# X-ray absorption magnetic circular dichroism of (La,Ce)MnO₃ thin films

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Creating a bipolarity of semiconductors has been a key technology to develop recent advanced semiconductor devices. Such bipolarity for manganese oxides, of which "hole-doped manganites" exhibit a rich variety of electric transport and magnetic properties, has been of great importance. Although theoretical calculation predicts the presence of ferromagnetic "electron-doped manganites" with doping tetravalent cations [Q. Zhang and W. Zhang, Phys. Rev. B **68**, 134449 (2003)], the ferromagnetic origin in experiments has been controversial due to the lack of direct experimental evidence. Here, we investigate the ferromagnetism in (La,Ce)MnO₃ thin films by measuring the magnetic circular dichroism in soft x-ray absorption (XMCD). Despite the presence of $Mn^{2+}$, i.e., electron doping for manganese, the $Mn^{2+}$ amount did not correlate with the Curie temperature, indicating the minor magnetic contribution of $Mn^{2+}$. More crucially XMCD measurements clarified that the ferromagnetism is not caused by the presence of $Mn^{2+}$ but by self-hole doping for manganese.

PACS number(s): 75.70.−i, 71.30.+h, 75.50.−y, 75.75.+a

## I. INTRODUCTION

Hole-doped rare-earth manganites $(R_{1-x}A_x MnO_3)$, in which the rare earth in the parent compound is partially replaced by a divalent cation such as Ba, Ca, Sr, and others, have been intensively investigated due to many interesting physical properties including colossal magnetoresistance (CMR), charge ordering (CO), and metal-insulator transition (MIT),[1] as well as their potential for device applications.[1–16] As to the hole doping in the parent compound $LaMnO_3$, a proportionate amount of $Mn^{3+}$ with the electronic configuration of $t_{2g}^3 e_g^1$ is replaced by $Mn^{4+}$ resulting in holes in the $e_g$ band. The holes permit charge transport in the $e_g$ band, inducing ferromagnetism through double exchange interaction between $Mn^{3+}$ and $Mn^{4+}$. On the other hand, recent attempts to create electron-doped manganites with the $t_{2g}^3 e_g^2$ and $t_{2g}^3 e_g^1$ electronic configuration by doping tetravalent cations, including Ce,[2–5] Sn,[6] and Te,[7] have attracted attention since the first report by Mandal and Das.[2] The realization of such electron-doped manganites is very interesting not only for fundamental physics in the context of the emergence of ferromagnetism in that electronic configuration[8] but also for the device application, e.g., the *p-n* homojunctions of both hole- and electron-doped manganites would be possible and promising for unique functional spintronic devices in future.[5] Although many investigations as for so-called electron-doped manganites with the $t_{2g}^3 e_g^2$ and $t_{2g}^3 e_g^1$ electronic configuration consistently reported the presence of MIT, ferromagnetic (FM) transition, and CMR effect,[2–7] the stoichiometry of such tetravalent cation doped manganites, i.e., the phase pure nature, has been questioned.[9–14] For example, fabricating a single phase of bulk Ce-doped $LaMnO_3$ system was found to be unfeasible using conventional solid-state reaction method due to the thermal stabilization of $CeO_2$.[9] On the contrary, fabricating a single phase of Ce-doped $LaMnO_3$ showing no impurity phases in the x-ray diffraction (XRD) data was reported to be possible only in the form of thin film using a pulsed laser deposition (PLD) technique.[3–5] Although the

presence of $Mn^{2+}$ within the (La,Ce)MnO₃ thin films has been demonstrated,[15,16] the magnetic contribution of $Mn^{2+}$, which is in fact crucial information, has not been clarified so far. Here, we present the valence specific magnetic information of (La,Ce)MnO₃ thin films by measuring the magnetic circular dichroism in soft x-ray absorption (XMCD).

## II. EXPERIMENT

$La_{0.7}Ce_{0.3}MnO_3$ epitaxial films were grown on $[(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}]$ (LSAT) (001) ($d=3.868$ Å) substrate by the PLD technique (ArF excimer, $\lambda=193$ nm) in an oxygen atmosphere. The thickness of the films fabricated was in the range of 1500–2000 Å. The oxygen pressure $P_{O_2}$ and the substrate temperature $T_s$ during depositions were 1 Pa and 700 °C, respectively.[12,13] To investigate the effect of the transition temperature variation, several films were then annealed at 600 °C in flowing argon at atmospheric pressure for 10 h. The crystallinity was characterized by a four-axis XRD measurement, showing the film epitaxy to the substrate and also the absence of Ce-rich impurities on the XRD level[12,13] (see also the inset of Fig. 1). The compositions of the films were measured using electron probe microanalyzer (EPMA) coupled with energy dispersion spectroscopy (EDS). The film composition was almost consistent with the nominal value within the resolution of EDS.[13] The magnetic properties were evaluated using a superconducting quantum interference device (SQUID) magnetometer. We measured XMCD for thus well-defined thin films at BL23SU beamline of SPring-8 to identify the origin of ferromagnetism in $La_{0.7}Ce_{0.3}MnO_3$ films. The measurements were performed at 20 and 100 K under an applied magnetic field of 3 T, which was much higher than saturating magnetic field, along the surface normal of the sample. To prevent contamination, the samples had been capped with $SrTiO_3$ (1–2 nm thickness) without atmospheric exposure, which remained on the samples during the measurements. The XMCD spectra were measured by switching the photon he-
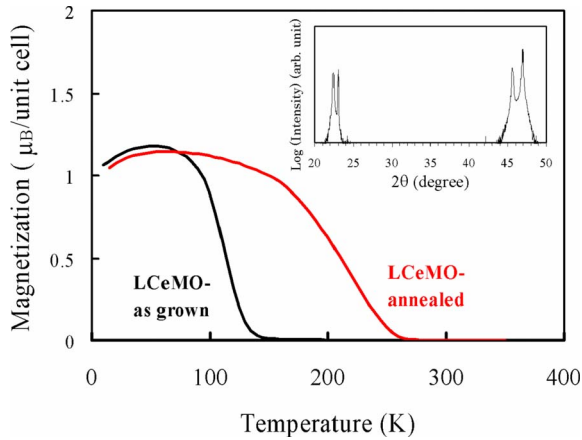
FIG. 1. (Color online) Temperature dependences of magnetization for LCeMO films. Data of both as-grown and annealed LCeMO films are shown for the comparison. The measurements were performed under field cooling of 100 Oe in the temperature range of 5–350 K. The inset displays the typical XRD pattern of LCeMO film, showing the absence of observable impurities on the XRD level. $F$ and $S$ denote the LCeMO film and the LSAT substrate, respectively.

licity being parallel ($I_+$) and antiparallel ($I_-$) to the fixed magnetization at each photon energy employing the total electron yield (TEY) mode with an energy resolution of 0.1 eV. The degree of circular polarization was better than 90%. We assume our XMCD measurements to be representative of entire LCeMO films because the probing depth of the TEY method is approximately 5 nm or deeper.

### III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of magnetization for as-grown and annealed $La_{0.7}Ce_{0.3}MnO_3$ (LCeMO) thin films fabricated by PLD. The lack of impurities on the XRD level for the as-grown film can be seen in the inset XRD data. The variation in Curie temperature $T_C$ was found to range from 140 to 265 K,[13] which is consistent with previous reports.[2–5] In fact, such observed ferromagnetism has been frequently thought to be the evidence of electron-doped manganites.[3–5] The as-grown film is insulating and the annealed film exhibits the metal-insulator transition, as reported elsewhere.[13] However, subsequent reports have raised concerns about the suggested intrinsic nature of ferromagnetism in these materials due to the possibility of self-hole doping effects[9–14] where cation vacancies and/or nanoscale impurities of doped cations are created under overoxidizing atmosphere, providing charge carriers even for thin films. This situation clearly calls for more detailed studies of Ce-doped manganites to establish or refute the premise of the intrinsic nature in magnetism. One of the important criteria for electron-doped manganites to be intrinsic is suggested to be the observation of the presence of $Mn^{2+}$ by electron doping.[15] Mitra *et al.*[15] and Chang *et al.*[16] observed the presence of $Mn^{2+}$ within the films using x-ray absorption spectroscopy (XAS). It should be noted that in the context information not only about the valence state but also the

contribution of $Mn^{2+}$ to ferromagnetism are crucial to identify the intrinsic origin of ferromagnetism observed in many electron-doped manganites. However, to the best of our knowledge investigating the magnetic contribution of each manganese valence state in Ce-doped manganites has not been reported at all so far. In Sec. IV, we present the XMCD in LCeMO epitaxial thin films since this technique provides spectral features only from those components that exhibit ferromagnetism.

Figure 2(a) shows the Mn $2p_{3/2}$ XAS ($I_+ + I_-$) spectra of as-grown ($T_C \approx 145$ K) and annealed ($T_C \approx 255$ K) films of LCeMO in comparison with the spectra of lightly hole-doped manganites ($La_{0.84}Sr_{0.16}MnO_3$) (Ref. 17) and $Ga_{0.975}Mn_{0.025}As$ as a reference of $Mn^{2+}$.[18] The spectral shape for the annealed film was nearly identical to the previous results of LCeMO films with $T_C \approx 260$ K.[15] Since it has been theoretically[19,20] and experimentally[21] found that $Mn^{2+}$ ion produces the distinct feature at around 640 eV, our spectra confirm the presence of $Mn^{2+}$ within the LCeMO films. Theoretical calculations[19,20] also demonstrated that the major distinct feature at around 640 eV due to $Mn^{2+}$ is common even varying the crystal field, allowing the comparison between the perovskite manganese and Mn-doped GaAs. It is noted that XMCD measurements are representative of bulk LCeMO films rather than only the surfaces because of the deep probing depth of the method and the use of cap layer.[18] The comparison of the spectral weight of $Mn^{2+}$ peak indicates that the as-grown films have higher $Mn^{2+}$ content than the annealed films. There should be certain relationship between the amount of $Mn^{2+}$ and the Curie temperature since within the framework of the double exchange interaction mechanism, the amount of $Mn^{2+}$, i.e., the carrier density in electron-doped systems, should increase with the Curie temperature.[22] The comparison between films in terms of the $T_C$ and the $Mn^{2+}$ content indicates that the lower the $Mn^{2+}$ content is, the higher the Curie temperature is, as shown in the inset of Fig. 2(a). Therefore our results indicate that the $Mn^{2+}$ component does not increase the Curie temperature of LCeMO films. These XASs indicate that there is no clear evidence for the contribution of $Mn^{2+}$ to the ferromagnetism in LCeMO systems.

The contribution of $Mn^{2+}$ to the ferromagnetism in LCeMO system was further studied by the MCD ($I_+ - I_-$) spectra as shown in Fig. 2(b). Although there is a significant difference in the $Mn^{2+}$ content, the shapes of the XMCD spectra of the LCeMO thin films were very similar to each other, and almost no characteristic signatures around 640 eV expected for $Mn^{2+}$ component were observed, demonstrating no significant magnetic contribution of $Mn^{2+}$ to the ferromagnetism of LCeMO systems in both as-grown and annealed films. In addition, the MCD spectra of LCeMO thin films were similar to that of $(La, Sr)MnO_3$ (LSMO) (spin-aligned $Mn^{3+}$ and $Mn^{4+}$). Further comparisons are shown in Fig. 2(c) as the difference between LCeMO and LSMO in the MCD spectra. Clearly the subtracted spectra were not consistent with the spectra of (Ga,Mn)As, which is the MCD reference of $Mn^{2+}$ induced ferromagnetism. Since above MCD measurements were performed at 100 K relatively near $T_C$ around 150 K, the MCD measurement at 20 K well below $T_C$ was performed for as-grown LCeMO film. The MCD
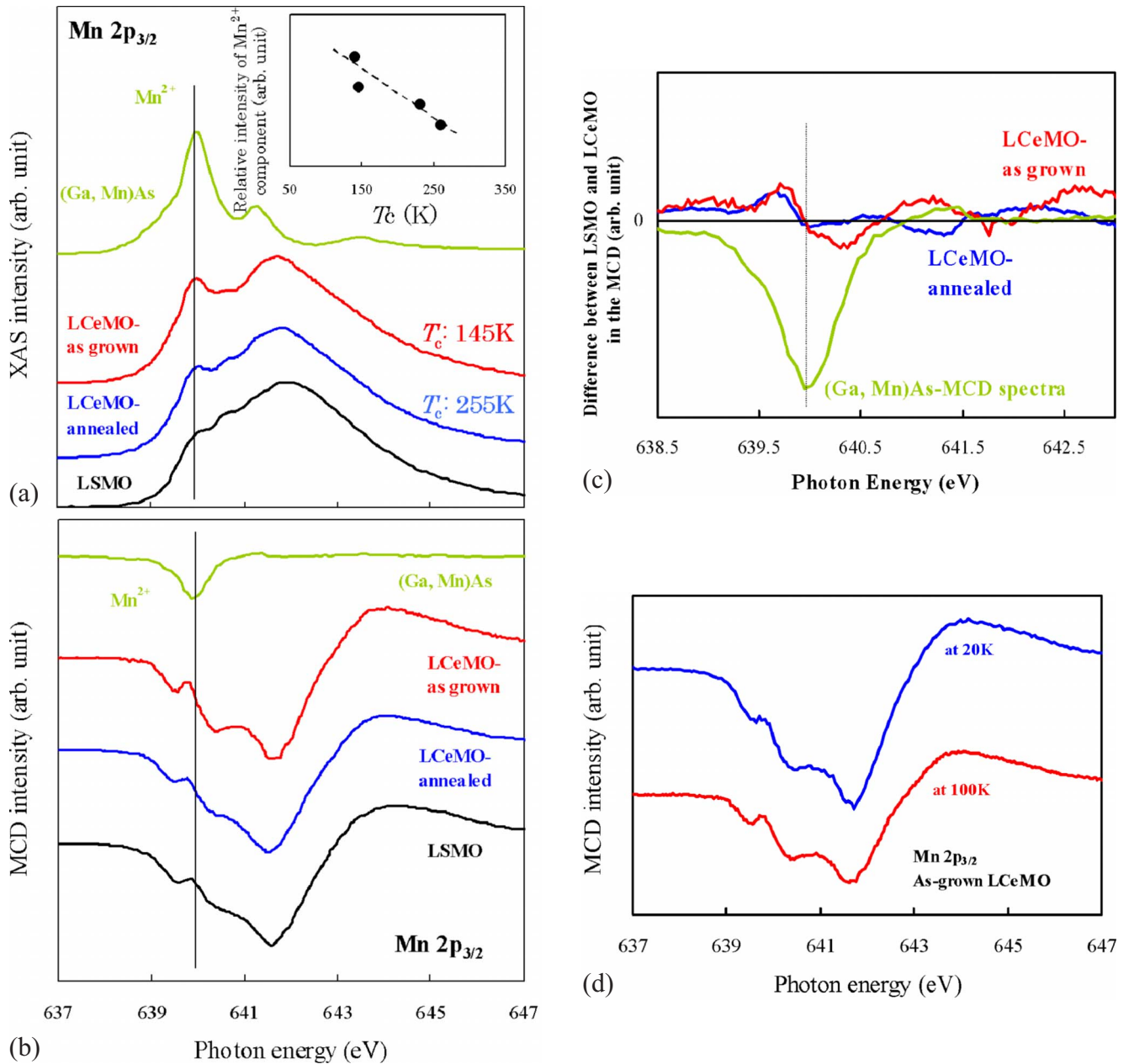
FIG. 2. (Color online) Mn $2p_{3/2}$ XAS and XMCD spectra of LCeMO films. (a) XAS spectra of LCeMO films in comparison with the spectra of (Ga,Mn)As film as the $Mn^{2+}$ reference and LSMO single crystal as the reference of hole-doped manganites. The inset shows the relationship between the relative intensity of $Mn^{2+}$ at the photon energy around 640 eV and the Curie temperature $T_C$. (b) XMCD spectra of LCeMO films, (Ga,Mn)As film, and LSMO single crystal. The photon energy around 640 eV, corresponding to the magnetic contribution of $Mn^{2+}$, is shown as the line for the comparison. The inset shows the relationship between the relative intensity of $Mn^{2+}$ at the photon energy around 640 eV and the Curie temperature $T_C$. (c) Difference between LCeMO films and LSMO in the MCD spectra. The significant discrepancy between the subtracted spectra and the spectra of (Ga,Mn)As film as the $Mn^{2+}$ reference was seen. (d) Comparison of MCD spectra measured at 20 and 100 K using as-grown LCeMO film. The spectra showed the same trend even at 20 K well below the Curie temperature $T_C$.

spectra were shown in Fig. 2(d). It can be seen that the major trend of MCD was independent of the temperature for MCD measurements. This suggests that the major origin of ferromagnetism in the LCeMO films is due to the double exchange interaction between $Mn^{3+}$ and $Mn^{4+}$ even in the presence of $Mn^{2+}$. Chang *et al.*[16] discussed experimentally and theoretically the hole-type nature of LCeMO ferromagnetism even with the proper Ce doping. In addition to their interpre-

tations based on the magnetotransport, XAS spectra, and optical reflectance data, our present XMCD data gave the direct experimental evidences to support the hole-type nature of the LCeMO ferromagnetism even in the presence of $Mn^{2+}$. We can thus conclude that the magnetic contribution of $Mn^{2+}$ to the ferromagnetism is rather negligible, considering all the observed facts including (i) the absence of correlation between the amount of $Mn^{2+}$ in the XAS spectra and the Curie

temperature, (ii) no characteristic signatures of the presence of $Mn^{2+}$ in the XMCD spectra, and (iii) the similarity of the XMCD spectra with those of hole-doped manganites. Thus this study gives the direct experimental evidence for the speculation in some previous investigations,[10–14] which the formation of Ce-rich nanoclusters, the resultant La-deficient $La_{1-\delta}MnO_3$, and/or overoxidized $LaMnO_{3+\delta}$ (Ref. [23]) are responsible for the ferromagnetism of LCeMO films. The ferromagnetism arising from the self-hole doping effects on $LaMnO_3$ is well known phenomena.[19] The experimental findings in the present XMCD measurements highlight that such self-hole doping is crucial on emerging ferromagnetism in LCeMO systems. In addition the robustness of the $Mn^{3+}$ and $Mn^{4+}$ network even in the presence of $Mn^{2+}$ is also indicated, in contrast to the theoretical calculation[8] that predicts the existence of ferromagnetism based on a double exchange interaction between $Mn^{2+}$ and $Mn^{3+}$. In order to explore such mechanism, investigating an experimentally ideal system, in which the self-hole doping, i.e., $Mn^{4+}$, is negligible as the theoretical prediction assumed, is essential to clarify the role of $Mn^{2+}$ on the magnetism.

## IV. CONCLUSION

We have investigated the ferromagnetism in LCeMO systems by measuring both XAS and XMCD. The XAS spectra clearly demonstrated the presence of $Mn^{2+}$ within the films, while the amount of $Mn^{2+}$ did not correlate to the Curie temperature. More crucially XMCD measurements showed no characteristic features due to $Mn^{2+}$, indicating the minor contribution of $Mn^{2+}$ on the ferromagnetism. These experimental findings highlight that the origin of ferromagnetism in LCeMO is a double exchange interaction between $Mn^{3+}$ and $Mn^{4+}$ due to self-hole doping effects even in the presence of $Mn^{2+}$.

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