

Anomalous magnetic ordering in b -axis-oriented orthorhombic Ho Mn O 3 thin films

T. H. Lin, C. C. Hsieh, H. C. Shih, C. W. Luo, T. M. Uen, K. H. Wu, J. Y. Juang, J.-Y. Lin, C.-H. Hsu, and S. J. Liu

Citation: [Applied Physics Letters](#) **92**, 132503 (2008); doi: 10.1063/1.2904649

View online: <http://dx.doi.org/10.1063/1.2904649>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/92/13?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Dielectric properties of a -axis-oriented orthorhombic HoMnO 3 thin films](#)

J. Appl. Phys. **106**, 024106 (2009); 10.1063/1.3182822

[Strong coupling of magnetic and dielectric properties in the a -axis-oriented orthorhombic HoMnO 3 films](#)

Appl. Phys. Lett. **94**, 082502 (2009); 10.1063/1.3089361

[Multiferroic properties of Ho Mn O 3 films and capacitor trilayers](#)

J. Appl. Phys. **101**, 09M108 (2007); 10.1063/1.2715848

[Physical properties of multiferroic hexagonal Ho Mn O 3 thin films](#)

Appl. Phys. Lett. **90**, 142902 (2007); 10.1063/1.2718512

[Neutron-scattering studies of magnetism in multiferroic Ho Mn O 3 \(invited\)](#)

J. Appl. Phys. **99**, 08E301 (2006); 10.1063/1.2162090

The advertisement features a dark blue background with white and orange text. At the top left, it reads 'NEW! Asylum Research MFP-3D Infinity™ AFM' in large white letters, followed by 'Unmatched Performance, Versatility and Support' in orange. On the right, the Oxford Instruments logo is shown with the tagline 'The Business of Science®'. Below the text are several images: a blue textured surface, a brown textured surface, a yellow and red patterned surface, and a stack of yellow and red rectangular samples. On the right side, there is a photograph of the MFP-3D Infinity AFM instrument, which is a white and blue device with a sample stage and a probe head.

NEW! Asylum Research MFP-3D Infinity™ AFM
Unmatched Performance, Versatility and Support

OXFORD INSTRUMENTS
The Business of Science®

Stunning high performance

Simpler than ever to GetStarted™

Comprehensive tools for nanomechanics

Widest range of accessories for materials science and bioscience

Anomalous magnetic ordering in *b*-axis-oriented orthorhombic HoMnO₃ thin films

T. H. Lin,^{1,a)} C. C. Hsieh,¹ H. C. Shih,¹ C. W. Luo,¹ T. M. Uen,¹ K. H. Wu,¹ J. Y. Juang,^{1,b)} J.-Y. Lin,² C.-H. Hsu,³ and S. J. Liu⁴

¹Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan

²Institute of Physics, National Chiao Tung University, Hsinchu 30010, Taiwan

³National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan

⁴Department of Materials Engineering, Mingchi University of Technology, Taipei 24301, Taiwan

(Received 8 January 2008; accepted 27 February 2008; published online 1 April 2008)

Orthorhombic HoMnO₃ films with well-aligned crystallographic orientations were deposited on LaAlO₃(110) single crystal substrates by using pulsed laser deposition. The nearly perfect *b*-axis-oriented films provide the opportunity of investigating the orientation-dependent physical property of this material. The temperature dependent magnetization evidently displays an antiferromagnetic ordering near 42 K, irrespective to the direction of applied field. Furthermore, the theoretically expected lock-in transition was clearly observed at around 30 K when field was applied along the *c* axis and was undetectable along the *a* and *b* axes. The 30 K transition was suppressed to 26 K when the applied field increased from 100 to 500 Oe. © 2008 American Institute of Physics. [DOI: 10.1063/1.2904649]

Multiferroic materials with magnetic ordering-induced improper ferroelectricity have been of significant research interest owing to the intriguing underlying physics and the anticipated multifunctional applications for next generation electronics.^{1–5} In particular, Sergienko *et al.*⁶ have theoretically predicted that the double-exchange driven polar displacement manifested in the *E*-type magnetic structure of orthorhombic HoMnO₃ (*o*-HMO) and possibly other similar compounds might give rise to a ferroelectric polarization orders of magnitude larger than those exhibited in helical magnetic ordering-induced ferroelectricity. Unfortunately, *o*-HMO is not the thermodynamically stable phase at the ambient conditions; thus, the few available reported results were all obtained from polycrystalline samples prepared either by high-temperature high-pressure synthesis^{7–10} or by the citrate-based soft chemistry method.^{11,12} For these samples, the neutron scattering¹² showed that *o*-HMO indeed exhibited an incommensurate (IC) antiferromagnetic (AF) transition around 42 K, and at lower temperatures, the magnetic order locks into a temperature independent commensurate wave vector as expected. However, the minute ferroelectric polarization ($P \approx 2\text{--}5$ nC/cm²) derived from pyroelectric current measurements and the suggestive involvement of Ho³⁺ moments in the low-temperature dielectric anomalies had stirred debates about the relevant physical mechanisms.^{7,13} Since within the frameworks of various microscopic mechanisms the magnetic ordering and associated ferroelectricity are intimately related to specific crystallographic orientations, consequently in order to gain more insight toward understanding these intriguing physical properties, it is essential to obtain samples capable of revealing the relevant properties along the respective crystallographic orientations. In this letter, we report the magnetization behaviors of the collinear *E*-type magnetic phase with the field applied along the respective crystallographic orientations, which is realized by courtesy of the success of growing the

well-aligned *b*-axis-oriented *o*-HMO films on LaAlO₃(110) [LAO(110)] substrates.

Because of the small ionic size of the Ho³⁺, *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 the *o*-HMO films with controllable orientations, it is crucial to select the suitable substrates. In this study, we chose the LAO(110) substrates. The lattice constants along the [110] and [001] directions of LAO are 5.358 and 7.578 Å, respectively,¹⁵ and are quite suitable to accommodate the *ac* plane of *o*-HMO. Sintered ceramic pellet of stoichiometric HoMnO₃ was prepared by conventional solid-state reaction method and used as a target for the subsequent pulsed laser deposition (PLD), which was carried out by using a 248 nm KrF excimer laser operated at a repetition rate of 3 Hz with an energy density of 2–4 J/cm². The substrate temperature and oxygen pressure were optimized at $T_s = 850$ °C and $P(\text{O}_2) = 0.1$ Torr, respectively. The film thickness was around 180 nm. The film structure was extensively characterized by various x-ray diffraction (XRD) schemes and by atomic force microscopy (AFM). The temperature dependent magnetization [$M(T)$] was measured by using a Quantum Design® superconducting quantum interference device system.

Figure 1(a) 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. The inset of Fig. 1(a) exhibits the rocking curve of the (020) peak, displaying a full width of half maximum of 0.68°. Furthermore, as shown in Fig. 1(b), the φ scan of the (110) reflection of the *o*-HMO displays a clear twofold symmetry, indicating that the films were indeed epitaxial and well aligned with the substrate. We note that the nearly perfect epitaxial relation between *o*-HMO(110) and LAO(010) peaks shown in Fig. 1(b) is quite consistent with the expected lattice mismatches of -2.95% along the [001] direction and -1.91% along the [110] direction for growing

^{a)}Electronic mail: mumuhair.ep95g@nctu.edu.tw.

^{b)}Electronic mail: jyjuang@cc.nctu.edu.tw.

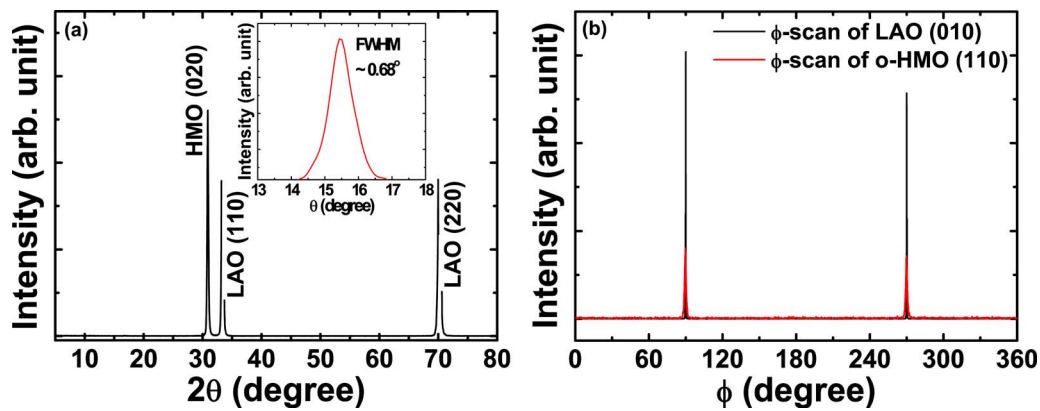


FIG. 1. (Color online) (a) The typical θ - 2θ diffraction pattern of *o*-HMO films grown on LAO(110) substrate. The inset in (a) shows the rocking curve of the *o*-HMO(020) peak. (b) The azimuthal ϕ scans of the (110) peak of the *o*-HMO films, displaying the nearly ideal alignment of crystallographic orientations between film and substrate.

o-HMO on the LAO(110) substrates. 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, 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 2 shows the AFM image of the *o*-HMO displaying the elongated but uniform grain morphology. Since the LAO(110) substrate has slightly larger lattice constants than that of the *o*-HMO,¹² significant in-plane tensile strain is expected to accumulate with increasing film thickness. The fact that no microcracks or voids were observed suggests that the spindlelike grains of the *o*-HMO film must have aligned along the specific crystallographic directions of the LAO substrate and the growth might have been accompanied by significant uniform strain. From the previous analyses, we schematically depict the elongated axis and short axis of the grains as being along the *a* and *c* axes of *o*-HMO, respectively. Perhaps, the most significant implication of the present results is that it allows us to probe the physical properties of the *o*-HMO along the different major crystal orientations.

Figure 3(a) shows the temperature dependent magnetization [$M(T)$] behaviors probed by the zero-field-cooled (ZFC) scheme with a 100 Oe field applied along the different crystal orientations. As is evident in Fig. 3(a), all the three ZFC $M(T)$ curves clearly exhibit an ordering transition near 42 K, which is consistent with the recent neutron diffraction results^{11,12,16} and can be assigned as the usual AF ordering of Mn moment for *o*-HMO. Another feature to be noted in Fig. 3(a) is the significantly larger magnetization level along the *b* axis over the whole temperature range. According to the neu-

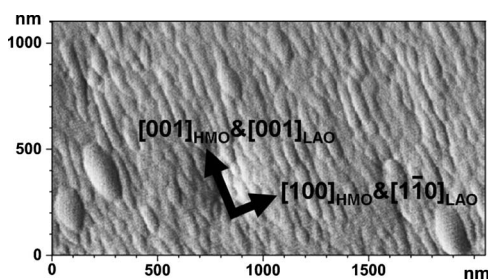


FIG. 2. The AFM image of a 180-nm-thick *o*-HMO film deposited on LAO(110) substrate. The arrows indicate the growth direction of *o*-HMO grains.

tron 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* axes the easy axis in the *Pbnm* group symmetry setting. Thus, it explains that, in the entire temperature range, the magnetization along the *b* axis is larger than that along the *a* or *c* axes. 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. Finally, we note that around 30 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 IC-commensurate transition to conform to previous theoretical⁶ and experimental⁷ anticipations, there are, nevertheless, several points needed to be clarified. First, 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). Second, the ordering temperature (30.4 K) is much higher than the Ho^{3+} moment ordering temperature (11–15 K),^{7,12} thus preventing it from being relevant to Ho^{3+} ordering.⁷ Third, despite of the above mentioned inconsistencies, we note that it is, nevertheless, consistent with the neutron diffraction results reported by Brinks *et al.* (left inset of Fig. 5 of Ref. 11); in that, an abrupt increase in magnetic reflection along [001] of *o*-HMO was clearly observed, which disappeared when measured along [011].

In order to further examine this anomalous *c*-axis magnetization, we plot the results measured at 100 and 500 Oe in Fig. 3(b) for comparison. As is evident from the results, the AF ordering remains around 42 K [see also the 500 Oe FC and ZFC results shown in the inset of Fig. 3(b)]. However, the 30 K transition has been pushed down to about 26 K with a much broadened feature by merely increasing the measuring field from 100 to 500 Oe. Although field-induced suppression of the lock-in temperature has been previously observed,¹⁷ the fields involved, however, were all in the order of tesla and the suppression was much less significant than the present case. It appears that, whatever this magnetic ordering might be, it is very susceptible to the applied field.

Perhaps, the most intriguing question to be asked here is whether this anomalous *c*-axis magnetic ordering has anything to do with the ferroelectric polarization. According to

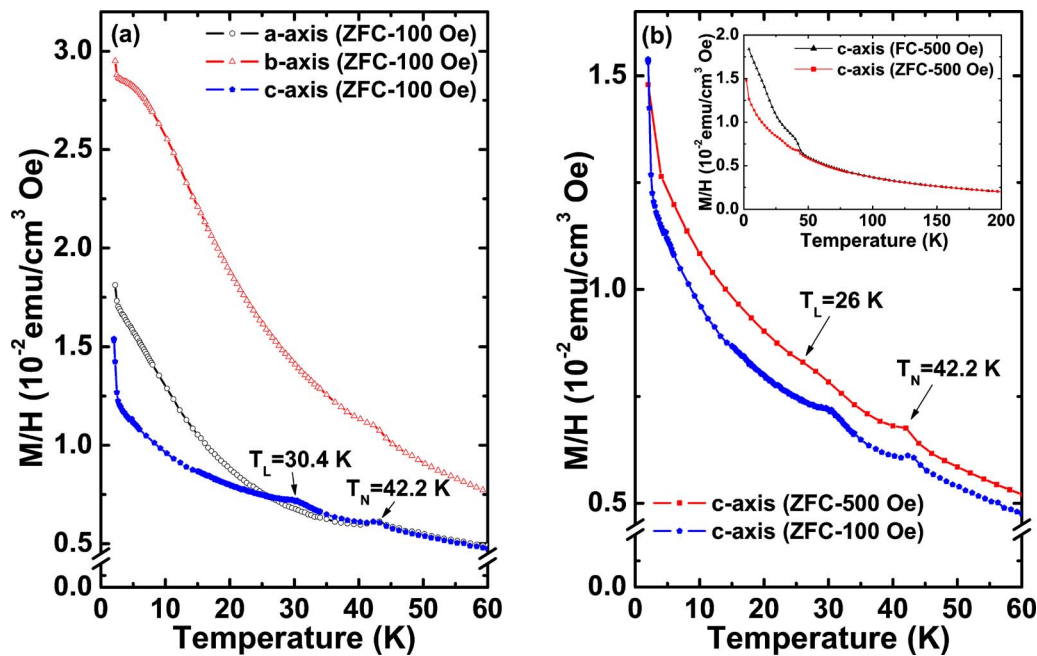


FIG. 3. (Color online) (a) The zero-field-cooled temperature dependent magnetizations [ZFC- $M(T)$] for o -HMO film probed along the different crystal orientations with an applied magnetic field of 100 Oe. (b) The ZFC- $M(T)$ along the c axis measured at 100 and 500 Oe. The inset in (b) shows full temperature range of the FC- and ZFC- $M(T)$ measured at 500 Oe. Notice the 30 K anomalous ordering along the c axis and the significant suppression of it by applying merely 500 Oe.

the recent first-principles calculations,¹³ in o -HMO, the multiferroicity could be simultaneously driven by both lattice and electronic mechanisms, although the ordering was assumed to occur within the a - b plane (a - c plane in $Pnma$ space group setting used in Ref. 13). Thus, it could be that the magnetic ordering in c axis somehow distorts the lattice, which, in turn, induces the lock-in transition in b axis and the associated polarization along the a and c axes. In any case, further investigations are certainly needed to delineate these interesting phenomena.

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 AF ordering expected for the o -HMO, an anomalous c -axis magnetic ordering near 30 K was evidently observed. This ordering temperature, although coincides very well with the lock-in temperature associated with the IC-commensurate magnetic ordering transition revealed by neutron diffraction and dielectric constant anomaly, is, however, very susceptible to applied field. Furthermore, the temperature is well above and should be irrelevant to the ordering temperature of Ho^{3+} moments. Finally, the fact that the ordering occurs along the c axis (in $Pbnm$ setting) is surprising and certainly demands further extensive studies.

This work was supported by the National Science Council of Taiwan, R.O.C. through Grant Nos. NSC95-2112-M-

009-035-MY3, NSC95-2112-M-009-038-MY3, and NSC95-2112-M-213-005 and MOE ATU program

- ¹T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, *Nature (London)* **426**, 55 (2003).
- ²N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S.-W. Cheong, *Nature (London)* **429**, 392 (2004).
- ³W. Eerenstein, N. D. Mathur, and J. F. Scott, *Nature (London)* **442**, 759 (2006).
- ⁴D. I. Khomskii, *J. Magn. Magn. Mater.* **306**, 1 (2006).
- ⁵S.-W. Cheong and M. Mostovoy, *Nat. Mater.* **6**, 13 (2007).
- ⁶I. A. Sergienko, C. Sen, and E. Dagotto, *Phys. Rev. Lett.* **97**, 227204 (2006).
- ⁷B. Lorenz, Y.-Q. Wang, and C. W. Chu, *Phys. Rev. B* **76**, 104405 (2007).
- ⁸F. Ye, B. Lorenz, Q. Huang, Y. Q. Wang, Y. Y. Sun, C. W. Chu, J. A. Fernandez-Baca, P. Dai, and H. A. Mook, *Phys. Rev. B* **76**, 060402(R) (2007).
- ⁹B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, *Phys. Rev. B* **70**, 212412 (2004).
- ¹⁰J.-S. Zhou and J. B. Goodenough, *Phys. Rev. Lett.* **96**, 247202 (2006).
- ¹¹H. W. Brinks, J. Rodríguez-Carvajal, H. Fjellvåg, A. Kjekshus, and B. C. Hauback, *Phys. Rev. B* **63**, 094411 (2001).
- ¹²A. Muñoz, M. T. Casáis, J. A. Alonso, M. J. Martínez-Lope, J. L. Martínez, and M. T. Fernández-Díaz, *Inorg. Chem.* **40**, 1020 (2001).
- ¹³S. Picozzi, K. Yamauchi, B. Sanyal, I. A. Sergienko, and E. Dagotto, *Phys. Rev. Lett.* **99**, 227201 (2007).
- ¹⁴J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, and M. T. Fernández-Díaz, *Inorg. Chem.* **39**, 917 (2000).
- ¹⁵S. C. Chae, Y. J. Chang, S. S. A. Seo, T. W. Noh, D.-W. Kim, and C. U. Jung, *Appl. Phys. Lett.* **89**, 182512 (2006).
- ¹⁶A. Muñoz, J. A. Alonso, M. T. Casais, M. J. Martínez-Lope, J. L. Martínez, and M. T. Fernández-Díaz, *J. Phys.: Condens. Matter* **14**, 3285 (2002).
- ¹⁷T. Kimura, G. Lawes, T. Goto, Y. Tokura, and A. P. Ramirez, *Phys. Rev. B* **71**, 224425 (2005).