Physical properties of multiferroic hexagonal $HoMnO_3$ thin films

P. Murugavel, J.-H. Lee, D. Lee, T. W. Noh, Younghun Jo, Myung-Hwa Jung, Yoon Seok Oh, and Kee Hoon Kim

Citation: Applied Physics Letters **90**, 142902 (2007); doi: 10.1063/1.2718512
View online: http://dx.doi.org/10.1063/1.2718512
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/90/14?ver=pdfcov
Published by the AIP Publishing

Physical properties of multiferroic hexagonal $HoMnO_3$ thin films

P. Murugavel,[a)] J.-H. Lee, D. Lee, and T. W. Noh[b)]
ReCOE and FPRD, Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Korea

Younghun Jo and Myung-Hwa Jung
Quantum Material Research Team, Korea Basic Science Institute, Daejeon 305-333, Korea

Yoon Seok Oh and Kee Hoon Kim
CSCMR and FPRD, Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Korea

(Received 9 January 2007; accepted 26 February 2007; published online 2 April 2007)

The authors investigated the magnetic and ferroelectric properties of hexagonally grown $HoMnO_3$ thin films. The magnetic measurements revealed bulklike magnetic phase transitions with an additional spin-glass-like behavior feature below the Néel temperature. The ferroelectricity in the films was distinctly different from the suggested bulk behavior. Below 40 K, the $HoMnO_3$ films showed typical ferroelectric character: their remnant polarization and coercive field values at 20 K were 3.7 $\mu C/cm^2$ and 0.69 MV/cm. Above 40 K, however, the films exhibited an unusual antiferroelectriclike behavior, with more pronounced features appearing at higher temperatures. These intriguing physical properties make $HoMnO_3$ films a potential candidate material for numerous future applications. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2718512]

Due to the complexity in their ferroelectric and magnetic ordering, studies on hexagonal manganites have continued since their discovery in the early 1960s.[1–10] Interest in the system was renewed with the finding that the magnetic phase in hexagonal $HoMnO_3$ crystals could be controlled by an external electric field.[8] In hexagonal $HoMnO_3$, the Mn^{3+} ion forms triangular lattices in the *a*-*b* plane, which are then stacked in alternating fashion along the *c* axis with Ho^{3+} layers in between.[11] At low temperature, the Mn^{3+} spins order antiferromagnetically at $T_N \approx 72$ K forming a noncollinear 120° spin structure in a $P6_3'c'm$ magnetic symmetry.[12] Around 40 K,[3,6,12] $HoMnO_3$ displays a spin reorientation transition, when the Mn^{3+} spins rotate 90°, resulting in a change in magnetic symmetry to $P6_3'cm'$. At about 5 K, a second spin reorientation transition appears in the $P6_3cm$ magnetic symmetry, which is accompanied by a strong increase in Ho antiferromagnetic (AFM) ordering.[3,13] Taken together, $HoMnO_3$ possesses a novel magnetic-field-induced reentrant phase with the most complex phase diagram of all hexagonal manganites.[6]

It was recently suggested that the origin of the ferroelectric distortion in hexagonal $YMnO_3$ is generated by the buckling of the MnO_5 polyhedral bonds accompanied by the displacement of the Y ions.[7] Despite the extensive research on the magnetic and magnetoelectric properties of bulk $HoMnO_3$, its ferroelectric properties have rarely been investigated. Although $HoMnO_3$ is reported to show a saturation polarization (P_s) of 5.6 $\mu C/cm^2$ at a high Curie temperature ($\approx$875 K), most of our present understanding is based on limited older data.[1,2] For this study, we fabricated epitaxial hexagonal $HoMnO_3$ thin films by pulsed laser deposition (PLD) techniques to conduct a comprehensive study of their magnetic and ferroelectric properties. Contrary to reported bulk ferroelectric properties, our hexagonal $HoMnO_3$ films showed an interesting antiferroelectriclike (AFE-like) feature starting around 40 K.

$HoMnO_3$ films were deposited by the PLD method on $Pt(111)/Al_2O_3(0001)$ and yttrium stabilized zirconia (111) [YSZ(111)] substrates. A sintered ceramic pellet of stoichiometric $HoMnO_3$ was used as a target for the PLD. Ablations were effected using a 248 nm wavelength KrF excimer laser (Lambda Physik) with fluence on target of 1.5 J cm^{-2}. To obtain high quality films, the substrate temperature and oxygen pressure were optimized at 850 °C and 100 mTorr. Deposited film thickness was estimated to be around 100 nm. The crystal structure of the films was analyzed by high resolution x-ray diffraction. For the ferroelectric measurements, Au top electrodes of 100 μm diameter were sputtered through a shadow mask. The polarization hysteresis loops were measured using a low temperature probe station (Desert Cryogenics) and a T-F analyzer (aixACCT) at 2 kHz. The capacitance was measured using an *LCR* meter with an 50 mV, 100 kHz ac signal. Low temperature magnetization measurements were performed using a magnetic property measurement system (Quantum Design).

High quality epitaxial $HoMnO_3$ thin films were obtained under these optimized growth conditions. Figure 1(a) shows the x-ray diffraction (XRD) θ-2θ patterns for the $HoMnO_3$ films on $Pt(111)/Al_2O_3(0001)$ and YSZ(111) substrates. The patterns reveal pure (000*l*)-oriented hexagonal $HoMnO_3$ reflections without a trace of an impurity or additional phases. To investigate the in-plane texture of the films, we measured the x-ray ϕ scans around the $(11\bar{2}2)$ $HoMnO_3$ and (200) Pt reflections. As shown in Fig. 1(b), the ϕ scans of $HoMnO_3$ also display sixfold symmetry, suggesting epitaxial growth of the hexagonal $HoMnO_3$ film.[10] From the XRD, we evaluated the in-plane (*a*) and out-of-plane (*c*) lattice parameters of the $HoMnO_3$ on $Pt(111)/Al_2O_3(0001)$ to be 6.20 and 11.40 Å, respectively. The respective values on YSZ(111) substrate are 6.15 and 11.37 Å. The comparison with the bulk values

[a)]Present address: Department of Physics, Indian Institute of Technology Madras, Chennai-600 036, India.
[b)]Electronic mail: twnoh@snu.ac.kr

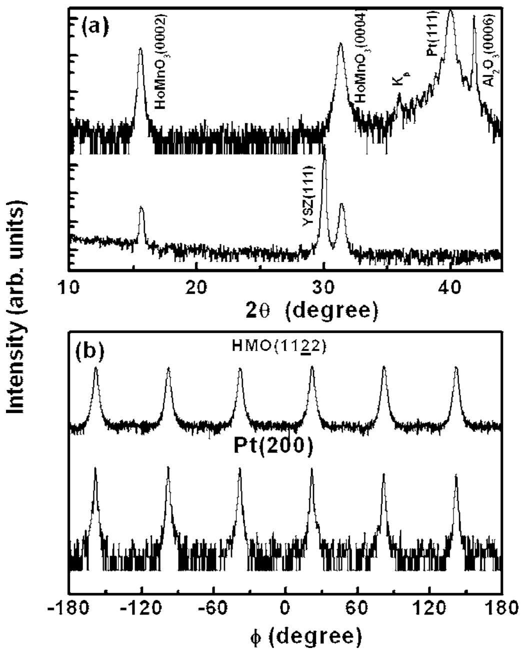

FIG. 1. (a) θ-2θ XRD scans of $HoMnO_3$ films on $Pt(111)\|Al_2O_3$ and YSZ(111) substrates. (b) ϕ scan plot of the $HoMnO_3(11\underline{2}2)$ and Pt(200) reflections.

of $a=6.13$ Å and $c=11.40$ Å demonstrates that the $HoMnO_3$ films were grown under tensile strained condition. Note that the c lattice parameter of the film on $Pt(111)/Al_2O_3(0001)$ substrate remains the same as the bulk value, indicating a possible oxygen nonstoichiometry of the film.

In the magnetic property studies, the magnetic background signal from the Pt/Al_2O_3 substrate was found to be very large.[10] Therefore, we epitaxially deposited the $HoMnO_3$ films on an YSZ(111) substrate rather than on $Pt(111)/Al_2O_3(0001)$. Figure 2 shows the magnetization versus temperature curves measured under the zero-field cooled (ZFC) and the field cooled (FC) conditions. Both curves show anomalies near 50 and 38 K. These anomalies are clearly seen in the inverse susceptibility versus temperature ($1/\chi$ vs T) plot of the ZFC data shown as solid squares in Fig. 2. The inverse susceptibility undergoes a sharp decrease at $\sim$70 K, reaching a first minimum at 50 K followed by another at 38 K. The 50 K minimum could have originated

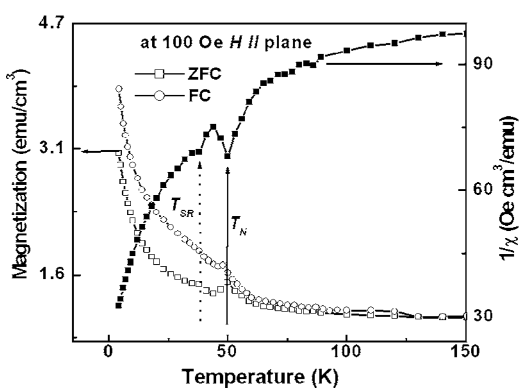

FIG. 2. (a) Magnetization vs temperature plot of a $HoMnO_3$ film on an YSZ(111) substrate, measured under zero-field cooled condition (open squares) and a 100 Oe field cooled condition (open circles). The solid squares represent the inverse susceptibility vs temperature plot measured under a zero-field cooled condition.

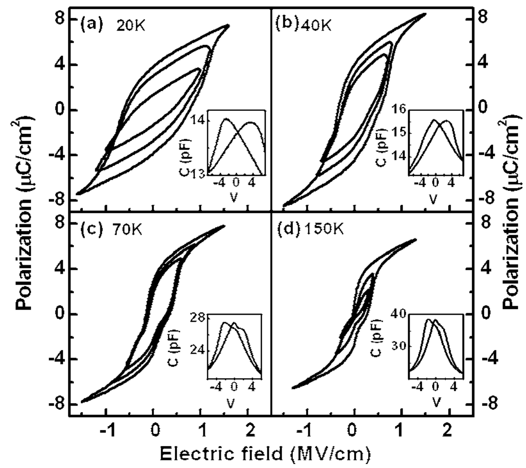

FIG. 3. Polarization vs electric field hysteresis loops for a $HoMnO_3$ film measured at (a) 125 K, (b) 40 K, (c) 70 K, and (d) 150 K. The inset shows the capacitance vs voltage plot measured at the same temperatures.

from the AFM ordering of the Mn^{3+} spins in their triangular lattice, while the 38 K could have come from the Mn^{3+} spin reorientation transition. In addition, the steep fall in $1/\chi$ below 10 K may be attributable to the Ho^{3+} spin ordering.

When compared to its bulk counterpart, the $HoMnO_3$ films exhibited interesting magnetic properties. First, the AFM ordering temperature T_N of our film is about 50 K, significantly lower than the corresponding bulk value of 72 K. However, the spin reorientation temperature T_{SR} of our film is similar to that of the reported bulk value, i.e., about 40 K. Fiebig *et al.* stated that the AFM ordering of the Mn^{3+} spin comes from the in-plane exchange interaction and that the spin reorientation could be attributed to the magnetic superexchange interaction between the Mn^{3+} and the Ho^{3+} spins along the c axis.[14] Tensile stress, applied to the $HoMnO_3$ film, can lower the exchange interaction and hence T_N. However, it will not affect the c-axis magnetic interaction significantly, causing little change in T_{SR}. Second, the $HoMnO_3$ film shows a spin-glass-like behavior below T_N, as seen in the hysteresis between the ZFC and FC magnetization data shown in Fig. 2. Munoz *et al.* reported no difference between the ZFC and FC susceptibilities in bulk $HoMnO_3$ polycrystalline samples.[3] Although the spin-glass-like behavior could be related to the geometrical frustration of antiferromagnetically coupled Mn^{3+} spins, it is not yet clear why our film's magnetic susceptibility data are so different from the reported bulk behavior.

The electric properties of the hexagonal $HoMnO_3$ films also display surprisingly different behavior than the accepted view that $HoMnO_3$ has a ferroelectric phase with a P_s of 5.6 $\mu C/cm^2$ and a very high Curie temperature of about 875 K.[1,2] We measured the polarization versus electric field (P-E) hysteresis loops between 4 and 220 K (leakage current problems around room temperature, due to possible oxygen nonstoichiometry, prevented higher temperature measurements). Figures 3(a)–3(d) show the P-E loops measured at 20, 40, 70, and 150 K, respectively, for several values of maximum applied E. All of the P-E hysteresis loops show nearly saturating behaviors, indicating that the leakage current provides negligible contributions below 150 K. At 20 K, the P-E loops indicate a clear ferroelectric hysteresis character with remnant polarization (P_r) and coercive field (E_c) values of 3.7 $\mu C/cm^2$ and 0.69 MV/cm. Surprisingly, above

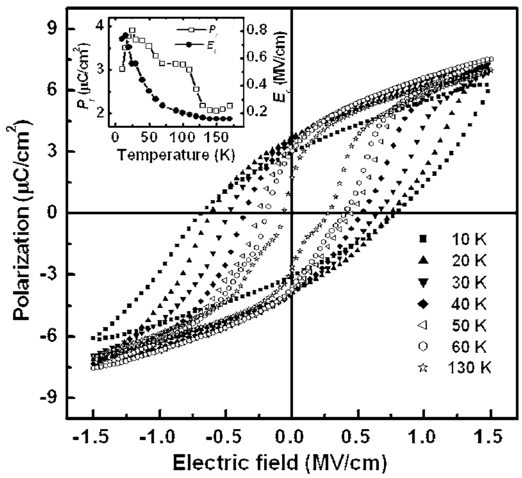

FIG. 4. Polarization vs electric field hysteresis loops for a $HoMnO_3$ film measured at various temperatures. The inset shows the temperature dependence of the remnant polarization and coercive field.

40 K, the *P-E* loops appear different from conventional ferroelectric loops. In particular, at 70 K, the *P-E* loop shows an AFE-like shape whose features become clearer with increasing *T*.

Figure 4 shows the systematic development of the AFE-like feature with increasing temperature. To prevent dielectric breakdown, the maximum applied field was limited to 1.5 MV/cm above 30 K, when the *P-E* hysteresis loops showed saturation. The inset of Fig. 4 presents the P_r and E_C values plotted against *T*. Apart from the sharp decrease in P_r due to the unsaturated *P-E* loop below 30 K, both the P_r and E_C trends became higher with decreasing *T*. The increase in E_C might be explained in terms of an increase in domain pinning effects at low temperature.[15,16] However, the AFE-like behavior in our $HoMnO_3$ films could not be attributed to these domain pinning effects because then the AFE-like behavior should be stronger at lower temperature, contrary to our observations. In addition, the unusual AFE-like properties are further demonstrated in the double butterfly-shaped capacitance versus electric field loops shown in the insets of the respective graphs in Fig. 3.

We believe that, with the exception of $YMnO_3$, complete *P-E* loop data are not available for either bulk or thin films of hexagonal manganites. The *P-E* loop for the hexagonal $YMnO_3$ film shows a typical ferroelectric response. As the ionic sizes of Y^{3+} and Ho^{3+} ions are quite similar, the AFE-like behavior in our $HoMnO_3$ films is quite unexpected. However, the lack of available data on bulk $HoMnO_3$ makes it difficult to conclude that the observed AFE-like properties are unique to the $HoMnO_3$ thin films.

Using epitaxial stabilization techniques,[10,17] we were recently able to fabricate hexagonal $TbMnO_3$ and $DyMnO_3$ films, with their orthorhombic equilibrium phases. In these artificial materials, we observed similar AFE-like properties. Note that the Y^{3+} ions do not have spin, but that the Ho^{3+}, Dy^{3+}, and Tb^{3+} ions do. The observation of the AFE-like behavior only for films with magnetic spins is quite intriguing and strongly supports further systematic investigations.

In summary, good quality epitaxial hexagonal $HoMnO_3$ films were fabricated on both $Pt(111)/Al_2O_3(0001)$ and YSZ(111) substrates. At low temperatures, the films revealed several magnetic transitions, including antiferromagnetic, spin reorientation, and Ho^{3+} ordering transitions displayed in order with decreasing temperature. The $HoMnO_3$ films differ from the bulk material in both a significantly lower Néel temperature and in a spin-glass-like behavior. In addition, contrary to general belief, the $HoMnO_3$ films showed antiferroelectriclike features starting at 40 K. The present work strongly promotes the need for better understanding of these hexagonal manganite thin films, which could lead to novel applications for these materials.

This research was financially supported by the Creative Research Initiatives (Functionally Integrated Oxide Heterostructure) of MOST/KOSEF.

[1]E. F. Bertaut, F. Forrat, and C. R. Fang, Acad. Sci., Paris, C. R. **256**, 1958 (1963).

[2]P. Coueuré, F. Guinet, J. C. Peuzin, G. Buisson, and E. F. Bertaut, in *Proceedings of the International Meeting on Ferroelectrcity*, edited by V. Dvorák (Institute of Physics of the Czechoslovak Academy of Science, Prague, 1966), p. 332.

[3]A. Munoz, J. A. Alonso, M. L. Martinez-Lope, M. T. Casais, J. L. Martinez, and M. T. Fernandez-Diaz, Chem. Mater. **13**, 1497 (2001).

[4]T. Katsufuji, S. Mori, M. Masaki, Y. Moritomo, N. Yamamoto, and H. Takagi, Phys. Rev. B **64**, 104419 (2001).

[5]Th. Longai, D. G. Tamuta, U. Amann, J. Ihringer, R. W. A. Hendrikx, D. M. Tobbens, and J. A. Mydosh, Phys. Rev. B **69**, 134108 (2004).

[6]B. Lorenz, A. P. Litvinchuk, M. M. Gospodinov, and C. W. Chu, Phys. Rev. Lett. **92**, 087204 (2004).

[7]B. B. Van Aken, T. T. M. Palstra, A. Filipetti, and N. A. Spaldin, Nat. Mater. **3**, 164 (2004).

[8]T. Lottermoser, T. Lonkal, U. Amann, D. Hohlwein, J. Ihringer, and M. Fiebig, Nature (London) **430**, 541 (2004).

[9]M. Fiebig, J. Phys. D **38**, R123 (2005).

[10]J. H. Lee, P. Murugavel, H. Ryu, D. Lee, J. Y. Jo, J. W. Kim, H. J. Kim, K. H. Kim, Y. Jo, M. H. Jung, Y. H. Oh, Y. W. Kim, J. G. Yoon, J. S. Chung, and T. W. Noh, Adv. Mater. (Weinheim, Ger.) **18**, 3125 (2006).

[11]H. L. Yakel, W. C. Koehler, E. F. Bertaut, and E. F. Forrat, Acta Crystallogr. **16**, 957 (1963).

[12]M. Fiebig, D. Frohlich, K. Kohn, St. Leute, Th. Lottermoser, V. V. Pavlov, and R. V. Pisarev, Phys. Rev. Lett. **84**, 5620 (2000).

[13]H. Sugie, N. Iwata, and K. Kohn, J. Phys. Soc. Jpn. **71**, 1558 (2002).

[14]M. Fiebig, C. Degenhardt, and R. V. Pisarev, Phys. Rev. Lett. **88**, 027203 (2002).

[15]J. Y. Jo, Y. S. Kim, T. W. Noh, J.-G. Yoon, and T. K. Song, Appl. Phys. Lett. **89**, 232909 (2006).

[16]J. Y. Jo, D. J. Kim, Y. S. Kim, S.-B. Choe, T. K. Song, J.-G. Yoon, and T. W. Noh, Phys. Rev. Lett. **97**, 247602 (2006).

[17]J. H. Lee, P. Murugavel, D. Lee, T. W. Noh, Y. Jo, M.-H. Jung, K. H. Jang, and J.-G. Park, Appl. Phys. Lett. **90**, 012903 (2007).