Journal of Physics: Conference Series **200** (2010) 012227 doi:10.1088/1742-6596/200/1/012227

# Polarization-dependent x-ray absorption spectroscopy of hexagonal and orthorhombic $TbMnO_3$ thin films

**K H Wu[1*], I C Gou[1], C W Luo[1], T M Uen[1], J-Y Lin[2], J Y Juang[1], T Kobayashi[1], C K Chen[3], J M Lee[1,3], J M Chen[3]**

[1]Department of Electrophysics, National Chiao Tung University, Hsinchu 300, Taiwan, R.O.C.
[2]Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan, R.O.C.
[3]National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, R.O.C.

E-mail: khwu@cc.nctu.edu.tw

**Abstract.** Pure phase $TbMnO_3$ manganite thin films with hexagonal ($h$-TMO) and orthorhombic ($o$- TMO) crystal structures were prepared by pulsed laser deposition. The distinctive orientation alignments between film and substrate obtained here have allowed us to perform the x-ray absorption near edge spectroscopy (XANES) measurements with the electric field applied along the three major crystallographic directions. The XANES results, as expected, display significantly different spectral features for the $h$-TMO and $o$-TMO films. In addition, the XANES spectra also exhibit strong polarization dependence at O $K$ and Mn $L$ edges for both samples.

## 1. Introduction

Multiferroic rare earth manganites $ReMnO_3$ (RMO, R = rare earth) have been investigated extensively in materials science and condensed-matter physics recently. These complex adaptive materials exhibit the coexistence and mutual coupling of different order parameters, namely the ferroelastic strain, electric polarization and magnetization [1-4]. It is found that the ferroelectricity can be induced by either the complex lattice distortion in hexagonal RMO ($h$-RMO) or by the spin spiral structure in the orthorhombic RMO ($o$-RMO). More importantly, the coupling between the electric polarization and magnetization enables the manipulation of the magnetic state of a material through the application of the electric field, or vice versa. In order to understand the physical mechanisms of the coexistence and coupling of magnetic and ferroelectric orders and to design the devices for accomplishing the potential applications of RMO manganites, it is essential to prepare the thin films with the two relevant hexagonal and orthorhombic crystalline structures and to investigate how the crystalline structure affects the manifestations of multiferroicity in the same compound.

It is possible to grow $h$-RMO or $o$-RMO thin films of the same compound on different substrates [5-7] by utilizing the technique of epitaxial strain stabilization. Recently, we have grown $h$-$YMnO_3$ ($h$-$HoMnO_3$, $h$-$TbMnO_3$) and $o$- $YMnO_3$ ($o$-$HoMnO_3$, $o$-$TbMnO_3$) thin films with well-aligned in-plane orientation respectively and studied their anisotropic electrical, magnetic properties and ultrafast dynamics [5, 6]. In the present work, pure phase $h$-TMO

 

and $o$-TMO manganite thin films were prepared and their anisotropic electronic structures were probed by the polarization-dependent x-ray absorption spectroscopy (XAS). Consequently, the polarization-dependent XAS measurement can elucidate distinctly the anisotropic property of Mn-O bonding and the factor responsible for the magnetoelectric anisotropy of these samples [8-10].

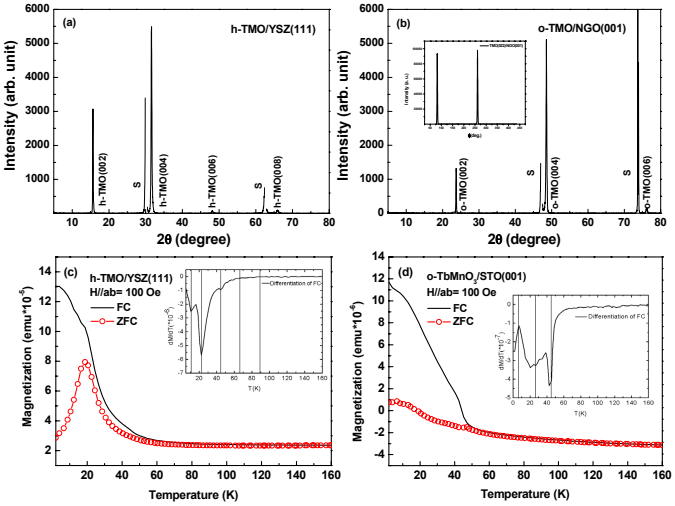


**Figure 1.** The $\theta$-$2\theta$ XRD pattern for the as deposited (a) (00l) $h$-TMO/YSZ(111) films (b) (00l) $o$-TMO/$NdGaO_3$(001) films. The inset of figure 1(b) shows the $\phi$ scan of the $o$-TMO(022) and displays a clear two-fold symmetry. Temperature dependent magnetization (M-T) curves for the (c) $h$-TMO/YSZ(111) films and (d) $o$-TMO/$SrTiO_3$(001) with the applied magnetic field in the $ab$- plane ($H \| ab$) of the film, the inset shows the corresponding dM/dT curves.

## 2. Experiment

The pure phased $h$-TMO and $o$-TMO films used in this study were prepared by pulsed laser deposition. A KrF excimer laser operating at a repetition rate of 3-5 Hz with an energy density of 2-5 J/cm$^2$ was used. The $h$-TMO films were deposited on YSZ(111) substrate, while the $o$-TMO films were deposited on $SrTiO_3$(001) and $NdGaO_3$(001) substrates. The thicknesses of $h$-TMO and $o$-TMO films were around 80 nm and 120 nm, respectively. Figs. 1(a)-1(d) show the typical X-ray diffraction (XRD) patterns and magnetization (M-T) curves of $h$-TMO and $o$-TMO films. Fig. 1(a) shows the $\theta$-$2\theta$ XRD scans for the as deposited $h$-TMO/YSZ(111) films. The diffraction peaks reveal pure (00l)-oriented $h$-TMO reflections without discernible impurity phase, indicating the formation of a pure $c$ axis $h$-TMO thin film. Similar results for $o$-TMO/$NdGaO_3$(001) films is shown in Fig. 1(b). Besides, as shown in the inset of Fig. 1(b), the $\phi$ scan of the $o$-TMO(022) displays a clear two-fold symmetry, indicating that the films were indeed epitaxial and well aligned in the surface of the substrate. Figs. 1(c) and 1(d) show the M-T curves for the $h$-TMO and $o$-TMO films with the applied field in the $ab$-plane ($H \| ab$), respectively. The XAS measurements at the O $K$- and Mn $L$- edges were carried out using high- energy spherical grating monochromator (HSGM) beamline and Dragon beamline at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, operating at 1.5 GeV with a maximum stored current of 200 mA. The O $K$- edge XAS spectrum was recorded in the surface-sensitive total electron yield (TEY) mode and bulk-sensitive x-ray fluorescence yield mode. The Mn $L$- edge XAS spectrum was recorded in TEY mode.

## 3. Results and Discussion

### *3.1. XAS of o-TMO thin films*

Figs. 2(a) and 2(b) show the O $K$- edge and Mn $L$- edge XAS spectra of an $o$-TMO/NGO(001) thin film, respectively. The polarizations $E \| a$, $E \| b$, and $E \| c$ could be measured individually in this sample. The results are similar to the XAS spectra of $o$-TMO single crystal that reported in

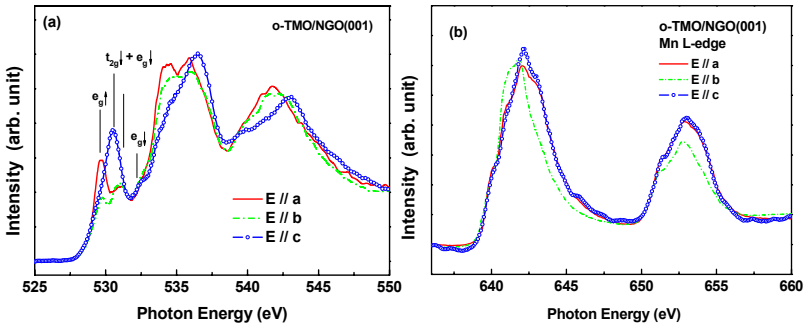


**Figure 2.** (color online) Polarization-dependent (a) O $K$-edge and (b) Mn $L$-edge XAS of $o$-$TbMnO_3$/NGO(001) thin film for the polarizations $E\|a$, $E\|b$ and $E\|c$. The assignments of absorption features are described in the text.

[10]. The Mn $3d$ region consists of four pre-edge peaks, which appear at 529.7, 530.6, 531.2, and 532.2 eV. The broad structure located around 535 eV is attributed to the O $2p$ states hybridized with the Tb $5d$ states, whereas the peak near 542 eV is associated with transitions into the Mn $4sp$ and Tb $6s$ states. According to the LDA+U calculation [10] in $o$-TMO, the pre-edge peaks below 533 eV are identified respectively as the transitions into empty O $2p$ states hybridized with the majority-spin Mn $e_g(\uparrow)$ bands, the minority-spin Mn $t_{2g}(\downarrow)$ and Mn $e_g(\downarrow)$ bands, and the minority-spin Mn $e_g(\downarrow)$ bands, as denoted in Fig. 2(a).

It is noted that the features of the O $K$- edge XAS and Mn $L_{2,3}$- edge XAS spectra exhibit significant anisotropy when measuring along the three principal crystallographic directions, which are in contrast to the conclusions drawn in [9]. In that, although the spectra of the hexagonal manganites exhibit strong polarization dependence at both Mn $L_{2,3}$- and O $K$ edges, the orthorhombic manganites barely show polarization dependence in the similar absorption edges. However, since the in-plane orientation of the films they used was indistinguishable, therefore, only $E\|ab$ and $E\|c$ spectra were measured. In fact, when we measured the spectra of the (001) $o$-TMO thin film deposited on the STO(001) substrate, in which the $a$- and $b$- axes are indistinguishable, or when we took the average of the $E\|a$ and $E\|b$ distributions for the (001) $o$-TMO/NGO sample, the results ($E\|ab$ and $E\|c$ spectra) were similar to that shown in Fig. 4 of Ref. [9]. Therefore, the present data are actually consistent with those in Ref. [9]. More importantly, we confirm that the XAS spectra for $o$-TMO are strongly polarization dependent both for the O $K$- edge and Mn $L$- edge along the three principal crystallographic directions, particularly in the region of the Mn $e_g(\uparrow)$-O $2p$ hybridization.

*3.2. XAS of h-TMO thin films*

Figs. 3(a) and 3(b) show the O $K$- edge and Mn $L$- edge XAS spectra ($E\|c$ and $E\|ab$) of the $h$-TMO thin film deposited on YSZ(111) substrate, respectively. The intensity distribution and the peak positions of the XAS spectra are distinctly different from those of $o$-TMO described above, which indicates that the local environment, geometrical arrangement and crystal field around Mn and O ions are different for both phases. The O $K$- edge XANES spectrum of the $h$-TMO thin film is very similar to that reported in [9] and can be divided into three parts, corresponding to Mn $3d$, Y $4d$, and Mn $4sp$/Y $5sp$ regions. There are four pre-edge peaks in the Mn $3d$ region and are attributed to $a_{1g}(\uparrow)$, $e_{1g}(\downarrow)$, $e_{2g}(\downarrow)$, and $a_{1g}(\downarrow)$, as denoted in Fig. 3(a), respectively. The spectrum also exhibits strong polarization dependence in the Mn $3d$ and Y $4d$ regions, indicating the existence of strong Mn $3d$-O $2p$ and Y $4d$- O $2p$ bond anisotropy. It is noted that the Mn $L_{2,3}$- edge XAS of the $h$-TMO thin film (Fig. 3(b)) also shows the

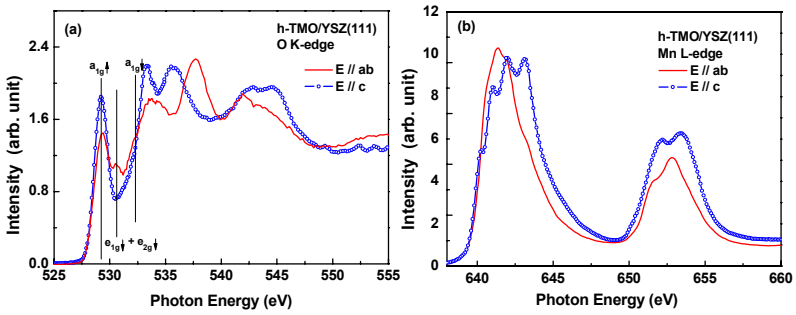


**Figure 3.** (color online) Polarization-dependent (a) O $K$- edge (b) Mn $L$- edge XAS of $h$-TMO/YSZ(111) thin film for polarizations $E\|ab$ and $E\|c$.

strong polarization dependence and is very close to the spectral of $h$-$YMnO_3$ sample reported previously. As described in [9], these electronic and bond anisotropies of $h$-RMO are closely related to the ferroelectricity of these materials. Therefore, these results provide new insight into the microscopic understanding of the magnetoelectric anisotropy exhibited in many RMO manganites.

## 4. Summary

In summary, we have prepared pure hexagonal and orthorhombic TMO thin films for XAS measurements. It is evident that there are significant differences in the electronic structures of $h$-TMO and $o$-TMO thin films, indicating that the type and strength of hybridization between the Mn and O ions are different for both samples. Moreover, the XAS of $E\|ab$ and $E\|c$ spectra for $h$-TMO and the $E\|a$, $E\|b$, and $E\|c$ spectra for $o$-TMO all exhibit strong polarization dependence at both O $K$ and Mn $L$ edges. These electronic and bond anisotropies are closely related to the magnetoelectric anisotropy and multiferroicity exhibited in these materials.

## Acknowledgements

This project is financially sponsored by the National Science Council (grant no. NSC 95-2112-M-009-037-MY3) and the Ministry of Education (2007 MOE ATU program at NCTU) of Taiwan.

## References

[1] Fiebig M, 2005 *J. Phys. D* **38**, R123
[2] Kimura T, Goto T, Shintani H, Ishizaka K, Arima T and Tokura Y, 2003 *Nature* **426**, 55
[3] Khomskii D I, 2006 *J. Magnetism and Magnetic Materials* **306**, 1
[4] Cruz C D, Yen F, Lorenz B, Wang Y Q, Sun Y Y, Gospodinov M M, and Chu C W, 2005 *Phys. Rev. B* **71**, 060407
[5] Lin T H, Hsieh C C, Shih H C, Luo C W, Uen T M, Wu K H, Juang J Y, Lin J -Y, Hsu C H, Liu S J, 2008 *Appl. Phys. Lett.* **92**, 132503
[6] Hsieh C C, Lin T H, Shih H C, Hsu C-H, Luo C W, Lin J Y, Wu K H, Uen T M, Juang J Y, 2008 *J. Appl. Phys.* **104**, 103912
[7] Lee J H, Murugavel P, Ryu H, Lee D, Jo J Y, Kim J W, Kim H J, Kim K H, Jo Y, Jung M H, Oh Y H, Kim Y W, Yoon J G, Chung J S, Noh T W, 2006 *Adv. Mater.* **18**, 3125
[8] Edwards D M, 2002 *Adv. Phys.* **51**, 1259
[9] Chen J M, Lee J M, Chen C K, Chou T L, Lu K T, Haw S C, Liang K S, Chen C T, Jeng H T, Huang S W, Yang T J, Shen C C, Liu R S, Lin J Y, Hu Z, 2009 *Appl. Phys. Lett.* **94** 044105
[10] Cho D Y, Kim J Y, Park B G, Rho K J, Park J H, Noh H J, Kim B J, Oh S J, Park H M, Ahn J S, Ishibashi H, Cheong S W, Lee J H, Murugavel P, Noh T W, Tanaka A, Jo T, 2008 *Phys. Rev. Lett.* **98**, 217601