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Effects of compressive epitaxial strain in the b-axis on the magnetization response of orthorhombic $HoMnO_3$ thin films

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Abstract. The orthorhombic phase $HoMnO_3$ (*o*-HMO in *Pbnm* symmetry setting) thin films were prepared on $LaAlO_3$(110) (LAO(110)) substrates by pulsed laser deposition. While for films grown on LAO(110) substrates, the compressive strain along the *b*-axis was resulted from the tensile strain in the *a*-*c* plane. The films provide the opportunity of investigating the effects of strain, hence lattice elasticity, on the physical properties of this material. For *o*-HMO films an antiferromagnetic ordering with $T_N \sim 42$ K, irrespective to the direction of applied field was clearly observed. However, an additional magnetic ordering occurring around 26.4 K was observed when the field was applied along the *c*-axis of *o*-HMO. This transition, however, was absent when the field was applied along *a*- and *b*-axis. These results indicate that the second magnetic ordering observed along the *c*-axis could be more relevant to the Mn moments lying along the partially strained *b* direction of the *o*-HMO which has been theoretically expected to result in incommensurate-commensurate lock-in transition.

1. Introduction

Magnetoelectric materials with symmetry-breaking magnetic structure induced improper ferroelectricity have attracted much interest due to the intriguing fundamental physics and promising multifunctional applications for next generation electronics [1-5]. Among them, the rare-earth perovskite manganite $RMnO_3$ (R=Y, Ho, and Er) have drawn enormous attention recently [6, 7]. In particular, Picozzoi *et al*. [8] have theoretically proposed that the quantum-mechanical effects of electron orbital polarization manifested in the *E*-type magnetic structure of orthorhombic $HoMnO_3$ (*o*-HMO) and further predicted polarization might be orders of magnitude larger than those exhibited in helical magnetic ordering-induced ferroelectricity. Unfortunately, under ambient conditions, the *o*-HMO samples were all inevitably polycrystalline prepared either by high-temperature high-pressure synthesis [6-7, 9-10] or by the citrate-based soft chemistry method [11-12]. For these samples, the neutron scattering [12] showed that *o*-HMO indeed exhibited an incommensurate (IC) antiferromagnetic (*AFM*) transition around 42 K and at lower temperatures the magnetic order locks into a temperature-independent commensurate wave vector as expected. However, pyroelectric current measurements on bulk polycrystalline *o*-HMO revealed the minute ferroelectric polarization ($P \approx$ 2-9 nC/cm^2) and the suggestive involvement of Ho^{3+} moments in the low temperature dielectric anomalies had stirred debates about the relevant physical mechanisms [6, 8]. The discrepancies were ascribed to

the unavailability of single crystalline samples and alternate ways of preparing orientation-specific orthorhombic $HoMnO_3$ films have received extensive attention lately [13]. In order to gain more insight toward understanding these intriguing correlations between the spin, charge and lattice degree of freedoms, it is essential to obtain samples capable of revealing the relevant physical properties along the distinctive crystallographic orientations. In this paper, we report the observation of compressive strain along the *b*-axis in *o*-HMO films and its influence on introducing additional magnetic ordering along *c*-axis in the system.

2. Experimental details

Because of the small ionic size of the Ho^{3+}, *o*-HMO is structurally highly distorted with lattice constants of a = 5.26 Å, b = 5.84 Å, and c = 7.36 Å (in *Pbnm* setting), respectively [14]. Thus, in order to stabilize the phase and epitaxially grow *o*-HMO films with controllable orientations, it is crucial to select the suitable substrates [13]. In this study, we chose the LAO(110) substrates. Sintered ceramic pellet of stoichiometric $HoMnO_3$ was prepared by conventional solid-state reaction method and used as a target for the subsequent pulsed laser deposition (PLD), which was carried out using a 248 nm KrF excimer laser operated at a repetition rate of 3 Hz with an energy density of 2-4 J/cm^2. The substrate temperature and oxygen pressure were optimized at T_s = 850℃ and $P(O_2)$ = 0.1 Torr, respectively. The film thickness was around 180 nm. The film structure was extensively characterized by various x-ray diffraction (XRD) schemes. The temperature dependent magnetization ($M(T)$) was measured using a Quantum Design® SQUID system.

3. Results and discussion

Figure 1 shows the θ-2θ XRD scans for the as-deposited *o*-HMO films on LAO(110) substrates. The diffraction peaks reveal pure (020)-oriented *o*-HMO reflections without discernible impurity phase, indicating the formation of a pure *o*-HMO. By comparing the parameters listed in Table 1 and consider the scenario depicted in Ref. 13, one obtains that, with the *a*-axis and *c*-axis of *o*-HMO aligning with the [001] and [1$\bar{1}$0] directions of LAO(110) substrate, the expected in-plane mismatches between film and substrates are only about 2.9% and 1.9%, respectively. Consequently, the lattice constants obtained here are a = 5.28 Å, b = 5.80 Å, and c = 7.51 Å, respectively. Compare to a = 5.26 Å, b = 5.84 Å, and c = 7.36 Å for the bulk *o*-HMO [12], it is clear that the film is under tensile strain within the *ac*-plane and compressive along the *b*-axis, even when its thickness reaches 180 nm.

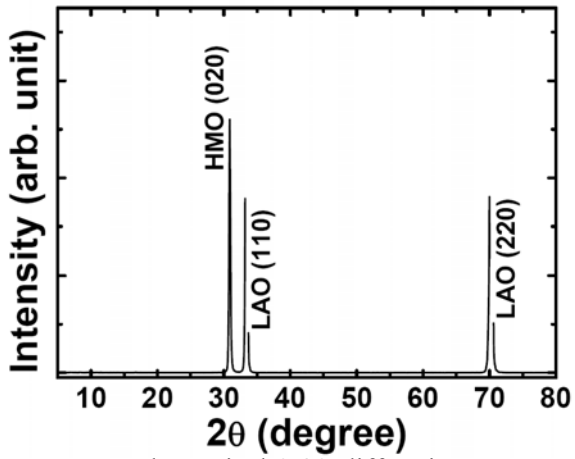

Figure 1. The typical θ-2θ diffraction pattern of *o*-HMO films grown on LAO(110) substrate.

Table 1. The fitting parameters and in-plane mismatch calculations between *o*-HMO thin films and substrates used in this study.

	a (Å)	b (Å)	c (Å)	V (Å^3)
Database	5.26	5.84	7.36	226.1
o-HMO on LAO(110)	5.28	5.80	7.51	229.9
LAO(110) substrates (in plane length)	5.36		7.58	
In-plane mismatch with substrate	1.9%		2.9%	
Strain factor	0.38%	-0.68%	2.04%	1.68%

Figure 2 shows the temperature dependent magnetization ($M(T)$) behaviors probed by the zero-field-cooled (ZFC) scheme with an 500 Oe field applied along different crystal orientations. As is evident in Figure 2, all the three ZFC $M(T)$ curves clearly exhibit an ordering transition near 42 K, which is consistent with the recent neutron diffraction results [11, 12, 15] and can be assigned as the usual *AFM* ordering of Mn moment for *o*-HMO. Another feature to be noted in Figure 2 is the significantly larger magnetization level along the *b*-axis over the whole temperature range. According to the neutron diffraction results [12], the magnetic ordering of the Mn^{3+} ions is uniaxial, and the moments are parallel to the *b* direction, making the *b*-axis the easy axis in the *Pbnm* group symmetry setting. Thus explains that, in the entire temperature range, the magnetization along the *b*-axis is larger than that along *a*- or *c*-axis. At lower temperatures, however, the magnetic moment of Ho^{3+} will eventually come into play below $T = 20\sim25$ K [12]. The latter might account for the enhancement of the *a*-axis magnetization for $T < 25$ K. As for the notably increase of magnetization around $T = 2$ K, it has been suggested to result from metamagnetic transition of Ho^{3+} ions [12]. Finally, we note that around 26.4 K an interesting anomaly in the *c*-axis $M(T)$ curve signifying a second ordering transition is clearly observed. Although, it is tempting to identify it as the lock-in temperature (T_L) of the incommensurate-commensurate transition to conform to previous theoretical [16] and experimental [6] anticipations, there are, nevertheless, several points needed to be clarified. Firstly, this second ordering occurs only along the *c*-axis and is undetectable in either *a*- or *b*-axis, which is in contrast to the generally conceived scenario of regarding the collinear Mn^{3+} moments being aligned within the *a*-*b* plane (*Pbnm* space group setting). Secondly, the ordering temperature (26.4 K) is much higher than the Ho^{3+} moments rotation ordering temperature (11-15 K) [6, 12], thus preventing it from being relevant to Ho^{3+} ordering. Thirdly, despite of the abovementioned inconsistencies, we note that it is, nevertheless, consistent with the neutron diffraction results reported by Brinks et al. (left inset of Figure 5 in Ref. 11), in that an abrupt increase in magnetic reflection along [001] of *o*-HMO was clearly observed, which disappeared when measured along [011].

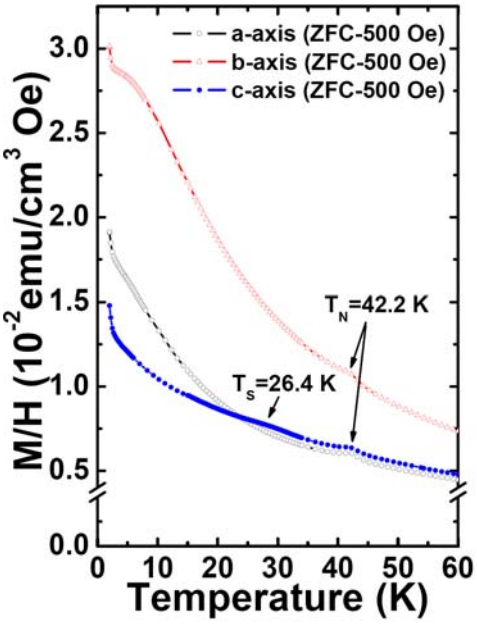

Figure 2. The zero-field-cooled temperature-dependent magnetizations (ZFC-$M(T)$) for *o*-HMO film probed along different crystal orientations with an applied magnetic field of 500 Oe.

4. Conclusions

In summary, we have grown *o*-HMO films with well-aligned crystallographic orientations on LAO(110) substrates by PLD. The samples provide the possibility of accessing the orientation-dependent physical properties of this system. The $M(T)$ measurements showed that, in addition to the 42 K *AFM* ordering expected for the *o*-HMO, an anomalous *c*-axis magnetic ordering near 26.4 K was evidently observed. This ordering temperature, although coincides very well with the lock-in temperature associated with the incommensurate-commensurate magnetic ordering transition revealed by neutron diffraction and dielectric constant anomaly. Furthermore, the temperature is well above and should be irrelevant to the ordering temperature of Ho^{3+} moments. Finally, the facts that the compressive strain along the *b*-axis in *o*-HMO films and its influence on introducing additional magnetic ordering along *c*-axis (in *Pbnm* setting) are surprising certainly demand further extensive studies.

Acknowledgments

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