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2009 J. Phys.: Conf. Ser. 150 042114

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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 $T_N \approx 42$ 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, Picozzi 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
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 $T_s = 850^\circ$C 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 $\theta$-2$\theta$ 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 [110] 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.

| 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   | 5.36            | 7.58            |                |                 |
| (in plane length)     |                 |                 |                |                 |
| In-plane mismatch with substrate | 1.9% | 2.9% |
| Strain factor         | 0.38%           | -0.68%          | 2.04%           | 1.68%           |

Figure 1. The typical $\theta$-2$\theta$ diffraction pattern of o-HMO films grown on LAO(110) substrate.
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 $T = 20$--25 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](image_url)

**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
This work was supported by the National Science Council of Taiwan, R.O.C. through grant NSC95-2112-M-009-035-MY3, NSC95-2112-M-009-038-MY3, NSC95-2112-M-213-005 and MOE ATU program.

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