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Magnetic transition anisotropies in orthorhombic $LuMnO_3$ and $HoMnO_3$ multiferroic thin films

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Abstract. We have successfully prepared the *b*-axis-oriented orthorhombic $LuMnO_3$ (LuMO) and $HoMnO_3$ (HMO) thin films by pulsed laser deposition on (110)-$LaAlO_3$ substrates. The nearly perfect alignment between the film growth orientation and the substrate allows us to study the magnetic transitions along the respective crystal orientation, which has displayed marked anisotropic behaviours. In particular, with the largest ionic size difference between Lu and Ho for the family of $RMnO_3$ displaying the *E*-type AFM, the effects of lattice distortion on the magnetic transition are compared.

1. Introduction

Orthorhombic phase rare-earth manganites ($RMnO_3$ with R = Ho, Er, Tm, Yb, and Lu) are expected to exhibit an incommensurate antiferromagnetism (ICAFM) to *E*-type AFM transition with an induced ferroelectric polarization to accompany the magnetic transition [1-4]. However, direct demonstration of these fascinating phenomena has been hindered by the challenges in obtaining samples with the desired phase and, especially with definite crystallographic orientations, namely single crystals. Indeed, previous measurements performed on bulk polycrystalline orthorhombic $HoMnO_3$ (*o*-HMO) revealed only a minute ferroelectric polarization ($P \approx 9$ nC/cm^2) with evidences suggesting the possible involvement of Ho moments in the development of P [5, 6]. In trying to clarify some of these seemingly disputable issues, we have recently succeeded in preparing orientation-specified *o*-HMO thin films on various substrates [7-9]. These films, in addition to exhibiting the ICAFM transition with $T_N \sim 42$ K and expected magnetoelectric effects, have displayed distinctive magnetic transition anisotropies at lower temperatures, which are believed to arise from the strain-induced effect on the ICAFM to commensurate *E*-phase AFM transition. However, owing to the overwhelming paramagnetic background from the Ho moments, the conclusions drawn from the temperature dependent magnetic susceptibility, $\chi(T)$, need further experimental supports. Moreover, as pointed out by Muñoz *et al*. [10], the size of the rare-earth ion may also affect the magnetic ground states of $RMnO_3$ manganites due to the tilting of the MnO_6 octahedra and presence of the Jahn-Teller distortion. Recent neutron powder diffraction study on orthorhombic $LuMnO_3$ (*o*-LuMO) polycrystalline sample synthesized under high-pressure has shown that, in this material, Mn-moments display an AFM transition with $T_N \sim 40$ K and transform into an *E*-type AFM magnetic structure near 10 K, which is much lower than that of *o*-HMO [11]. Previously, it has also been suggested that epitaxial strain existing in substrate-stabilized orthorhombic $YMnO_3$ (*o*-YMO) films may modify the magnetic structure, and hence the accompanying induced polarization [12].

It is thus interesting to investigate the roles played by lattice strain in shaping the eventual magnetic structure and associated magnetoelectric effect in these multiferroic perovskite maganites. In this study, we compare the effects of lattice strain, resulting from both the ionic size difference and the film/substrate epitaxial relations, on the anisotropic characteristics of magnetic transitions exhibited in *o*-LuMO and *o*-HMO films.

2. Experimental details

Sintered ceramic pellets of stoichiometric LuMO and HMO were prepared by conventional solid-state reaction method and used as targets for the subsequent pulsed laser deposition (PLD). The as-prepared bulk samples were all hexagonal manganites. For growing thin films, a 248 nm KrF excimer laser operated at a repetition rate of 3 Hz with an energy density of 2-4 J/cm^2 was used. The growth temperature and oxygen pressure were optimized at T_g = 800 °C and 850 °C for LuMO and HMO, respectively, with $P(O_2)$ = 0.1 Torr. The deposited film thickness were about 150 nm (LuMO) and 180 nm (HMO), respectively, as determined by α-step measurements and confirmed by x-ray reflectivity measurements. The crystalline structure and corresponding lattice constants of the as-grown films were characterized by four-circle high resolution x-ray diffraction (XRD) with both θ-2θ and ϕ-scans. The temperature dependent magnetic susceptibility ($\chi(T)$) was measured using a Quantum Design® SQUID system.

3. Results and discussion

Figure 1 shows the $\chi(T)$ results of the as-prepared hexagonal phase $HoMnO_3$ and $LuMnO_3$ powders. It is apparent that there is a magnetic structure transition occurring around 85 K for $LuMnO_3$ [13], while it is indistinguishable for $HoMnO_3$ presumably due to the near two orders of magnitude larger paramagnetic background arising from the Ho moments. The magnetic structure transition for these hexagonal manganites is believed to be the frustrated AFM ordering of the Mn moments, which might also explain the peculiar rising in the zero-field-cooled (ZFC) $\chi(T)$ of $LuMnO_3$ for $T < T_N$. The magnetic susceptibility of $HoMnO_3$ is, nonetheless, dominated by the Ho moments over the entire temperature range measured. Figure 2 shows the results of the θ-2θ and ϕ-scans of four-cycle high resolution x-ray diffraction (XRD) for the *o*-LuMO and *o*-HMO films grown on $LaAlO_3$(110) substrates. It is evident that the films not only are of pure orthorhombic phase but also exhibit nearly perfect orientation alignment with the substrates. That is it allows one to probe the physical properties of these films along the three principal crystalline axes. The lattice constant analyses also indicate that owing to the in-plane stretch along the *a*- and *c*-axis, the *b*-axis of both films is under compressive strain. Since it is the crystalline axis along which the commensurate magnetic wave vector propagates when the ICAFM to CM-collinear *E*-phase transition takes place [10-11], one expects that some extrinsic effects might arise due to the *b*-axis compressive strain.

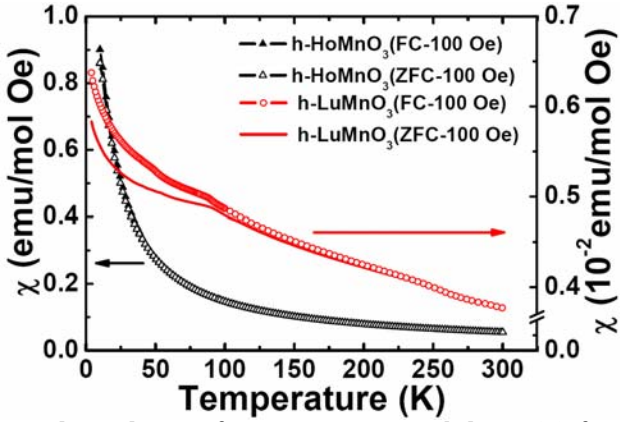

Figure 1 The temperature dependence of magnetic susceptibility $\chi(T)$ for the hexagonal $HoMnO_3$ and $LuMnO_3$ powders. The symbols are for field-cooled (FC) measurements, while the lines are the zero-field-cooled (ZFC) results.

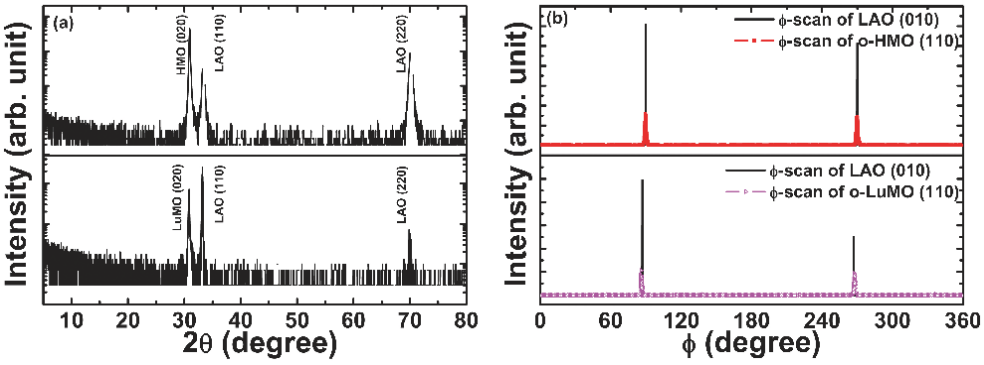

Figure 2 (a) The θ-2θ scans around 85 K of the films grown on $LaAlO_3$(110) substrates, showing that the films are single-phase *b*-axis-oriented orthorhombic perovskite manganites (in *Pbnm* space group settings). (b) The ϕ-scans of the same films displayed in (a), showing the nearly perfect in-plane alignments between films and substrates in both cases.

As shown in Fig. 3, the χ(*T*) measured along the respective principal crystalline axis exhibits apparent anisotropic characteristics in terms of temperatures at which the magnetic structure transition occurs as well as the magnitude of susceptibility itself. At first, the expected AFM transition at 42 K can be easily indentified in each case and it appears to be extremely robust against the lattice strains. Nevertheless, a closer examination immediately indicates dramatic differences in magnetization behaviors of these two structurally similar materials. Previously, we have indicated that, for *o*-HMO films, since the *b*-axis (in *Pbnm* group symmetry setting) is the easy axis which explains the larger *b*-axis magnetization observed over the entire temperature range [7-9]. Furthermore, the spin reorientation (T_s ~ 26.4 K) identified in the χ(*T*) of the *c*-axis might be attributed to the ICM to CM magnetic structure transition, which has been affected by the compressive epitaxial strain. On the other hand, as is evident from Fig. 3(b), the magnetization along the *b*-axis of the *o*-LuMO film is much smaller than that probed along the *c*-axis. Since both materials are having similar magnetic and crystal structures, and the lattice parameter analyses also indicate about the same amounts of epitaxial strain existing, the current results thus might have something to do with the ionic size effect.

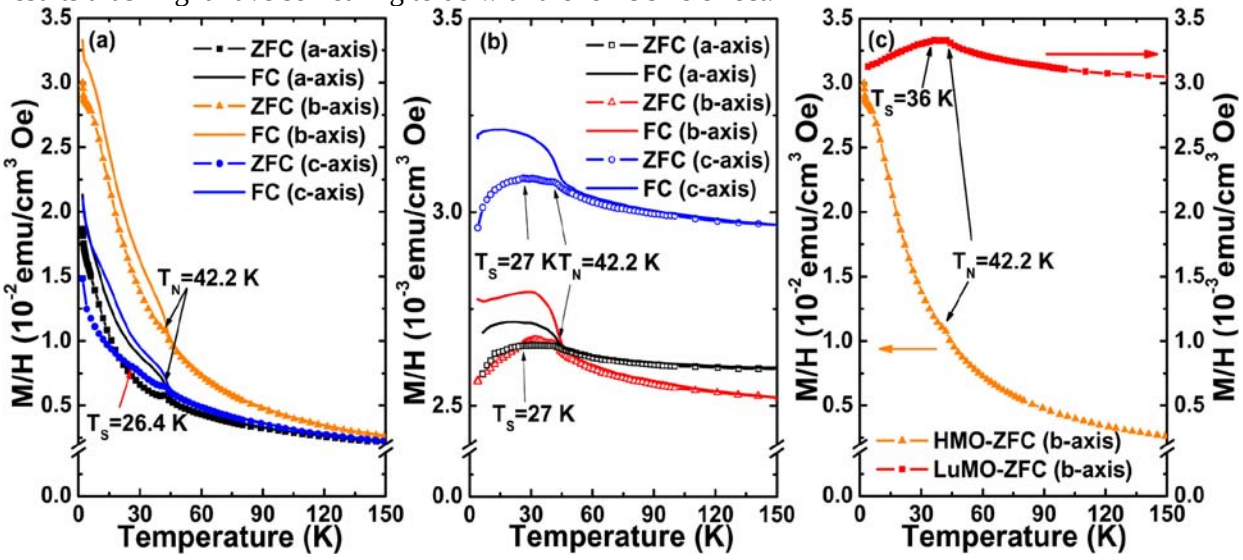

Figure 3. (a) The χ(*T*) of the *o*-HMO films probed along the respective crystalline axis at an applied field of 500 Oe; (b) Similar measurements as that displayed in (a) for the *o*-LuMO films; (c) Comparison of the ZFC χ(*T*) taken along the *b*-axis for both films. Notice that the different scales are used.

The strongly distorted manganites although favor the stabilization of AFM-*E* spin configuration [3], further decrease in the rare-earth ion size may induce some unexpected modifications in the low temperature magnetic structures, especially when incorporates with severe external strains. Finally, it is also worthy to note that the spin reorientation transition in *o*-LuMO is also anisotropic with $T_s \sim 27$ K when probing along the *a*- and *c*-axis and $T_s \sim 36$ K when measuring along the *b*-axis (Fig. 3(c)). To the best of our knowledge, this is the first time that such transitions are directly observed from the $\chi(T)$ measurements. Understanding the details of how the magnetic transition when incorporate with the inevitable external strains would affect the magnetism-induced ferroelectricity should be an interesting future work.

4. Conclusions

In summary, we have prepared both the hexagonal phase and orthorhombic phase of $LuMnO_3$ and $HoMnO_3$ and compared the similarities and differences between their magnetization behaviors. For $HoMnO_3$, due to the large Ho moments, the paramagnetic background dominates the $\chi(T)$ signal over the entire temperature range. Nevertheless, both materials were found to exhibit significant anisotropic characteristics when probing along respective crystalline axis. In particular, it is suggestive that both the external strain from film/substrate epitaxial relations and the internal lattice strain originates from the decreasing rare-earth ion size as well as the Jahn-Teller distortion accompanied with magnetic structure ordering may have played intriguing roles in determining the eventual ground state magnetic structures.

Acknowledgments

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