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Journal:	*Inorganic Chemistry Frontiers*
Manuscript ID	QI-RES-05-2021-000670.R1
Article Type:	Research Article
Date Submitted by the Author:	13-Jul-2021
Complete List of Authors:	Fan, Longlong; Tianjin Normal University, College of Physics and Materials Science Zhang, Linxing; University of Science and Technology Beijing, Liu, Hui; University of Science and Technology Beijing, Chen, Yu-Sheng; University of Chicago Advanced Photon Source,, ChemMatCARS Ren, Yang; Argonne National Laboratory, Xing, Xianran; University of Science and Technology Beijing, School of Metallurgical and Ecological Engineering Chen, Jun; University of Science and Technology Beijing, Department of Physical Chemistry

In situ determination on the interplay of structure and domain under subcoercive field in $BiScO_3$-$PbTiO_3$

Longlong Fan,[a,†] * Linxing Zhang,[c] Hui Liu,[b] Yu-sheng Chen,[†] Yang Ren,[d] Xianran Xing,[e] Jun Chen[b, e]

[a] College of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China
[b] School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, China
[c] Institute for Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China
[d] X-Ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA
[e.] Beijing Advanced Innovation Center for Materials Genome Engineering, Institute of Solid State Chemistry, University of Science and Technology Beijing, Beijing 100083, China
[†] NSF's ChemMatCARS Beamline@APS, The University of Chicago, Argonne, IL, 60439, USA

Abstract

The extraordinary performances for phase-coexisting ferroelectrics are significantly affected by not only the phase constitution but also the motion of domain walls. The study on the role of phase coexistence in the formation of ferroelectric and ferroelastic domain microstructures is of great importance to explain the enhanced piezoelectric properties. In-situ high-energy diffraction and Rayleigh law are utilized to reveal the interplay of phase constitution and domain configuration to the macroscopic electromechanical coupling effect in the morphotropic phase boundary composition $0.365BiScO_3$-$0.635PbTiO_3$ during the application of weak electrical loading in the present study. It is found that anisotropic phase transition and domain switching occur in the polycrystalline ferroelectric ceramics and a phase transition occurs dramatically beyond the coercive field. Taking into account the important role of coupled ferroelectric and ferroelastic domain microstructures, we conceived a configuration of the monoclinic domains coexisting with and bridging the tetragonal domains. The existence of bridging domains would bring an insight into the interplay of phase and domain and explains the piezoelectric performance in the vicinity of morphotropic phase boundaries.

Keywords
ferroelectrics, in-situ diffraction, Rayleigh law, MPB, $BiScO_3$-$PbTiO_3$

Introduction

In piezoelectric materials, the motion of domain walls is known to significantly affect their dielectric, piezoelectric, and ferroelectric properties. Understanding not only the ferroelectric domain but also the ferroelectric domain boundary becomes more essential for the development of piezoelectric materials and devices. For example, investigations demonstrated that the formation of nanodomains assists ferroelastic domain switching and reduces the threshold field for the domain propagation.[1] The movement of ferroelastic domain walls significantly enhanced the piezoelectric coefficient of the ferroelectric thin film.[2] A significant reduction of the stiffness at the domain boundary promoted the switching of domains to enhance piezoelectric properties.[3] The pinning of ferroelectric domain boundary motion induced the polarization fatigue in the ferroelectric thin film.[4]

Thermodynamically, the phase coexistence in ferroelectric compounds accessing the morphotropic phase boundary (MPB) regions also improves dielectric, piezoelectric properties, and electromechanical coupling.[5-7] That the MPB of the solid solution separates the phase components possessing an approximate energetic landscape with different orientations of polarization. The flatted free energy around MPB benefits the field-driven phase transformation, facilitating the alignment of polar in domains under electric field as reported in PZT,[8,9] $PbTiO_3$-$BiScO_3$, [10,11]and et al.. Meanwhile, a strong synergy between the reversible phase transition and enhanced domain switching exists near MPBs and plays an important role in improving the piezoelectric responses.[10,12] These studies provide a broad aspect of the MPB phase coexistence phenomenon. Since advancements including transmission electron microscopy (TEM) have revealed that the existence of mottled nanometer ferroelectric domains for MPB composition would be highly related to the phase composition and be the crucial factor responsible for the excellent piezoelectric response,[13,14] the role of phase coexistence in the change of ferroelectric and ferroelastic domain microstructures must be considered in order to account for the enhanced

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* Corresponding authors. Email: longl.fan@gmail.com

piezoelectric properties.

Experimentally, X-ray and neutron Bragg scattering techniques would be versatile tools to be utilized to quantitively investigate ferroelastic domain wall motion and phase transition in polycrystalline materials. Because, crystallographically, the lattice deformation and average displacement of domain walls can be tracked from the changes in peak position and crystallographic texture observed during the loading process.[15] Hence, in-situ X-ray diffraction combined with two-dimensional (2D) scattering geometry technology would be helpful to construct a comprehensive picture of structural evolution and domain switching behavior, that the information of phase transition, intrinsic effects (including polarization vector rotation and lattice distortion under an external stimulus), and extrinsic effects (mainly including domain wall motion) can also be simultaneously extracted to elaborate their contributions to the piezoelectric behavior. Because Pb/Bi-based perovskites exhibit extremely high T_C and large piezoelectricity and in some cases multiferroic behavior, binary systems of $PbTiO_3$-$BiMeO_3$ have been intensely researched. In the present study, the high-T_C and high performance MPB piezoceramics of $0.365BiScO_3$-$0.635PbTiO_3$ (0.365BS-0.635PT) was employed to investigate the role of phase coexistence on the domain walls motion. To assess the total influence of the domain wall and interphase boundary motion on the piezoelectric behaviors, the Rayleigh law in association with in-situ high-energy diffraction was used. Based on the fact that the relative nonlinear contributions in the Rayleigh coefficient orientate from the displacements of ferroelectric domain walls and/or phase boundary, the change of converse piezoelectric coefficient and in-situ diffraction profiles convince that a phase transition occurs dramatically beyond the coercive field. A landscape of the tetragonal domains bridged by the monoclinic phase or domains has been constructed to elaborate the piezoelectric performance. It is suggested that a transition area would exist between the domains of the tetragonal and monoclinic phase, and the transition area play a pivotal role in the piezoelectric performance.

Experimental section

The solid-state reaction method was used to prepare samples of 0.365BS-0.635PT. The analytically pure starting powders of PbO, Bi_2O_3, TiO_2, and Sc_2O_3 were stoichiometrically mixed and milled in a mortar with ethanol for 2h. After drying, the mixture was calcined at 750 °C for 4h, and the green ceramic pellets were sintering at 1125 °C for 2 hours in a closed crucible with covering sacrificial powder.Then, a powder XRD pattern of the ground ceramic powder confirmed the phase purity and coexistence of tetragonal and monoclinic phase at the MPB as stated in prior observations [16-18]. The pellets were polished on abrasive paper, and gold electrodes were deposited on the top and bottom surfaces. Polarization and strain loops of 0.36BS-0.64PT ceramic were characterized on initially unpoled materials by a ferroelectric analyzer at various field amplitudes and frequencies (TF Analyzer 1000, aixACCT). The piezoelectric parameter was measured by a Berlincourt d_{33} meter (ZJ-3, China Academy of Acoustics, China) after the samples are poled at the electrical loading as high as 7kV/mm. The measurements of strain responses of the poled samples were repeated under bipolar field amplitudes varying below and near the coercive field.

In-situ high-energy synchrotron XRD (HEXRD) investigations using a wavelength of 0.11165 Å were performed on beamline 11-ID-C at Advanced Photon Source, Argonne National Laboratory. The beam size incident on the material was 0.5 mm by 0.5 mm. The samples for in situ experiments were prepared by cutting into dimensions of 1 mm x 1.2 mm x 5 mm. The electric field was applied perpendicular to the beam direction using a high voltage amplifier. Diffraction patterns were measured in forwarding scattering geometry (transmission mode) on a Perkin-Elmer amorphous silicon area detector placed at approximately 1600 mm from the sample stage. The high energy X-ray penetrated the thick Pb/Bi-based ceramics and was adapted for the investigation of the bulk response under an external electric field.

To determine the evolution of phase structure as a function of the electric field, a triangular step shape waveform with an amplitude of 6 kV/mm and a step size of 0.5 kV/mm was applied. Relatively longer duration (about 60 s) for data collection was carried out to collect high-quality diffraction data for reliable structure determination. Hence, the bipolar cycling frequency is about 0.33 mHz. During the diffraction analysis, the Debye rings under different electric fields were divided into different azimuthal sectors at intervals of 15° to integrate the diffraction intensities. Considering the symmetric nature of the diffraction data, only the first quadrant, $0 \leq \varphi \leq \pi/2$ of the data is presented in this work. The diffraction patterns collected at the 0° sector, which is parallel to the direction of the electric field, are utilized to extract the domain volume and lattice deformation under the electrical stimulus. According to our previous investigation, the diffraction data achieved at the 45° sector is utilized for the crystal structure analysis.

The structural refinements were performed with the FULLPROF program.

Results and discussion

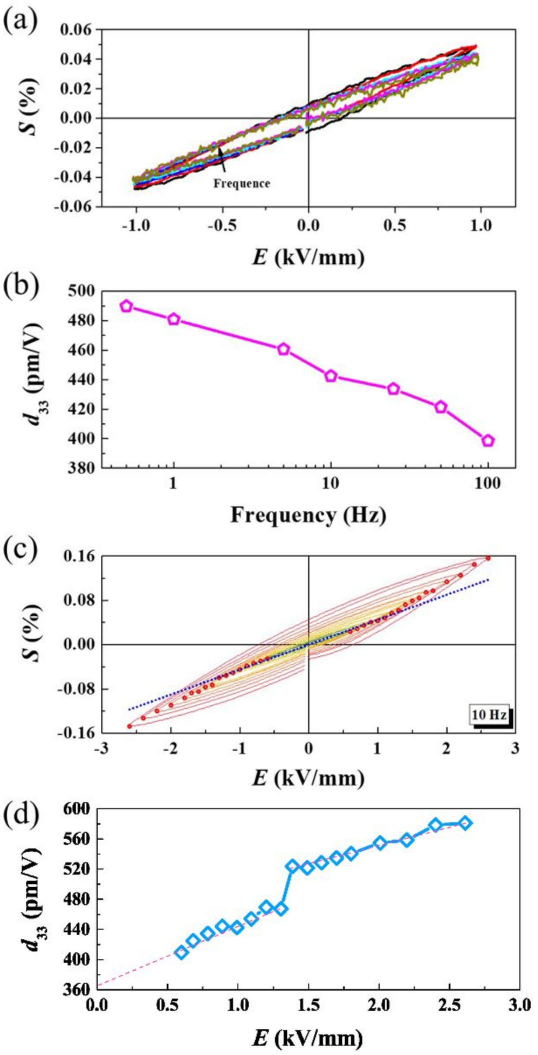

FIG. 1. (a)Strain and (b)piezoelectric coefficient measurements at 1 kV/mm under various frequencies. (c)Strain and (d)piezoelectric coefficient measurements progressively increasing sub-coercive electrical loading up to 2.6 kV/mm at 10 Hz. The error in the piezoelectric coefficient is less than 5%.

The ferroelectric compounds of $BiScO_3$-$PbTiO_3$ at the MPB have been widely studied for their known excellent properties. Herein, the piezoelectric and ferroelectric properties of 0.365BS-0.635PT are prudent to quantitatively measured, the direct piezoelectric coefficient was measured as about 440 pC/N. The coercive field (Ec) has been determined as about 2.7 kV/mm from the polarization and strain measurements in response to bipolar electric field amplitudes at ±7 kV/mm at a frequency of 1 Hz (FIG. S1). The maximum and remanent polarization reach up to 49 and 38 $\mu C/cm^2$, respectively, and the peak-to-peak strain measured is 0.55%. After poling under 7 kV/mm, the piezoelectric coefficient is measured as a function of the frequency of ac electrical loading, at an ac electrical loading of ~1 kV/mm. The maximum strain values measured in the positive and negative field directions were used to calculate the converse piezoelectric coefficient as a function of frequencies ranging from 0.5 to 100 Hz. Results are shown in FIG. 1a and 1b. The piezoelectric coefficient decreases monotonically with the logarithm of the frequency and could be well represented with the linear equation $d_{33}(\omega) = d_0+\beta\ln(1/\omega)$, where d_0 and β are 481.7 and 16.4pm/V, respectively. Herein, the piezoelectric coefficient measured by Berlincourt d_{33} meter is lower than the d_0, while it is approximate to the $d_{33}(\omega)$value at about 10 Hz. The change of frequency dependent piezoelectric coefficient would be due to the randomly pinning of domain walls.

That both reversible and irreversible components are frequency dependent in the ferroic systems which interface pinnings are randomly distributed.[19]

Then, increasing cyclic electric fields up to 2.6 kV/mm, which is in close proximity to the ferroelectric Ec, were progressively applied to the sample in order to study the total influence of intrinsic and extrinsic effects (including domain wall and interphase boundary motion) to the piezoelectric performance. FIG. 1c and 1d show the strain measurements and field amplification dependent piezoelectric coefficients. Under a weak field (below Ec/2 ≈ 1.4 kV/mm), the field dependent piezoelectric coefficient can be described by a relationship analogous to the Rayleigh law: $d_{33}(E\text{max}) = d_{\text{init}} + \alpha E\text{max}$, where the Emax is the amplitude of ac electric field, d_{init} includes reversible contributions such as intrinsic piezoelectric displacement and reversible interface motion and α represents contributions from the irreversible interface displacements.[20] Herein, dinit and α are equal to 368.3 pm/V and 79.7×10^{-18} m^2/V^2, respectively. Due to the measurements under a high frequency, both of the dinit and α are lower than that reported in 0.36BS-0.64PT.[21,22] Once the electric field exceeds Ec/2, there exhibits a "leap" for the field dependent piezoelectric coefficient. The d_{init} and α become 446.2 pm/V and 52.9×10^{-18} m^2/V^2, respectively. Intriguingly, the ratio of α/d_{init} at the weak field is 0.22×10^{-6} m/V, higher than the value of 0.12×10^{-6} m/V measured above Ec/2. For the Rayleigh parameters allow for a quantitative determination of the domain wall contributions, the higher α/d_{init} means that the irreversible contributions are stronger below Ec/2 and become weak as the electric field access Ec.[20] To reveal the nature of piezoelectric behaviors, it becomes essential to study the motion of domains and reconstruction of domain boundaries under in-situ conditions.

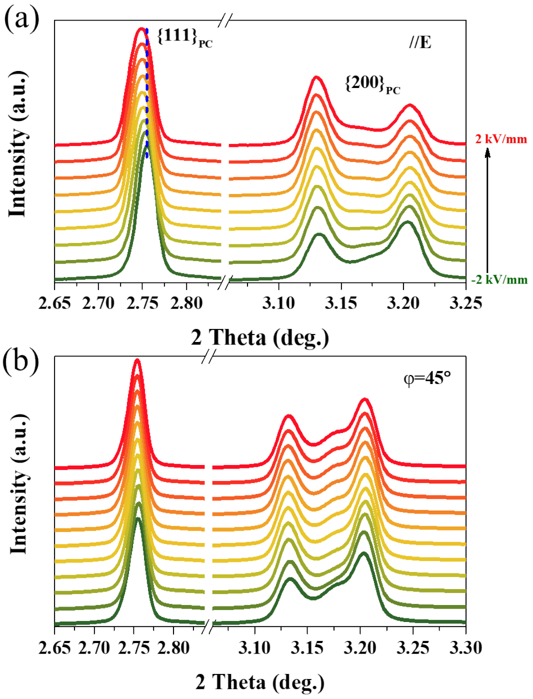

FIG. 2. The diffraction profiles corresponding to the $\{111\}_{\text{PC}}$ and $\{200\}_{\text{PC}}$ reflections (a) parallel to the electric field and (b) at φ = 45° sector during the application of a bipolar electric field with the amplitudes below coercive field amplitude (Ec).

FIG. 2a and 2b illustrate the HEXRD patterns in the region of the $\{111\}_{\text{PC}}$ and $\{002\}_{\text{PC}}$ reflections, where PC refers to the pseudocubic setting, during the application of a linear bipolar electric field with the amplitudes below the Ec. At φ = 0° sector, it exhibits a change in the average $\{111\}_{\text{PC}}$ interplanar spacing, accompanying with significant intensity changes for the $\{002\}_{\text{PC}}$ diffraction profile. The changes in intensities are orientated from domain switching under the influence of external stimuli.[12,21,23,24] Between the tetragonal $\{002\}_{\text{T}}$ ($2\theta \approx 3.13$) and $\{200\}_{\text{T}}$ ($2\theta \approx 3.21$) reflections, the additional Bragg scattering was suggested to be related to the existence of 002M and 220M reflections of a monoclinic phase[10,25]. Due to overlap from the tetragonal $\{002\}_{\text{T}}$ and $\{200\}_{\text{T}}$ reflections and diffuse scattering, the monoclinic $\{220\}_{\text{M}}$ and $\{002\}_{\text{M}}$ reflections are not easily resolved and considered as a single profile in the following analysis. Under the electrical loading of -1.5 to 2.0kV/mm, the diffraction profile from monoclinic phase reflections at $\varphi = 0°$ sector almost remain unchanged(FIG. 2a), which has been discussed in the following. While at $\varphi = 45°$ sector, both the peaks position and relative intensities of the $\{111\}_{PC}$ and $\{002\}_{PC}$ reflections present mild change with varying of the electric loading (FIG. 2b). Similar to the results reported in our previous investigation on rhombohedral, tetragonal, and MPBs compounds,[8,10,12,26] it is supposed that the diffraction data collected at $\varphi = 45°$ sector get rid of influence from the intergranular strain and texture induced by domain switching. The data of the $\varphi = 45°$ sector was used for structure refinement in the following analysis to evaluate the phase evolution in 0.365BS-0.635PT under the applied electric field.

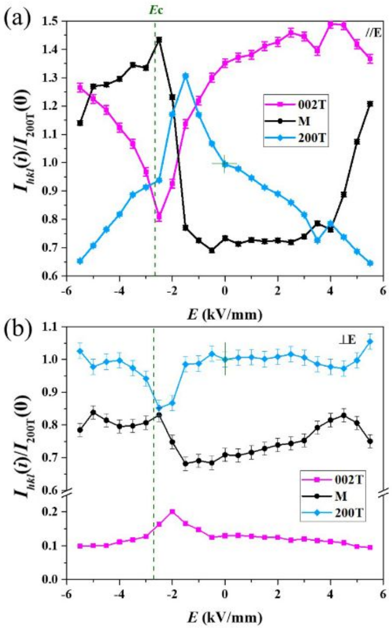

FIG. 3. The evolution of relative intensities on the $\{200\}_{PC}$ reflections (a) parallel and (b) perpendicular to the electric field during the application of a bipolar electric field.

For piezoelectric ceramics with applying external stimuli, the diffraction intensities of characteristic peaks are mainly susceptible to not only the multiplicity factor but also the structural factor.[24] Taking considering the structure change of the ferroelectric phase under electrical loading, therefore, it should be more difficult to accurately estimate the variation of domain volume by the specific peak intensity change. Nevertheless, investigations on the tetragonal phase illustrate that the $\{h00\}_T$ peaks present both stable structural factors and peak profiles under the different electric fields and their intensity change can be utilized for deducing the process of domain motion by evaluating the relative volume change of 001-orientated domains perpendicular to the electric field.[24] Herein, the characteristic reflections of $\{200\}_{PC}$ at $\varphi = 0°$ and $\varphi = 90°$ achieved during both the positive and negative electric field are fitted by three pseudo-Voigt peaks to integrate intensities of the tetragonal $\{002\}_T$ and$\{200\}_T$ and the reflections from a monoclinic phase. FIG. 3a and 3b show the changes of their relative intensity to the $\{200\}_T$ at poled state ($I_{hkl}(i)/I_{200T}(0)$, where $I_{hkl}(i)$ is the intensities of *hkl* reflections at electric field of *i* kV/mm, and $I_{200T}(0)$ is the intensity of $\{200\}_T$ reflections at 0 kV/mm) as a function of electrical loading. At the sector of $\varphi = 0°$ (FIG. 3a), the relative intensity of $\{200\}_T$ monotonously decreases with increasing electric field from -1.5 to 3 kV/mm, while the relative intensity of $\{002\}_T$ changes in the opposite. It should be noted that the intensity increment of $\{002\}_T$ and intensity decrement of$\{200\}_T$ is similar between ±1.5 kV/mm, that means the 90° domains equivalently switch between the direction of parallel and perpendicular to the electric field as applying an electrical loading lower than *E*c/2. Besides, the peak intensity for the monoclinic phase almost stays the same at the $\varphi = 0°$ sector in the range of -1.5 to 3 kV/mm, implying that no phase transition has happened in this condition. Comparely, FIG. 3b exhibits that the relative intensity of $\{200\}_T$ at the $\varphi = 90°$ sector keeps a constant in the range of -1.5 to 3 kV/mm, and the change of $\{002\}_T$ peak intensity and monoclinic phase intensity have an opposite tendency. It can thus be seen that anisotropic phase transition and domain switching occurs in the polycrystalline ferroelectric ceramics. Furthermore, it is worth noting that the peak intensities at $\{002\}_{PC}$ position exhibit tremendous changes between -1.5 and -2.5 kV/mm. This mutation would originate from the reconstruction of ferroelastic domains as discussed in the following sections.

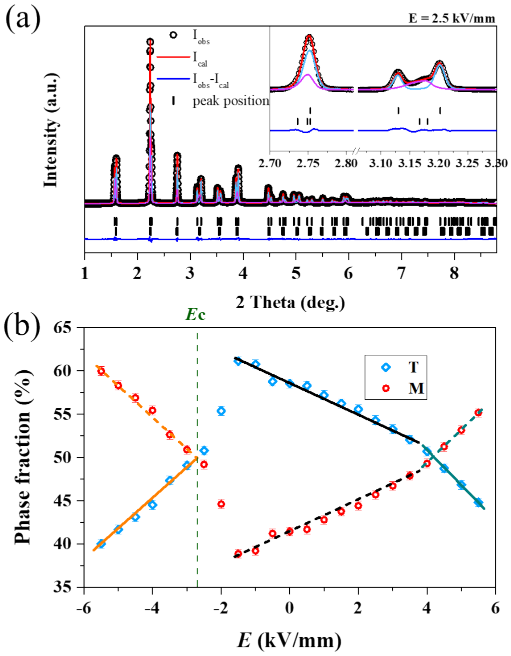

FIG. 4. (a)Structure refinement results of 0.365BS-0.635PT collected at 2.5 kV/mm. (b) Monoclinic-tetragonal phase fraction in 0.365BS-0.635PT with applying bipolar electrical loading.

Generally, once the displacement of domains is limited under the application of the electric field, the phase transformation would be enhanced and vice versa. At the orientations access to $\varphi = 45°$, the electric-field-driven phase transformation become remarkably improved. Considering that no intergranular strain and preferred orientation induced by domain switching were detected at $\varphi = 45°$ sector, the structure refinement rather than peak fitting was employed for phase analysis in order to illustrate the relationship between domain motion and phase transition and their contribution to the piezoelectric performance. For structure refinement, the monoclinic-tetragonal phase coexistence was employed as primitive structure models. To get steady refinements and minimize the number of variables, the coordinates of atoms of the monoclinic phase[8] were kept fixed for the applied bipolar electric field. In terms of the existence of an electrostatic equilibrium between the external electric field, depolarization field, and average field over the volume of crystal cell in dielectrics by applying an electric field, the polarization in every grain should be equal to macroscopic polarization. Furthermore, the flattening of free energy profile near MPB[27,28] would promote the spontaneous polarization in the monoclinic phase adapting to the tetragonal level at around 47 $\mu C/cm^2$(Table S1). The well-refined structure results for 0.365BS-0.635PT under 2.5kV/mm have been shown in FIG. 4a. The detailed phase fraction was plotted in FIG. 4b. It shows that the phase transition occurs gently in the range of -1.5 to 3 kV/mm, and the rate of linearly phase transition is about 1.7 %/[kV/mm], which is lower than that measured by peak fitting on 0.36BS-0.64PT (4.2 %/[kV/mm]).[10] That would come from the difference between these two compounds in the phase construction. As the amplitude of the electric field is over ± 4 kV/mm, the transformation rate increases up to about 3.6 %/[kV/mm]. It should be noted that an electric field of transition "mutation" is prior to the coercive field. Around -1.5 and -2.5 kV/mm, the tetragonal phase rapidly transits to the monoclinic phase, and the transformation rate reaches up to 10.3 %/[kV/mm]. Why does the phase transition rate vary suddenly at the electric field of -1.5 kV/mm rather than the *E*c (-2.7 kV/mm)? There should have an intrinsic correlation between the phase transition and domain switching/domain wall motion for compositions around MPB as well, that the texture intensity change sharply accompanying a phase transition as observed at the 0° sector. In view of the fact that the weak-field piezoelectric coefficient changes near the field of ±1.5 kV/mm (FIG. 1), unveiling the correlation of phase transition and domain switching would furtherly elaborate the fundamental nature of the above-mentioned piezoelectric and ferroelectric performance.

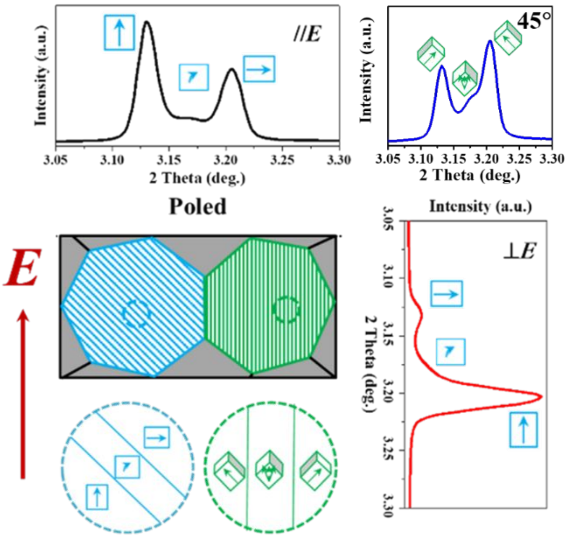

Fig. 5 The schematic diagram of {002}$_{PC}$ diffraction profile of 90°domains in 001-oriented (cyan) and 101-oriented (green) grains. Herein, the 1-domain (↑) and 2-domain (→) corresponds to the domains parallel and perpendicular to the electric field, respectively. The oblique arrow represents the monoclinic domains. In the 101-oriented grains, their polarization direction of the tetragonal phase makes a 45° angle with the electric field.

The MPB ferroelectrics should be spatially heterogeneous systems due to coexisting of multiphase and multidomain microstructures. To explain the role of phase coexistence and enhanced piezoelectricity around MPBs, it needs to be solved as a priority that what about the phase-matching of ferroelectric phases and the mechanism of the phase transition between ferroelectric phases such as rhombohedral/monoclinic and tetragonal phase across MPB. It is well known that the total free energy in ferroelectrics includes bulk phase free energy, domain wall energy, long-range electrostatic, and elastostatic energies.[29] For the monoclinic phase near the MPB, its lower free energy could ascribe to the rotational polarization instabilities, and its emergency would dramatically decrease the domain wall energy.[30] To minimize the total free energy near the MPB, it is thus conceived that the tetragonal domains would be bridged by the monoclinic phase or domains. We propose the domain distribution around the MPB as the schematic diagram shown in FIG. 5. The existence of monoclinic bridging domains could lower the domain wall energy of the tetragonal phase caused by electrostatic and elastostatic functions.[29] The monoclinic bridging domains offer a low energy path for the transition of polarization between various polar axes in tetragonal phase, that the rotational polarization in monoclinic bridging domains makes the polarization vary continuously in MPB grains, facilitating the domain switching under external stimuli.

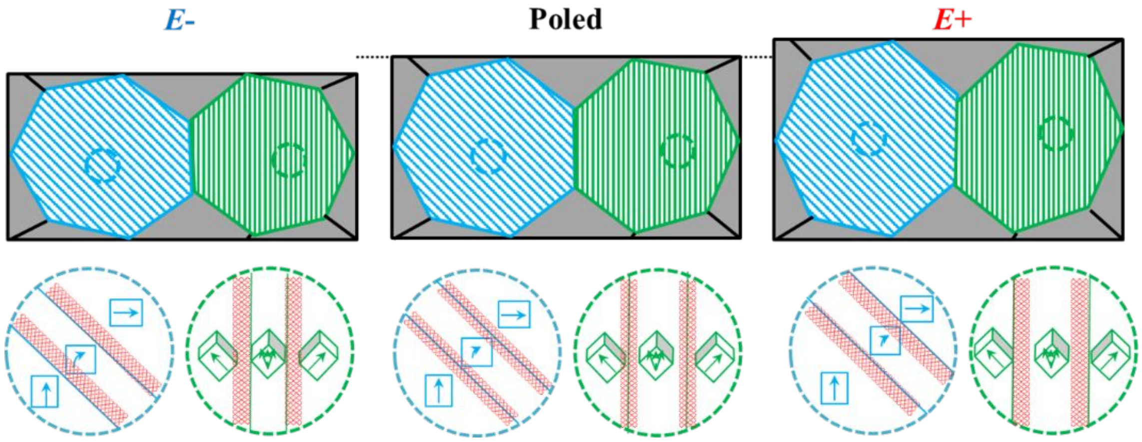

FIG. 6. The schematic diagram of domain switching in MPB ferroelectric polycrystals under subcoercive field. The red zone between the monoclinic and tetragonal phases was defined as a transition area.

In FIG. 5, the diffraction profiles of domains from 001- and 101-oriented grains in poled 0.365BS-0.635PT have also been plotted. Correspondingly, the 1-domains marked as "↑" show stronger $(002)_T$ textured at the sector of 0° and $(200)_T$ textured at the sector of 90°. For 2-domains marked as "→", their related $\{200\}_{PC}$ reflections are weaker than that in the 1-domains. These phenomena is in accord with the switching of domains parallel to the electric field. In the 101-oriented grains, the domains of the tetragonal phase compete to transfer to monoclinic domains rather than domain switching due to their polarization direction makes a 45° angle with the electric field. Thus the intensity of $\{200\}_{PC}$ reflections for tetragonal and monoclinic phase vary with changing of electrical loading and exhibit texture-free characteristics at the sector of 45°. To furtherly account for the motion of domain walls in present MPB ferroelectric polycrystalline, a series of schematic diagrams of domain distribution under subcoercive field was proposed as shown in FIG. 6. Herein, a transition area was introduced in the schematic diagram. It is hypothesized that the domain wall motion and phase transition would occur initiatively at the transition area, in terms of the investigation results of above-mentioned in-situ diffraction, that the intensity of $\{200\}_{PC}$ reflections of monoclinic phase keeps constant or change linearly under subcoercive field (-1.5-2.5 kV/mm). Besides, the domain wall and phase boundary would surmount a small potential barrier to move across the pinning at the transition area, that the d_{33} increases rapidly at the weak field ($\alpha/d_{init} = 0.22 \times 10^{-6}$ m/V). Once the electrical loading exceeds Ec/2, the transition area would expand and the pinned tetragonal/monoclinic phase start to transform to an alternative phase, hence a high phase transition rate was observed. The destruction and reconstruction of the transition area would activate the pinned domains to promote their switching, resulting in enhanced piezoelectric performance. It is therefore concluded that the change of converse piezoelectric coefficients of 0.365BS-0.635PT below Ec is collectively contributed from domain wall motion in tetragonal and phase transition to monoclinic phases. The existence and reconstruction of bridging monoclinic domains promote the switching of domains. Regulating the configuration of domains and domain boundary would be furtherly helpful to improve the ferroelectric and piezoelectric performance in MPB materials.

Conclusion

In summary, the Rayleigh model and in-situ high-energy diffraction were used for studying the nonlinear converse piezoelectric response in the MPB composition of $0.365BiScO_3$-$0.635PbTiO_3$ to investigate the role of phase coexistence on the domain walls motion. It is shown that the nonlinear response below the coercive field obeys the Rayleigh law. Using synchrotron-based X-ray diffraction, the evolution of domains and phase transformation has been evaluated. Both the change of Rayleigh variables and characteristic peak profiles imply that a phase transition occurs dramatically beyond the coercive field. Based on the present investigation, we constructed a configuration of the tetragonal domains bridging with the monoclinic phase or domains to explain the role of phase coexistence and enhanced piezoelectricity. It is speculated that the domain switching and phase transformation would take place firstly at a transition area between the tetragonal and monoclinic domains. The present investigation would bring an insight into the character of phase coexistence to enhanced piezoelectric response and would be furtherly beneficial to improve the ferroelectric and piezoelectric performance in MPB materials in the way of controlling the configuration of domain walls.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (Grants 21701126, 21801013, 21825102, 21731001, and 21590793) and the Fundamental Research Funds for the Central Universities, China (Grant FRF-TP-18-001C2). L.F. is thankful for the financial support from the China Scholarship Council and the help from Naike Shi. NSF's ChemMatCARS Sector 15 is principally supported by the Divisions of Chemistry (CHE) and Materials Research (DMR), National Science Foundation, under Grant No. NSF/CHE-1834750. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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