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Probing the domain structure of BiFeO₃ epitaxial films with three-dimensional reciprocal space mapping

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High-resolution 3-Dimensional Reciprocal Space Mapping (3D-RSM) has been performed on mixed-phase BiFeO₃ (BFO) epitaxial films on (001)-oriented LaAlO₃ substrates. Our results demonstrate that 3D-RSM is an effective way to present a structural overview of the different BFO polymorphs, domain variants, and even the interfacial regions between coexisting triclinic phases. The dislocation-free boundaries between the triclinic phases revealed by these 3D-RSMs are believed to be responsible for the large electromechanical response found in mixed-phase BFO films. This study demonstrates the unique merits of the 3D-RSM technique for the structural characterization of ferroic films with complicated domain structures. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4875579>]

Ferroelastic materials, analogous to ferroelectricity and ferromagnetism, exhibit at least two spontaneous strain states that can be switched by external stress, and thus have attracted great attention in past decades due to their interesting physics and practical applications in mechanical sensors and actuators.¹ Although ferroelastic materials are not necessarily ferroelectric or ferromagnetic, most practical ferroelastic materials are either one or the other, where coupling between lattice strain and electric-polarization or magnetization facilitates electric- or magnetic-field controllable mechanical response or the inverse effect. In ferroelectric-ferroelastic materials such as PbZr_{1-x}Ti_xO₃ (Refs. 2 and 3) or highly strained BiFeO₃ (BFO),^{4,5} domains form to minimize the total free energy of the depolarization field and the strain energy.⁶⁻⁸ Accurate determination of crystal phases/domains and their evolution under applied external field is crucial for understanding the large piezoelectric effect found in these materials.

Bulk BFO is rhombohedral with spontaneous polarization along pseudocubic $\langle 111 \rangle$ directions.⁹ When epitaxially grown on (001)-oriented LaAlO₃ (LAO), a super tetragonal (T)-like BFO phase with a giant c/a ratio of ~ 1.24 is stabilized by the large compressive strain,^{4,5} as predicted in recently published temperature-strain phase diagrams.¹⁰ However, once the film thickness exceeds 30 nm, the BFO transforms into a multi-phase structure, with two tilted triclinic BFO phases (Tri-1 and Tri-2) forming within the parent T-like phase to accommodate the large misfit strain. A large electromechanical response of $\sim 5\%$ is found in this multi-phase BFO system, which is believed to originate from the ease of transition

between the triclinic phases.^{4,5,11,12} It is then of great interest to determine and understand the details of this BFO domain structure. Recently, various structural analyses have been performed on this system with methods such as transmission electron microscopy (TEM),^{4,13} scanning probe microscopy (SPM),^{11,12,14} and conventional x-ray diffraction (XRD).^{4,5,15-17} However, the measured crystal/domain structure of this system can be easily misinterpreted, since the triclinic BFO phases tilt along both the H00 and 0K0 directions in reciprocal space (where H00 and 0K0 are parallel to the pseudocubic $[100]$ and $[010]$ directions, respectively), and each phase produces eight domain variants with different orientations.⁵ Such a configuration makes for a complex representation in reciprocal space, as illustrated in Fig. 1(a).

Due to the penetrating capability of hard x-rays, x-ray reciprocal space mapping (RSM) is a well-known approach for the study of domain structures.¹⁸ Determining the 3D nature of domains and their interaction requires 3D probing of reciprocal volumes. This can be done non-destructively with x-ray RSM, which provides volume-averaged information on the morphology, strain state, and size of different domains. When the results are combined with local probes (e.g., x-ray nanoprobe, TEM, SPM, etc.), an accurate 3D real-space model of the microstructure can be reconstructed, leading to improved computational models and better understanding of domain morphologies and their interactions.¹⁹ X-ray 3D-RSM has been regarded as an excessively time-consuming technique, but recent developments in high-speed area detectors and advances in computing capabilities have made it more practical. Several works have been performed recently using 3D-RSM, exhibiting its unique merits for characterizing polar nano-regions,²⁰ morphology of crystallites,^{21,22} and nano-particles strained *in situ*.²³ Here, using a mixed-phase

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FIG. 1. (a) Illustration of reflections of mixed-phase BFO films, as well as traces of conventional 1D- (dotted line) and 2D-XRD (grey plane) scans, in the reciprocal space around LAO (002) Bragg spot. (b) Typical AFM topography of mixed-phase BFO films. (c) Experimental 1D- and (d) 2D-XRD scans of the 40-nm-thick BFO/LAO film.

BFO film as a model system, we show how information on domain morphology and interfaces can be determined in ferroelastic heterostructures with this technique.

Epitaxial BFO films were grown on (001)-oriented LAO single crystal substrates using pulsed laser deposition at 700 °C under an oxygen pressure of 100 mTorr. A 40-nm-thick BFO film was selected for the 3D-RSM study. Diffraction data were obtained at the BL14B beamline of the Shanghai Synchrotron Radiation Facility (SSRF, $\lambda = 1.2398 \text{ \AA}$) with an image-plate detector, and at the 33ID-D beamline of Advanced Photon Source (APS, $\lambda = 0.6889 \text{ \AA}$) with a CCD detector. The final 3D-RSMs were reconstructed from a series of 2D patterns obtained while rotating the sample and are plotted in reciprocal lattice units of the LAO ($\text{r.l.u.} = 2\pi/3.789 \text{ \AA}^{-1}$). Conventional 1D- and 2D-XRD scans were performed at the SSRF with a point detector. Surface morphology was measured using atomic force microscopy (AFM) (Asylum Research MFP-3D).

In the AFM topography of a typical mixed-phase BFO film (Fig. 1(b)), the bright flat areas correspond to the T-like phase, while the darker areas with stripe contrast correspond to regions with Tri-1 and Tri-2 phases, according to previous studies.^{5,11,14} For this BFO film, the Bragg reflections of the various BFO phases and domain variants around LAO (002) Bragg point are schematically illustrated in three dimensional reciprocal space in Fig. 1(a).⁵ As seen, the reflections from all eight domain variants of Tri-1/Tri-2 BFO phases are displaced off the 00L specular rod. A scan along 00L (indicated by the dotted line in Fig. 1(a)) will overlook such tilted phases; an example scan is shown in Fig. 1(c). Although a 2D-RSM in the HL plane (Figs. 1(a) and 1(d)) exhibits the multi-phase nature of the film, it is difficult to accurately perceive how the Tri-1, Tri-2 phases fit within the domain structure without information from the third dimension. Hence, we performed 3D-RSM at the SSRF and the APS with area

detectors and reconstructed the 3D reciprocal space map of the Bragg reflections.

Figure 2 shows the experimental approach for obtaining 3D-RSM data from the BFO/LAO sample. In reciprocal space, when the x-rays irradiate the sample at a fixed incident angle ($\vec{k}_{in}$), the Bragg spots that fall on the Ewald sphere fulfill the Laue law and generate outgoing reflections along vector $\vec{k}_{out}$, and the projected pattern on the area detector represents a curved slice through reciprocal space. In practice, the sample is oriented to a particular HKL reflection and then rotated in small steps about the theta-axis, so that, the reflection is swept through the Ewald sphere, and a series of curved slices are projected onto the area detector (illustrated by the insets of Fig. 2), which contains the intensity distribution of reflections in a volume of reciprocal space. The resolution of each CCD image is determined by CCD pixel size, the CCD-sample distance, and geometrical parameters. The step in theta determines the Q-space resolution along normal direction of the detector.

For the experiment at the APS, the CCD detector was centered at $\theta = 18^\circ$ and placed 80 cm away from the sample; the pixel size was $20 \times 20 \mu\text{m}$. The incident beam divergence was $70 \mu\text{rad}$ vertically and $120 \mu\text{rad}$ horizontally, so the experimental setup provided an in-plane reciprocal spatial resolution better than $\delta Q = \delta \left(\frac{4\pi \times \sin \theta}{\lambda} \right) = \frac{4\pi \times \cos \theta}{\lambda}$

$\times \delta \theta = \frac{4\pi \times \cos \theta}{\lambda} \times \sqrt{(120 \mu\text{rad})^2 + \left(\frac{20 \mu\text{m}}{80 \mu\text{m}} \right)^2} = 1.3 \times 10^{-3} \text{ r.l.u.}$ According to the Shannon-Nyquist sampling theorem,²⁴ the domain size, the film thickness, and the spatial resolution (sampling rate) required for measuring the detailed structural information should not be worse than $\frac{2\pi}{2d} = \frac{2\pi}{2 \times 40 \text{ nm}} = 4.7 \times 10^{-3} \text{ r.l.u.}$, where d is the larger value

FIG. 2. Schematic diagram of 3D-reciprocal space mapping for BFO/LAO film around (002). Inset: XRD patterns obtained by the CCD detector with varied incident angles. The positions of the Tri-1(002), Tri-2(002), and T-like(002) Bragg reflections are indicated by the dotted lines.

between film thickness and domain size. Therefore, 0.05° was used as the step size in theta when rocking the sample, which provided an out-of-plane resolution of 2×10^{-3} r.l.u.

For the data processing, each pixel in the raw CCD images (1340×1300 pixels) was first converted into reciprocal coordinates (Q_x, Q_y, Q_z) according to the geometrical parameters. Then, a 3D grid with an interval of $0.001 \times 0.001 \times 0.001$ r.l.u. was created in this limited Q-space and data interpolation was performed within it. Finally, the 3D-RSMs were reconstructed with a Matlab program and presented as both static isosurfaces of equal intensity and animations (see Figure S1 in the supplementary material²⁵).

In Figure 3, isosurfaces of different values are presented to illustrate the diffraction intensity distribution in the 3D-RSMs. These 3D-RSMs provide an overview of the domain structure: as seen, all the 002 reflections of the various BFO polymorphs, including the T-like phase and the Tri-1 and Tri-2 phases, are simultaneously represented as well as the four-fold symmetric alignment of the eight domain variants of the tilted Tri-1/Tri-2 phases. In addition, the morphology of a diffraction spot in reciprocal space represents the Fourier transform of the average morphology of the crystal domain in real space. For example, the elongated shape of the Tri-1 002 reflection indicates that the Tri-1 domains are thin and narrow along the elongating directions with (002) planes 2.6° -tilted with respect to the surface normal. Furthermore, the tails between the domain reflections indicate lattice distortion in the interfacial region. As shown in Fig. 3(a), the tails from the Tri-1 reflections to the central rod indicate that the (002) crystal plane of the Tri-1 gradually tilts back to the substrate normal direction when closer to the domain boundary. A similar analysis of the Tri-2 reflection suggests similar behavior exists for the Tri-2

domains. As seen in Figs. 3(c) and 3(d) as well as in the supplementary Fig. S1,²⁵ a vertically anisotropic rod stretches upward from the T-like 002 reflection, implying relaxation of the elongated c lattice parameter of T-like BFO. Finally, the most important information that can be deduced from such 3D-RSMs is the accurate coordinates and quantitative intensities of diffraction spots. As shown quantitatively in the supplementary material,²⁵ the integrated intensities of the eight reflections of Tri-1 domains are quite different, indicating an unequal ratio of domain orientations in the film.

Any specific slice in the reciprocal space can be obtained by interpolating within the measured volume provided by the 3D-RSMs. As an example, Figs. 4(a) and 4(b) present HK slices at $L = 1.81$ and 1.62 , crossing the Tri-1, Tri-2 002 reflections, respectively. Previous AFM studies have revealed that the structural origin for the huge electromechanical response found in this system is the tunable phase balance between the coexisting BFO polymorphs, and that the important structural unit is the tilted Tri-1 domain and the adjacent oppositely tilted Tri-2 domain. The volume ratio of Tri-1/Tri-2 seems as a fixed value dominated by temperature and film thickness.¹¹ Consistent with this AFM result, the diffraction intensity distribution shown in Figs. 4(a) and 4(b) represents this relationship, as the lower intensity Tri-1 reflections (e.g., Tri1-2 and Tri1-3) lie in quadrants in reciprocal space opposite to those of the lower intensity Tri-2 reflections (e.g., Tri2-6 and Tri2-7). Exactly which domains are adjacent to each other in real space remains unclear. However, this can be elucidated with quantitative analysis of the integrated intensities, where, for example, it becomes clear that the nearest neighbors of the Tri1-1 domains are the Tri2-5 domains rather than the Tri2-6 domains, as indicated by the circles in Figs. 4(a) and 4(b), which was verified in a recent in-plane piezoelectric force microscopy (PFM) study¹⁴ (see Figs. S2 and S3 in the supplementary material and the associated discussion²⁵).

FIG. 3. 3D-RSMs of BFO/LAO film around LAO (002) Bragg spot, reconstructed with the help of Matlab and represented as isosurfaces in reciprocal lattice units of LAO. Isosurface values are (a) 1700, (b) 800, (c) 3000, (d) 12 000, and (e) 24 000, respectively. (f) is a HK view of the plot.

FIG. 4. 2D slices obtained from the 3D-RSMs via interpolation: (a) HK slice at $L = 1.81$, crossing Tri-1 domains; (b) HK slice at $L = 1.62$ crossing Tri-2 domains; (c) specific vertical slice crossing coexisting Tri-1 and Tri-2 domains, as indicated by the dotted line in (a) and (b).

Details on the diffuse tail between the adjacent Tri-1 and Tri-2 phases can be determined from Fig. 4(c), which shows a specific cut along a vertical plane 10°-clockwise rotated from the H0L plane with respect to the 00L axes (indicated by the dotted line in Figs. 4(a) and 4(b)). Since the incident beam size is relatively large, the reflections from regions with different domain morphology (shown in AFM) cause overlap of the diffuse tails. The diffuse tails pointing from the Tri-1 phase ($L = 1.81$) to the central rod are clear, while those from the Tri-2 phase ($L = 1.62$) are obscured (indicated by the white arrows). These diffuse tails are anisotropic with respect to the centers of reflections, suggesting they are not only caused by a domain size effect but also by lattice relaxation at the interface region between adjacent domains. Therefore, the orientation of the diffuse tail indicates the lattice-relaxation path of the domain. These tails merge at a single point on the specular rod (referred as OP), revealing an intimate relationship between the Tri-1 and Tri-2 domains in real space, i.e., the interfacial region between these polymorphs is homoepitaxial, and the crystal lattices of adjacent domains vary continuously to reach the same lattice parameter indicated by OP. This point of view was supported by a previous high-resolution TEM result, where dislocations were not found at the interfacial boundary.⁴ Therefore, a relatively low energy barrier to phase transformation is believed to exist, making it easy for the domain walls to move back and forth between the adjacent Tri-1 and Tri-2 domains. This should be the microstructural origin for the ease of transition between the Tri-1 and Tri-2 domains, which results in the huge electromechanical response of BFO/LAO film, as verified by recent nano-probe experiments.^{12,13} Furthermore, due to the broken inversion symmetry at this interfacial region, magnetic order may exist there and couple with ferroelectric order to present intriguing multiferroic functionalities.^{26,27} Last, but not least, as shown in Fig. 4(c), the intense tails connecting OP/Tri-2 and T-like BFO indicate an existing lattice deformation corresponding to the structural transition in the BFO film during the cooling process after deposition on a LAO substrate at high temperature. Future temperature and field-dependent 3D-RSM studies and 3D-RSM with an x-ray nanoprobe could help to reveal such domain dynamics and their underlying physics.

In summary, high-resolution 3D-RSM has been performed and analyzed for mixed-phase BFO films and is found to be an effective way to visualize the BFO polymorphs, domain variants, and even the interfacial regions between adjacent Tri-1 and Tri-2 BFO domains. The epitaxial relationship and lattice gradient found at the interface, revealed by these 3D-RSMs, are believed to be the microstructural origin for the ease of phase transition between Tri-1 and Tri-2, and result in a large electromechanical response recently found in mixed-phase BFO/LAO films. This study demonstrates the unique merits of the XRD 3D-RSM technique, which can be extended to the investigation of other ferroic films with complicated domain structures. These kinds of studies can also be extended to *in-situ* studies under an applied field for the study of domain dynamics.

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- ¹E. K. H. Salje, *Annu. Rev. Mater. Res.* **42**, 265 (2012).
- ²B. Noheda, D. E. Cox, G. Shirane, J. A. Gonzalo, L. E. Cross, and S. E. Park, *Appl. Phys. Lett.* **74**, 2059 (1999).
- ³D. Vanderbilt and M. H. Cohen, *Phys. Rev. B* **63**, 094108 (2001).
- ⁴R. J. Zeches, M. D. Rossell, J. X. Zhang, A. J. Hatt, Q. He, C. H. Yang, A. Kumar, C. H. Wang, A. Melville, C. Adamo, G. Sheng, Y. H. Chu, J. F. Ihlefeld, R. Ermi, C. Ederer, V. Gopalan, L. Q. Chen, D. G. Schlom, N. A. Spaldin, L. W. Martin, and R. Ramesh, *Science* **326**, 977 (2009).
- ⁵Z. 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. Bellaiche, and L. Chen, *Phys. Rev. B* **84**, 094116 (2011).
- ⁶A. L. Roitburd, *Phys. Status Solidi A* **37**, 329 (1976).
- ⁷S. K. Streiffer, J. A. Eastman, D. D. Fong, C. Thompson, A. Munkholm, M. V. Ramana Murty, O. Auciello, G. R. Bai, and G. B. Stephenson, *Phys. Rev. Lett.* **89**, 067601 (2002).
- ⁸D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, and C. Thompson, *Science* **304**, 1650 (2004).
- ⁹G. Catalan and J. F. Scott, *Adv. Mater.* **21**, 2463 (2009).
- ¹⁰C. Ederer and N. A. Spaldin, *Phys. Rev. Lett.* **95**, 257601 (2005).
- ¹¹A. R. Damodaran, C. W. Liang, Q. He, C. Y. Peng, L. Chang, Y. H. Chu, and L. W. Martin, *Adv. Mater.* **23**, 3170 (2011).
- ¹²C. Beekman, W. Siemons, T. Z. Ward, M. Chi, J. Howe, M. D. Biegalski, N. Balke, P. Maksymovych, A. K. Farrar, J. B. Romero, P. Gao, X. Q. Pan, D. A. Tenne, and H. M. Christen, *Adv. Mater.* **25**, 5561 (2013).
- ¹³J. X. Zhang, B. Xiang, Q. He, J. Seidel, R. J. Zeches, P. Yu, S. Y. Yang, C. H. Wang, Y. H. Chu, L. W. Martin, A. M. Minor, and R. Ramesh, *Nat. Nanotechnol.* **6**, 98 (2011).
- ¹⁴L. You, Z. Chen, X. Zou, H. Ding, W. Chen, L. Chen, G. Yuan, and J. Wang, *ACS Nano* **6**, 5388 (2012).
- ¹⁵Z. 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).
- ¹⁶H. 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).
- ¹⁷Z. Luo, Z. Chen, Y. Yang, H. J. Liu, C. Huang, H. Huang, H. Wang, M. M. Yang, C. Hu, G. Pan, W. Wen, X. Li, Q. He, T. Sritharan, Y. H. Chu, L. Chen, and C. Gao, *Phys. Rev. B* **88**, 064103 (2013).
- ¹⁸P. F. Fewster, *Crit. Rev. Solid State Mater. Sci.* **22**, 69 (1997).
- ¹⁹Y. L. Li, S. Y. Hu, Z. K. Liu, and L. Q. Chen, *Acta Mater.* **50**, 395 (2002).
- ²⁰G. Xu, Z. Zhong, H. Hiraka, and G. Shirane, *Phys. Rev. B* **70**, 174109 (2004).
- ²¹S. O. Mariager, C. M. Schlepütz, M. Aagesen, C. B. Sørensen, E. Johnson, P. R. Willmott, and R. Feidenhans'l, *Physica Status Solidi A* **206**, 1771 (2009).
- ²²T. W. Cornelius, D. Carbone, V. L. R. Jacques, T. U. Schüllli, and T. H. Metzger, *J. Synchrotron Radiat.* **18**, 413 (2011).
- ²³T. W. Cornelius, A. Davydok, V. L. R. Jacques, R. Grifone, T. Schüllli, M. I. Richard, G. Beutier, M. Verdier, T. H. Metzger, U. Pietsch, and O. Thomas, *J. Synchrotron Radiat.* **19**, 688 (2012).
- ²⁴C. E. Shannon, *Proc. Inst. Radio Engineers* **37**, 10 (1949).
- ²⁵See supplementary material at <http://dx.doi.org/10.1063/1.4875579> for quantitative analysis of the reflection intensity and animations of the 3D-RSM with varied isosurface values or rotating angles.
- ²⁶I. C. Infante, J. Juraszek, S. Fusil, B. Dupé, P. Gemeiner, O. Diéguez, F. Pailloux, S. Jouen, E. Jacquet, G. Geneste, J. Pacaud, J. Íñiguez, L. Bellaiche, A. Barthélémy, B. Dkhil, and M. Bibes, *Phys. Rev. Lett.* **107**, 237601 (2011).
- ²⁷K.-T. Ko, M. H. Jung, Q. He, J. H. Lee, C. S. Woo, K. Chu, J. Seidel, B. Jeon, Y. S. Oh, K. H. Kim, W. Liang, H. Chen, Y. Chu, Y. H. Jeong, R. Ramesh, J. Park, and C. Yang, *Nat. Commun.* **2**, 567 (2012).