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Spectroscopic evidence of electron doping in $La_{0.7}Ce_{0.3}MnO_3$

J.-Y. Lin[a,*], W.J. Chang[b], J.Y. Juang[b], T.M. Wen[b], K.H. Wu[b], Y.S. Gou[b], J.M. Lee[c], J.M. Chen[c]

[a] *Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan, ROC*
[b] *Department of Electrophysics, National Chiao Tung University, Hsinchu 300, Taiwan, ROC*
[c] *National Synchrotron Research Center, Hsinchu 300, Taiwan, ROC*

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Abstract

X-ray absorption near edge spectroscopy was used to investigate the hole states in the $La_{0.7}Ce_{0.3}MnO$ (LCeMO). A substantial decrease in the spectral weight of the e_g orbital was observed in LCeMO compared to that in the hole-doped $La_{0.7}Ca_{0.3}MnO$. This directly proves that electron doping occurs in LCeMO.

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Keywords: CMR; XANES; Electron doping

The colossal magnetoresistance (CMR) phenomenon in hole-doped rare-earth manganites $R_{1-x}A_xMnO_3$ (R: trivalent rare-earth element; A: divalent alkaline earth ions) has attracted enthusiasm for its dramatic MR effects near the Curie temperature (T_C) and the generous phase diagram. The doping of divalent cations leads Mn^{3+} of the undoped manganite to form a mixture of Mn^{3+} and Mn^{4+}, and drives a ferromagnetic metallic transition. In electron-doped manganites, a mixture of Mn^{2+} and Mn^{3+}, the analogy to hole-doped manganites are still not clear. Unfortunately, the cerium-doped manganese oxide is usually mixed with unbinding Ce^{4+}, which are in CeO_2 state. For polycrystalline samples, the effects of CMR are from hole doping (lanthanum deficient) rather than electron doping. Very recently, the single-phase $La_{0.7}Ce_{0.3}MnO_3$ (LCeMO) epitaxial thin films have been successfully grown by pulsed laser deposition, using KrF excimer laser [1,2]. This breakthrough could provide a novel opportunity to study the physical properties of electron-doped manganites and an alternative to reach CMR.

Although the single-phase LCeMO in the thin film form has been confirmed, its electronic structure has to be further investigated. Manganese has been verified to be in a mixture of Mn^{2+} and Mn^{3+} valence states [3]. However, whether the electron doping occurs in the electronic structure of LCeMO is crucial to further studies of the properties and applications of this material. X-ray absorption near edge spectroscopy (XANES) has proven to be an effective tool to

*Corresponding author. Tel.: +886-3-573-1653; fax: +886-3-572-0728.
E-mail address: ago@cc.nctu.edu.tw (J.-Y. Lin).

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investigate the hole states in the complex compounds. In this paper, XANES clearly shows the evidence of the electron doping in the e_g states of Mn in LCeMO.

Epitaxial LCeMO films were grown on $SrTiO_3$ (1 0 0) (STO) substrates by pulsed laser deposition (PLD), using a KrF (248 nm) excimer laser with a repetition rate of 5 Hz. For this study, the oxygen pressure of 0.35 Torr was set for all experiments as it gave the best results. X-ray diffraction data demonstrated the formation of single-phase LCeMO in the thin films. The O K-edge and Mn L-edge X-ray absorption spectra were carried out at $T = 300$ K using linear polarized synchrotron radiation from 6-m high-energy spherical grating monochromator beamline located at NSRRC in Taiwan. The energy resolution of the monochromator was about 0.2 and 0.1 eV for the O K-edge and Mn L-edge energy range, respectively. Details of XANES experiments can be found in Refs. [4,5]. The O K-edge and Mn L-edge spectra were in the fluorescence and the total electron mode, respectively. The saturation (or "self-absorption") effects were corrected for all measured O K-edge spectra.

DC magnetization $M(T)$ and the resistivity $\rho(T)$ of the LCeMO thin film are shown in Fig. 1. The ferromagnetic magnetic ordering happens at $T_C \approx 255$ K judged by the inflection point of the $M(T)$ curve. A "metal-to-insulator" transition for $\rho(T)$ follows the magnetic ordering at almost identical temperature. The same phenomenon has been observed in the well-studied $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) with similar T_C. Beyond these superficial similarities, it is of interest to investigate the underlying mechanism in further detail. The magnetic and transport properties in LCMO are associated with the e_g orbital. The unoccupied states in e_g^1 lead to the magnetic ordering and the consequent $\rho(T)$ through the double exchange mechanism. In the following, XANES results reveal a different electronic structure of LCeMO from that of LCMO.

Fig. 2 shows the Mn L-edge spectra of LCeMO, LCMO, and standard samples. In comparisons, it is clearly demonstrated that the mixed valence of Mn is between +2 and +3 in LCeMO, in contrast to that between +3 and +4 in LCMO. These

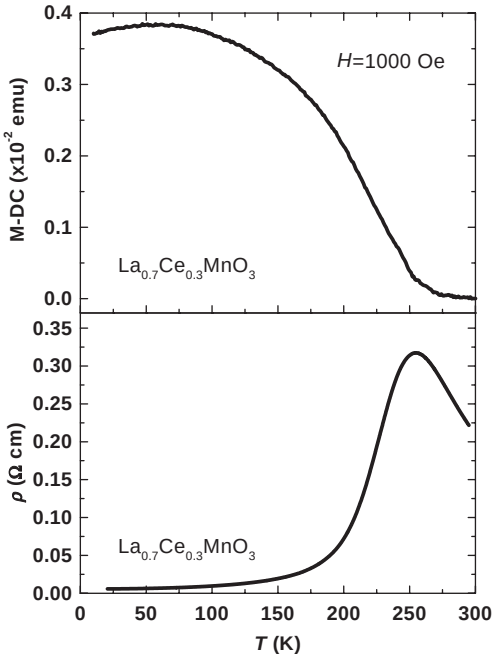

Fig. 1. The DC magnetization $M(T)$ and the resistivity $\rho(T)$ of the LCeMO thin film. $M(T)$ was measured under field cooling.

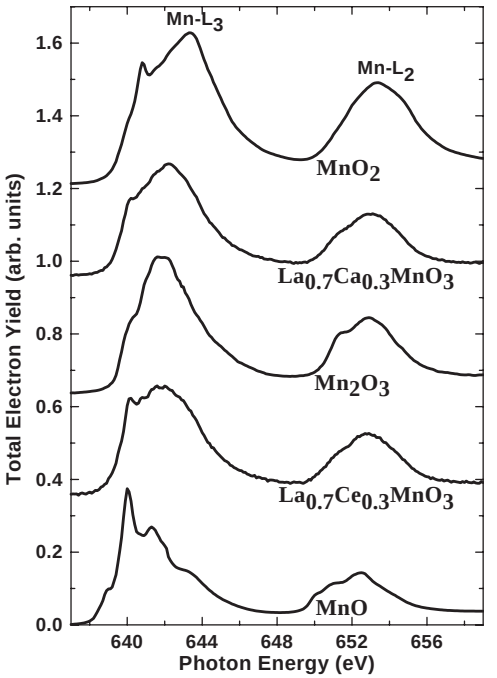

Fig. 2. Mn L-edge XANES spectra show that Mn is in the mixture of +2 and +3 states.

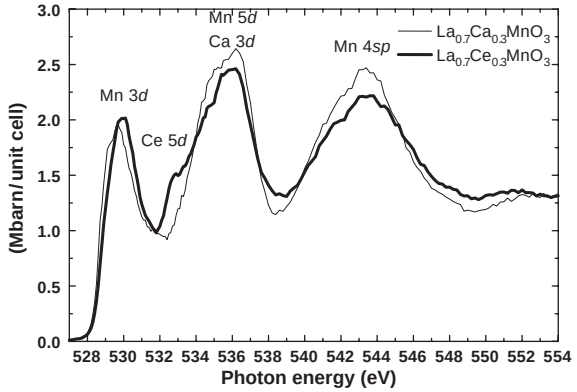

Fig. 3. Comparisons of the O K-edge XANES spectra of LCeMO and LCMO indicate the electron doping in the e_g states of LCeMO.

results can be taken as an indication of electron doping in LCeMO and are consistent with the previous report [3]. O K-edge spectra are shown in Fig. 3 and provide further evidence. The O 2p states are hybridized with Mn 3d and other states. In Fig. 3, these assignments were labeled to the associated spectral peaks. For the Mn 3d peak, the onset in LCeMO occurs at a higher energy than in LCMO. This is consistent with the electron doping by the rigid band model. More obviously, the spectral weight of the shoulder at 529 eV in LCMO, which is assigned to the $e_g\uparrow$ states [6], is much reduced in LCeMO. Therefore, there are more occupied $e_g\uparrow$ states in LCeMO.

In summary, XANES provides strong evidence of electron doping in LCeMO. Whether the doped holes reside in the $e_g^2\uparrow$ or $t_{2g}\downarrow$ states as proposed by Ref. [2] remains to be further investigated. More XANES measurements at low temperatures are currently underway.

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