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# Magnetoresistive properties of the $La_{0.7}Ce_{0.3}MnO_3$ bulks and epitaxial thin films

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The $La_{0.7}Ce_{0.3}MnO_{3+\delta}$ compounds and epitaxial thin films were fabricated by the solid-state reaction and the pulse laser deposition methods, respectively. The XRD patterns, the temperature dependence of resistivity, the temperature dependence of the magnetization and the temperature dependence of the heat specific of these samples were measured. We thought the sample $La_{0.7}Ce_{0.3}MnO_{3+\delta}$ was electron doped system. Both the bulk sample and the thin film sample show paramagnetic-ferromagnetic transition and metal-insulator transition phenomena. In addition, both them display a prominent giant magnetoresistance (CMR) around the Curie temperature. However, the temperature of paramagnetic-ferromagnetic transition and CMR between them was different.

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*Keywords*: $La_{0.7}Ce_{0.3}MnO_3$, Magnetoresistance, Phase transition

## 1. Introduction

Recently there has been renewed interest in studying the Magnetoresistive properties of the perovskite type of Mn oxides ($R_{1-x}A_xMnO_3$, R=rare earth). The reason is that the $R_{1-x}A_xMnO_3$ has many fascinating physical properties including colossal magnetoresistance (CMR) phenomena. The rare earth R in the manganites can be partially replaced by a divalent cation such as Ca, Ba, Sr [1,2] or a tetravalent cation including Ce, Sn and others [3,4,5]. In general, the majority carriers in divalent cation doped compounds are holes. For the hole-typed rare-earth manganites, we can understand the physics mechanism of the CMR from an interplay of a strong Hund's rule coupling and the Jahn-Teller (JT) distortion [3]. The divalent cations in these compounds bring the manganese from a $Mn^{3+}$ valence state into a mixed state of $Mn^{3+}$ and $Mn^{4+}$. Double exchange between two cations drives the insulating antiferromagnetic (AFM) or weak paramagnetic (PM) state into a ferromagnetic (FM) metallic state below the Curie temperature $T_c$. In these hole doped manganites the cation $Mn^{3+}$ is the JT ion. However, the majority carriers in the Ce-doped compounds are debated. If the Ce-doped compound is a type of electron system, the mixture valence state should be $Mn^{3+}$ and $Mn^{2+}$ [6,7]. Mitra et al., [8] claimed that the ferromagnetism in this compound might be brought about by the double exchange between $Mn^{2+}/Mn^{3+}$ ions. 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.

In addition, in both the hole doped manganites and the electron doped manganites the insulator–metal transition accompanied with PM–FM transition was observed [9]. The existence of an electron doped manganite is not merely of academic interest since it also opens up possibilities for fabricating bipolar devices using the electron and hole doped manganites where both spin and charge are utilized. Many researchers hope these two systems can be used to the p–n homojunctions [10,11].

Mitra et al. [12] argued that the difficulties is the compound of $La_{1-x}Ce_xMnO_3$ in single phase only exist in the epitaxial thin film form, deposited through the energetic pulsed laser ablation process. In the compound of bulk sample $La_{1-x}Ce_xMnO_3$ fabricated by the solid state reaction exist the impurity phases of $CeO_2$ [13], they thought that $CeO_2$ is a highly stable refractory material. Therefore, for polycrystalline samples, the effects of CMR are from hole doping rather than electron doping [14]. On the other hand Mandal and Das [15] claimed that they had acquired the bulk sample $La_{1-x}Ce_xMnO_3$ in single phase by the solid state reaction. It is interesting that Zhao et al. [16] observed the impurity phases of $CeO_2$ in both the thin film sample deposited through the pulsed laser (PLD) ablation process and the bulk sample fabricated by the solid state reaction. Therefore, whether all the doped Ce go into the La site or partially go into the La site are not clear yet.

In this paper, the bulk samples of $La_{0.7}Ce_{0.3}MnO_3$ compounds were fabricated by the solid state reaction and the film samples of $La_{0.7}Ce_{0.3}MnO_3$ compounds were grown on $SrTiO_3(100)$ substrates by a pulse laser ablation system, the temperature dependence of resistivity was measured with a magnetic field. In addition we measured the specific heat of the $La_{0.7}Ce_{0.3}MnO_3$ and $La_{0.9}MnO_3$ compounds. The phase separation, CMR ratio, peak temperature was discussed.

## 2. Sample and experimental

Samples of nominal composition $La_{0.7}Ce_{0.3}MnO_3$ were prepared by conventional solid-state reaction methods. A stoichiometric mixture of $La_2O_3$, $CeO_2$, $Mn_3O_4$ powder was heated in air at 900 °C for 24 h and then 1100 °C for 24 h respectively with intermediate grindings. The $La_2O_3$ powder was preheated at 900 °C for 12 h. The reacted powder was ground, pressed into pancakes with a diameter of 10mm and thickness of 1 mm. The samples of $La_{0.7}Ce_{0.3}MnO_3$ were sintered at 1400 °C and 1300 °C for 24 h respectively with intermediate grindings for homogenization and were named A1, B1, subsequently the as-prepared samples of A1 were annealed in oxygen gas at 900°C for 10h and 4h respectively in oxygen and were named C1,D1. The epitaxial thin film samples of $La_{0.7}Ce_{0.3}MnO_3$ were fabricated by the PLD technique. The as-grown samples were named as A2, then the sample A2 was annealed in a flowing oxygen gas at 800 °C for 10 h and subsequently was annealed in a flowing gas($Ar/O_2$:3/1) at 760 °C for 3 h and was named B2, eventually we named the sample annealed in a flowing oxygen gas at 800 °C for 10 h C2. In addition, a stoichiometric mixture of $La_2O_3$, $Mn_3O_4$ powder was heated in air at 900 °C for 24 h and then 1100 °C for 24 h respectively with intermediate grindings. The reacted powder was ground, pressed into pancakes with a diameter of 10 mm and thickness of 1 mm. The samples of $La_{0.9}MnO_3$ were sintered at 1400 °C, subsequently was annealed in oxygen gas at 900 °C for 10 h and was named C3.

The x-ray diffraction patterns were collected at room temperature in the $20° < 2\theta < 90°$ range using a standard Cu-anode powder diffractometer (Siemens D5000). The resistivity was measured by a standard four-probe method. The magnetoresistance measurement and specific-heat measurement were performed on a commercial Physical Property Measurement System (Quantum Design PPMS). The speed of temperature decreases at a ratio of 3K/min. Magnetization was measured using a Quantum Design superconducting quantum interference device (SQUID).

## 3. Results and discussions

Zhao et al. [16] argued that a $CeO_2$ impurity phase always existed in both Ce-doped LMO bulk and thin films, and the presence of $CeO_2$ introduced vacancies on the La sites. More importantly, their thermopower measurement indicated their Ce-doped LMO films to be hole doped systems. The observed CMR effect can be explained in terms of the doping of holes due to these vacancies. In addition their results of the transport and magnetic property of the Ce-doped LMO are similar to the self-doped LMO. So they concluded all of the $CeO_2$ didn't go into the La cite.

Fig. 1 The XRD patterns of the bulk samples $La_{0.9}MnO_3$ and $La_{0.7}Ce_{0.3}MnO_3$. No impurity phases present in the XRD patterns of the self-doped $La_{0.9}MnO_3$ sample and there is a few peaks of $CeO_2$ phase in the XRD pattern of the samples of $La_{0.7}Ce_{0.3}MnO_3$. The similar result was reported in the Ref. [13]. Analysis shows that these peaks can be well fitted both in angles and intensities by the peaks of $CeO_2$ with index. So we conclude the bulk samples of $La_{0.7}Ce_{0.3}MnO_3$ were not a single phase but included an impurity phase of $CeO_2$. On the other hand, whether even though a bit of the doped Ce don't go into the La site. In fact the electric property and specific heat between the composition $La_{0.7}Ce_{0.3}MnO_3$ and $La_{0.9}MnO_3$ are completely different. So we conclude that the doped Ce should partially go into the La site. Fig. 2 displays the temperature dependence of the heat specific $C_p$ measured at H=0T for the samples C1 and C3. The anomaly in $C_p$ is observed for the sample C1, which has two phase transitions around about 45K and 237K respectively. For the sample C3 two prominent phase transitions were also observed around about 45K and 114K respectively. For the sample C3 we think the phase transition around 114K correspond to the establishment of an antiferromagnetic-spin ordering ($T_N$). In addition the transition at 45K suggests the existence of magnetic frustration in very low temperature range. It was ascribed to the development of a spin canting in the antiferromagnetic structure.

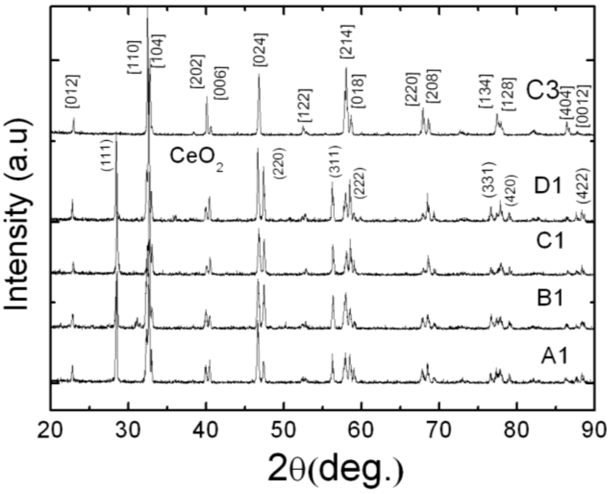

*Fig. 1. X-ray patterns of the $La_{0.9}MnO_3$ sample named C3 and the $La_{0.7}Ce_{0.3}MnO_3$ samples named as A1, B1, C1, D1, respectively.*

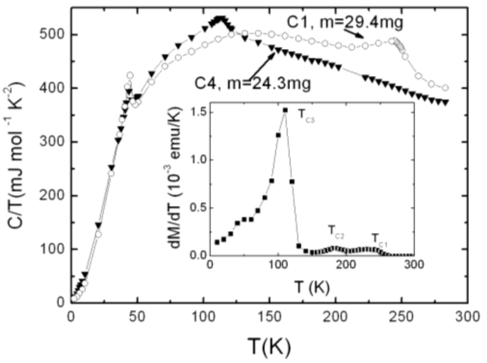

*Fig. 2. Temperature dependence of the specific heat of the sample C1, C3.*

Fig. 3 shows the temperature dependence of resistivity with different magnetic field of the samples C1and C2 respectively. In comparisons, it is clearly demonstrated that the resistivity of the bulk sample C1 was much higher than the thin film sample C2. In addition, in Fig. 3(a) the metal-insulator transition peaks were about 226K and 227K and the peak temperature was almost not changed with the magnetic field increasing. Whereas, every curve in Fig. 3(b) shows a metal-insulator transition peak and with the magnetic field increasing the peak temperature increase from 285K to 303K 319K 332K. It is clear that all the peak temperatures were higher than that of the sample C1 shown in the Fig. 3(a).

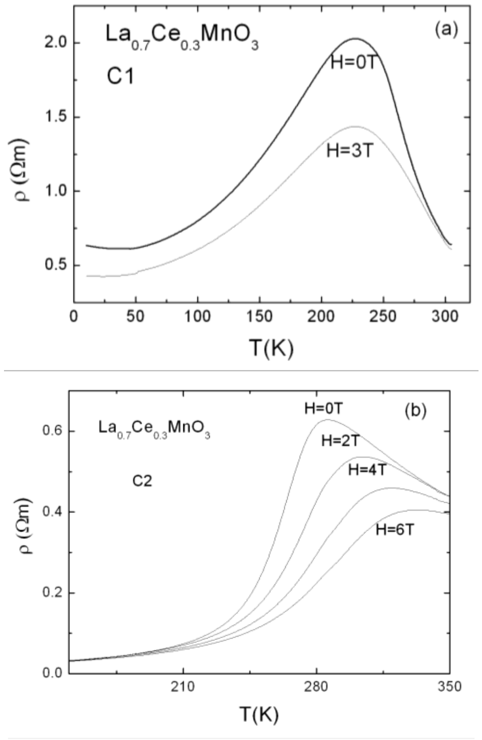

*Fig. 3. (a) Temperature dependence of the resistivity at zero-field and the 3T field for the sample C1.(b) Temperature dependence of the resistivity at different magnetic field for the sample C2.*

In Fig. 4 we have measured the M-T loop from 5 to 300K and then down to 5K at 100 Oe with zero-field cooling (ZFC). The temperature of the paramagnetism-ferromagnetism transition was about 240K and this result has been confirmed in the ρ–T curve of the sample C1.

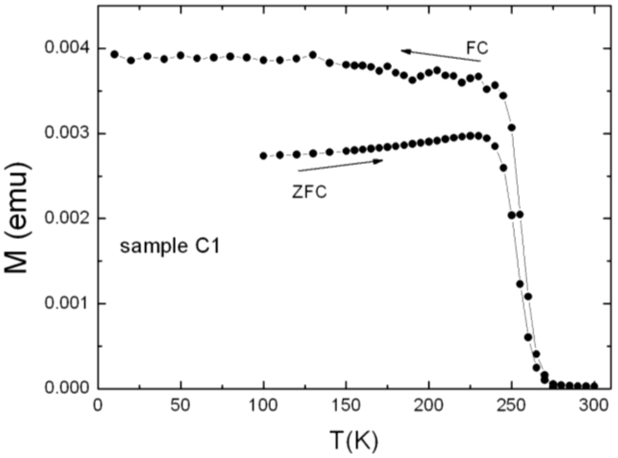

*Fig. 4. The temperature dependence of the magnetization measured at 0 Oe with zero-field cooling for sample named as C1.*

Fig. 5(a) shows the MR-T curves of the samples C1, D1. For the sample D1 annealed at 900°C for 4h their transitions were 190K.However the transition temperature of metal-insulator for sample C1 annealed for 10h was about 237K and it was in good agreement with the temperature T=240K appeared in the $C_p$-T curve of the sample C1. This proved a ferromagnetic-paramagnetic transition accompanying a transition of metal-insulator exist in the sample. In addition, the curie temperature $T_c$ increased from 190K to 240K with increasing the post-annealing time and the similar result has been reported in Ref.[9].

Fig. 5(b) shows the MR-T curves of the sample C2. We found that the CMR ratio was about 178% under the magnetic field H=6T, even the magnetic field was only 2T the CMR ratio reached 61%. However, for the bulk samples C1 the CMR ratio at the transition of metal-insulator with a magnetic field H=3T was only 42%.

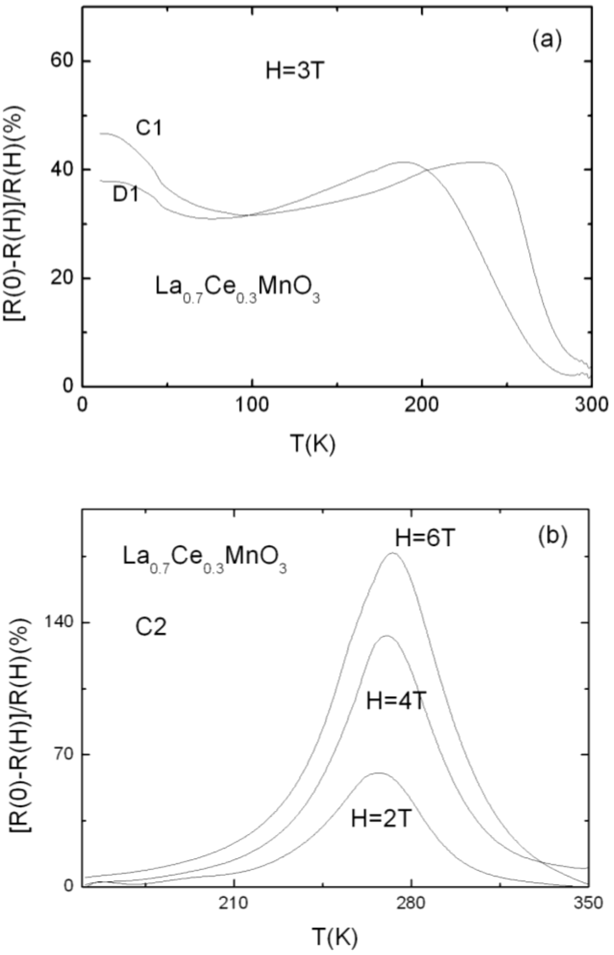

*Fig. 5. (a) Temperature dependence of the magnetoresistance ratio for samples C1, D1 at H=3T. (b) Temperature dependence of the magnetoresistance ratio at H=2T, 4T, 6T respectively for the sample C2.*

In general manganite system, manganese can have three valence states: $Mn^{2+}$, $Mn^{3+}$ and $Mn^{4+}$. It is well known that in a divalent ion doped manganite system the manganese ion exists in trivalent and tetravalent states, but if the rare-earth ion is partially replaced by some tetravalent ion the corresponding amount of manganese will be converted into a divalent state. Mandal and Das [15] investigated the LCeMO and confirmed the double-exchange mechanism could be applied to LCeMO as well as LCaMO. In addition, the compounds of LCeMO show the CMR effect and a ferromagnetic-paramagnetic transition. The ferromagnetism and metallic conductivity appear to be due to the double-exchange interaction between the mixed-valent manganese ions, and their relative amount can be controlled by altering the doping level and oxygen stoichiometry.

In the case of CMR films, strain is one of important issues on the thin film properties. Because of the strong strain effect induced by the substrate, thin films could reveal many novel phenomena which never occurred in bulk material. In this paper, the epitaxial $La_{0.7}Ce_{0.3}MnO_3$ thin films were grown on single crystal of $SrTiO_3(100)$. We found that the $T_p$ increased with increasing the magnetic field and the peak resistivity of the metal-insulator transition in the thin film was depressed significantly by an applied magnetic field. For the bulk samples, the $T_{IM}$ was almost not changed even though the peak resistivity was depressed by an applied magnetic field. More importantly is that the $T_p$ of C2 is much higher than that of C1.

Yao et al., [17] investigated the $La_{0.9}Sr_{0.1}MnO_3$ thin films. According the formula

$$2d\sin\theta=n\lambda$$

their result implied that as the thickness of films decreases, the out-of-plane lattice parameter increases, and then the epitaxial strain compression of the lattice induced by the substrate increases. The compressive strain may cause a reduction of the static JT distortion and an increase of double exchange interaction, and subsequently the IM transition was induced. For our samples it was evident that there is a pronounced difference for the magnetotransport properties between thin films and bulk materials, and these differences have been attributed to substrate-induced biaxial strain in the thin film structures due to lattice mismatch. In the CMR manganites, the strong electron lattice coupling [3] is known to play a key role demonstrated by the oxygen isotope effect [18]. One particular mechanism for this coupling is the JT effect lifting the degeneracy of the Mn $e_g$ levels in a cubic environment by a biaxial distortion [3]. According to this theory, the effect of a biaxial distortion induced by substrate strain is expected to be different from the effect of bulk (compressive) strain driving the lattice towards cubic symmetry and to strongly affect the subtle interplay between spin, charge, structural, and orbital degrees of freedom.

Lu et al.,[19] investigated the effect of strain and tetragonal lattice distortions in hole doped perovskite manganite thin films $La_{2/3}Ca_{1/3}MnO_3/SrTiO_3$. They implied that the effect of a biaxial distortion induced by substrate strain is expected to be different from the effect of bulk. At last the parameter c of the thin film is higher than the bulk sample but the $T_p$ of thin film is lower than the bulk sample.

For our samples LCeMO, the $T_p$ of thin film is much higher than that of bulk sample. In the Ref. [20] the author claimed that the single phase electron-doped LCeMO manganite thin films can be very sensitive to the substrate. It appears that in-plane tensile strain tends to deteriorate $T_p$, while the compressive strain does the opposite. This is indicative of a strong coupling between the electron and the lattice degree of freedom existent in this system. The relaxation of the in-plane tensile strain (reflected by increasing c parameter) evidently enhances the double-exchange interaction and then $T_p$. This theory is accordant with our experimental results.

## 4. Conclusions

The bulk and thin film samples of $La_{0.7}Ce_{0.3}MnO_3$ and the bulk samples of $La_{0.9}MnO_3$ have been successfully fabricated. After the electric transport and magnetic properties of the samples were measured, we concluded that the compound $La_{0.7}Ce_{0.3}MnO_3$ should be a hole doped manganite. In addition, the bulk samples and the thin film samples show different CMR effect. We think that the strain effect induced by the substrate in the thin film sample lead to the difference.

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