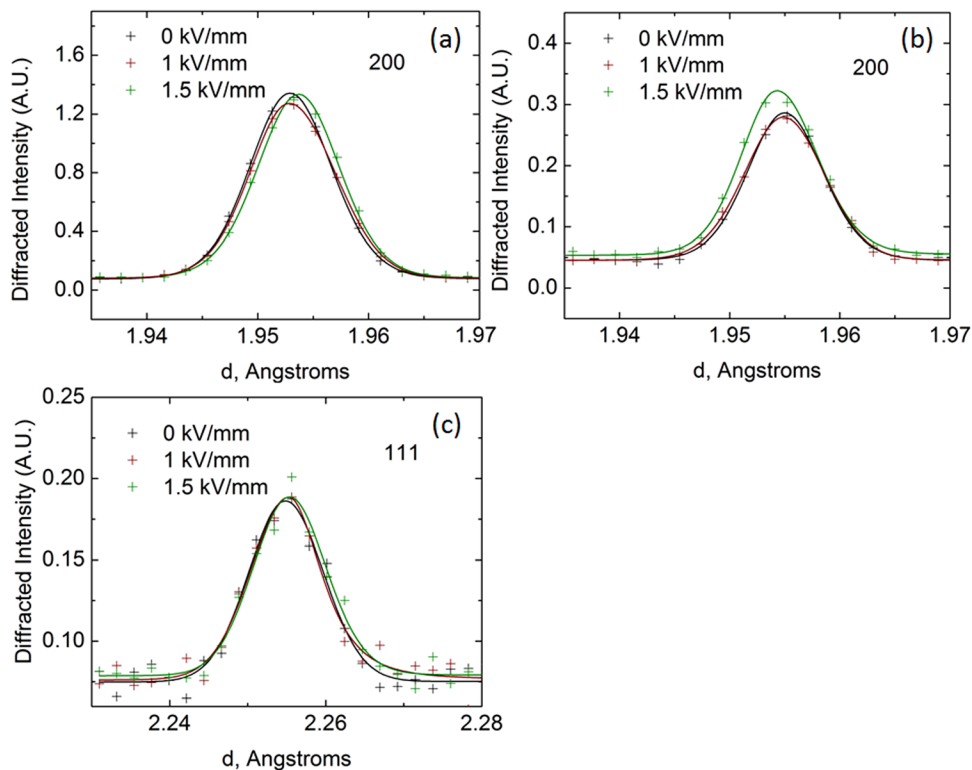

FIG. 5. Changes in the $(200)_{PC}$ diffraction peak profile for the $(100)_{PC}$ textured specimen, (a) parallel, and (b) transverse, to the direction of the applied electric field. Fig. (c) shows changes in the $(111)_{PC}$ diffraction peak profile for the same specimen, parallel to the direction of applied electric field.

NBT-KBT based system, a faster rate of applied electric field rate was found to induce structural transformations.[24] The absence of structural transformation under slower field rate was attributed to internal stresses caused by domain switching during poling, which occurs at the coercive field, because poling before structural transformation increases the required field for phase transformation to a large extent. Internal stresses can be generated during the poling process due to differences in non-180° domain switching behavior of adjacent grains with different orientations.[31] Therefore, it is proposed that the lower coercive field observed in the textured NBT-BT (Fig. 3) specimen facilitates poling, and the resultant internal stresses inhibit further structural transformation. Due to the pseudocubic nature of the diffraction peaks of the textured specimen, non-180° domain switching cannot be clearly identified from structural measurements during the application of electric fields. Nevertheless, large strains associated with non-180° domain switching has been found to play a vital role in the overall structural behavior of various other ferroelectric systems.[32–35] Further examination of the physical origins for such different behaviors of both the types of specimens is currently underway from TEM investigations and detailed Rietveld refinements of neutron diffraction data.

In summary, the lead-free piezoelectric $(Na_{0.5}Bi_{0.5}TiO_3)$-$BaTiO_3$ (NBTBT) textured in $(001)_{PC}$ orientation was found to depict a high longitudinal piezoelectric constant of 322 pC/N contrary to ~160 pC/N observed in randomly oriented NBTBT ceramics. *In situ* neutron scattering experiments revealed electric field induced structural phase transformation in the randomly oriented NBT-7BT ceramic, which was, however, absent in the textured ceramic of the same composition. The absence of *E*-field induced structural phase transformation in the textured NBT-7BT is tentatively attributed to smaller coherence length scales of PNRs and/or inhibition due to internal stress generated by domain switching which precedes a structural transformation. We further conclude that the phase instability is not a necessary condition to achieve enhanced piezoelectric response in NBT-BT.

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