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Strain-induced effects on antiferromagnetic ordering and magnetocapacitance in orthorhombic $HoMnO_3$ thin films

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Abstract

We investigated the magnetic and ferroelectric properties of *c*-axis oriented orthorhombic phase $HoMnO_3$ (*o*-HMO in *Pbnm* symmetry setting) thin films grown on Nb-doped $SrTiO_3$(001) substrates. The *o*-HMO films exhibit an antiferromagnetic ordering near 42 K, irrespective of the orientation of the applied field. However, an additional magnetic ordering occurring around 35 K was observed when the field was applied along the *c*-axis of *o*-HMO, which was absent when the field was applied in the *ab*-plane. The magnetocapacitance measured along the *c*-axis showed that although there is evidence of dielectric constant enhancement when the temperature is below 35 K the expected abrupt change in dielectric constant appears at a much lower temperature and reaches maximum around 13.5 K, indicating that the low-temperature *c*-axis polarization might be related to the ordering of the Ho^{3+} moment. The lattice constant analyses using x-ray diffraction and the observation of a slight magnetization hysteresis suggest that the weak second magnetic transition along the *c*-axis at 35 K might be more relevant to the strain-induced effect on antiferromagnetism.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The rich physics and potential practical applications involved in manipulating the coupling between the magnetic and ferroelectric orders existent in multiferroic rare-earth manganites ($RMnO_3$) have evoked tremendous research interest recently [1–4]. Unfortunately, since the ferroelectricity and magnetism for most hexagonal $RMnO_3$ originate independently, the antiferromagnetic (AFM) Néel temperature (T_N) and ferroelectric (FE) Curie temperature (T_C) are usually very far apart (e.g. for $YMnO_3$, $T_C \sim 920$ K and $T_N \sim 80$ K), resulting in virtually no coupling between the two orders. However, very recently it was reported that for orthorhombic $TbMnO_3$ not only is T_C (~ 30 K) lower than T_N(~ 40 K), but also the FE ordering is evidently driven by transition between specific configurations of magnetic structures [1, 5]. This so-called improper magnetic ferroelectricity [3, 6] is of particular interest because it represents the possibility of manipulating magnetic order (polarization) by applying an electric (magnetic) field. Indeed, the switching of the electric polarization by a magnetic field has been demonstrated in single crystal orthorhombic $TbMnO_3$ [1]. The microscopic origin of ferroelectricity in orthorhombic $TbMnO_3$ results from the lock-in transition of a collinear incommensurate sinusoidal magnetic order to a spiral magnetic order at some temperature below T_N in frustrated magnets [7]. However, the spiral magnetic structure is not the only source of magnetic ferroelectricity. In particular, the magnitude of FE polarization

along the *a*-axis (in *Pbnm* group symmetry setting) in the *E*-type orthorhombic $HoMnO_3$ (*o*-HMO) has been theoretically estimated to be about two orders of magnitude larger than those exhibited in helical magnetic ordering-induced ferroelectricity [6, 8]. However, experimental confirmation of this extraordinary enhancement of the magnetic order-induced FE polarization along the *a*-axis in *E*-type orthorhombic $RMnO_3$ has been hampered by a lack of availability of suitable samples.

For $RMnO_3$ manganites with a rare-earth ionic size smaller than that of Dy the thermodynamically stable phases are the hexagonal ones [9]. Thus, for example, the *o*-HMO samples obtained previously were prepared either by soft chemical procedures [10–12] or by high-pressure synthesis [13–15] and were all inevitably polycrystalline in nature. This, in turn, has limited the capability to directly test the predicted properties. The temperature-dependent FE polarization obtained from the high-pressure synthesized *o*-HMO samples, though clearly displaying a mild enhancement below the lock-in temperature of Mn^{3+}, had a magnitude about 2–3 orders smaller than expected [15]. There is, however, an abrupt increase in FE polarization around 15 K, at which the Ho moments rotate in the *ab*-plane and form a noncollinear magnetic structure. The involvement of the rare-earth moment in inducing the magnetic ferroelectricity thus appears to be indispensable [15, 16]. In order to understand these intriguing correlations between the spin, charge and lattice degree of freedoms, it is essential to have a means of probing the relevant physical properties along specific crystallographic orientations. Very recently we have grown well-aligned *o*-HMO thin films on various substrates, which revealed the magnetic ordering anisotropy along the principal crystal axes [17]. However, the insulating nature of the substrates has been hindering the direct measurement of polarization associated with the magnetic ordering. Here we report an attempt to use the conductive Nb-doped $SrTiO_3$(001) (Nb:STO) for preparing the epitaxial *o*-HMO thin films. The resultant *c*-axis oriented *o*-HMO film allows direct measurements of the dielectric properties along the *c*-axis and the anisotropy of the magnetic properties along the *c*-axis and in the *ab*-plane. Our data confirm again a possible magnetic ordering transition occurring around 35 K along the *c*-axis as previously delineated in a *b*-axis oriented *o*-HMO film [17]. The lattice constant analyses as well as the hysteretic field-dependent magnetization (*M*–*H* curve) (see below) suggest that the second Mn^{3+} moment ordering along the *c*-axis might be more relevant to the distortion-induced effect, although in the *E*-type *o*-HMO neither lock-in magnetic ordering nor FE polarization was anticipated to take place along the *c*-axis [6, 8]. Moreover, the results also reveal unexpected FE order appearing along *c*-axis, which peaks around 13.5 K and is indicative of the involvement of the rare-earth moment ordering in stabilizing the FE order [15, 16].

2. Experimental procedures

$HoMnO_3$ thin films were grown on (001)-oriented 0.5%-Nb:STO substrates (500 μm thick) by pulsed laser deposition (PLD) using a KrF excimer laser (wavelength 248 nm and pulse duration about 30 ns) operating at a repetition rate of 3 Hz and with an energy density around 2–4 J cm^{-2}. The $HoMnO_3$ target was prepared by using a standard solid state reaction technique. The substrate temperature and oxygen pressure were kept at $T_s = 850\,^{\circ}C$ and $P(O_2) = 100$ mTorr, respectively. The film thickness was 202 nm as determined by x-ray reflectivity (XRR) and α-step measurements. The film structure and crystalline orientation were characterized by x-ray diffraction (XRD). The magnetic properties were measured in a Quantum Design® superconducting quantum interference device (SQUID) system. For dielectric property measurements, a 4 mm diameter gold top electrode was sputtered on the film surface through a shadow mask. The temperature-dependent dielectric constant $\varepsilon(T)$ was measured using a physical property measuring system (PPMS) equipped with a *LCR* meter. A 10 kHz ac signal with amplitude of 5 mV (corresponding to a poling field of about 3×10^4 V m^{-1}) was used in the present study.

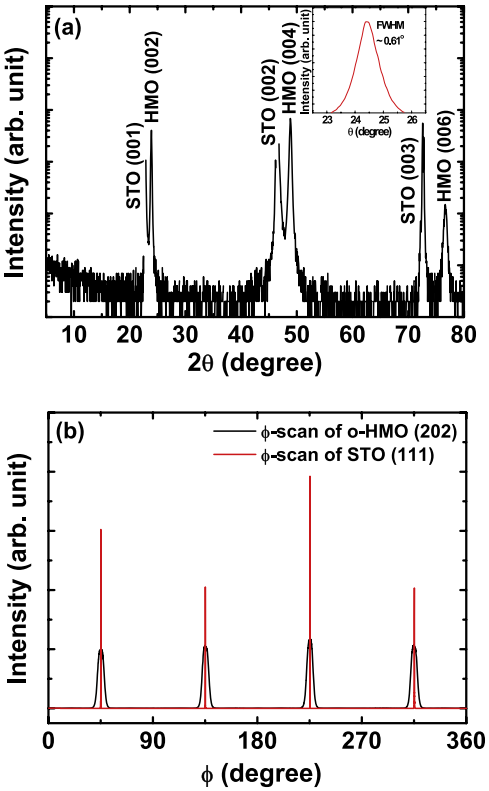

Figure 1. The XRD results of the *o*-HMO thin films grown on Nb:STO(001) substrates. (a) The θ–2θ scans (intensity plotted on a logarithmic scale) reveal that HMO films are indeed orthorhombic with a nearly perfect *c*-axis oriented characteristic. The inset shows the rocking curve of the *o*-HMO (004) peak. (b) The ϕ-scan plot of the (202) peak of the *o*-HMO films indicates a clear four-fold symmetry, suggesting that the film is well-aligned along (001)-orientation; however, it is of *ab* mixing character in the film plane.

3. Results and discussion

Figure 1(a) shows the x-ray diffraction (XRD) θ–2θ pattern for the obtained *o*-HMO films grown on Nb:STO(001) substrate. The XRD data evidently confirm the formation of pure

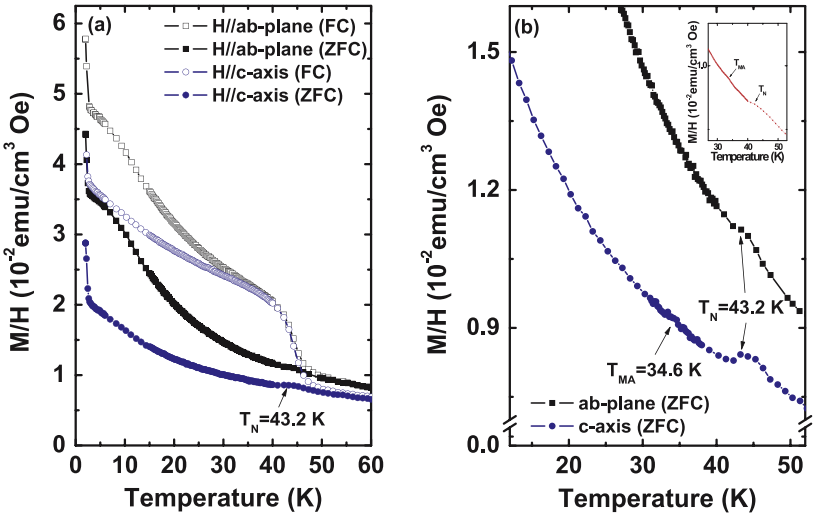

Figure 2. The temperature-dependent magnetization ($M(T)$) of *o*-HMO probed along the *c*-axis and the *ab*-plane. (a) The ZFC (solid symbols) and FC (open symbols) $M(T)$'s measured with a magnetic field of 100 Oe applied along the *c*-axis and in the *ab*-plane. Both reveal an AFM transition temperature of 43.2 K. (b) An enlarged version of the ZFC curves displayed in (a). Magnetic ordering near 34.6 K is evident in the *c*-axis. The inset of (b) shows that the feature can be seen more clearly by plotting M/H as a function of T.

orthorhombic $HoMnO_3$ with the *c*-axis (space group: *Pbnm*) oriented normal to the film surface. The inset of figure 1(a) displays the rocking curve (ω-scan) of the (004) reflections. The full width at half maximum (FWHM) ($\sim$0.61°) indicates the good crystalline quality and grain alignment of the *o*-HMO films. To further examine the in-plane texture of the films, we also measured the ϕ-scan around the *o*-HMO (202) reflection. As shown in figure 1(b), the ϕ-scans display an evenly behaved four-fold symmetry, indicating that the in-plane grain alignment is randomly mixed in the *ab*-plane.

Figure 2(a) shows the temperature dependence of magnetization $M(T)$ for *o*-HMO measured with an external field of 100 Oe applied either in the *ab*-plane or along the *c*-axis. The zero-field-cooled (ZFC) and field-cooled (FC) $M(T)$ curves all show a clear transition around 43.2 K in both field directions. It is noted that the sharp rise in the magnetization near $T = 43.2$ K in the FC $M(T)$ curves in both directions deviates somewhat from the standard AFM transitions. One of the possible origins of this magnetization enhancement below the Néel temperature (T_N) is the uncompensated AFM spins existing in the vicinity of the domain boundaries between the AFM domains. For instance, weak ferromagnetism is frequently observed in the AFM nanoparticles [18, 19], due to the significant fraction of uncompensated spins produced by the high surface/volume ratio of the nanoparticles. Alternatively, the weak ferromagnetism can also result from the canted AFM state, in that a relatively abrupt magnetization is expected. Either the uncompensated spin or the canted AFM state will presumably result in hysteretic field-dependent magnetization (M–H curve).

In addition to the magnetization enhancement described above, a closer look at the data further reveals that when the field is applied along the *c*-axis the ZFC $M(T)$ clearly exhibits another magnetization anomaly at $T_{MA} \sim 35$ K. This feature, nevertheless, is undetectable in the *ab*-plane ZFC $M(T)$ (figure 2(b)). This is consistent with the results observed in the *b*-axis oriented *o*-HMO films [17], where a similar secondary magnetic ordering was observed around 30.4 K when the field was applied along the *c*-axis. According to the neutron diffraction results obtained from polycrystalline *o*-HMO samples, the Mn^{3+} spin moments exhibit an incommensurate AFM (ICM-AFM) ordering with sinusoidal modulation around 42 K, which locks into a commensurate (CM) *E*-type at a lower temperature T_L ($T_L \sim$ 26–29.6 K) with a constant magnetic modulation vector ($k_b = 1/2$) propagating along the *b*-axis [10, 11, 13]. Although it is tempting to associate the observed *c*-axis magnetic ordering anomaly with the lock-in transition between the ICM–CM magnetic structures, since it was not observed in the polycrystalline *o*-HMO samples and there has been no theoretical model predicting *c*-axis magnetic ordering for *o*-HMO [6, 8, 20], we believe that another origin should be responsible. Moreover, since it occurs at a temperature much higher than that of the rotation ordering of Ho moments [15], the two are possibly irrelevant to each other.

In order to search for a reasonable origin, we note that in addition to being markedly higher than T_L ($\sim$26–29.6 K), T_{MA} ($\sim$35 K) also appears to be quite sensitive to the film microstructures and/or strain states. To illustrate the latter point, we obtained the respective lattice constants for the present *c*-axis film and the *b*-axis films grown on LAO [17] by using four-circle XRD. The measured lattice constants for *a*, *b* and *c* were 5.25 (5.28), 5.76 (5.80) and 7.47 (7.51) Å for the *c*-axis (*b*-axis) *o*-HMO films, respectively. Compared to $a = 5.26$, $b = 5.84$ and $c = 7.36$ Å for the bulk *o*-HMO [12], the *b*- and *c*-axes of the films are apparently under compressive and tensile stresses, respectively. It has been proposed [21] that in the hexagonal phase of HMO canting of the Mn^{3+} spins out of the basal *xy*-plane can drastically reduce the magnetic symmetry and hence induce a magnetoelectric effect. Thus, in order to check whether or not the current *c*-axis ordering anomaly is a result of

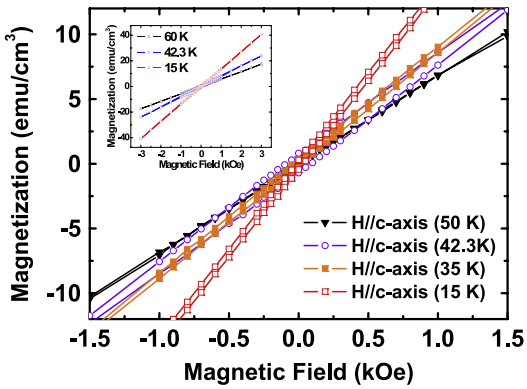

Figure 3. The field-dependent magnetization (M–H) measured at four temperatures. The hysteretic behavior exhibited when $T < T_N$ indicates the presence of weak ferromagnetism.

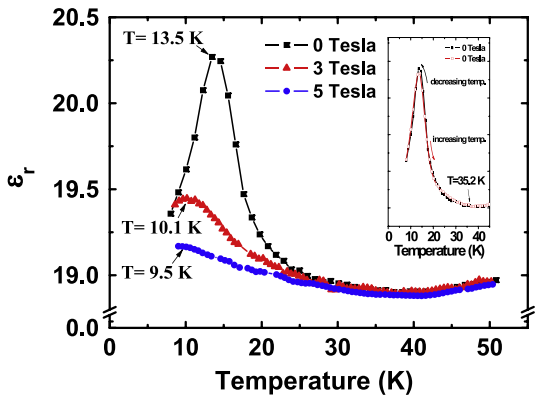

Figure 4. The dielectric constant as a function of temperature measured along the c-axis of the o-HMO film. Significant suppression of the enhancement and peak temperature by the applied field are evident. The inset shows that the dielectric enhancement is non-hysteretic in temperature.

similar canting effects, we measured the M–H curves at several temperatures below and above the c-axis ordering temperature. As is evident from the results displayed in figure 3, the M–H curve becomes clearly hysteretic when $T < T_N$ (∼43 K), indicating a weak ferromagnetism emerging immediately after the system gets into the AFM state. This is also consistent with the magnetization enhancement occurring at T_N as described in the previous paragraph. However, the $M(H)$ loop appears to shrink with decreasing temperature and then remains essentially constant after $T < 30$ K (see figure 3 and its inset). This indicates that the weak ferromagnetism below T_N might have arisen from an imbalance in the number of 'up' and 'down' spins [22], instead of the similar canting effects observed in hexagonal HMO [21]. In the latter, the magnetic moment is not expected to decrease with temperature. Since, there exists significant lattice mismatch-induced epitaxial strain in our films which might interrupt the formation of long-range AFM order. The short-range ordering nature of the AFM domains inherent in these frustrated manganites, in turn, gives rise to significant incomplete spin compensation and the sharp magnetization enhancement below T_N. On the other hand, the slight shrinkage of the $M(H)$ loop towards $T_{MA} \sim 35$ K may be attributed to the ICM–CM AFM transition, which, though it has been drastically affected by the lattice distortion, could cause some rearrangement of the uncompensated spins.

The other important question to be addressed is: does any of this magnetic ordering actually lead to the gigantic polarization as expected? Figure 4 shows the temperature and magnetic field dependences of the dielectric constant directly measured along the c-axis with the external magnetic field applied parallel to the surface (**H** ∥ ab-plane) of the film. It is clear that on going below the AFM temperature (∼42 K) there is no sign of ferroelectric transition occurring along the measuring c-axis. As the temperature is lowered across T_{MA} (∼35 K) the relative dielectric constant starts to increase slowly, but no abrupt change is evident. However, with further lowering of temperature, the dielectric constant grows rapidly when $T < 20$ K and reaches a maximum around $T = 13.5$ K and appears to be non-hysteretic in temperature (see inset of figure 4)[5]. Moreover, the enhancement of dielectric constant is drastically reduced with a downshift of the maximum temperature when an external magnetic field was applied. It is noted that similar behaviors have previously been observed in polycrystalline o-HMO and were attributed to transition of the Ho moment from b-axis collinear to a noncollinear alignment below 15 K [13, 15]. However, in that case the noncollinear structure was expected to give rise to a FE displacement along the a-axis (in *Pbnm* group symmetry) instead of along the c-axis observed here. Moreover, the effect of the applied external field in suppressing the dielectric constant enhancement observed in the present case is apparently much more drastic than that reported in [13]. The present results thus imply that, despite the strong magnetic effect on the dielectric enhancement (figure 4), the interplay between the magnetic ordering and the induced FE might be more subtle than previously conceived, in particular when external stress also comes into play.

Since the current results suggest that T_{MA} is probably a manifestation of the reordering of Mn^{3+} spins due to the compressed b-axis, it is natural to ask: is the 30–35 K magnetic ordering along the c-axis relevant to the so-called lock-in temperature (T_L)? And what role does it play in the magnetic ferroelectricity? Very recently, the microscopic origin of the FE order in E-type orthorhombic HMO has been proposed to be originate simultaneously from two mechanisms: lattice and electronic [8]. For the electronic origin, the magnetic ordering induces hybridization of electronic orbitals, which in turn leads to a polar charge distribution [23, 24]. On the other hand, the AFM coupled FM zigzag spin chains within the ab-plane of the o-HMO can lead to buckling distortion of the oxygen octahedra allowing for the formation of a polar displacement along the a-axis [6]. In both microscopic mechanisms, neither magnetic ordering nor induced polarization was expected to take place

[5] Our preliminary electric field-dependent polarization measurements performed on these films, though still suffering from a leakage current problem, have clearly shown ferroelectric polarization emerging at $T \sim 36.2$ K (slightly higher than the ICM–CM transition temperature) and saturated for $T < 20$ K.

along the *c*-axis of *o*-HMO (in the *Pbnm* space group). Thus, if the 35 K *c*-axis ordering is relevant, it could somehow be acting as a trigger of the subsequent lock-in ordering transition at a slightly lower temperature. Unfortunately, the availability of either *b*-axis or *a*-axis oriented *o*-HMO films has been limited to non-conductive substrates. Thus, direct measurements of polarization along the other two principal axes are not accessible at present. Finally, we would like to point out that there was no further magnetic ordering transition, except for the AFM ordering near 43 K, observed along either the *a*-axis or the *b*-axis, as is evident from figure 2 or in [17]. The reason for this might be because that the lock-in transition involves mainly the commensuration between the periodicity of the magnetic ordering structure and that of the underlying lattice and there is no significant change in the total moments to be resolved in magnetization measurements.

4. Summary

In summary, we have grown *c*-axis oriented orthorhombic $HoMnO_3$ thin films on conductive Nb-doped $SrTiO_3$(001) substrates, which allowed us to perform direct measurements of orientation-specific magnetic ordering-induced ferroelectricity in this material. Surprisingly, the films exhibit an anomalous magnetic ordering around 35 K as well as an abrupt dielectric enhancement starting around 20 K and reaching a maximum around 13 K along the *c*-axis. In addition, the dielectric enhancement and its peak temperature was markedly suppressed when an external magnetic field (in the several tesla range) was applied in the *ab*-plane. We argue that although the existence of weak second magnetic ordering, induced ferroelectricity, and magnetoelectric coupling along the *c*-axis of the orthorhombic $HoMnO_3$ are not compatible with most of the available theoretical models proposed, it is evidently demonstrated to be closely related to the strain-induced effect on the ordering of Mn^{3+} moments. Nevertheless, further investigations are certainly needed to delineate how coupling to Ho^{3+} moments gives rise to the dielectric enhancement at lower temperatures.

Acknowledgments

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