



Effect of Crystallographic Texture on the Field-Induced-Phase Transformation Behavior of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}7\text{BaTiO}_3\text{-}2\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$

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Effect of Crystallographic Texture on the Field-Induced-Phase Transformation Behavior of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - 7\text{BaTiO}_3 - 2\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$

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The electric-field-induced phase transformation of $\{001\}_{\text{pc}}$ oriented $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - 7\text{BaTiO}_3 - 2\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ bulk ceramics with a 8.3 multiples of a random distribution fiber texture was investigated using *in situ* diffraction. Field-dependent diffraction suggests that the high strain is a result of an electric-field-induced pseudo-cubic to tetragonal phase transformation, where the induced tetragonal phase has a strong domain texture. The effect of electric field direction was investigated by applying the electric field parallel and perpendicular to the fiber texture axis. Applied field direction affected the lattice spacing of the induced phase, domain texture, and increased poling field to induce the phase transformation.

Keywords: Preferred Orientation, Electric-Field-Induced Phase Transformation, Bismuth Sodium Titanate

Piezoelectric materials are used in a variety of applications such as actuators, sensors, and transducers.[1] Because of the high strain response, systems that exhibit an electric-field-induced pseudo-cubic to polar transformation have received strong interest as a potential alternative to lead-based ceramics.[1–4] One promising system is the solid solution $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - x\text{BaTiO}_3 - y\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (BNT- x BT- y KNN).[3] At room temperature, BNT-6BT-2KNN exhibits a $S_{\text{max}}/E_{\text{max}}$ of 567 pm/V at 8 MV/m with a low d_{33} of 30 pm/V.[3] The origin of the high strain has been attributed to reversible field-induced transformation, where the addition of KNN into the BNT- x BT decreased the depolarization temperature below room temperature.[2]

In recent years, *in situ* diffraction experiments have been used to investigate field-induced phase transformations [5–10] and domain texture evolution.[5,6,11] Recent *in situ* studies have suggested BNT-7BT undergoes an oriented electric-field-induced transformation from pseudo-cubic to tetragonal.[5,6] It has also been reported that BNT-6BT-2KNN undergoes a reversible field-induced transformation from pseudo-cubic to a tetragonal and rhombohedral phase mixture.[9] While

in situ studies have investigated the phase evolution of single crystals [12] and bulk ceramics,[5–8] the effect of crystallographic texture on the electric-field-induced phase transformation behavior of bulk BNT-based ceramics has only recently been investigated.[13] Here, we investigate the effect crystallographic texture and electric field direction has on the electric-field-induced phase transformation behavior of BNT-7BT-2KNN using *in situ* X-ray diffraction.

In situ scattering experiments were performed at beamline 5-BM-D at the Advanced Photon Source at Argonne National Laboratory using 65 keV (0.1907 Å) X-rays. Tungsten beam slits were used to limit the incident beam to a $500 \times 500 \mu\text{m}$ spot size. A Mar 345-image plate positioned approximately 1.6 m from the sample was used to collect diffraction images. Diffraction data were collected while a static electric loading was applied perpendicular to the incident X-rays to emulate the electric poling process. Detailed reports of the experimental setup have been previously published.[14,15]

Samples with a $\{00l\}_{\text{pc}}$ fiber texture were prepared using the tape cast method as reported elsewhere.[16] Two sets of bulk ceramics were prepared for *in situ*

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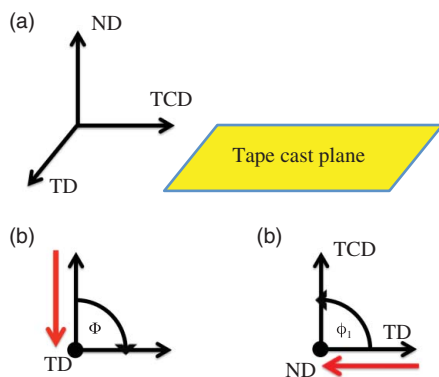


Figure 1. Schematic of the (a) processing coordinate system and a 2D projection of the processing coordinate system from the perspective of the incident X-rays for a field applied along (b) ND and (c) TD, where the angle from applied field, (b) and (c), are defined in terms of Bunge Euler rotation angles (ϕ_1, Φ, ϕ_2).

diffraction; 20 layer stacks, and 80 layer stacks. Samples used for *in situ* diffraction were rectangular bars with of $xyz = 5 \times 1 \times 1$ and $4 \times 1 \times 1$ mm for and electric field applied along the sample normal direction (ND) and transverse direction (TD), respectively. Sintered ceramics developed a 8.3 multiples of a random distribution (MRD) $\{001\}_{pc}$ fiber texture. The crystallographic texture was calculated by refining zero field diffraction using the software package materials analysis using diffraction with a harmonic orientation distribution function model.[17] See supplementary information for details of the texture refinements. To investigate the effect of the applied field direction, relative to the fiber texture axis, the electric field was applied parallel and perpendicular to the fiber axis (processing ND). Applying the electric field perpendicular to the fiber axis probes a different distribution of crystallites because all $\{00l\}_{pc}$ are equally probable at all orientations in the plane perpendicular to the fiber axis.

A coordinate system can be defined relative to the initial processing axis with; ND, tape-cast direction, and TD, as shown in Figure 1(a), with the direction of the applied field is defined relative to this coordinate system, Figure 1(b) and 1(c). By projecting the sample coordinate system along the axis of the incident X-ray, the angle between the applied field and the diffraction vector ($\hat{k}$) is defined in terms of Euler angles (ϕ_1, Φ, ϕ_2), where the rotation between the scatter vector and electric field is defined as ($\phi_1, 0, 0$) and ($0, \Phi, 0$) for an applied poling field along TD and ND, respectively.

Prior to the application of the electric field, the diffraction signal, Figures 2(a) and 3(a), showed no peak splitting, shoulders, or superlattice reflections associated with a distorted or mixed phase structure; henceforth, this zero-field structure will be referred to as pseudo-cubic. Diffraction signal as a function of angle from the applied field, Figures 2(c) and 3(c), highlights the difference in

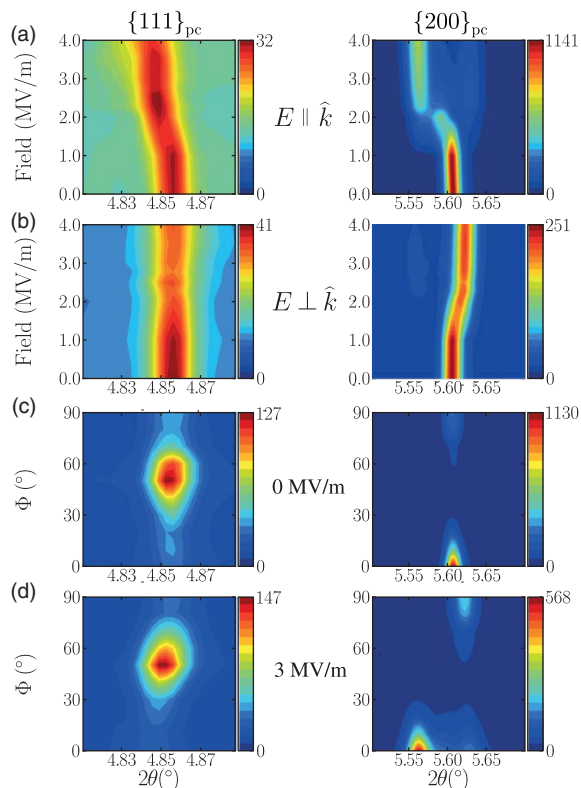


Figure 2. Evolution of the $\{111\}_{pc}$ (left) and $\{200\}_{pc}$ (right) diffraction signal with increasing field (a) parallel and (b) perpendicular to the applied field along ND. Diffraction signal at an angle Φ away from the applied field axis at (c) zero field and (d) 3 MV/m.

the $\{00l\}_{pc}$ distribution relative to the applied field, where the $\{200\}_{pc}$ diffraction signal has either two maxima ($\Phi = 0$ and 90) or remains constant for all angles, for a field applied along ND and TD, respectively. The large grain size, $\sim 25 \mu\text{m}$, gives rise to intensity variation in the $\{111\}_{pc}$ and $\{200\}_{pc}$ diffraction signal, Figure 3(c) and 3(d), due to poor sampling.

Increasing the applied poling field above 1 MV/m induces peak splitting in the (002) diffraction signal, while the $\{111\}_{pc}$ diffraction signal shows no splitting, as shown in Figures 2(a) and 2(b) and 3(a) and 3(b). A lack of $\{111\}_{pc}$ splitting suggests the observed peak splitting is consistent with a pseudo-cubic to tetragonal transformation, but the diffraction data cannot definitively determine the field-induced transformation to be a pseudo-cubic to a single tetragonal phase. Field-dependent diffraction data show the pseudo-cubic to tetragonal transformation proceeds across a wide electric field range (1–3 MV/m), and the resulting tetragonal phase shows a strong domain texture where minimal (002) diffraction signal was measured perpendicular to the applied poling field, as shown in Figures 2(d) and 3(d). Close inspection of the (002) diffraction signal at 4 MV/m shows the pseudo-cubic to tetragonal transformation results in a stronger domain texture when the electric field is applied along ND, as

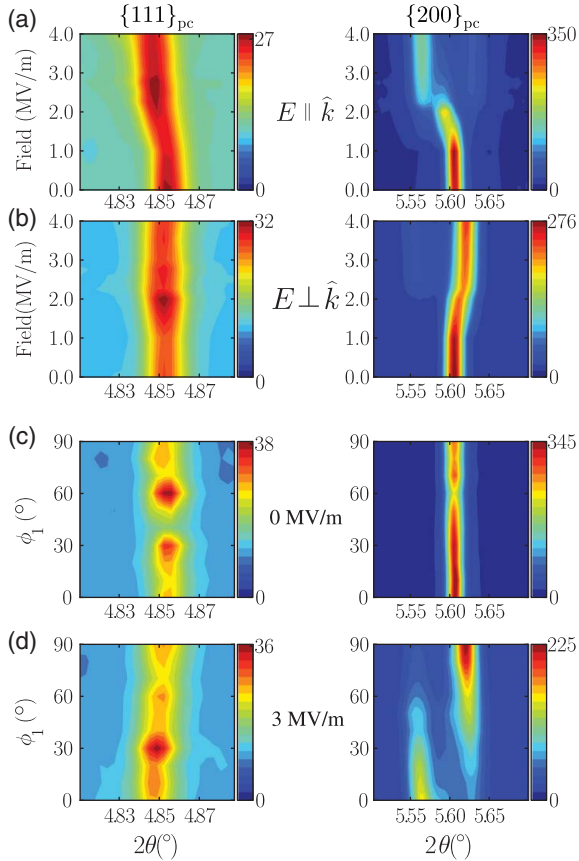


Figure 3. Evolution of the $\{111\}_{pc}$ (left) and $\{200\}_{pc}$ (right) diffraction signal with increasing field (a) parallel and (b) perpendicular to the applied field along TD. Diffraction signal at an angle ϕ_1 away from the applied field axis at (c) zero field and (d) 3 MV/m.

seen in a reduction in (002) diffraction signal parallel to the applied field, Figure 2(a). *In situ* electric field experiments of randomly oriented BNT–7BT, at 3 MV/m, showed the pseudo-cubic to tetragonal transformation resulted in the formation of a moderate domain texture (1.27 MRD₀₀₂), [6] and at 6 MV/m a rhombohedral and tetragonal phase mixture was observed with both phases having a domain texture of 2.8 MRD₁₁₁ and 1.9 MRD₀₀₂, respectively. [18] The difference in domain texture associated with an applied field; along ND, TD, and in randomly oriented ceramics suggest crystallographic texture affects the grain constraints preventing domain alignment with the applied field. In addition to a different domain texture development, applying the electric field along TD and ND affects the phase transformation behavior, where the onset field and completeness of the pseudo-cubic to tetragonal phase transformation is affected by the applied field direction. The onset of the tetragonal transformation occurs at 1 and 1.4 MV/m for an applied field along ND and TD, respectively. When a 4 MV/m field is applied along TD the $\{200\}_{pc}$ diffraction signal shows a pseudo-cubic fraction remains, as observed by a smearing between the (002)_T and (200)_T reflections in Figure 3(b).

Without comparable *in situ* studies for randomly oriented BNT–7BT–2KNN, it is not possible to determine if the $\{00l\}_{pc}$ texture promotes the field-induced transformation to the tetragonal phase. *In situ* diffraction of BNT–5.6BT single crystals has shown that the field-induced-phase transformation is only dependent on the field direction if the field material is above the relaxor transition temperature. [19] The modification of BNT–BT with KNN has been reported to decrease the relaxor transition temperature below room temperature, [4] suggesting a $\{001\}_{pc}$ crystallographic texture can affect the field-induced phase transformation, potentially by promoting polarization extension/rotation along the field direction. [20] Sub-coercive field *in situ* neutron scattering experiments have shown textured BNT–7BT maintains a pseudo-cubic structure while randomly oriented ceramics develops peak splitting in both the 200 and 111 peaks. [13] The authors suggested the suppression of the transformation could result from a difference in the coherence length of the polar nano regions or a microstructural effect. Without *in situ* data collected for a stronger applied electric loading, it is unclear if the final field-induced phase or phase transformation electric field is affected by the $\{001\}_{pc}$ texture.

The $\{111\}_{pc}$ diffraction signal shows distinctly different field-dependent behaviors parallel, Figure 2(a) and 3(a), and perpendicular, Figures 2(b) and 3(b), to the applied field. Perpendicular to the applied field, both peak shape and position show minimal variation with increasing field, while the diffraction signal parallel to the applied field shows two distinct inflection points with increasing field at (1 and 2 MV/m) and (1 and 2.25 MV/m) for an applied field along ND and TD, respectively. These inflection points correspond well to the electric field range where BNT–7BT–2KNN transforms from pseudo-cubic to tetragonal. The higher electric field inflection point occurs at a lower electric field than inflection points measured in polarization and strain measurements, suggesting the observed strain increase is the result of further domain alignment with increasing field, a polarization and strain loop is reported in the supplementary information.

The lattice parameters of the induced tetragonal phase were measured by fitting the diffraction data using three peaks, [5] two split pseudo-Voigt functions to model the (002) and (200) diffraction peaks and a pseudo-Voigt function to fit the pseudo-cubic fraction. Prior to applying the electric field the lattice parameter of the pseudo-cubic structure was 3.89702 (5) Å for both applied field directions. The lattice parameters of the induced tetragonal phase are graphed in Figure 4 for an applied field range of 2–4 MV/m. The larger error in the measured *a* and *c* lattice parameter is the result of peak overlap between the induced phase and the initial pseudo-cubic phase. For both applied field directions, the lattice spacing of the induced tetragonal phase, Figure 4(a) and 4(b) shows a trend of *c*-axis expansion and *a*-axis contraction with

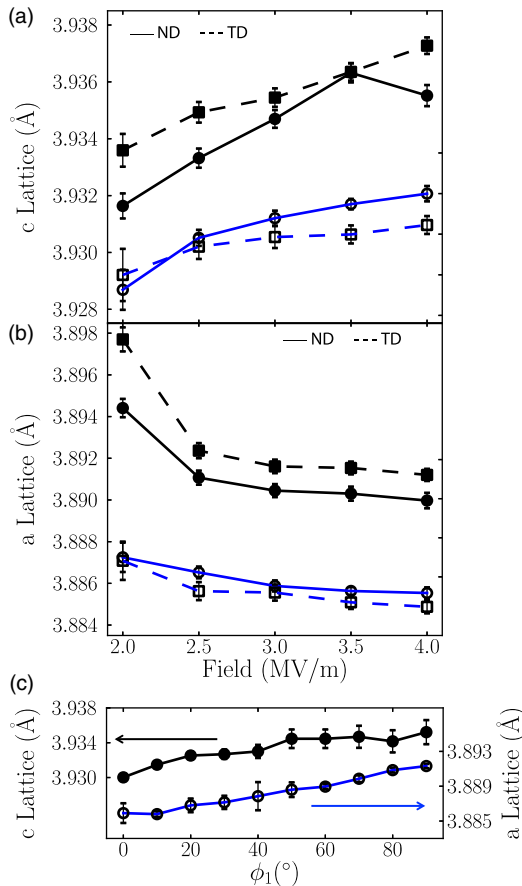


Figure 4. Electric field-dependent tetragonal lattice parameters (a) c -axis and (b) a -axis measured parallel (open) and perpendicular (solid) to the applied field, and (c) angular-dependent tetragonal lattice parameters for a 3 MV/m applied field along TD. Error bars represent the 99% confidence band from the respective peak fit.

increased poling field. Applied field direction has a direct affect on the lattice parameter of the induced phase, where an applied field along ND induced a longer c -axis parallel to the applied field and shorter a -axis perpendicular to the applied field. This result is attributed to an increase in the constraints imposed by neighboring grains that arises from applying the electric field parallel to the fiber texture axis, where an electric field applied along ND has minimal misalignment between the $\{001\}_{pc}$ and the electric field direction because ND is the fiber texture axis. Applying the electric field perpendicular to the fiber texture axis probes the tape-cast plane where all $\{001\}_{pc}$ are equally probable, resulting in significant misalignment of the $\{001\}_{pc}$ variants and the applied field direction.

Angular-dependent lattice parameters of the induced tetragonal phase for a field applied along ND show the average a and c lattice expand with increased angle (ϕ_1) from the applied field. The (002) and (200) diffraction peaks show an asymmetric profile with the asymmetric tails overlap between the (002) and (200) peaks. A lack of $\{200\}_{pc}$ diffraction signal at various Φ angles prevented

an accurate determination of the angular-dependent lattice parameters of the induced tetragonal for an applied field along ND. The lattice parameters measured parallel and perpendicular to the applied field follow this trend suggesting the direction of the applied field is not the cause of this expansion. This trend can be attributed to the intrinsic piezoelectric response of the tetragonal phase, where a positive d_{31} piezoelectric coefficient would promote both a and c axis expansion perpendicular to the applied field.

In summary, *in situ* diffraction of $\{00l\}_{pc}$ oriented BNT–7BT–2KNN bulk ceramics show an oriented field-induced pseudo-cubic to tetragonal transformation for both applied field directions. The direction of the applied electric field, with respect to the processing coordinate system, affects the field-induced phase transformation behavior. Applying a poling field along TD imposes grain constraints that results from applying the electric field inside the tape-cast plane where all $\{001\}_{pc}$ are equally probable, resulting in a shorter c -axis parallel to the applied field, lower domain texture, and increased poling field to induce the phase transformation.

Supplementary online material. A more detailed information on experiments is available at <http://dx.doi.org/10.1080/21663831.2013.800606>.

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