Review Article

Characterization of Multiferroic Domain Structures in Multiferroic Oxides

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Multiferroic oxides have been received much attention due to that these materials exhibit multiple ferroic order parameters (e.g., electric polarization in ferroelectrics, magnetization in ferromagnetics, or spontaneous strain in ferroelastics) simultaneously in the same phase in a certain temperature range, which offer an exciting way of coupling between the ferroic order parameters. Thus, this provides a possibility for constructing new type of multifunctional devices. The multiferroic domain structures in these materials are considered to be an important factor to improve the efficiency and performance of future multiferroic devices. Therefore, the domain structures in multiferroic oxides are widely investigated. Recent developments in domain characterization techniques, particularly the aberration-corrected transmission electron microscopy (TEM), have enabled us to determine the domain structures at subangstrom scale, and the recent development of *in situ* TEM techniques allows ones to study the dynamic behaviors of multiferroic domains under applied fields or stress while the atomic structure is imaged directly. This paper provides a review of recent advances on the characterization of multiferroic domain structures in multiferroic oxides, which have been achieved by the notable advancement of aberration-corrected TEM.

1. Introduction

In recent years multiferroic materials have attracted much interest because they possess more than one type of ferroic order parameters in the same phase, which brings out novel physical phenomena and offers the possibilities for developing new multiferroic devices [1–3]. The defining characteristic of a ferroic material is ferroic order parameter (e.g., electric polarization in ferroelectrics, magnetization in ferromagnets, or spontaneous strain in ferroelastics) that has different, energetically equivalent orientations; the orientation of which can be selected using an applied field. For example, in the magnetoelectric multiferroics there exists a coupling between the electric and magnetic fields, or named as magnetoelectric effect, which describes the induction of magnetization (M) by an electric field (E) or polarization (P) generated by a magnetic field (H). The multiferroic materials may have domains with differently oriented regions, separated by domain walls, coexisting in a sample. In the magnetoelectric multiferroics, both ferroelectric and magnetic domains exist simultaneously. In addition,

“ferroelectric domain switching controlled by magnetic field” and “magnetic domain switching controlled by electric field” are also available, which lead to the possibilities for designing new multiferroic devices [4]. In the multiferroic oxides, the possible domain structures are much more complex than that in either ferroelectric or ferroelastic materials due to the multiple coupling between the primary ferroic order parameters. Aizu [5] analyzed the numbers of ferroic domain states in multiferroics, and found that the possible domain walls, was given by the ratio of the point group orders of the high- and low-symmetry phases, although Shuvalov et al. [6] argued that a higher number of domains (super-orientational states) could be permissible than given by the Aizu rule, as indeed observed in ferroelastic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [7]. The multiferroic domain structures in these multiferroic oxides are considered to be important factors to improve the efficiency and performance of future magnetoelectric devices. Therefore, multiferroic domain structures in multiferroic oxides have been extensively investigated. Meanwhile, both the techniques and instruments of transmission electron microscopy (TEM), which is one of the most powerful

tools of the domain analysis, have been much improved in the last decade. As advances in aberration-corrected TEM have enabled ones to determine three-dimensional structures of materials with subangstrom resolution, the recent development of *in situ* TEM techniques also allows ones to study the dynamic behaviors of multiferroic domains under applied fields or stress while the atomic structure is directly imaged simultaneously [8–10]. Therefore, the new generation high-resolution TEM (HRTEM) and scanning transmission electron microscopy (STEM) facilities equipped with Cs-corrector will benefit for the characterizations of multiferroic domain structures in multiferroic oxides. Recently, much progress in this direction has been achieved by the notable advancement of aberration-corrected TEM. In this paper, an overview of the characterizations of multiferroic domain structures in multiferroic oxides is presented, and the future challenges of the characterizations on the domain structures of multiferroic oxides are also discussed.

2. Multiferroic Domain Structures in Multiferroic Oxides

Multiferroic oxides can be classified four categories based on their different microscopic nature for multiferroic behaviors [1]. The first type is lone pair multiferroics (examples such as BiFeO_3 , BiMnO_3 , and PbVO_3 , in which the A-site cation (Bi^{3+} , Pb^{2+}) has a stereochemically active $6s^2$ lone-pair electrons, distorting the geometry of the BO_3 anion, resulting in ferroelectricity); the second one is charge-ordered multiferroics (certain “noncentrosymmetric” arrangements of ions induce ferroelectricity in magnetic materials, one prominent example is LuFe_2O_4); the third one is magnetic-ordered multiferroics (as exemplified in DyMnO_3 , TbMnO_3 , and TbMn_2O_4 , ferroelectricity is induced by magnetic long-range order in which the arrangement of magnetic dipoles lacks reflection symmetry); and the fourth one is geometrical frustration multiferroics (as exemplified in REMnO_3 ($\text{RE} = \text{Y}$, Dy , Tb , etc.), in which long-range dipole-dipole interactions and rotations of oxygen atoms generate a stable ferroelectric state). In multiferroics, the possible domain structures are much more complex than that in either ferroelectric or ferroelastic materials due to the multiple coupling between the primary ferroic order parameters. In this work, we will focus on the multiferroic domain structures in multiferroics revealed by TEM and aberration-corrected HRTEM/STEM.

2.1. Multiferroic Domain Structures in BiFeO_3 Thin Films. Perovskite-type BiFeO_3 , as one of the few known single-phase magnetoelectric multiferroics, exhibits a coexistence of simultaneous ferroelectric and magnetic order parameters above room temperature. Thus, it offers exciting potential for room temperature device integration and has been the topic of intensive studies as an interesting model multiferroics [11]. Structurally, BiFeO_3 crystallizes in a rhombohedrally distorted perovskite structure with $R3c$ space group at room temperature, of which the lattice constants were determined as $a_h = 5.587 \text{ \AA}$, $c_h = 13.867 \text{ \AA}$ in the hexagonal unit cell containing six formula or $a_R = 5.638 \text{ \AA}$, $\alpha = 59.348^\circ$ in

the rhombohedral unit cell containing two formula units [11]. Three main distortions are responsible for the existence of spontaneous polarization along the $[001]_{\text{hex}}$ direction (i.e., $[111]_{\text{cub}}$). Therefore, in the BiFeO_3 with a rhombohedral structure, there exists eight different polar domains, and three possible types of ferroelectric domain walls, namely as 71° , 109° , and 180° domain walls. Recently, a new kind of vortex-like nanodomain arrays (toroidal domain patterns) were reported in the epitaxial BiFeO_3 thin films grown on TbScO_3 substrates, which were revealed by aberration-corrected STEM [12]. Figure 1(a) is dark-field TEM image of the vortex nanodomain arrays formed at the interface between the BiFeO_3 film and TbScO_3 substrate, and Figure 1(b) is the plotting of the D_{FB} vectors (D_{FB} defined as the atomic displacement in the image plane of the Fe cation from the center of the unit cell formed by its four Bi neighbors) for a 109° domain wall which forms a vortex domain by addition of a pair of 180° triangle domains, where the polarization rotates about the intersection of two 109° and two 180° domain walls to form a vortex domain structure. The formation of such complex domain structures tends to reduce the depolarization fields produced at the surface of the TbScO_3 insulator substrates. And along with the interface epitaxy constraints, a local broadening of the walls is produced, which makes the polarization rotation quasicontinuous.

2.2. Multiferroic Domain Structures in Hexagonal YMnO_3 Single Crystals. Hexagonal YMnO_3 is the representative geometrical frustrated multiferroics, which has received much attention not only from a fundamental but also a technological point of view because of its large coupling between the two (magnetic and electric) ferroic orders. The magnetic and electric coupling can be utilized for higher density data storage or highly sensitive sensor devices. The ferroelectric and magnetic domain structures in this multiferroic material are considered to be an important factor for improving the efficiency and performance of future multiferroic devices. Therefore, multiferroic domain structures in multiferroic hexagonal YMnO_3 are extremely studied. In the past years, domain structures in YMnO_3 have been studied by various methods, such as surface etching [13], SEM [13], second-harmonic near-field imaging [14], piezo-response force microscopy [15, 16], and conventional TEM [17, 18]. In recent years, a characteristic cloverleaf domain structure and topologically protected multiferroic vortex-antivortex pairs have been revealed by conventional dark-field TEM images [19, 20], as shown in Figure 2. Figure 2(a) shows a combination of dark-field TEM image (bottom grey-scale layer) and conductive atomic force microscopy (top colored layer) image of cloverleaf domain pattern, which shows six crystallographic domains joining at a defect line with positive and negative polarization (+ and – signs in the conductive atomic force microscopy image, resp.) alternating around the defect. The TEM dark-field image was obtained by using the $1\bar{3}1$ diffraction spot (the Miller index is based on $\text{P}63\text{cm}$), in which six antiphase domains (α - β - γ - α - β - γ) form 60° wedges and merge from one central point. These six structural domains represent the minima of free energy of

FIGURE 1: (a) Dark-field TEM images of the vortex nanodomain arrays formed at the interface between the BiFeO_3 film and TbScO_3 substrate. (b) Plotting of the D_{FB} vectors (defined as the atomic displacement in the image plane of the Fe cation from the center of the unit cell formed by its four Bi neighbors) for a 109° domain wall which forms a vortex domain by addition of a pair of 180° triangle domains, where the polarization rotates about the intersection of two 109° and two 180° domain walls [12].

FIGURE 2: (a) Cloverleaf domain patterns in ferroelectric YMnO_3 [19, 20]. The combination of TEM (bottom grey-scale layer) and conductive atomic force microscopy (top colored layer) images shows six crystallographic domains joining at a defect line with positive and negative polarization (+ and – signs in the conductive atomic force microscopy image, resp.) alternating around the defect. The TEM dark-field image is obtained by using the $1\bar{3}1$ diffraction spot. (b) Contour plot of the free energy of hexagonal YMnO_3 , where the six minima correspond to six structural domains. The arrows in the direction of the minima (colored blue and red) indicate the direction describing these states. The red and blue arrows also encode the sign of electric polarization. The dashed arrow connecting two neighboring minima is a lowest-energy domain wall. (c) and (d) Vortex and antivortex configurations correspond to the cloverleaf defect, respectively. The α , β , and γ antiphase domains correspond to the three options for the origin of trimerization.

the system, rotated by 60° angles, as depicted in Figure 2(b). The domain walls separating the structural domains are trajectories beginning in one minimum and ending in another. The lowest-energy domain walls connecting two neighboring minima are depicted by the dashed line in Figure 2(b). As is evident from the cloverleaf defects are therefore vortices where around the defect the phase angle goes successively through all six phases. This leaves only two possible domain sequences: $\alpha+$, $\beta-$, $\gamma+$, $\alpha-$, $\beta+$, and $\gamma-$ (vortex) and $\alpha+$, $\gamma-$, $\beta+$, $\alpha-$, $\gamma+$, and $\beta-$ (antivortex). Therefore, the electric alternating sign of polarization of neighboring domains, such domain walls flip the electric polarization. The polarization changes sign at each domain wall (Figures 2(c) and 2(d)).

Such vortices are stable topological defects that cannot be unwound by local lattice distortions. The 60° rotation of spins at domain boundaries implies that the cloverleaf defects are also magnetic vortices where lattice distortions and spins rotate together. It would be interesting to find out whether this amazingly complex interplay between structural, electric and magnetic properties of defects can lead to new magneto-electric phenomena. Similarly, the cloverleaf domain patterns in YMnO_3 thin films are also reported by Matsumoto et al. [21], as shown in Figure 3. In a low-magnification dark-field TEM image (Figure 3(a)), the multiferroic cloverleaf domains are elongated along the c -axis of the specimen as indicated

with an arrow. Some vortices can be observed in the field-of-view and an enlargement of a vortex as designated by a white rectangle is shown in Figure 3(b) (as a false-color image). After numerous TEM observations, it is found that vortices with at least two domain boundaries along the c -axis (transverse domain wall, TDW) are stable during TEM observations. Along with TDW, no charge is exposed whereas a small amount of charge is exposed at the longitudinal domain boundary (LDW) at the core. In contrast, an unstable vortex is shown in the center of Figure 3(c), which appears as a four-leaves-like vortex. The contrast appeared to be blurred near the vortex and all of the boundaries were found to be mostly perpendicular to the c -axis. A fair amount of charges are exposed along the LDW making such a vortex structure unstable under the electron irradiation. The ferroelectric and antiferromagnetic domains have been confirmed to be interlocked with each other by a simultaneous observation by contact AFM and low temperature MFM [22]. Anisotropic conduction through the domain boundary was also observed, which could lead to tunable and flexible design of multiferroic devices [23]. To better understand the physical and chemical mechanism of multiferroicity in multiferroic hexagonal YMnO_3 , a visualization technique based on spherical aberration-corrected STEM with atomic resolution has been employed to characterize the charge and

FIGURE 3: (a) A conventional dark-field TEM image of the multiferroic cloverleaf domains in the YMnO_3 crystal near the $[110]$ zone axis [21]. Note that the domains are elongated along the c -axis as indicated with an arrow. (b) An enlargement of the vortex designated by a white rectangle is shown as a pseudocolor representation. (c) An instable vortex observed in some field of view.

FIGURE 4: High-resolution ABF-STEM image of the YMnO_3 single crystal recorded along the $[110]$ direction, where five different kinds of domain structures (marked as Up, Down, TDW, LDW, and STEP in the figure) are observed [21].

uncharged domain walls in multiferroic hexagonal YMnO_3 , where the annular bright-field (ABF) imaging technique is also used to reveal the light atomic element of oxygen. To further reduce the residual and statistical noises in the STEM images, multivariate statistical analysis (MSA) technique is also used [24]. Figure 4 demonstrates a high-resolution ABF-STEM image recorded along the $[110]$ direction from a part of the field-of-view shown in Figure 3(b), where five different kinds of domain structures (marked as Up, Down, TDW, LDW, and STEP in the figure) are observed in the same field of view in the image [21]. The MSA reconstructed score images from the LDW region and TDW region with color obtained from the HAADF (a, c) and ABF (b, d) images are shown in Figure 5, respectively. It is clear that the transition between the two opposite polarization is atomically sharp in both images. The separation was found to be as good as that for an artificial image group constructed from

upward only and downward only region (Up and Down in Figure 4). Therefore, with the aid of MSA technique, unbiased and quantitative maps of ferroelectric domain structures with atomic resolution have been obtained. Such a statistical image analysis of the transition region between opposite polarizations has confirmed the atomically sharp transitions of ferroelectric polarization both in antiparallel (uncharged) and tail-to-tail 180° (charged) domain boundaries. Based on these analyses, a correlated subatomic image shift of the Mn–O layers with that of Y layers, exhibiting a double-arc shape of reversed curvatures, has been elucidated. The amount of image shift in Mn–O layers along the c -axis is statistically significant as small as 0.016 nm, roughly one-third of the evident image shift of 0.048 nm in Y layers. In addition, such a subatomic image shift in Mn–O layers vanishes at the tail-to-tail 180° domain boundaries. By using aberration-corrected high-angle annular-dark-field (HAADF) imaging technique the domain configurations and atomic structures of the vortex in multiferroic hexagonal YMnO_3 has been directly identified along the $[100]$ direction, as shown in Figure 6 [25]. Due to the Z-contrast characteristics of the HAADF imaging, the big bright spots correspond to Y atoms and the small bright spots correspond to Mn atoms. Note that $[100]$ direction is the most suitable for imaging the DWs and identifying the location of the vortex core, where the shift of Y ions can be observed without overlapping. The different configurations of Y_{up} and Y_{down} atoms comparing to the MnO_5 polyhedra, which appears wavy-like, indicate that YMnO_3 has two opposite polarized states, which are indicated by the yellow upward and blue downward arrows, respectively. Since the HAADF contrast is generally less affected by small variation of specimen thickness, therefore, mapping the atomic position of heavier ions using HAADF approach is a reliable method to measure ion displacements and to further calculate the polarization. Six ferroelectric domains can be distinguished clearly by the up-down-down and down-up-up arrangements of Y ions and their polarizations are marked by upward arrows and downward arrows, respectively, as shown in Figure 6. It is found the six DWs can

FIGURE 5: MSA (multivariate statistical analysis) reconstructed score images from the LDW region and TDW region with color obtained by from (a, c) the HAADF and (b, d) ABF images [21].

be classified into two types by their displacements across the DWs: type-I $1/6$ [210] and type-II $1/3$ [210]. Six translation-ferroelectric domains denoted by $\alpha+$, $\gamma-$, $\beta+$, $\alpha-$, $\gamma+$, and $\beta-$, respectively, were recognized, demonstrating interlocking nature of the antivortex domain. The core region of nearly zero polarization was found to be about four unit cells width. These results demonstrated that the polarization reverse can be realized efficiently by the adjustments of displacements of Y ions within several unit cells at both DWs and the antivortex core, demonstrating the trimerization nature of improper ferroelectricity of YMnO_3 . These findings provide a solid evidence for the understanding of topological behaviors and intriguing physics of the vortex in RMnO_3 and pave the way for further theoretical calculation.

2.3. Multiferroic Domains in Charge-Ordered LuFe_2O_4 Multiferroics. Recently multiferroicity is observed in LuFe_2O_4 , which is due to ferroelectricity originating from $\text{Fe}^{2+}/\text{Fe}^{3+}$

charge order at the ferromagnetic transition temperature. The crystal structure of LuFe_2O_4 consists of the alternate stacking of triangular lattices of rare-earth elements, iron and oxygen. An equal amount of Fe^{2+} and Fe^{3+} coexists at the same site in the triangular lattice. Compared with the average iron valence of $\text{Fe}^{2.5+}$, Fe^{3+} , and Fe^{2+} are considered as having an excess and a deficiency of half an electron, respectively. The Coulombic preference for pairing of “oppositely” signed charges (Fe^{2+} and Fe^{3+}) is considered to cause the degeneracy in the lowest energy for the charge configuration in the triangular lattice, similarly to the triangular antiferromagnetic Ising spins. Thus, RFe_2O_4 is considered to be a charge-frustrated system of triangular lattices, where ferroelectricity is originated from the electron distribution. It is expected that real-space observations of the charge-ordered domains will provide crucial information for a deeper understanding of the process of frustrated charge ordering in the triangular lattice. Since frustrated charge ordering gives rise to only weak

FIGURE 6: HAADF image of the antivortex domains in multiferroic YMnO_3 [25]. Yellow and blue rectangles are used to mark the upward and downward polarized unit cells, respectively. The yellow upward and blue downward arrows indicate the different direction of polarization, respectively. Two white horizontal lines are superposed on the image to identify the relative translation relationship among α , β , and γ domains. The DWs are marked by red dotted lines and the red circle is used to mark the region of the vortex core. The types of six DWs are also outlined by the white vertical lines, labeled by type-I and type-II. The schematics of the three translation domains are presented at the bottom. The broken rectangles are used to indicate the same polarized unit cells. The black ruler is scaled by the lattice periodicity projected along the $[100]$ direction. The positions of the broken rectangles relative to the short vertical lines in the black ruler reflect their translation relationship.

satellite reflections (i.e., diffuse scattering), so the technique of energy-filtered TEM is employed to significantly improve the visibilities of electron diffraction patterns and the dark-field images obtained using such weak reflections. Figure 7 shows the morphology of charge-ordered domains in LuFe_2O_4 [26]. Figure 7(a) is the selected area electron diffraction pattern of LuFe_2O_4 recorded at 299 K, which exhibits a feature of a characteristic diffuse scattering caused by charge ordering in LuFe_2O_4 , as marked by the black arrows in Figure 7(a). The diffuse scattering is accompanied by streaks in the direction of c^* axis due to suppression of interlayer correlation between Fe double layers, which are separated by Lu–O sheets. The trace of diffuse scattering is not linear; instead, it has a slightly zigzag shape. This modulation can be explained by a small peak shift perpendicular to the c^* axis whose magnitude depends on the index l . X-ray diffraction patterns of the LuFe_2O_4 single crystals reveal that the diffuse scattering has intensity maxima at approximately $(h/3, h/3, l + 3/2)$ in reciprocal space, where h and l are the Miller indices [27, 28]. Based on the full width at half maximum (FWHM) of the diffuse scattering pattern measured perpendicular to the c^* axis at the position of the intensity maxima, the sizes of charge ordering domains are estimated to be ~ 4.7 nm at 299 K. To determine the charge-ordered domain structure in real space, a dark-field image (Figure 7(b)) was obtained by using the diffuse scattering indicated by the circle in the inset. That reveals the

nanometer-scale charge-ordered domains, which exhibit as the bright dots in Figure 7(b). The size of bright dots seems smaller than the correlation length (~ 4.7 nm) deduced from the FWHM. It appears likely that the bright dots represent the portions which show a significant degree of charge ordering, for example, the inner portions of charge-ordered domains. In other words, the outskirts regions having a lower degree of charge ordering than the inner portions do not provide sufficient brightness in the dark-field image. To determine the average spacing between the bright dots observed by dark-field imaging at 299 K, the number of nanometer-scale dots (N), such as those indicated by red points in Figure 7(c) is calculated. With respect to agglomerations observed in the dark-field image, it was difficult to determine the true positions of individual charge-ordered domains. Because of these uncertainties, the observations of N were dispersed from 132 to 190.

Based on the above results it can be concluded that dark-field imaging revealed a spot-like contrast of the charge-ordered domains. Although electron diffraction patterns demonstrated the development of charge ordering upon cooling, the observable domain size remained on a nanometer scale (i.e., smaller than 10 nm) over a wide temperature range between T_{CO} (~ 310 K) and 88 K. These findings indicate that the charge ordering is constrained by the geometric aspects of the crystal structure, such as the triangular lattice and the discreteness of the Fe double layers. An average spacing between neighboring domains (spacing between domain centers) of was determined to be 5–7 nm at 299 K. This value was comparable with the in-plane (c plane) correlation length (~ 4.7 nm) deduced from the FWHM of the diffuse scattering. It is conjectured that there are only small charge-disordered regions separating neighboring charge-ordered regions. Such small ferroelectric domains are free from the lattice distortion as observed by dark-field TEM, which can assist the realization of an extremely small ferroelectric element in high density ferroelectric random access memory. Such a fascinating potential for electron-ordered ferroelectricity will be pioneered in future research.

3. Concluding Remarks

In this paper, we have reviewed the recent progress in the characterizations of multiferroic domain structures in multiferroic oxides. Due to the existence of two or three primary ferroic order parameters simultaneously in the same phase multiferroics and intricately coupling each other, new amazing multiferroic properties and/or phenomena are realized by combinations of distinct nanometer-scale charge-ordered domains, cloverleaf domain structures, and topological defects such as multiferroic vortex-antivortex pairs. Therefore, the importance of multiferroic domain analyses will be enhanced in the future. However, in order to explore these complex and nano-scaled structures with high precision, improvements on the microscopic methods should be sustained. Recent development of spherical aberration correction is revolutionizing the performance of HRTEM/STEM instruments, which allows ones to achieve a spatial resolution

FIGURE 7: Morphology of charge-ordered domains in LuFe_2O_4 [26]. (a) SAED pattern of LuFe_2O_4 recorded at 299 K. (b) Dark-field TEM image of the charge-ordered domains obtained by using the diffuse scattering indicated by the circle in the inset. The charge-ordered domains are imaged as bright dots. (c) Nanometer-scale bright dots (indicated in red) representing the charge-ordered domains, which are used to determine the average spacing between the neighboring charge-ordered domains.

better than 0.08 nm and an energy resolution better than 100 meV. Such breakthrough would bring us to see and thoroughly explore the multiferroic domain structures at subangstrom scale. Another fascinating task is to combine the measurements of multiferroic physical properties (e.g., ferroelectric, magnetic, and magnetoelectric coupling properties) with the multiferroic domain analysis as performed here. This type of simultaneous measurements will be necessary for further understanding of the ferroelectric, magnetic and/or magnetoelectric coupling between the small domains. An exciting new era for multiferroic domain characterizations in multiferroic oxides is on the horizon!

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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