Ferroelectric domains in the multiferroic phase of ErMnO$_3$ imaged by low-temperature photoemission electron microscopy

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Abstract. Low-temperature photoemission electron microscopy (PEEM) is used to image and compare the distribution of ferroelectric domains in multiferroic ErMnO$_3$ above and below the magnetic ordering temperature ($T_N = 80$ K). Our temperature-dependent PEEM data demonstrate that the ferroelectric domain structure is robust against the onset of magnetic long-range order and the emergence of antiferromagnetic domains. The observed persistence indicates that antiferromagnetic domain walls adopt the position of ferroelectric walls – and not vice versa – developing a multiferroic domain-wall pattern congruent with the ferroelectric domain-wall distribution observed above $T_N$.

1. Introduction

Hexagonal manganites RMnO$_3$ ($R =$ Sc, Y, In, Dy to Lu) are among the most intensively studied multiferroics, exhibit unusual geometrically driven ferroelectricity and intriguing magnetoelectric coupling, as well as functional domain walls [1][2][3][4][5]. The synthesis of RMnO$_3$ was already reported in 1963 [6] and, in the same year, their ferroelectric and magnetic properties were characterized [7][8][9]. Despite more than half a century of research, however, the multiferroic domain structure emerging in this material class keeps puzzling physicists and materials scientist. The room-temperature ferroelectric domains in RMnO$_3$ were first visualized in 1967 by Safrankova and co-workers [10]. Such domains regained tremendous interest in 2010, when modern high-resolution techniques revealed the formation of topologically protected singularities within the domain structure, as well as exotic domain-switching physics [11][12]. At low-temperature the frustrated spin system in RMnO$_3$ orders antiferromagnetically ($T_N \approx 100$ K), constituting the multiferroic nature of this family of materials [1]. The corresponding multiferroic domain structure was imaged by Fiebig et al. using optical second harmonic generation (SHG) [13]. The spatially resolved SHG data demonstrated the...
coexistence of antiferromagnetic and multiferroic (ferroelectric + antiferromagnetic) domain walls at 6K. The presence of purely ferroelectric domain walls was not observed. The latter suggests that all ferroelectric domain walls become multiferroic walls for $T < T_N$. With a resolution of $\gtrsim 1 \mu m$, however, the SHG microscopy experiments did not resolve the characteristic length scale and fine-structure of the ferroelectric domain distribution. This raises the question if the multiferroic domain-wall pattern at $T < T_N$ reproduces the room-temperature ferroelectric domain structure in all its details, or if the emergence of magnetic long-range order possibly leads to local modifications due to the strong magnetoelectric coupling and magnetostrictive effects.

Here, we address this open question studying the evolution of ferroelectric domains in ErMnO$_3$ across the multiferroic phase transition. Using X-ray photoemission electron microscopy (X-PEEM) we image the ferroelectric domain distribution above and below the Néel-temperature, $T_N$, and compare the position of the respective domain walls with a resolution of about 50 nm. The high-resolution X-PEEM measurements provide direct experimental evidence for the persistence of the ferroelectric domain pattern in the multiferroic phase and its robustness against the onset of magnetic long-range order. Our findings show that the multiferroic walls are formed by antiferromagnetic walls adopting the position of preexisting ferroelectric walls. This implies that their functionality can be engineered even before entering the multiferroic phase by manipulating the ferroelectric domain walls.

2. Experimental Results

For studying the ferroelectric domains in ErMnO$_3$, high-quality single crystals were grown by the pressurized floating-zone method [14]. Oriented platelets with out-of-plane polarization (P $\parallel$ (001)) and dimensions of about 5 x 5 x 1 mm$^3$ were cut and chemo-mechanically polished. The polishing allowed us to prepare flat surfaces with a roughness in the order of one nanometer.

![Figure 1](image1.png)

**Figure 1.** Ferroelectric domain structure in ErMnO$_3$ imaged by PFM and X-PEEM at room-temperature. (a) PFM scan (out-of-plane contrast) taken on (001)-oriented ErMnO$_3$. Domains of opposite polarization are clearly distinguishable due to their bright and dark contrast levels. (b) X-PEEM image gained at room-temperature at a photon energy of 640.9 eV. Dark and bright areas correspond to $-P$ and $+P$ domains, respectively. (c) X-PEEM image gained at room-temperature at the same sample position shown in (b) after cooling to 180 K while continuously irradiating the sample with X-rays at 640.9 eV. The white dashed line indicates the position of the ferroelectric domain wall in (b) with arrows reflecting the direction in which the wall moved during the applied cooling cycle.

2.1. Piezoresponse force microscopy

As a first step, we imaged the room-temperature ferroelectric domain structure of our ErMnO$_3$ samples to investigate the characteristic distribution and size of the as-grown domains. Figure 1(a) displays a piezoresponse force microscopy (PFM) scan taken with an AC voltage of 5 V at ambient conditions on a (001)-oriented sample, i.e., with the spontaneous polarization $P$ normal to the image plane. The
image shows the out-of-plane PFM contrast with dark and bright areas corresponding to opposite domain orientations with $P$ pointing into and out of the plane, respectively. The probed ferroelectric domain structure reflects the six-fold meeting points of $+P$ and $-P$ domains that are characteristic for the hexagonal $R$MnO$_3$ family [11][12]. The ferroelectric domains have an average size of a few micrometers.

2.2. Photoemission electron microscopy

After determining the room-temperature ferroelectric domain state in our samples by PFM measurements, we applied X-PEEM to address the evolution of the ferroelectric domains across the multiferroic phase transition. For this purpose we used the aberration corrected photoemission electron microscope, PEEM-3, at beamline 11.0.1 of the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory (LBNL).

Figure 2. Comparison of the ferroelectric domain structure above and below the multiferroic phase transition in ErMnO$_3$. (a) Integrated second harmonic generation data adapted from ref. [19] tracking the onset of antiferromagnetic ordering and hence multiferroicity in ErMnO$_3$. The dashed line highlights the Néel temperature and red arrows indicate the temperatures at which the X-PEEM measurements shown in (b) and (c) were conducted. (b) X-PEEM image taken at 90 K at a synchrotron energy of 640.9 eV. (c) Spatially resolved X-PEEM data showing the ferroelectric domain distribution in the multiferroic phase ($T = 35$ K).

In Fig. 1(b) we present spatially resolved X-PEEM data taken at room-temperature at a photon energy of 640.9 eV. Two contrast levels are distinguishable revealing a pattern that clearly resembles the ferroelectric domain structure seen in Fig. 1(a) in shape and size. X-PEEM contrasts, however, can originate from various sources such as bound surface charges, screening by internal charge carriers and defects, external screening by adsorbates, as well as band structure and other surface effects [15][16][17]. Thus, in order to demonstrate that the obtained contrasts relate to the ferroelectric domains in ErMnO$_3$, we performed the following test experiment: After recording the image presented in Fig. 1(b), we cooled the sample down to 180 K while irradiating it with synchrotron radiation at an energy of 640.9 eV. Due to the reduced temperature, the conductivity of the semiconducting sample drops. As a consequence, the sample charges positively at the surface and in surface-near regions because the material cannot fully compensate for the emitted photo-electrons [18]. We then increased the temperature back to room-temperature and recorded the X-PEEM image shown in Fig. 1(c). A comparison of Figs. 1(b) and 1(c) reveals that the dark regions have grown at expense of the brighter ones in cause of the X-ray induced positive charging. Based on this behavior, we can conclude that
dark regions correspond to \(-P\) domains with the spontaneous polarization pointing into the image plane, whereas brighter regions are \(+P\) domains of opposite polarization orientation. The charging induced domain growth further indicates that the ferroelectric domain walls can move freely and hence excludes strong domain wall pinning effects.

After demonstrating that the obtained X-PEEM contrasts relate to the ferroelectric domain distribution in ErMnO\(_3\), a platinum (Pt) capping-layer with a thickness of about 1.5 nm was grown on the single-crystal using DC sputtering. We note that no special surface treatment was applied prior to the Pt deposition. Due to the Pt-layer the aforementioned X-ray induced charging effects were completely suppressed so that it was possible to gain X-PEEM images at temperatures down to 30 K.

In Fig. 2(a) we present SHG data adapted from ref. [19] showing the transition temperature \((T_N = 80 \text{ K})\) below which multiferroicity emerges in ErMnO\(_3\). Red arrows indicate the temperature at which the X-PEEM images in Figs. 2(b) and (c) were obtained. Figure 2(b) shows an X-PEEM image (640.9 eV) of the ferroelectric domains at 90 K, i.e., above the multiferroic phase transition. Although the X-PEEM contrasts are less pronounced compared to Fig. 1(b) and (c), a difference in the photoelectron emission from \(+P\) and \(-P\) domains is still clearly visible. We attribute the reduced contrast to the Pt capping-layer. The sample was then cooled down to 35 K and spatially resolved X-PEEM data was recorded in the multiferroic phase as seen in Fig. 2(c). The highlighted area in Fig. 2(c) corresponds to the region shown in Fig. 2(b). The analysis of the domain structure in Figs. 2(b) and 2(c) revealed that the ferroelectric domain walls are unaffected by the magnetic phase transition and that they keep their initial position within the resolution of the experiment (\(\sim 50 \text{ nm}\)).

3. Discussion

By applying low-temperature X-PEEM, we imaged the ferroelectric domains in ErMnO\(_3\) above and below the magnetic phase transition at 80 K. By comparing the set of X-PEEM data we find a one-to-one correspondence concerning the position of the ferroelectric domain walls demonstrating that the onset of magnetic long-range order has no detectable influence on the ferroelectric domain distribution. We note that our low-temperature X-PEEM data provides the first direct evidence for the persistence of the room-temperature ferroelectric domain pattern across the multiferroic phase transition. In all previous RMnO\(_3\) microscopy studies the ferroelectric domains have been resolved at room-temperature and then compared with low-temperature data [20][21]. The observed persistence, however, is by no means trivial as the strong magnetoelectric coupling in RMnO\(_3\) and pronounced magnetostrictive effects that occur at the multiferroic phase transition may locally influence the ferroelectric domain walls.

Based on our findings we conclude that multiferroic domain walls in RMnO\(_3\) are formed by antiferromagnetic walls adopting the position of already existing ferroelectric walls which is consistent with the literature data [13][20][21][22]. The fact that no pure ferroelectric domain walls were observed in previous SHG studies suggest that every ferroelectric domain wall serves as such a pinning centre, so that the multiferroic walls establish a pattern that is identical to the ferroelectric one seen e.g. in Fig. 1(a). In consequence, it is possible to control the density and distribution of the multiferroic domain walls by acting on the room-temperature ferroelectric domains. Under strain the ferroelectric structure in Fig. 1(a), for instance, transforms into stripe patterns [23], bubble-shaped domains can be induced by thermal treatment [24], and completely new ferroelectric domain and domain wall states emerge in highly doped samples [25]. In addition, the position of the ferroelectric domain walls and their transport properties can be tuned by electric field poling [4][12][26]. Thus, it is possible to pre-determine functional aspects of the multiferroic domain walls even before entering the multiferroic phase.
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