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Effects of Strain and Ordering of Rare-Earth Element Moments on Magnetic-Reordering in Orthorhombic Multiferroic Manganites

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Orthorhombic multiferroic manganite thin films with various orientations and strain states were prepared to show the effects of anisotropic strain and antiferromagnetic (AFM) ordering of rare-earth f-electrons on the orientation of the incommensurate-to-commensurate AFM reordering. Systematic analyses suggest that the low-temperature AFM ordering of the rare-earth f-electrons may have played a decisive role in causing the orientation changes in AFM reordering, although the *b*-axis strain does have a significant influence on the zero-field magnetization behaviors.

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The anticipated applications promised by manipulating the ferromagnetic (FM) and ferroelectric (FE) orders coexisting in various multiferroic materials with external electric and/or magnetic fields have triggered extensive research interests over the last decade.^{1–4)} However, since the magnetic-ordering-induced electric polarization originally observed in TbMnO₃ was rather weak,¹⁾ seeking new materials with enhanced magnetism-induced electric polarization became a hotly pursued task. In 2006, Sergienko et al.⁵⁾ theoretically predicted that, the incommensurate-to-commensurate (ICM–CM) transition occurring below the Néel temperature (T_N) of the E-type antiferromagnetic (AFM) HoMnO₃ (o-HoMO) might induce FE polarization orders of magnitude larger than that observed in the improper magnetic ferroelectrics with helical AFM ordering. Unfortunately, the rare-earth manganites (ReMnO₃) with E-type AFM structures are not the thermodynamically stable phases under ambient conditions. Thus, the metastable orthorhombic bulk samples can only be prepared by means of high-temperature high-pressure synthesis or by the citrate-based soft chemistry method.^{6–8)} The polycrystalline nature of these bulk samples has inevitably blurred the expected magnetism-induced ferroelectricity. Very recently, Lee et al.⁹⁾ have successfully grown o-HoMO single crystals and reported some prominent unexpected results. Namely, it was shown that, in contrast to the theoretical prediction, the electric polarization along the *a*-axis was partially vanished and the spin wave vector along the *b*-axis was no longer 0.5. Specifically, the exchange striction between Ho–Mn was identified to be responsible for the large polarization along the *c*-axis emerging at $T < T_N$. This is also consistent with some of the earlier observations made in substrate-stabilized ReMnO₃ systems, wherein unexpected polarization along the *c*-axis^{10,11)} and orientation of magnetic ordering deviated from the theoretical predictions^{10–14)} were observed.

On the other hand, owing to the successes of growing o-ReMnO₃ thin films with specific out-of-plane and in-plane orientations,^{10–16)} it is suggested that the existence of the *b*-axis strain may have played an important role in enhancing the magnetization when measuring along a specific crystallographic axis and altering the ordering behaviors of magnetic moments in o-YMnO₃ thin films.^{15,16)} Very recently, Jiménez-Villacorta et al.¹⁷⁾ reported that the AFM state of o-YMnO₃ thin films can even shift from E-type to A-type and

eventually cross into a spiral spin state, depending on the substrates onto which the films were epitaxially grown. These observations strongly indicate that the structural strains could also play an important role in tuning the ordering of the AFM states and, hence, the detailed electric polarization behaviors in multiferroic manganites. It appears that both the coexistence of Mn–Mn and Re–Mn interactions as well as the strain states in the films are affecting the eventual orientation of magnetic ordering transition and, hence, the electric polarization. The question is which one is the more dominant factor? In order to address this issue in a more systematic manner, in this study, we performed detailed magnetization measurements on o-YbMnO₃ (o-YbMO) and o-TmMnO₃ (o-TmMO) films grown on different substrates to produce different strain states. The systems were intentionally chosen such that the magnetic moments of the rare-earth ions vary from $S = 1/2$ for Yb³⁺ to $S = 1$ for Tm³⁺, as compared with $S = 2$ for Ho³⁺. The results indicate that the epitaxy-induced strain along the *b*-axis appears to have a negligible effect on changing the orientation of magnetic reordering, although it does noticeably affect the behaviors of temperature-dependent magnetization. On the other hand, comparisons made among the rare-earth elements with different f-electrons moments suggest that AFM ordering of these f-electrons moments and the coexistence of magnetic interactions between Mn–Mn and Re–Mn ions may play an even more important role in the orientation of magnetic reordering transition. Moreover, increasing the applied external field has evidently decreased the reordering transition temperature and the magnitude of magnetization, which is consistent with that observed in our earlier work on o-HoMO thin films.^{11–13)}

The sizes of the Yb³⁺ and Tm³⁺ ions are 0.858 and 0.869 Å, respectively. They are smaller than Y³⁺ (0.9 Å) and Ho³⁺ (0.901 Å). Thus, when stabilized into the orthorhombic phase, o-YbMO and o-TmMO are structurally even more distorted than o-YMnO₃ and o-HoMnO₃. The lattice constants of o-YbMO (o-TmMO) are $a = 5.216$ Å (5.228 Å), $b = 5.799$ Å (5.809 Å), and $c = 7.299$ Å (7.318 Å) (in *Pbnm* setting).^{14,18)} Thus, in order to stabilize the phase and epitaxially grow the o-TmMO and o-YbMO thin films with controllable orientations, it is necessary to select the suitable substrates. In this report, we chose Nb (0.5 wt %) doped SrTiO₃(110) (NSTO) substrates to grow o-YbMO(100) and

o-TmMO(100) films, whereas STO(100) substrates was chosen to grow o-YbMO(001) film. Zhang et al.¹⁹ had demonstrated that although Nb-doping could enhance the conductivity of STO dramatically, no ferromagnetism was observed in temperature range of 5–365 K, even co-doped with magnetic ions. Thus the choice of NSTO should not affect the magnetic properties of the deposited films. Sintered ceramic pellets of stoichiometric YbMO and TmMO were prepared by the conventional solid-state reaction method and used as targets for the subsequent pulsed laser deposition (PLD). The substrate temperature and oxygen pressure were optimized to within the window between 800–900 °C and 50–100 mTorr, respectively. The thickness of thin films was around 140 to 200 nm, as independently determined by α -step and atomic force microscopy (AFM) measurements. The crystal structures of the as-grown films were characterized by X-ray diffraction (XRD) with a monochromatic Cu-K α radiation. The temperature-dependent magnetization [$M(T)$] was measured using a Quantum Design superconducting quantum interference device system (SQUID).

Figure 1(a) shows the θ - 2θ XRD scan for the as-deposited o-YbMO(100), o-YbMO(001), and o-TmMO(100) films on selected substrates, respectively. The diffraction peaks reveal only reflections of preferred orientations of o-YbMO and o-TmMO, and no other discernible impurity phase was observed. Furthermore, as shown in Fig. 1(b), the ϕ -scans of the o-YbMO(100) and o-TmMO(100) films display a clear twofold symmetry, indicating that the films are indeed epitaxially aligned with the substrate. On the other hand, the o-YbMO(001) film evidently exhibits fourfold symmetry characteristics in the ϕ -scan results, implying that the in-plane a -axis and b -axis of this film are undistinguishable. The nearly perfect epitaxial relation revealed in the ϕ -scan results is consistent with the expected lattice alignments between the targeted film orientation and specifically chosen substrate, although the initial mismatches between respective film/substrate orientations were significant in some cases.

Taking the o-TmMO(100) on NSTO(110) as an example, the bulk lattice constants of o-TmMO ($b = 5.809 \text{ \AA}$, $c = 7.318 \text{ \AA}$)¹⁸ and the in-plane lattice constants of the NSTO(110) substrate ($[1\bar{1}0] = 5.522 \text{ \AA}$, $[002] = 7.810 \text{ \AA}$) are expected to result in initial mismatches of -4.94 and 6.72% along the b -axis and c -axis of the film, respectively. For comparison, using the lattice constants of the out-of-plane and respective in-plane orientations determined from the θ - 2θ and ϕ -scan measurements, the residual strains calculated with the formula $(d_{\text{film}} - d_{\text{bulk}})/d_{\text{bulk}}$ are -1.77 and 0.97% along the b -axis and c -axis of the o-TmMO(100)/NSTO(110) films, respectively. This implies that during the film growth process, the initial mismatch strain has been relaxed drastically, namely, by 3.17 and 5.75% along the b -axis and c -axis, respectively. It is noted that, although it is unusual to have such a substantial residual strain remaining in films with thickness of ~ 150 nm, similar results were in fact ubiquitously observed in similar manganite films.^{15,16} Results obtained from films with different growth orientations are summarized in Table I together with that of o-HoMnO₃ films and the respective bulk values reported in the literature for comparison.¹¹ It is evident from Table I that all films appear to be under compressive strain along the

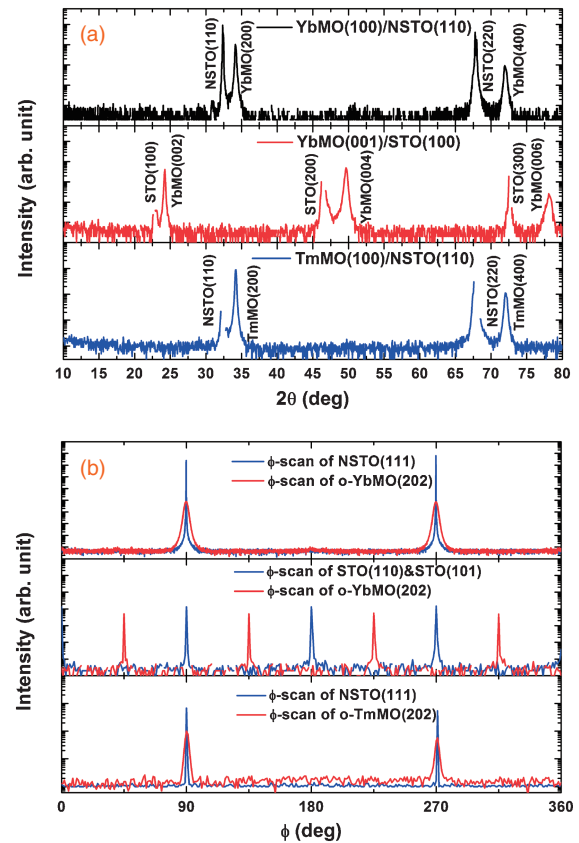


Fig. 1. (a) θ - 2θ diffraction patterns of o-YbMO(100)/NSTO(110), o-YbMO(001)/STO(100), and o-TmMO(100)/NSTO(110) films. (b) Azimuthal ϕ -scan of (202) peaks of o-YbMO and o-TmMO films.

b -axis, which is the orientation along which the collinear AFM ordering relevant to multiferroicity occurs.

Figure 2 shows the zero-field-cooled (ZFC) [$M(T)$] probed with a field strength of 300 Oe applied along various crystallography orientations of the o-YbMO(100) films. An apparent ordering transition near 43 K is evident in $M(T)$ curves obtained with the field applied along the three major orientations, which is consistent with the AFM ordering of Mn³⁺ moments for o-YbMO obtained from specific heat measurements.¹⁸ However, substantial magnetization is also attained after the AFM transition, indicating that a moderate ferromagnetism may have occurred in these o-YbMO(100) films. The other feature to be noted in Fig. 2 is an additional broad peak around 36 K, which appears only when the field is applied along the b -axis and is absent when probing along the a -axis and c -axis. According to the specific heat measurements¹⁸ and neutron diffraction results,²⁰ we consider that the broad peak should be the manifestation of the magnetic reordering transition of o-YbMO.

Figure 3 shows the results obtained from similar $M(T)$ measurements performed on the o-YbMO(001) films. Apparently, the $M(T)$ behaves very differently as compared with that of the o-YbMO(100) films. In this case, although the AFM transition still occurs at around 43 K when probed either with the field applied in-plane or out-of-plane, the ZFC magnetization appears to follow the typical AFM behavior without exhibiting apparent ferromagnetism at lower temperatures. Moreover, as displayed in Fig. 3(b), the reordering temperature of the o-YbMO(001) films is

Table I. Strain factors defined as $(d_{\text{film}} - d_{\text{bulk}})/d_{\text{bulk}}$ within respective crystallographic axes, spin quantum number of rare-earth f-electrons,²⁴⁾ and corresponding orientations of magnetic reordering transition for various films grown on selected substrates. The polarization orientation was determined by dielectric or polarization measurement.^{9,12–14,25)}

Oriented films/substrate	a (Å) (strain factor %)	b (Å) (strain factor %)	c (Å) (strain factor %)	Spin moments (S)	Magnetic reordering orientation T_{ro} (K)	Polarization orientation
o-HoMO single crystal ⁹⁾	5.2689	5.8450	7.3698	2		c
(100)/NSTO(110) ²⁵⁾	—	—	—	2	a (26)	a
(010)/LAO(110) ¹¹⁾	5.28 (0.38)	5.80 (−0.69)	7.51 (2.04)	2	c (30.4)	
(001)/NSTO(100) ¹²⁾	5.25 (−0.19)	5.76 (−1.37)	7.47 (1.49)	2	c (34.6)	c
(001)/NSTO(100) ¹³⁾	5.251 (−0.11)	5.767 (−1.16)	7.464 (1.40)	2	c (34.2)	c
o-TmMO bulk ¹⁸⁾	5.228	5.809	7.318	1		
(100)/NSTO(110) ¹⁴⁾	—	—	—	1	a (32)	a
(100)/NSTO(110)	5.231 (0.06)	5.706 (−1.77)	7.389 (0.97)	1	a (36)	
o-YbMO bulk ¹⁸⁾	5.216	5.799	7.299	1/2		
(100)/NSTO(110)	5.241 (0.48)	5.702 (−1.67)	7.458 (2.18)	1/2	b (35.8)	
(001)/STO(100)	5.520 (5.83)	5.533 (−4.59)	7.374 (1.03)	1/2	ab (38)	

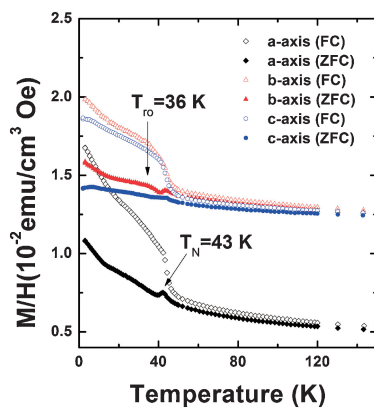


Fig. 2. FC (open symbol) and ZFC (solid symbol) $M(T)$ curves of o-YbMO(100) film probed along different crystal orientations at 300 Oe.

observed only when the field is applied in-plane and is fairly sensitive to the strength of the applied field, namely, changing from $T_{\text{ro}} = 38$ K for $H = 200$ Oe to $T_{\text{ro}} = 33$ K for $H = 1000$ Oe. Whereas for o-YbMO(100) films, the T_{ro} has been identified to be around 36 K for $H = 300$ Oe (Fig. 2) and it was virtually unrecognizable for $H = 1000$ Oe. These observations clearly indicate that the magnetic reordering is not only dependent on the applied field strength as seen in o-HoMnO₃ films,¹¹⁾ but also sensitive to the film strain state. Nevertheless, unlike that observed in o-HoMnO₃ films,^{11–13)} the b -axis strain in o-YbMO films (Table I) appears to have no influence on the orientation of magnetic reordering.

In order to further elucidate the effect of f-electron moment and strain on the magnetic reordering transition, a series of o-TmMO(100) films were prepared. In that, Tm³⁺ has two unpaired f-electrons, whereas Yb³⁺ and Ho³⁺ have one and four f-electrons, respectively. As is evident from Fig. 4(a), T_{N} is around 43 K for o-TmMO(100) films, regardless of the applied field orientation. However, the

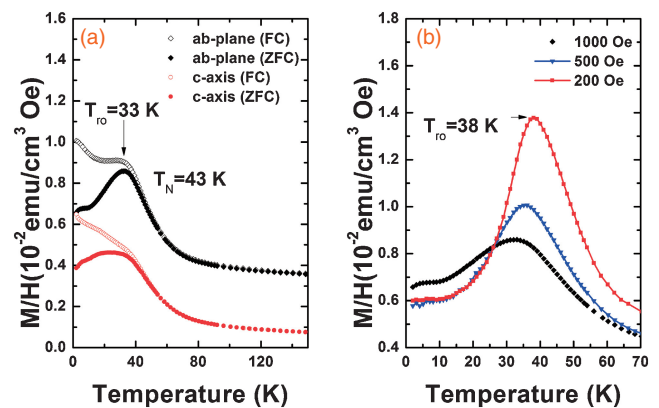


Fig. 3. (a) ZFC (solid symbols) and FC (open symbols) $M(T)$ curves of o-YbMO(001) film probed along c -axis and ab -plane at 1000 Oe. (b) ZFC- $M(T)$ along the ab -plane measured at 200, 500, and 1000 Oe.

magnetic reordering transition occurring around 36 K can only be observed when the probing field is applied along the a -axis, in contrast to the reordering along the b -axis in YbMO films described above. Furthermore, Fig. 4(b) shows that T_{ro} is suppressed to lower temperatures with increasing applied field, which is consistent with that seen in Fig. 3(b) and in a previous report.¹³⁾ It is interesting to note that, although all films are subjected to compressive strain along the b -axis (Table I), the orientation of magnetic reordering transition appears to be irrelevant to the strain state existing in these orthorhombic manganite films. This observation leads us to believe that the magnetic interaction between Mn³⁺ and Re³⁺ might be the primary reason driving the reordering transition of the Mn moment away from the expected crystallographic axis, the b -axis. According to Picozzi et al.,²¹⁾ high- and low-spin states of the Re³⁺ ions could change the magnetic ground state energy, which implies that the spin quantum number of Re³⁺ may

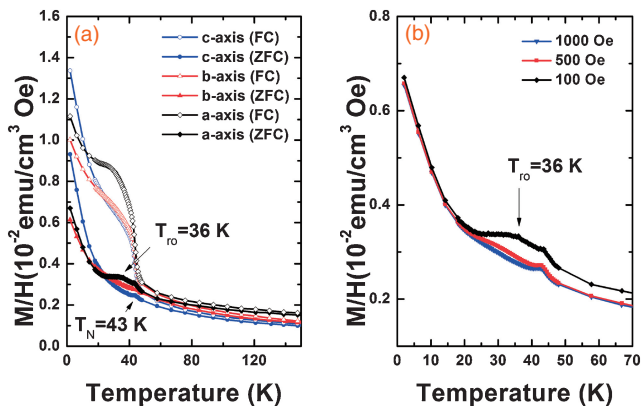


Fig. 4. (a) $M(T)$ of FC (open symbol) and ZFC (solid symbol) for o-TmMO film probed along the different crystal orientations at 100 Oe. (b) ZFC- $M(T)$ along a -axis measured at 100, 500, and 1000 Oe.

significantly disturb the magnetic behaviors of o-ReMO. Lee et al.⁹⁾ reported that the existence of weak polarization along the c -axis resulting from the exchange striction could be attributed to the coupling between the Ho^{3+} moment and AFM ordering of the Mn^{3+} ions. As summarized in Table I, the fact that the eventual magnetic reordering orientation changes from along the b -axis for YbMO ($S_{\text{Yb}^{3+}} = 1/2$) to along the a -axis for TmMO ($S_{\text{Tm}^{3+}} = 1$), and finally, to along the c -axis for HoMO ($S_{\text{Ho}^{3+}} = 2$) seems to indicate that the spin quantum number of the rare-earth elements is indeed a more relevant factor. Since the orientation of the magnetic reordering is intimately related the exchange striction-induced polarization and has not been explicitly taken into account theoretically, it is not surprising that extensive experimental results reported for various E-type orthorhombic multiferroic manganites exhibit deviations from theoretical predictions. Alternatively, it has been demonstrated recently that the competition between the E-type and cycloidal magnetic orders has played a prominent role in giving rise to spin canting towards c -axis in YMnO_3 , even though there is no f -electron involved.^{22,23)} However, since the existence of competing magnetic ordering has not been identified in systems discussed here, the possibility of the alternative thus remains open and further investigations are certainly needed.

In summary, a series of o-YbMO and o-TmMO films with well-aligned crystallographic orientations on selected substrates have allowed us to access the orientation-dependent physical properties of these intriguing multiferroic systems. The $M(T)$ measurements showed that the b -axis strain is relatively irrelevant to the deviations of magnetic reordering orientation occurring at temperatures slightly below the antiferromagnetic transition temperature, although it does result in significantly different magnetization behaviors. Instead, we observed that the spin quantum number of f -electrons of the rare-earth elements might have contributed substantial complex magnetic interactions with the moments

of manganese ions, which in turn causes the reordering orientation to deviate from the theoretically predicted b -axis. Our results suggested that, in order to fully comprehend the rich emergent magnetoelectric properties of these strongly correlated systems, it is necessary to include the exchange interactions between the rare-earth element and manganese ions.

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