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Ferroelectric annular domains in hexagonal manganites

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Abstract

Experimental observations and theoretical simulations for the ferroelectric (FE) domains in multiferroic RMnO_3 ($\text{R} = \text{Ho-Lu, Y and Sc}$) demonstrate that annular domains can appear in the topological Kosterlitz-Thouless (KT) phase in coexistence with the ‘cloverleaf’ vortices. Moreover, the annular domains often adopt the multi-layered structures as indexed by its annular number. The double-layered FE domains, an energetically favored structure, are commonly found in RMnO_3 . Thermal annealing experiments directly show exchanges between large annular domains and ‘cloverleaf’ vortices above the trimerization-structural transition temperature T_c . The temperature evolution of the FE domains has been analyzed by using the six-state clock model through Monte Carlo simulations. Based on careful in-situ SEM observations, the dynamic properties of annular domains and interplay among domain walls have been briefly discussed.

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Multiferroic materials have received much attention because of their wide range of applications such as the nonvolatile random-access memory, the nanoscale sensors, the photonic crystals, and the biologically inspired nanostructures [1-4]. There are three well-known forms of the ferroic orders in correlation with the spontaneous magnetization (ferromagnetism), the electric polarization (ferroelectricity), and the spontaneous strain (ferroelasticity), respectively. Ferroelectricity often accompanies ferroelastic strain, so ferroelectric (FE) domains tend to form in simple elongated configurations such as stripes [5,6]. On the other hand, it is also noted that the localized magnetic and FE domains have been also investigated in certain remarkable systems, e.g. the magnetic bubbles, have been observed in magnetic films under applied magnetic fields and used to build experimental devices that are of great interest in engineering practical electronic devices [7-9]. In this paper we will report on structural features and polarization configurations for the annular domains observed in hexagonal manganites. In addition, it is also demonstrated by using Monte Carlo simulations based on the six-state clock model that annular domains can appear in a large temperature range and often coexist with vortex domains in KT ordered state.

Recent investigations of layered hexagonal RMnO_3 ($\text{R} = \text{Ho-Lu, Y and Sc}$) have revealed interesting FE domain structures and remarkable physical properties, such as ‘cloverleaf’ vortex structures [10] and anisotropic conductivity at domain walls [11]. In order to clearly reveal the microstructural features of the ferroelectric domains at a high spatial resolution, we combined transmission electron microscopy (TEM), scanning electron microscopy (SEM), and piezoresponse force microscopy (PFM) for

our analysis. In particular, we have demonstrated that scanning secondary-electron microscopy with operating voltage (V_0) less than 1kV could be a powerful technique to directly reveal the FE domain/wall structures [12]. In addition, we also performed Monte Carlo simulations on the 2-dimensional six-state clock model for the triangular lattice with the periodic boundary conditions, as similarly reported in Ref. 13 and 14.

We begin by considering the experimental data obtained from as-grown ErMnO_3 crystals. Figures 1(a) and (b) show two typical SEM images, illustrating the structural features of FE domains on the a-b plane. It is recognizable in Fig. 1(a) that microstructure features in this area are apparently dominated by circular domains with amazing profiles. Furthermore, we also performed our extensive observations on the structures of domain walls, in particular for circle-like domains with the sizes between 0.5 and 5 μm . Our observations demonstrate that, though a certain single-wall domains can be observed, a large fraction of these annular domains in ErMnO_3 adopt a double-wall structure as typically shown in the inserted image of Fig. 1(a), in which the two domain walls can be clearly seen as two bright circles. These facts suggest that the double-wall structure could be an energetically favored structural pattern in ErMnO_3 , certain similar domain walls have been also observed by Chae *et al.* [13].

In addition to the annular domains, extended stripe domains as generally discussed in conventional ferroelectric materials, such as PbTiO_3 [15,16], also appear in the as grown ErMnO_3 crystals. Actually, we can often see notable domain bands caused evidently by the interplay among stripe and annular domains. In Fig. 1(b), we show a set of stripe domains and domain bands lining up roughly along the $[110]$ -axis direction. It is notable that each domain band originates from a rectilinear ferroelectric

domain which exhibits visible interaction with the annular domains, as a result, the stripe domains in Fig. 1(b) often adopt zigzag profiles surrounded by circular domains. Since stripe domain patterns are considered to be the ground state [13], then the appearance of annular domains reveals that the system enters a low-energy excited state.

Another important issue concerned in present study is the three-dimensional structural features of the annular domain structures. We therefore performed our observations perpendicular to the c-axis direction to reveal the side views of domain walls. Figures 1(c) and (d) show two examples of SEM and PFM image obtained for ErMnO_3 crystals, respectively. It is recognizable that the side views of FE domains in ErMnO_3 usually have elongated shapes along the c-axis direction due to the essential anisotropic properties of RMnO_3 crystals. It is remarkable that certain domain walls are closed within the crystals yielding annular domains in present system. Circle domain with one shell wall and annular domain with double shell walls can be clearly observed on this surface with some elongation along c-axis. These results demonstrate that the energetically unfavorable charged domain walls can be protected not only by the vortex cores [17], but also by annular structures. It is noted that the poling configuration of annular domains shows up very similar properties in comparison with the artificial structure as illustrated in Ref. 18 which is considered to be potential electronic device elements used for spatial conductivity modulation. Careful analysis of experimental images taken along relevant orientations suggests that the FE domains in present system frequently adopt annular structures composed of concentric

shells. In Fig. 2, we show a series of structural models for FE circular domains with different shell structures (Fig. 2(a)) and the relevant experimental images of domain walls as observed by SEM (Fig. 2(b)). It is recognizable that these circular structures can be well indexed respectively by its annular number n (i.e. the domain shells). Importantly, it is also recognizable that FE onion domains with $n = 1$ show very similar structural features with the known magnetic bubble domains which have been used commonly to build electronic devices [8,9], these facts suggest that these ferroelectric bubbles might be modulated by electric field.

In order to understand the essential structural features for the annular domains, we have employed the Monte Carlo simulations on the 2-dimensional six-state clock model for the triangular lattice, and the Hamiltonian used in our study is similar with that in Ref. 13 and 14. The six distinctive states in the theoretical model correspond respectively to the known six domains, i.e. α^+ , β^- , γ^+ , α^- , β^+ and γ^- [10]. Figure 2(c) shows a typical result for structural domains within the KT phase after 3500 Monte Carlo steps (MCS) per lattice at temperature of $T = 0.1J/k$, where J is the coupling constant and k is the Boltzmann constant. It is visible that, in addition to vortex-antivortex pairs, the double-wall annular domains appear in many areas in the KT phase in good agreement with our experimental observations, as shown in the lower panel of Fig. 2(c). As the transition between long range order and KT order is accompanied with variation of correlation function and free energy, a large quantity of annular domains condense while the vortex pairs are protected by their logarithmic entropy. However, a few residual annular domains still coexist with vortex pairs in the

KT phase. So the so-called KT phase is a little different from the low-temperature-phase in X-Y model in which only vortex-type topological excitations exist. This conclusion is demonstrated by our experimental and simulated results. The coexistence of circular-type and vortex-type excitations is also observed on the side surface parallel to the c axis. It suggests potential for experimental 3D six-state clock model study. Moreover, the structural configurations, as well as the poling features, for each domain can be directly read out from this simulated image as clearly illustrated in the inserted images. According to our theoretical data, the double-wall structure could have the configurations of $(\alpha^{+/-} \beta^{-/+} \gamma^{+/-})$ or $(\alpha^{+/-} \gamma^{-/+} \beta^{+/-})$. On the other hand, it is also noted that the annular domains could commonly appear at room temperature in RMnO₃ crystals. This fact suggests that this kind of domains can also be arrested by slow kinetic and strong pinning features as discussed in Ref. 13.

We now consider the atomic structures in correlation with the poling configurations and mechanism for the formation of annular domains in RMnO₃. Experimental investigations in the RMnO₃ materials revealed that the FE domain structures can be evidently affected by the defect structures, especially the antiphase boundary. Previous study demonstrated that FE and antiphase domains in RMnO₃ result essentially from the phase transition from $P6_3/mmc$ to a superstructure phase ($P6_3cm$), this superstructure phase adopts a $\sqrt{3} \times \sqrt{3}$ supercell and often contains three types of antiphase domains (so called α , β and γ) and two types of antiphase boundaries as recognizable by relative phase shifts [13,19]. Actually, a clear view of the local polarization and antiphase boundaries (APB) can be directly obtained in the

atomic resolution TEM images taken perpendicular to the c-axis direction. Figure 3(a) shows a typical aberration-corrected TEM image illustrating the alteration of poling direction crossing a FE domain wall (dotted line). In area A of the TEM image, the visible upward distortion for the two thirds of the Er ions in a trimerized pattern suggests an upwards polarization in this area. On the other hand, the downward distortion of two thirds of Er ions in the area B demonstrates a reversed poling feature. In Fig. 3(b), we show a schematic illustration in the upper panel for the Er displacements as measured qualitatively for an Er layer as indicated by an arrow in Fig. 3(a). In order to facilitate the comparisons and structural analysis, we show three schematic pictures illustrating structural features of interlocked ferroelectric and antiphase boundaries in the lower panel of Fig. 3(b), it is exhibited that the ferroelectric boundaries can be interlocked respectively with two types of antiphase boundaries, i.e., (FEB + APB1) and (FEB + APB2). In comparison with the experimental data, we can conclude that the observed domain wall in Fig. 3(a) can be characterized as FEB + APB1. In Figs. 3(c) and (d), we show two simplified models for the concentric circular domains interlocked with the antiphase structures based on our experimental data, respectively. Figure 3(c) exhibits a structural model arising from a regular configuration of $\dots\alpha^+\beta^-\gamma^+\alpha^+\beta^-\gamma^+\dots$ for three types of antiphase domains. This model is in good agreement with the simulated data on the six-state clock model as illustrated in above context. Figure 3(d) shows a possible structural model based on the alternative appearance of only two types of antiphase domains (i.e. $\alpha^+\beta^-\alpha^+\beta^-\alpha^+\beta^-$), which seldom appear in the simulations. It implies that this type of structure is

unstable in this system and the two circle walls can be coalesced together and vanished.

In previous literatures, structural changes of the vortex domains in YMnO_3 have been studied under applied electric fields to reveal its dynamic features [11]. Based on our recent investigations, both the vortex and annular domains in RMnO_3 could show visible dynamic phenomena depending on electron beam intensity during our SEM observations. Actually, we can see clear movements of domain walls and alternation of the domain configurations under an acceleration voltage of $V_0 = 1$ kV. Figures 4(a)-(d) show four frames taken from a video data for a crystal at different time. It is known that the average penetration depth of electron beam for $V_0 = 1$ kV is estimated to be 210 nm which could result in visible charge redistribution and changes of poling properties [12]. On the other hand, the secondary electrons in SEM in general are emitted from a very thin surface layer (about 5 ~ 10 nm), so the experimental images just reveal changes of surface domain structures. Take an annular domain for example, it has the double-layered walls as indicated by an arrow in Fig. 4(a), the polarization between these two walls can be determined to be along the view direction. Under electron irradiation, its outer wall tends to expand and, in contrast, the inner wall shrinks, then the outer wall touches and coalesces with a nearby vortex as shown in Fig. 4(b). As a matter of fact, the radius of the inner circle could decrease continuously and finally become totally disappears (see Fig. 4(c)). Moreover, the coalition between two single-layered domains has been also noted on the right part of these images (indicated by red arrows). In the present case, it is noted the domain

reorganizations turn to be stop about 10 seconds later and yield remarkable large FE domains as shown Fig. 4(b).

The interplay among domains walls of domains can be also observed in our experiments. As mentioned in above context, there are two kinds of domain walls, the experimental data clearly demonstrate that the boundary coalitions only happen among the same type of walls. In addition, according to our observations, two different kinds of walls never coalesce even they are close to each other. These facts suggest that the model shown in Fig. 3(c) is an energetically favored structure in present system.

We now go on to discuss the fundamental properties of multi-layered annular domains in RMnO_3 . Figure 5(a) shows a SEM image to display complex FE domain structures obtained in YMnO_3 crystal. The alternation of poling features from regular annuli at core area B to random vortices at areas A are clearly demonstrated by the PFM measurements shown in Fig. 5(b). In order to understand the evolutions of multi-layered annular domains in correlation with the vortices, we performed a series of thermal annealing experiments, and the domain patterns checked in the crystals were cooled down from different temperatures to room temperature. Our observations show that the multi-layered annular shells can be switched into the ‘cloverleaf’ patterns just above the critical temperature T_c . As a result, certain large ‘vortex’ and annular domains could also observe in some areas. Figure 5(c) shows two SEM images of TmMnO_3 single crystals clearly illustrating the thermal evolution and remarkable change of annular domain above the T_c . These crystals are observed after

cooling it down fast from 1170°C and 1250°C. Our observations demonstrate that the multilayered annular domains are rather stable below 1200°C, and, on the other hand, they change evidently in samples annealed above about 1200°C. It is important to point out that though the multilayered annular patterns with $n \geq 3$ have not been found in our theoretical simulations, this multi-layered annular domain structures have been widely observed in different samples such as YMnO_3 , ErMnO_3 , TmMnO_3 , LuMnO_3 and ScMnO_3 . Though the formation and structural properties of multi-layered domains have been investigated in a variety of samples based on our experimental observation, the mechanism for remarkable domains is still not clear. It is noted that the present structural defects or fissures (edges) in the crystals could evidently affect on the annular domain structures.

In summary, our experimental observations and theoretical simulations for the FE domains demonstrate that annular domains can be stable in a large temperature range in the multiferroic RMnO_3 materials, which appear in the KT phase coexisted with the ‘cloverleaf’ vortices at high temperature and also being visible at room temperature associated with stripe domains. It is believed that the ‘cloverleaf’ vortices and annular domains at low temperature are actually arrested by slow kinetic and strong pinning as discussed in Ref. 13. Based on in-situ SEM observations, the dynamic features as well the interaction of domain walls are analyzed. Moreover, the annular domains often show multi-layered structures, and thermal annealing experiments directly show that the annular domains could change into ‘cloverleaf’ vortices above the trimerization-structural transition temperature T_c . It is expected that the unique

structural features of annular domains could raise a series of new physical issues for further investigations, such as the poling and charging features on domain walls, the domain dynamics.

Acknowledgements

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Figure legends

FIG. 1. Structural features of ferroelectric domains in ErMnO_3 . (a) SEM image of circular domains in the a-b plane. The inset shows the double-wall structure. (b) SEM image showing the interaction of stripe domains (as indicated by arrows) with circular domains in the a-b plane. (c) SEM and (d) PFM images showing the side views of circular FE domains in the a-c plane. The annular structures can be recognized in certain areas.

FIG. 2. FE onion domains with shells of $n = 1, 2$ and multi-shell. (a) Structural models for FE onion domains observed in RMnO_3 . The $n = 1$ onion domain often shows poling features very similar to those of magnetic bubbles. Polarization in RMnO_3 occurs along the c-axis direction as indicated by the arrows. (b) SEM images showing the domain walls for FE domains with different annular numbers in the a-b plane. (c) The domain structures obtained from the six-state clock model in two dimensions through Monte Carlo simulations, showing the coexistence of ‘cloverleaf’ vortices and annular domains. Lower panel: The left insets show the structural features and poling configurations for a vortex and an annular domain from the square marked areas. The right one is an experimental image showing the coexistence of ‘cloverleaf’ patterns and annular domains obtained from an annealed ErMnO_3 sample.

FIG. 3. Atomic structure and interlocked FE domain walls in ErMnO_3 . (a) Cs-corrected TEM image shows the alternation of structural distortions crossing a

domain wall as indicated by dotted line, this image is taken along the [110] direction with $C_s = -13 \mu\text{m}$, and Er and Mn atoms are shown up as bright dots. (b) Upper panel: structural distortions of Er ions crossing the wall as measured from the indicated Er layer in Fig. 3(a). Lower panel: three schematic pictures for domain walls, FEB, FEB + APB1 and FEB + APB2. (c) Structural model for the annular domains arising from a periodic $\alpha^+\gamma^+\beta^+\alpha^+\gamma^+\beta^+\alpha^+\gamma^+\beta^+$ structure, the phase shifts at the boundaries are measured along the $\mathbf{k}$ -direction. (d) A simplified structural model for the circular domains from a periodic $\alpha^+\beta^-\alpha^+\beta^-\alpha^+\beta^-$ structure.

FIG. 4. Dynamic features of annular domains in RMnO_3 on the basic a-b plane. (a)-(d) Four frames taken from a video data reveal the motion of domain walls under electron irradiation. The evolution of an annular domain is indicated by a yellow arrow. The coalition between two single-layered domains is indicated by a red arrow.

FIG. 5. Ferroelectric annular domains in RMnO_3 on the basic a-b plane. (a) Annular pattern for a large onion domain in an YMnO_3 crystal; the vortex patterns appear at the outer shells (area A). (b) PFM image showing the alteration of polarization in the annular domains of Fig. 4(a). The polarizations of the typical domains of $+P_z$ and $-P_z$ are illustrated by “+” and “-” respectively. (c) Thermal annealing effect on a large annular domain above the critical temperature T_c . The upper figure shows a SEM image of multilayered annular pattern in annealed TmMnO_3 at 1170°C which is nearly the same as observed in the as-grown sample. The lower one is obtained from

the same area in the re-annealed sample at 1250°C.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5