Shear strain-induced anisotropic domain evolution in mixed-phase BiFeO$_3$ epitaxial films

Cite as: AIP Advances 9, 025114 (2019); https://doi.org/10.1063/1.5080709
Submitted: 11 November 2018 . Accepted: 30 January 2019 . Published Online: 19 February 2019

Han Xu, Zuhuang Chen, Xiaoyi Zhang, Yongqi Dong, Bin Hong, Jiangtao Zhao, Lang Chen, Sujit Das, Chen Gao, Changgan Zeng, Haidan Wen, and Zhenlin Luo

ARTICLES YOU MAY BE INTERESTED IN

Mixture domain states in PbTiO$_3$ film with potentials for functional application
Applied Physics Letters 114, 242901 (2019); https://doi.org/10.1063/1.5093798

Effect of “symmetry mismatch” on the domain structure of rhombohedral BiFeO$_3$ thin films
Applied Physics Letters 104, 182908 (2014); https://doi.org/10.1063/1.4875801

Ferroelectric or non-ferroelectric: Why so many materials exhibit “ferroelectricity” on the nanoscale
Applied Physics Reviews 4, 021302 (2017); https://doi.org/10.1063/1.4979015
Shear strain-induced anisotropic domain evolution in mixed-phase BiFeO$_3$ epitaxial films

Han Xu, Zuhuang Chen, Xiaoyi Zhang, Yongqi Dong, Bin Hong, Jiangtao Zhao, Lang Chen, Sujit Das, Chen Gao, Changgan Zeng, Haidan Wen, and Zhenlin Luo

AFFILIATIONS
1 National Synchrotron Radiation Laboratory & CAS Key Laboratory of Materials for Energy Conversion, Department of Physics, University of Science and Technology of China, Hefei 230026, China
2 Department of Materials Science and Engineering, University of California, Berkeley, California 94720, USA
3 X-Ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States
4 Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China

ABSTRACT
Understanding and controlling the domain evolution under external stimuli in multiferroic thin films is critical to realizing nanoelectronic devices, including for non-volatile memory, data storage, sensors, and optoelectronics. In this article, we studied the shear-strain effect on the domain evolution with temperature in highly strained BiFeO$_3$ thin films on rhombohedral LaAlO$_3$ substrates using a high-resolution synchrotron X-ray diffraction three dimensional-reciprocal space mapping (3D-RSM) technique. The results revealed significant biaxial, anisotropic, evolution behaviors of the mixed-phase ($M_C + R'/T'$ phases) BiFeO$_3$ ferroelectric domains along the in-plane [100] and [010] axes. These biaxial, anisotropic, evolution behaviors were attributed to the shear-strain-modulated transition pathways of the mixed-phase ferroelectric domains. This viewpoint was further verified in the BiFeO$_3$/LaSrAlO$_4$ (001) system in which no anisotropic evolution behaviors of the mixed-phase domains were found. This work sheds light on the quantitative analysis of domain evolution in multi-domain systems and demonstrates that the shear-strain effect could act as an effective tool to manipulate the domain behavior and control novel functionalities of ferroelectric thin films.

I. INTRODUCTION
Ferroelectric thin films usually form domains that minimize the total free energy of the system. The domain evolution with external stimuli (e.g., thermal, electric field, strain) has a profound impact on the dielectric permittivity, piezoelectric response, and polarization switching behavior. In addition, recent studies have shown that domain walls themselves can possess additional functionalities (e.g., electric conductivity and enhanced magnetization) and have the potential to exhibit other interesting effects. Therefore, it is important to deterministically control the domain evolution with external stimuli in ferroelectric thin films. Among ferroelectrics, BiFeO$_3$ has been extensively studied because of its room temperature multiferroicity with potential applications in nanoelectronic and spintronic devices. Detailed studies have reported that large compressive strains can induce a morphotropic phase boundary (MPB)-like behavior and create large piezoelectric responses in BiFeO$_3$ films. Multiple low-symmetry phases, including monoclinic $M_C$, $M_A$, and two tilted triclinic ($R'$ and $T'$) phases have been revealed in BiFeO$_3$ films grown on LaAlO$_3$ (001) substrates. On the other hand, strain engineering has been extensively studied to control the domain structure of various epitaxial ferroelectric films, with most researchers focused on the mismatch of the lattice parameters. To date, there have been few studies that consider the shear-strain effect...
that originates from symmetry mismatch (i.e., mismatch of the in-plane lattice angle).\textsuperscript{21–25} Previously, studies on BiFeO$_3$ (rhombohedral)/SrTiO$_3$ (cubic) have shown that the crystal symmetry of the system plays a critical role in the domain variant selection\textsuperscript{25,26} Unlike SrTiO$_3$ substrates, LaAlO$_3$ is a prototypical perovskite ferroelastic material and possesses a rhombohedral-distorted perovskite structure ($\alpha$ = 3.789 Å, $\alpha$ = 90.1$^\circ$) below 550 $^\circ$C.\textsuperscript{27–30} Thus, LaAlO$_3$ substrates could introduce an effective additional shear-strain $\sigma_s$ to the clamped BiFeO$_3$ lattice. Theoretically, the shear-strain provided by the rhombohedral-distorted substrate is uniaxial. Thus, we can expect anisotropic behaviors from the epitaxial film.

In this article, the domain evolution behavior of mixed-phase (monoclinic $M_C$, $M_A$, and two tilted triclinic $R'/T'$ phases) BiFeO$_3$ films grown on a LaAlO$_3$ substrate are systematically and quantitatively examined by employing a synchrotron-based X-ray diffraction three dimensional-reciprocal space mapping (3D- RMS) technique.\textsuperscript{17} It is found that along the in-plane pseudocubic [100] and [010] axes, biaxial anisotropy exists in the temperature-dependent evolution of the BiFeO$_3$ ferroelectric domains. The biaxial anisotropic behaviors are attributed to the in-plane uniaxial shear-strain $\sigma_s$, which is believed to modulate the transition pathways between the $R'$, $T'$, and $M_A$ domains. This interpretation is further supported by the domain evolution behavior of BiFeO$_3$ films epitaxially grown on tetragonal (001)-LaSrAlO$_3$ substrates in which no anisotropy was found. Our results reveal that modulating the shear-strain is an effective approach to engineer the domain structure and its evolution.

II. EXPERIMENTS

A. Thin film growth and microscopy characterizations

Epitaxial, BiFeO$_3$, thin films were grown on LaAlO$_3$ (001) and LaSrAlO$_3$ (001) single crystal substrates (CrysTech GmbH) using pulsed laser deposition (PLD) (KrF excimer laser, $\lambda$ = 248 nm) with a stoichiometric ceramic target of Bi$_2$Fe$_2$O$_5$ (MTI). The deposition temperature was maintained at 700 $^\circ$C and the oxygen pressure was at 100 mTorr. After the deposition, the films were cooled to room temperature at a rate of 5 $^\circ$C/min in oxygen at 760 mTorr. The thickness of the BiFeO$_3$ films was 50 nm on both the LaAlO$_3$ and LaSrAlO$_3$. The BiFeO$_3$/LaAlO$_3$ (001) samples with qualified LaAlO$_3$ ferroelastic domains were carefully checked using an OLYMPUS BX51 polarizing optical microscope in transmission mode. Atomic force microscopy (AFM) and piezoresponse force microscopy (PFM) were performed with a Bruker Dimension Icon microscope and Cypher scanning probe microscope, respectively.

B. Synchrotron three-dimensional x-ray reciprocal space mapping experiments

The 3D-RSM experiments were performed at the 11-1D- D and 12-1D-D stations of the Advanced Photon Source (APS) located at Argonne National Lab. The synchrotron photon energy was 13.14 KeV ($\lambda$ = 1.0598 Å). During the measurements, an area detector (Pilatus100k) was fixed at certain $2\theta$ positions (BiFeO$_3$/LaAlO$_3$ 003 peak: 42.2$^\circ$; BiFeO$_3$/LaAlO$_3$ -104 peak: 60.7$^\circ$; BiFeO$_3$/LaSrAlO$_3$ 002 peak: 29.3$^\circ$) and the sample was moved along the $\theta$-axis. Thus, a series of 2D diffraction patterns were collected in sequence. Then, Matlab programs were used to reconstruct the 3D diffraction patterns in reciprocal space using these 2D diffraction patterns. All diffraction patterns are presented in the reciprocal units of the utilized substrates (LaAlO$_3$ and LaSrAlO$_3$).

III. RESULTS AND DISCUSSION

A. Epitaxial BiFeO$_3$ films structure studies

It has been shown that annealing treatments reconstruct the ferroelastic domain structure of LaAlO$_3$ substrates.\textsuperscript{29} If the resulting domains are random, the shear-strain effect is averaged and cannot be detected. The initial step in studying the intrinsic uniaxial shear-strain effect in mixed-phase BiFeO$_3$ films is to eliminate the unqualified BiFeO$_3$/LaAlO$_3$ samples in which the LaAlO$_3$ ferroelastic domains are random. This step was performed by employing the transmission mode during a polarizing microscope analysis (see Fig. S1 for details) of the prepared BiFeO$_3$/LaAlO$_3$ samples. Large scale (40x40 $\mu$m) AFM results (Fig. 1(a)) reveal a qualified bare LaAlO$_3$ substrate with an in-plane uniaxial shear-strain $\sigma_s$ parallel to the [100] axis. The AFM and PFM results display the typical domain structure for the mixed-phase BiFeO$_3$ film that was composed of $M_C$ (transfers into $M_A$ at 90 $^\circ$C) + $R'/T'$ stripe domains (Figs. 1(b) and 1(d)). The saw-toothed $R'/T'$ stripe domains that were embedded in the $M_C$ phase matrix\textsuperscript{10,11} are labeled in Fig. 1(c).

The uniaxial $\sigma_s$ and $M_C + R'/T'$ mixed-phase domain structure enabled investigating the ferroelectric domain evolution while modulating the shear-strain. Thus, in-situ temperature-dependent 3D-RSM measurements were performed on the BiFeO$_3$/LaAlO$_3$ films from the room temperature mixed-phase state to the as-deposited high-temperature single phase state (Figs. 1(e)–1(f)). See Figs. S2 and S3 for details). Taking the 3D-RSM results at 30 $^\circ$C (Fig. 1(e)) as an example, the splitting of the diffraction patterns corresponds to the mixed-phase domain twins in real space (see Figs. S2 and S3 for details). At L = 2.75, the eight split diffraction spots represent the domain variants of the $R'$ phase. The $R'$ domains that tilt along the $\pm$H00 ($//\sigma_s$) and $\pm$0K0 ($\perp\sigma_s$) axes are denoted as $R'//$ and $R'\perp$ (labeled in Fig. 1(e)). Similarly, the diffraction spots at L = 2.45 represent the tilt domain variants of the $T'$ phase. The diffraction tails extend from $R'$ to the $T'$ diffraction spots and reveal the twin relationship of the adjacent $R'/T'$ domain. Consistent with previous temperature-dependent diffraction studies, the BiFeO$_3$/LaAlO$_3$ films experienced a sequence of phase transformations as the temperature increased: $M_C + R'/T' \rightarrow M_A + R'/T' \rightarrow M_A \rightarrow T'$, as shown in Fig. 1(f).

B. Shear-strain-modulated biaxial anisotropic ferroelectric domain evolution behavior

The 3D-RSM results of the $R'/T'$ mixed-phase domains were analyzed quantitatively. The results were first projected
on the HL (K = 0) and KL (H = 0) planes. Figures 2(a) and 2(b) present the temperature-dependent evolution of $R'_{//}/T'$ (Fig. 2(a)) and $R'_{\perp}/T'$ (Fig. 2(b)). Although the $T'$ phase shows no anisotropic behaviors, the difference between the temperature-dependent evolutions of the $R'_{//}$ and $R'_{\perp}$ phase domains are obvious. So, the diffraction spots of $R'_{//}$ and $R'_{\perp}$ were analyzed and are presented in Figs. 2(c)–2(e). The results reveal the significant biaxial anisotropy of the temperature-driven evolution for both domain volume ratios (normalized diffraction intensity), domain tilt angles, and the interfacial strains at the $R'_{//}/T'$ domain wall. Firstly, the normalized intensity of the diffraction spots indicates that the $R'_{\perp}$ disappeared much faster than the $R'_{//}$. For example, when the temperature increased from 30 to 200 °C, approximately 60% of the $R'_{//}$ still existed while only about 15% of the $R'_{\perp}$ remained (Fig. 2(c)). Secondly, the tilt behaviors of the $R'_{//}$ and $R'_{\perp}$ are significantly different, with $R'_{//}$ showing a faster rate of change. Finally, the interfacial strain at the $R'_{//}/T'$ domain wall increases with temperature, indicating a significant strain relaxation at higher temperatures.
$R'$, domains show different evolution tendencies. Figure 2(d) shows that the domain tilt angle of the $R'/T'$ increased abruptly above 130 °C. In contrast, the domain tilt angle of the $R'_1$ remained nearly the same during the phase transition. Thirdly, the interfacial strain at the $R'/T'$ domain wall was also analyzed (Fig. 2(e)). The out-of-plane lattice mismatch strain is defined as $c_R/c_T - 1$, where $c_R$ ($c_T$) is the out-of-plane lattice parameter of the $R'$ ($T'$) phase. It was observed that the interfacial strain in the $R'/T'$ domains increased quickly above 130 °C, while the interfacial strain in the $R'_1$ domains decreased gradually. The above analysis demonstrates a significant in-plane anisotropy for the BiFeO$_3$ ferroelectric domain evolution.

C. Shear-strain-modulated transition pathways

Further calculations were performed to understand how the uniaxial shear-strain $\sigma_s$ modulates the anisotropic ferroelectric domain evolution behavior of a mixed-phase BiFeO$_3$ film. Our results reveal that the shear-strain $\sigma_s$ modulates the transition pathways of the $M_3$ (transforms into $M_9$ at 90 °C) and $R'/T'$ mixed-phase domains. Previously, it has been shown that the mixed-phase domains are composed of two phase transition pathways: (i) the transition between the $R'$ and $T'$ phases; and (ii) the transition between the $R'$ and $M_9$ phases. The transition pathway-2 requires a minimal domain tilt (in-plane domain distortion $\approx 0.3°$, see Fig. S4 for details) while a relatively large distortion/tilt is needed for the transition pathway-1. The transition pathway-1 is accompanied by the domain wall shifting from $T'$ into $R'$ with lower inclined domain wall angles (from 34° to 24° during the transition). A previous high-resolution transmission electron microscope (HTEM) analysis revealed a remarkable epitaxial relationship between adjacent $R'$ and $T'$ domain twins, although the out-of-plane lattice mismatch reached up to 12%. Therefore, there should exist a geometrical relationship between adjacent $R'/T'$ domain twins for the transition pathway-1.

As shown in Fig. 3(a), the periodic $R'/T'$ domain twins form an extended domain stripe. The periodic structure shows that the changes of the saw-toothed $R'/T'$ domain stripe could be described as a fluctuating triangle, which is labeled in Fig. 3(b). The fluctuating triangle determines the geometrical structure of the $R'/T'$ domain twin (Fig. 3(c)), which is based on the epitaxial relationship between adjacent $T'$ and $R'$ phases. As shown in Fig. 3(d), the epitaxial lattice requires the geometrical polygon relationship (labeled as the blue polygon in Fig. 3(d)) between the lattice layer of the $T'$ and $R'$ phases,

$$c_R/sin(\alpha - \theta_R) = c_T/sin(\alpha + \theta_T),$$ (1)

where $c_R$ ($c_T$) is the out-of-plane lattice of the $R'$ ($T'$) phase, $\theta_R$ ($\theta_T$) is the domain tilt angle of the $R'$ ($T'$) domains, and $\alpha$ is the angle between the domain wall and the substrate (labeled in Figs. 3(c) and 3(d)). Thus,

$$\alpha = atan((\sin(\theta_T) + \mu \times \sin(\theta_R))/(\cos(\theta_T) + \mu \times \cos(\theta_R))),$$ (2)

where $\mu = c_R/c_T$. Using the parameters obtained at 30 °C ($\theta_R = 2.6°$, $\theta_T = 1.5°$, and $\mu = 4.66\text{Å}/4.17\text{Å}$), $\alpha$ was calculated to be 33.6°. This result is consistent with previous HTEM results (~34°), which confirms the effectiveness of the geometrical model. Subsequently, we further calculated the domain widths for the $R'$ and $T'$ phases (Fig. 3(c)),

$$w_R = h/tan(\theta_R) - h/tan(\alpha),$$ (3)

$$w_T = h/tan(\theta_T) + h/tan(\alpha),$$ (4)

where $h$ is the height of the fluctuating triangle, and $w_R$ and $w_T$ are the domain widths of the $R'$ and $T'$ phases, respectively (labeled in Fig. 3(c)). Therefore, the evolution of the $R'$ phase
through transition pathway-1 (between $R'$ and $T'$ phases) can be calculated,

$$P_R = \frac{V_R}{V_T + V_T}, \quad (5a)$$

$$S_{R/T} = w_T/(S_{R/T} + S_{R/T} + w_T), \quad (5b)$$

$$S_{\theta_{R/T}} = (1/\tan(\theta_T) - 1/\tan(\theta_T))/((1/\tan(\theta_T) + 1/\tan(\theta_T))), \quad (5c)$$

where $V_R$ is the domain volume of the $R'$ ($T'$) phase, $S_{R/T}$ is the cross-sectional area of the $R'/T'$ domain stripe, and $P_R$ is the domain proportion of the $R'$ phase in the $R'/T'$ domain twin.

Finally, the proportion of the $R'$ phase that transforms through transition pathway-1 (between $R'$ and $T'$) can be calculated (the values of all used parameters are labeled in the supplementary material Table I). By comparing these calculated $P_R$ with the experimental results (Fig. 2(c)), we evaluated the ratios of $R_{/T}$ and $R_{/T}$ that transform through the two transition pathways. The obvious discrepancy shown in Fig. 4(a) indicates that the uniaxial shear-strains indeed modulate the transition pathways of the $R'$ phase: (1) $R_{/T}$ transforms through both pathways with increasing temperature (27% pathway-1 + 15% pathway-2); and (2) the $R'$ primary goes through transition pathway-2 (between $R'$ and $M_A$), thus transforming mostly into the $M_A$ phase (10% pathway-1 + 74% pathway-2).

D. Study of BiFeO$_3$/LaSrAlO$_3$ 3D-RSM results

To further verify the observations in the previous section, mixed-phase BiFeO$_3$ epitaxial films grown on tetragonal symmetric substrates were fabricated and measured. The experimental results from a 50-nm-thick BiFeO$_3$ film grown on (001)-LaSrAlO$_3$ (tetragonal phase, $a = b = 3.75\, \text{Å}$, $c = 12.6 \, \text{Å}$) are presented in Figs. 5(a)–5(c). The AFM image indicates the typical surface morphology of a mixed-phase BiFeO$_3$ that consists of $M_C + R'/T'$ ferroelectric domains (Fig. 5(a)). The 3D-RSM results reveal a typical $M_C - M_A - T$ phase transition sequence as the temperature increased (see
Figs. S5 and S6 for details). Interestingly, further obtained temperature-dependent evolutions of the $R'$ phase domains that tilt along the H00 and OK0 axes (denoted $R'_{H00}$ and $R'_{OK0}$) are also similar to the $R'_{/}$ domains in the BiFeO$_3$/LaAlO$_3$ films (Fig. 2(d)), and no biaxial anisotropic behaviors were observed (Figs. 5(b) and 5(c)). This unambiguously demonstrates that the interfacial shear–strain is the origin of the anisotropic domain evolution behavior in the BiFeO$_3$/LaAlO$_3$ system.

IV. CONCLUSIONS

Our study demonstrates that by taking the intrinsic crystal symmetry of a substrate as the variable, ferroelectric domains could be engineered to reveal the anisotropic domain evolution process through modulation of the in-plane interfacial shear–strain. Our quantitative synchrotron X-ray diffraction 3D-DEP 3D-RSM results reveal that the domain volume, domain tilt angle, and interfacial strain at the domain wall of the mixed-phase ($M_C + R'_{/} + T$) phases BiFeO$_3$ films exhibit biaxial anisotropic evolutionary behavior. These behaviors could be attributed to two phase transition pathways ($R'_{/}$ and $R'_{/}$) which are strongly modulated by the uniaxial shear–strain field that originates from the symmetry mismatch between the LaAlO$_3$ substrates and BiFeO$_3$ films. This conclusion was further supported by comparing the BiFeO$_3$ epitaxial films grown on tetragonal LaSrAlO$_3$ substrates in which no biaxial anisotropic evolution behaviors were observed. Our work clearly demonstrates that shear-strain effect can be an effective tool to manipulate the ferroelectric domain structure to employ new properties and functionalities.

SUPPLEMENTARY MATERIAL

See the supplementary material for information on the Selection of qualified samples using polarizing microscope, Complete 3D-DEP 3D-RSM results of BiFeO$_3$/LaAlO$_3$. Tilt angle of BiFeO$_3$ domains in BiFeO$_3$/LaAlO$_3$. Table of parameters used for calculation, and 3D-DEP results of BiFeO$_3$/LaSrAlO$_3$.

ACKNOWLEDGMENTS

The authors thank the beamline staff at the Advanced Photon Source (APS) Sectors II-1D-D and 12-ID-D. This research was supported by the National key Basic Research Program of China (2016YFA0300102), the National Natural Science Foundation of China (11374010, 11675179, 11434009, U1532142, 51802057), and the Fundamental Research Funds for the Central Universities. Use of the APS, an Office of Science user facility, was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. This work was partially carried out at the USTC center for Micro and Nanoscale Research and Fabrication.

REFERENCES

1. C. T. Nelson, B. Winchester, Y. Zhang, S. J. Kim, A. Melville, C. Adamo, C. M. Folkman, S. H. Baek, C. B. Eom, D. G. Schlom, L. Q. Chen, and X. Q. Pan, Nano Lett. 11, 828 (2011).
2. J. Seidel, L. W. Martin, Q. He, Q. Zhan, Y. H. Chu, A. Rother, M. E. Hawke, P. Maksymovych, P. Yu, M. Gajek, N. Balke, S. V. Kalinin, S. Gemming, F. Wang, C. Catalan, J. F. Scott, N. A. Spaldin, J. Orenstein, and R. Ramesh, Nat. Mater. 8, 229 (2009).
3. J. Seidel, P. Maksymovych, Y. Batra, A. Katan, S. Y. Yang, Q. He, A. P. Baddorff, S. V. Kalinin, C. H. Yang, J. C. Yang, Y. H. Chu, E. H. Salje, H. Wornesteer, M. Salmeron, and R. Ramesh, Phys. Rev. Lett. 105, 197603 (2010).
4. Q. He, C. H. Yeh, J. C. Yang, G. S. Bhalia, C. W. Liang, P. W. Chiu, G. Catalan, L. W. Martin, Y.–H. Chu, J. F. Scott, and R. Ramesh, Phys. Rev. Lett. 108, 067203 (2012).
5. S. Y. Yang, J. Seidel, S. J. Byrnes, P. Shafer, C. H. Yang, M. D. Rossell, P. Yu, Y. H. Chu, J. F. Scott, J. W. Ager, L. W. Martin, and R. Ramesh, Nat. Nano. 5, 143 (2010).
6. J. Seidel, D. F. Su, S. Y. Yang, E. A. Lladó, J. Q. Wu, R. Ramesh, and J. W. Ager, Phys. Rev. Lett. 107, 126805 (2011).
7. D. Schmidt, L. You, X. Chi, J. L. Wang, and A. Rusydi, Phys. Rev. B 92, 075310 (2015).
8. D. Sando, A. Barthelemy, and M. Bibes, J. Phys.: Condens. Matter. 26, 475104 (2014).
9. J. Zeches, M. D. Rossell, I. X. Zhang, A. J. Hart, Q. He, C. H. Yang, A. Kumar, C. H. Wang, A. Melville, C. Adamo, G. Sheng, Y. H. Chu, J. F. Ihliefeld, R. Erni, C. Ederer, V. Gopalan, L. Q. Chen, D. G. Schlom, N. A. Spaldin, L. W. Martin, and R. Ramesh, Science 313, 977 (2009).
10. Z. H. Chen, Z. L. Luo, Y. J. Qi, P. Yang, S. X. Wu, C. W. Huang, T. Wu, J. L. Wang, C. Gao, T. Sritharan, and L. Chen, Appl. Phys. Lett. 97, 242903 (2010).
11. C. H. Chiu, W. J. Liang, C. W. Huang, J. C. Chen, Y. Y. Liu, Y. J. Li, C. L. Hsin, Y. H. Chu, and W. W. Wu, Nano Energy 17, 72 (2015).
12. K. Chu, B. K. Kang, J. H. Sung, Y. A. Shin, E. S. Lee, K. Song, J. H. Lee, C. S. Woo, S. J. Kim, S. Y. Choi, T. Y. Koo, Y. H. Kim, S. H. Oh, M. H. Jo, and C. H. Yang, Nat. Nano. 10, 972 (2015).
13. D. Schmidt, L. You, X. Chi, J. L. Wang, and A. Rusydi, Phys. Rev. B 92, 075310 (2015).
14. K. T. Ko, M. H. Jung, Q. He, J. H. Lee, C. S. Woo, K. Chu, J. Seidel, B. G. Jeon, Y. S. Oh, K. H. Kim, W. I. Liang, H. J. Chen, Y. H. Chu, Y. H. Jeong, R. Ramesh, J. H. Park, and C. H. Yang, Nat. Commun. 2, 567 (2011).
15. Q. He, Y. H. Chu, J. T. Heron, S. Y. Yang, W. I. Liang, C. Y. Kuo, H. J. Lin, P. Yu, C. W. Liang, R. J. Zeches, K. W. Cuo, J. F. Yan, J. T. Chen, C. T. Chen, A. Arezh, A. Scholl, and R. Ramesh, Nat. Commun. 2, 225 (2011).
16. Z. H. Chen, S. Prosandeev, Z. L. Luo, W. Ren, Y. J. Qi, C. W. Huang, L. You, C. Gao, I. A. Kornev, T. Wu, J. L. Wang, P. Yang, T. Sritharan, L. Bello and L. Chen, Phys. Rev. B 84, 094106 (2011).
17. Z. H. Chen, Z. L. Luo, H. Huang, X. Zhou, Z. H. Chen, Y. Yang, L. Wu, C. Zhi, W. Hwang, M. Yang, S. Hu, H. Wen, X. Zhang, Z. Zhang, L. Chen, D. D. Fong, and C. Gao, Appl. Phys. Lett. 104, 182901 (2014).
18. Z. H. Chen, Z. L. Luo, C. W. Huang, Y. J. Qi, P. Yang, L. You, C. S. Hu, T. Wu, J. L. Wang, C. Gao, T. Sritharan, and L. Chen, Adv. Funct. Mater. 21, 133 (2011).
19. Z. H. Chen, J. Liu, Y. J. Qi, D. Y. Chen, S. L. Hus, A. R. Demodaran, X. Q. He, A. T. NDiaye, A. Rockett, and L. W. Martin, Nano Lett. 15, 6506 (2015).
20. H. J. Liu, C. W. Liang, W. I. Liang, H. J. Chen, J. C. Yang, C. Y. Peng, G. F. Wang, F. N. Chu, Y. C. Chen, H. Y. Lee, L. Chang, S. J. Lin, and Y. H. Chu, Phys. Rev. B 85, 014104 (2012).
21. D. G. Schlom, L. Q. Chen, C. J. Fennelle, V. Gopalan, D. A. Muller, X. Q. Pan, R. Ramesh, and R. Uecker, MRS Bulletin 39, 118 (2014).
22. A. G. Zembilgotov, N. A. Pertsev, U. Böttger, and R. Waser, Appl. Phys. Lett. 86, 052903 (2005).
Z. Fan, J. Wang, M. B. Sullivan, A. Huan, D. J. Singh, and K. P. Ong, Sci. Rep. 4, 4631 (2014).

C. W. Huang and L. Chen, Materials 7, 5403 (2014).

Z. H. Chen, A. R. Damodaran, R. Xu, S. Lee, and L. W. Martin, Appl. Phys. Lett. 104, 182908 (2014).

C. J. M. Daumont, S. Farokhipoor, A. Ferri, J. C. Wojdeł, J. Íñiguez, B. J. Kooi, and B. Noheda, Phys. Rev. B 85, 014104 (2012).

K. H. Salje, Annu. Rev. Mater. Res. 42, 265 (2012).

R. J. Harrison, S. A. T. Redfern, and E. K. H. Salje, Phys. Rev. B 69, 144101 (2004).

C. Jutta and E. K. H. Salje, J. Appl. Phys. 85, 722 (1999).

E. K. H. Salje, M. Alexe, S. Kustov, M. C. Weber, J. Schiemer, G. F. Nataf, and J. Kreisel, Sci Rep 6, 27193 (2016).

J. Liu, C. W. Liang, W. I. Liang, H. J. Chen, J. C. Yang, C. Y. Peng, G. F. Wang, F. N. Chu, Y. C. Chen, H. Y. Lee, L. Chang, S. J. Lin, and Y. H. Chu, Phys. Rev. B 85, 014104 (2012).

A. R. Damodaran, C. W. Liang, Q. He, C. Y. Peng, L. Chang, Y. H. Chu, and L. W. Martin, Adv. Mater. 23, 3107 (2011).

H. G. Vlooswijk, B. Noheda, G. Catalan, A. Janssens, B. Barcones, G. Rijnders, D. H. A. Blank, S. Venkatesan, B. Kooi, and J. T. M. de Hosson, Appl. Phys. Lett. 91, 112901 (2007).

D. Zhu and W. Ma, Ceramics International 40, 6647 (2014).