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*Phys. Rev. Materials* **2**, 111403 — Published 15 November 2018

DOI: [10.1103/PhysRevMaterials.2.111403](https://doi.org/10.1103/PhysRevMaterials.2.111403)
Synergy between phase transformation and domain switching in morphotropic phase boundary ferroelectrics

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Abstract

Many applications of ferroic materials take advantage of the microstructural redistribution under an external stimulus. Despite extensive studies on the microstructural evolution during both domain switching and phase transformations of high performance ferroelectrics near morphotropic phase boundaries (MPB), the synergetic interactions between both leading factors remains unclear. Herein, we have illustrated and discerned the correlative response of phase transformation and domain switching in an archetypical piezoceramic of PbTiO3-BiScO3 using a combination of in-situ high-energy synchrotron x-ray diffraction and phase-field simulations. The direct structural evidence and domain development from simulations reveal a significant reversible orientation-dependent emerging phase transformation and enhanced domain switching. Increasingly populated polarization variants aligned with the applied electric field owing to this strong synergistic interaction plays an important role in enhancing the piezoelectric performances of MPB ferroelectrics. In
addition to providing a further insight into the microstructures of ferroelectrics, the present results have the potential to guide the design of high performance materials.
Understanding the effects of microstructures is the key to achieving the extraordinary properties of functional materials. For ferroelectrics, microstructures are inherently complex due to the structural symmetry breaking from ferroelectric/ferroelastic phase transitions. Morphotropic phase boundary (MPB) ferroelectrics are prime examples with complex domain structures that are widely used as sensors and actuators due to their excellent electromechanical properties and as memories due to their switchable polarization [1-7].

The utility of ferroelectric materials stems from a reversible microstructural redistribution in terms of domain switching, phase transformation, etc. under an external stimulus. Thus, it is important to understand these microstructure evolutions for the development and manipulation of these materials. Significant advances have been achieved to understand how domain switching influence the macroscopic properties of ferroelectrics by using various experimental methods including piezoresponse force microscopy (PFM), transmission electron microscopy (TEM), light microscope, and computer simulations et al [8-14]. On the other hand, electric-field-driven phase transformations have been commonly observed in ferroelectric bulk single crystals, epitaxial thin films, and polycrystalline ceramics. The examples are Pb/Bi–based ceramics [15-19], (Bi\(1/2\)Na\(1/2\))TiO\(_3\)–based, BaTiO\(_3\) ceramics [20-24], Pb(Zn\(1/3\)Nb\(2/3\))O\(_3\)–PbTiO\(_3\) (PZN-PT) single crystals [25], and BiFeO\(_3\) thin films [26]. In diverse susceptible MPB ferroelectrics, as we reckon, domain switching and phase transformation may invariably work cooperatively in response to external stimuli, which ultimately leads to desirable ferroelectric or piezoelectric properties.

Despite there have been extensive theoretical and experimental investigations on domain switching and phase transformation, the synergetic nature of both critical components remains unclear for the MPB polycrystalline ferroelectrics. The problem is mainly due to the lack of quantitative, in-situ, and comprehensive characterization techniques. Recently, the state-of-art in-situ high-energy synchrotron x-ray diffraction (SXRD) combined with 2D scattering geometry technology, and neutron scattering technique allow one to simultaneously extract the information on the phases, crystal
structures, and domain switching [15,27-29]. For examples, Hinterstein et al. have emphasized the structural contribution to the high piezoelectricity in soft PZT ceramics [16,19]. Jones et al. have investigated the domain wall displacement on various piezoelectric ceramics [24,30]. Our recent studies have revealed the quantitative relation between piezoelectric responses and electric-field-driven phase transformation [15] and the unique role of monoclinic phase in high-performance piezoelectrics [27-29].

In this Letter, the hidden correlation between the electric-field-driven phase transformation and domain switching has been ascertained in a high-$T_C$ and high-performance MPB piezoceramics of 0.64PbTiO$_3$-0.36BiScO$_3$ (PT-36BS) by in-situ high-energy SXRD combined with 2D scattering geometry technology. The electric-field-driven collective microstructure evolution and phase content are quantitatively analyzed, in which both domain switching and phase transformation are observed to exhibit distinct and correlated characters depending on the electric field direction. Intriguingly, a strong synergistic interaction has been revealed between emerging phase transformation and enhanced domain switching. Subsequent phase-field simulations confirm our experimental finding, which demonstrates a visualized and enhanced polarization variant alignment via the synergistic interaction between domain switching and phase transformation. The present results may provide new insights to other ferroic materials, such as ferroelastics and martensites.

The PT-36BS ceramics of MPB composition were prepared by a conventional solid-state method [31]. The ceramic samples were well sintered, which can be reflected by high value of piezoelectric coefficient ($d_{33} = 430\pm20$ pC/N) and the well saturated shape of bipolar $P$-$E$ and $S$-$E$ curves (see Fig. S1 of Supplemental Material [32]). In-situ high-energy diffraction experiments were performed at 11-ID-C at Advanced Photon Source (APS) at Argonne National Laboratory. The x-ray beam had a spot size of 0.5 mm $\times$ 0.5 mm, photon energy of about 110 keV and a wavelength of 0.11165 Å. The direction of electric field was perpendicular to the beam line. As shown in the experimental geometry (Fig. S2 of Ref [32]), it is important to note that the orientation parallel to the electric field is defined as $\varphi = 0^\circ$, while perpendicular to
the electric field as $\phi = 90^\circ$. Extensive experimental details are provided in the Supplemental Material.

Figure 1(a) and 1(b) shows the electric field evaluation of the $\{200\}_{pc}$ profile of PT-36BS at two representative directions of $\phi = 0^\circ$ and $90^\circ$, which exhibits a pronounced tetragonal (T) character. A strong domain texture ($f_{002,T}$) can be observed in PT-36BS similar to other ferroelectrics [33,34]. The relative intensity of tetragonal two reflections changes significantly with electric field. It indicates electric-field-driven rearrangement of domains at the $\phi = 0^\circ$ and $90^\circ$. However, if the orientation direction is shifted to $\phi = 45^\circ$, a strikingly different behavior is found in the middle peak between the two T ones [Fig. 1(c)]. All peaks markedly changes in intensity, in which the middle peak particularly increases while the other two T ones decrease with increasing electric field. It suggests electric-field-driven phase transformation occurs at the $\phi = 45^\circ$ but not $\phi = 0^\circ$ or $90^\circ$. As shown in Fig. 1(a)-(c), an interesting phenomenon is that phase transformation is orientation dependent. If depicting the intensity of $\{002\}_{pc}$ profiles as function of orientation at $E = 5$ kV/mm [Fig. 1(d)], the $\{002\}_{pc}$ profiles show a strong anisotropic at various orientation. The middle peak of second phase varies with orientation, which acts as a bridge smoothly connecting the two peaks of T phase.

As for the phase structure of the electric-field-driven middle peaks, it may be interpreted as the $(002)_{M}$ and $(220)_{M}$ reflections of monoclinic (M) phase ($Cm$) or the $(200)_{R}$ reflection of rhombohedral (R) phase [35,36]. However, due to the fact of two-phase coexistence, it is not reliable to determine the detailed crystal structure of electric-field-driven phase. It needs to note that the middle profile can be better fitted by a two-peak model, which signifies that the electric-field-driven phase is more likely the monoclinic one. Here, we define the electric-field-driven reflection as $\{002\}_{pc,R/M}$ based on the pseudo-cubic perovskite unit cell. In order to quantitatively evaluate phase fraction, and domain texture, the $\{002\}_{pc}$ profiles were fitted by four peaks using pseudo-Voigt function (Fig. S3 of Ref [32]). Since a similar pseudo-cubic structure is for tetragonal, rhombohedral, or monoclinic phase, the integrated area of the individual peak can be directly proportional to the volume phase fraction of each
phase. The percentage of the tetragonal \(\{002\}_{pc}\) peaks area with respect to the sum area represents the phase fraction of tetragonal phase (\(\xi_T\)). The peak intensity of T phase is utilized to quantify the electric-field-driven domain texture (\(f_{002,T}\)). The value of \(f_{002,T}\) is 1 for an unpoled state, and 3 for a saturated state. The details can be seen in the Supplemental Material.

Figure 2(a) shows phase fraction distribution as function of both electric field and orientation. It is interesting to find that the T phase exhibits an inhomogeneous distribution. It actually displays a U-shape distribution as function of electric field and orientation. As shown in Fig. 2(b), an interesting feature is that the magnitude of electric-field-induced phase transformation much depends on orientation (\(\phi\)). Large T phase content is observed at either \(\phi = 0^\circ\) or \(90^\circ\), which also keeps unchanged in the whole orientation. For example, at the \(\phi = 0^\circ\) parallel to the electric field, the T phase fraction is almost identical of 81% and 79% for 0 kV/mm (poled state) and 5 kV/mm, respectively. Intriguingly, as the orientation moves to the \(\phi = 45^\circ\), the phase transformation is trigged by loading electric field. For example, the T phase fraction decreases drastically from 76% at 0 kV/mm (poled state) to 53% at 5 kV/mm. The above results suggest that electric-field-driven phase transformation is energy favorable at the orientations of \(\phi\) near 45° but suppressed at \(\phi\) near 0° or 90°. Moreover, such orientation dependent electric-field-driven phase transformation is fully reversible. For example, the T phase fraction of \(\phi = 45^\circ\) manifests as a butterfly shape when a bipolar electric field is applied (Fig. S4 of Ref [32]). It is worth noting that the pronounced phase transformation was previously observed in soft PZT ceramics at similar 45° scattering geometry [16].

Domain switching is another important factor for ferroelectrics. Here, we utilize the difference in domain texture fraction [15,37], \(\Delta f_{002,T}^{E} = f_{002,T}^{E} - f_{002,T}^{E_0}\), to describe the relative change of domain switching with respect to the poled state at 0 kV/mm by loading electric field [Fig. 2(c) and (d)]. The value of \(f_{002,T}^{E_0}\) is the poled state at 0 kV/mm. As shown in Fig. 2(c), the domain texture also exhibits an inhomogeneous distribution, which is an inverted T-shape as function of orientation.
and electric field. This orientation dependent domain texture agrees with the previous reports [38,39]. At $\phi = 0^\circ$ parallel to electric field, the $\Delta f_{002,T}$ is increased to 0.54 at 5 kV/mm, while it is reduced to −0.34 for $\phi = 90^\circ$ perpendicular to electric field [Fig. 2(d)]. It indicates the common phenomenon that more domains are aligned the electric field direction ($\phi = 0^\circ$). At the above both orientations, domain switching exhibits most active. However, for $\phi$ near 45°, the domain switching ability is almost suppressed with the value of $\Delta f_{002,T}$ identical to 0 [Fig. 2(d)], which manifests as a negligible domain switching feature. It implies no energetic benefit for non-180° domain switching near this orientation.

If comparing Fig. 2 (a) and (c), one can capture an intuitive synergetic interaction between phase transformation and domain switching. To quantitatively estimate the tendency of domain switching and phase transformation response to electric field, the absolute values of $df_{002,T}/dE$ and $d\xi_T/dE$ were calculated as function of orientation [Fig. 3(a)]. At a fast glance, a synergetic interaction can be observed between domain switching and phase transformation. At the orientations of $\phi = 0^\circ$ or 90°, the $|df_{002,T}/dE|$ reaches the highest value, which is 0.102 (kV/mm)$^{-1}$, and 0.072 (kV/mm)$^{-1}$, respectively. It means that the domains of PT-36BS are most switchable at the directions parallel or perpendicular to the electric field. Simultaneously, no phase transformation occurs. The value of $d\xi/dE$ is close to 0 for both $\phi = 0^\circ$ and 90°. However, as the orientation changes to $\phi = \sim 45^\circ$, it is interesting to observe that the value of $|df_{002,T}/dE|$ is remarkable approximate 0, while the $d\xi/dE$ reaches the maximum value (4.2 %·(kV/mm)$^{-1}$). It means that at the orientation of $\phi = \sim 45^\circ$ domain switching is negligible but phase transformation is remarkably enhanced. For the intermediate orientations, both domain switching and phase transformation occur simultaneously. The roles of domain switching and phase transformation are complementary, which reveals the strong synergistic interactions. Overall, under application of electric field, when the ability of domain switching is limited, the phase transformation is enhanced, and vice versa. It is important to note that such interesting synergetic interaction is also observed in soft PZT ceramics which exhibit high-performance piezoelectric response ($d_{33} = 500$ pC/N) (Fig. S5 of Ref [32]).
In order to elucidate how such synergetic interaction determines the high piezoelectric response at the MPBs, we also have conducted in-situ experiments for non-MPB composition of T phase PT-34BS ($d_{33} = 260 \text{ pC/N}$) as a comparison. As anticipated, the macroscopic unipolar strain of the MPB composition is much higher than that of the non-MPB T phase [Fig. 3(c)]. For instance, at $E = 6 \text{ kV/mm}$, the strain is 0.31% and 0.22% for the MPB and non-MPB phases, respectively. Importantly, the synergistic interaction cannot be observed for the non-MPB T phase, in which there is only domain switching but not phase transformation (Fig. S6 of Ref [32]). Moreover, the ability of domain switching of the non-MPB T phase is much lower than that of the MPB one [Fig. 3(b)]. The role of such strong synergistic interaction can be directly reflected by the difference in lattice strain ($\varepsilon$) at $\phi = 0^\circ$, which of $\{111\}_{pc}$ profile is as large as 0.30% for the MPB composition ($5 \text{ kV/mm}$, $d_{33}^* = 600 \text{ pm/V}$), but 0.09% for the non-MPB phase ($5 \text{ kV/mm}$, $d_{33}^* = 180 \text{ pm/V}$) [Fig. 3(d)].

Phase-field modelling enables direct visualization of ferroelectric polarization switching via domain switching and phase transformation [40,41]. Here, we adopt a MPB PZT composition to interpret such synergistic interaction. The orientation dependent polarization switching behavior can be understood by applying an electric field along different directions. The initial domain structures are presented in Fig. 4(a). When the electric field applied along the $x$ axis ($\phi = 0^\circ$), the domains of T phase align with the electric field direction, while the limited phase transformation of T-to-R can be observed. A single domain structure can be observed at the maximum applied electric field [Fig. 4(b)]. While for the orientations of $\phi = 30^\circ$ and $45^\circ$ [Fig. 4 (c) and (d)], both domain switching and T-to-R phase transformation are observed. Two kinds of domains correspond to T and R phases. Intriguingly, at the final state of $\phi = 45^\circ$ the T phase completely transforms into the R phase with single domain. At $\phi = 45^\circ$ the unique engineered domain configuration for T phase leads to a negligible non-180° domain switching, if no phase transformation occurs. Since there is no energetic benefit for favoring one ferroelastic variations over another. However, in such case the polar axis of R/M phase is along or close to electric field direction. The reversible phase transformation of T-to-R/M can be triggered. Importantly, such a reversible
phase transformation has been widely utilized to enhance piezoelectric performance of single crystal via domain engineering, such as Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ [25]. The extensive final domain structures of different electric field orientations are shown in Fig. S7 of Ref [32]. Fig. 4(e) shows the individual phase fraction of T and R phases as function of orientation, which can be achieved through accumulating the domain fraction of each phase. It is interesting to observe a similar phase fraction distribution as function of orientation, which is well consistent with the experimental results [Fig. 2 (a) and (b)].

It is known that most ferroelectric materials adopted in technical applications are polycrystalline consisting of large number of randomly oriented grains. Owing to the inter-granular and domains constraints, domain switching depends on grain orientations [Fig. 3(a)]. Polarization tends to align as closely with the applied electric field direction as allowed by the crystallite orientation. The emergence of reversible phase transformation can activate some inactive domains, and promotes flexible polarization extension, which enables more polarization variations aligned along the electric field direction. The electric-field-driven T-to-R phase transformation is considered as 54° domain switching or polarization rotation to improve polarization alignment [19]. Such strong synergistic interaction between phase transformation and domain switching can minimize the electrostatic energy in polycrystalline ferroelectrics [42].

In summary, the electric-field-driven phase transformation and domain switching evolution have been investigated in polycrystalline MPB ferroelectrics by using a combination of in-situ high-energy SXRD technology and phase-field simulations. Under an external electric field, a strong synergy between an emerging reversible phase transformation and enhanced domain switching has been observed near MPBs. Such a strong synergy plays an important role in enhancing the piezoelectric responses near MPBs by enabling more polarization variants aligned with the applied electric field. The present results deepen the understanding of the microstructures in MPB ferroelectrics, and it will be helpful for the design of high performance piezoelectric materials.
Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21731001, 21590793, and 11504020), The National Program Support of Top-notch Young Professionals, and Program for Chang Jiang Young Scholars, and the Fundamental Research Funds for the Central Universities, China (Grant No. FRF-TP-17-001B). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. H. L. thanks the financial support from China Scholarship Council. L.-Q. C. is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-FG02-07ER46417.
1 References

Figure Legends

FIG. 1. Contour plots of diffraction patterns of \( \{200\}_pc \) profile. (a) 0° sector \((\varphi = 0°)\), (b) 90° sector \((\varphi = 90°)\) (c) 45° sector \((\varphi = 45°)\), and (d) as function of \( \varphi \) at max electric field \((E = 5 \text{ kV/mm})\).

FIG. 2. (a) Distribution of the tetragonal (T) phase fraction as function of both electric field and orientation \((\varphi)\). (b) The tetragonal (T) phase fraction \((\xi_T)\) as functions of electric field at various orientations. (c) Distribution of absolute changes of domain texture fraction \((|\Delta f_{002,T}|)\) as function of both electric field and orientation \((\varphi)\). (d) Changes of domain texture fraction \((\Delta f_{002,T})\) as function of electric field and orientation.

FIG. 3. (a) Strong synergy of phase transformation and domain switching for the composition of PT-36BS at MPB as function of orientation \((\varphi)\). (b) Domain switching of non-MPB tetragonal phase of PT-34BS as function of orientation \((\varphi)\). (c) Measured macroscopic strain. (d) Lattice strain \((\varepsilon)\) of the \(\{111\}_pc\) profile.

FIG. 4. Phase-field modeling of PZT single crystal under applied electric field with different directions. (a) The initial domain structure. Polarization switching evolution along different electric field directions (b) \(\varphi = 0°\), (c) \(\varphi = 30°\), and (d) \(\varphi = 45°\), and the enlarged square area shows the polar vectors. (e) T and R phase fraction of the final state as functions of the orientation of electric field \((\varphi)\).