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Nanoscale analysis of dispersive ferroelectric domains in bulk of hexagonal multiferroic ceramics

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ABSTRACT

The atomic nature of topologically protected ferroelectric (FE) walls in hexagonal $ReMnO_3$ oxides (R: Sc, Y, Er, Ho, Yb, Lu) creates an interesting playground to study effects of defects on domain walls. The 6-fold FE vortices in this multiferroic family lose the ordering by the rule of 6 in the presence of partial edge dislocations (PED) besides it can be modified by chemical doping. Therefore, it is essential to comprehend the cross coupling of FE walls and defects or vacancies in the lattice of multiferroics. Atomic resolution STEM is used to explore the correlative response of electrical polarization of FE domains in the presence of defects in multiferroic ceramics. Such level of resolution also allows the study of switching of FE domains on encounter of lattice defects. The driving force behind appearance of dispersed, small FE domains in images of piezo force microscopy is revealed by observation of lattice defects and FE boundaries simultaneously at the nano-scale. Planar defects and FE domain walls play their role of internal interfaces consequently such interplaying duly modifies the magnetic and FE properties of multiferroic oxides.

1. Introduction

Recent appearance of interlocking of ferroelectric domain walls and structural anti-phase boundaries in hexagonal lattices of $RMnO_3$ oxides pushed researchers to investigate properties of FE domains and rules governing their emergence [1–4]. It was shown that 6-fold vortices, also called cloverleaf patterns, consist of 6 FE domains of which the polarization direction (displacement of R ions with 4b Wyckoff sites) is reversed upon crossing the domain wall. Lattice energy at structural antiphase domain boundaries created at trimerization stage is decreased by switching the direction 4b R^{3+} ion displacements in coincidence with the phase shift by in-plane displacement of apical oxygen ions [2].

Vacancy doping of Mn or Lu cation sites duly modifies multiferroic properties of self-doped h-$LuMn_xO_{3\pm\delta}$ ceramics, as previously shown by one of us, where it was also found that self-poling introduces point defects in the lattice which interact with FE domain walls [5]. Manipulation of 6-fold FE vortices in h-$RMnO_3$ oxides has been achieved via controlled cooling rate [1], doping the lattice [6–8], oxygen vacancies [9,10] and mechanical strain [11]. The atomically sharp nature of FE domain walls makes their study feasible only with nano-analytic tools like TEM/STEM of sub-angstrom resolution to display R ion displacements and right identification of grains with adequate crystal orientation if one works with bulk ceramics [12,13]. These issues became the object of current research employing probe-corrected STEM to get distinct representations of FE domain switching upon meeting extended lattice defects in vacancy disordered lattices. Rare studies on polarization switching, or phase shifting of FE domains in the presence of lattice defects demand further investigation. To gain additional insight into interactions of defects and FE domain walls, self-doped ceramics with off-stoichiometric composition of either Lu, or Mn excess were selected for this study.

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2. Experimental Section

2.1. Sintering of Ceramics

The solid state reaction method with suitable mixing of the Lu_2O_3 (99.999%) and MnO_2 (99.999%) oxides was used to produce ceramic pellets. Firing of samples was done in three steps with intermediate grinding, ended at 1300 °C after 5 days annealing in air to obtain properly reacted ceramics [14]. All sintered ceramics present the $P6_3cm$ space group as main phase within the detection limit of XRD analysis (supplementary materials, Fig. S1).

2.2. Microscopy Analysis

TEM/STEM sample preparation was done by mechanical polishing down to 10 μm controlled by silicon transparency followed by gentle Ar^+ ion milling. Preliminary TEM analysis was done with the JEOL JEM2200FS FEG 200 kV electron microscope. HAADF-STEM images of sub-Angstrom resolution were taken using the C_s/probe-corrected Titan Themis TEM/STEM microscope operated at either 200 kV or 300 kV, 30 mrad convergence angle and over 80 mrad collection angle for HAADF detector.

3. Results and Discussion

Displacement of Lu ions in the HAADF-STEM image along [110] zone axis of sample $LuMn_{0.96}O_{3\pm\delta}$ in Fig. 1a is well resolved and shows upward FE polarization by Lu displacement [12]. Mn ions fill rows of weaker contrast between the rows of Lu ions in agreement to the $P6_3cm$ crystalline structure of $LuMnO_3$ phase. Close observation of the image revealed a boundary separating the regular hexagonal lattice of $P6_3cm$ symmetry (above) from a monoclinic-like distortion of the lattice (bellow) with c-axis tilted by approximate 2° in relation to the orthogonal direction with a-b plane, the orthogonal being given by the yellow line in Fig. 1a. In the upper half of the image the yellow line overlaps with the origin of FE periods. The white line on low-right gives the change in position of origin of corresponding FE periods in c-axis-tilted area. Border between the two areas coincides with anomalous

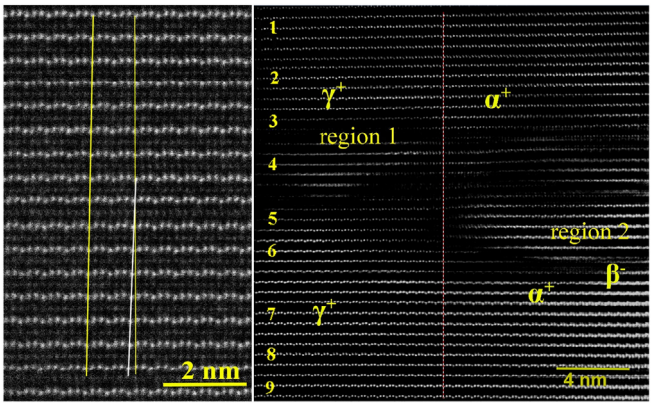

Fig. 1. HAADF-STEM images along [110] zone axis of two regions of a grain h-$LuMn_xO_{3\pm\delta}$ ceramics with x = 0.96 composition. a) One (001) boundary plane separates the regular hexagonal $LuMn_{0.96}O_{3\pm\delta}$ lattice (above) from distortion of hexagonal lattice with monoclinic axis (white line on right) with α = 90°, β ≅ 87.7° and γ = 120° showing a partial dislocation ribbon. b) HAADF-STEM image of the defective region of the same crystalline grain of (a). FE domains of same polarization direction, but of different phase are observed (indicated as α^+ and β^+). From left to right of the image, a low angle boundary of 1.12° rotates the planes of Lu ions under the effect underlying stacking faults. Areas marked 1 and 2 will be object for further analysis in Fig. 2. Numbers on the left of image give the atomic planes selected for calculation of ionic polarization along the vertical dash line in the middle of the figure.

interspacing of Lu-planes 20% wider than the regular spacing of the Lu planes. White line meets the reference yellow line at this boundary plane. The end of the lines on the low-right marks the position where the crystalline lattice returned to regular hexagonal alignment, the width of tilted band being approximately $4c_0$ (c_0, the c-constant of the unit cell). Development of this slightly tilted band of narrow width in the lattice of $LuMn_{0.96}O_{3\pm\delta}$ bears remarkable similarity with dislocation structures of another hexagonal lattice of ionic species, the crystalline lattice of corundum, the α-Al_2O_3, where gradual displacement of O^{2-} ions in the $[1\bar{2}10]$ direction of the quarter partial dislocation gliding in the basal plane is linked to simultaneous shift of Al^{3+} interstitials in octahedral sites, the gradual displacement of ions being distributed by fractional displacements over a dozen consecutive planes of the dislocation ribbon [15]. The Burger vector of displacement of the regular lattice of $LuMn_{0.96}O_{3\pm\delta}$ on upper half of Fig. 1a slipped by $\overrightarrow{b_p}$ in relation to the unslipped lattice bellow the tilted band is approximately $\overrightarrow{b_p} \cong 1/6[1\bar{1}0]$. The width $4c_0$ of the partial dislocation ribbon yields the shear strain $|\overrightarrow{b_p}|/c_0$ of 3.8% and shear angle 2.2°.

Examination of other areas of same particle showed defective areas with stacking faults and revealed switching FE polarization direction from upward to downward at several places. Also, analysis of Lu ion displacements shows phase shift along atomic planes of Lu ions with the constant FE polarization direction which breaks the ground rule of 6-fold vortices but is permitted by the presence of partial dislocations and correlated planar defects of crystalline lattices [8,16].

The strain field of a probable stacking fault in the center of Fig. 1b caused the phase shift of FE domains above and below the defect. Considering α^+ the phase of FE domains on the right side there is gradual change in the azimuthal angle which determines the phase of FE domains, ending in the γ^+ phase on the left [12] (Fig. S2 shows the phase shift from one domain to another one using a scale to determine the phase shift). Since this angle is defined by the shifting of the direction of apical oxygen from α^+ [2], appearance of a second phase with the same polarization of FE domains uncovers the effect of stacking fault on the tilting of MnO_5 bipyramids which resulted in breaking the rule of 6-fold vortices. FE vortices of different phase but one same polarization would not be energetically favorable in a regular h-$RMnO_3$ lattice [2]. But, the appearance of a phase shift in FE domains of fixed polarization direction in the lattice of $YMnO_3$ and $Y_{0.67}Lu_{0.33}MnO_3$ single crystals was explained by the concomitant presence of a partial edge dislocations (PED) coupled to vortex lines [8,16]. In aforementioned studies, on the boundary of the FE domains with same polarization, extra (030) atomic planes of the PEDs were detected thus creating phase shifts in the lattice. The PED's appeared linked to vortex cores whenever the lattice lost the ground symmetry of regular trimerization.

Although no evidence of extra atomic planes is found by moving from below to top of the image in Fig. 1b, twisting of Lu planes by 1.12° is detectable. On the right side of the defect polarization switching is not seen except at the low right corner, continued as Fig. 2a, where β^- phase appears, the domain wall (marked by the dashed line in this figure) is of type I (1/3 of unit cell) [13]. This domain wall displays combination of DW perpendicular to the polarization direction (transversal domain wall, TDW) and DW parallel to the polarization direction (longitudinal domain wall, LDW), a domain wall of type C [17]. This region of reverse polarization is small. It can be considered a nano-FE domain of negative polarization immerging in a composite area of positive polarization.

Split planes of Lu ions with positive and negative polarization facing each other were found at the border in region of Fig. 1b, propagated to the left and enlarged in Fig. 2b. The distance between two Lu planes of opposite polarization in the split pairs of the disordered region ranges from 0.15 nm to 0.23 nm in average and looks insufficient to interleave any Mn plane between them. The specific contrast of Mn planes in non-defective regions is missing in the image of Fig. 2b. In the regular lattice