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## Study of transport behavior for Fe-doping $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ perovskite manganese\*

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**Abstract:** Systematic studies of the transport properties of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  ( $x=0-0.3$ ) systems showed that with increasing Fe-doping content  $x$  the resistance increases and the insulator-metal transition temperature moves to lower temperature. For small doping content, the transport property satisfies metal transport behavior below the transition temperature, and above the transition temperature it satisfies the small polaron model. This behavior can be explained by  $\text{Fe}^{3+}$  doping, which easily forms  $\text{Fe}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$  channel, suppressing the double exchange  $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$  channel and enhancing the spin scattering of Mn ions induced by antiferromagnetic clusters of Fe ions.

**Key words:**  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ , Fe-doping, Crystal structure, Transport properties

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### INTRODUCTION

$\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  (Ln=rare earth, A=Ca, Ba, Sr, etc.) compounds have been popular subjects of intense research in recent years due to the existence of colossal magnetoresistance (CMR) (Chahara *et al.*, 1993; Von Helmolt *et al.*, 1993; Jin *et al.*, 1994). At room temperature, the perovskite compound  $\text{LnMnO}_3$  is antiferromagnetic insulator in which Mn is trivalent. The partial substitution of trivalent

Ln ions with divalent ions, such as Ca, Ba, Sr and Pb, etc., yields a new compound with strong ferromagnetism and high metallic conductivity. The transport property in these compounds can be partly explained in terms of the double exchange (DE) mechanism, which considers the magnetic coupling between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  (Zener, 1951). The DE model results from the motion of an electron across two partially filled  $d$  shells with strong on-site Hund's coupling. However, detailed researches showed that the DE model alone is insufficient in accounting for the various phenomena found in these compounds. Instead, a strong electron-phonon coupling due to the Jahn-Teller effect of  $\text{Mn}^{3+}$  ion was proposed to gain further understanding of these manganites (Hwang *et al.*, 1995; Millis *et al.*, 1995; Zhou and Goodenough, 1998).

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Element doping is an important method for clarifying the physical mechanism of CMR, especially on the Mn site, which is the heart of DE (Blasco *et al.*, 1997; Garathri *et al.*, 1997; Rubinstein *et al.*, 1997; Feng and Hwang, 1999; Ghosh *et al.*, 1999; Lee *et al.*, 1999; Sun *et al.*, 1999; Wang *et al.*, 1999). Many investigations on Fe-doped and doping-free (Jaime *et al.*, 1996; Ahn *et al.*, 1997; Cai *et al.*, 1997; Lanzara *et al.*, 1998; Ogale *et al.*, 1998; Ghosh *et al.*, 1999; Simopoulos *et al.*, 1999; Triki *et al.*, 2003) CMR materials have been conducted. It was shown that there exists a ferromagnetic transition. Firstly, Fe ion is one of the nearest neighbors of Mn ion in the periodic system and its radius is nearly that of Mn ion. The crystal lattice will not distort obviously because of Fe ion doping on the Mn site, and so will have little influence on the electron-phonon coupling. Secondly, as the 3rd subgroup of elements in the periodic system, Fe and Mn both have similar energy level structure and multiple valences, thus they would be able to substitute  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  and further influence the double exchange; for which reasons, Fe ion doping at Mn site shows some interesting physical properties and can provide a useful clue for understanding the physical mechanism in this system. Ghosh *et al.* (1999) studied the doping effect of various transition elements for  $\text{La}_{0.6}\text{Ca}_{0.3}\text{MnO}_3$  compound. Ahn *et al.* (1997) observed that the Fe substitution on Mn encourages an antiferromagnetic insulator behavior which opposes the DE effects. Ogale *et al.* (1998) observed the occurrence of a localization-delocalization transition in the compound of the  $\text{La}_{0.75}\text{Ca}_{0.25}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  system at a critical concentration. Cai *et al.* (1997) proposed to explain their experimental results on  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$  doped with  $\text{Fe}^{3+}$  ions using the formation of ferromagnetic and antiferromagnetic clusters and the competition between these clusters, which do not participate in the double-exchange process. Simopoulos *et al.* (1999) used Mössbauer spectroscopy to study the effect of Fe doping on the compound  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  and observed an antiferromagnetic coupling of Fe ion with the neighbor Mn ion. They found that the local strains were induced by the size mismatch between the dopant and

the host lattice, which dominate the magneto transport properties of perovskite manganese. In this paper, we present the results of related experimental studies on  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  ( $x=0-0.3$ ) system by transport, magnetic properties, and X-ray diffraction measurements. The transport characteristic of the samples can be explained by  $\text{Fe}^{3+}$  doping, which easily forms  $\text{Fe}^{3+}\text{-O}^{2-}\text{-Mn}^{4+}$  channel, suppressing the double exchange  $\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{4+}$  channel and enhancing the spin electron scattering by the spins of Mn ions induced by antiferromagnetic clusters of Fe ion.

## EXPERIMENT

The series of experimental samples  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  ( $x=0.00, 0.02, 0.04, 0.06, 0.08, 0.10, 0.30$ ) were fabricated by conventional solid state reaction methods. Stoichiometric proportions of  $\text{La}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}_2$  with purities not less than 99.99% were mixed, ground and heated in air at 1000 °C for 12 hours. After regrinding, the mixture was pressed into pellets and sintered in air at 1200 °C for 24 hours and 1300 °C for 24 hours with intermediate grindings. The diffractometer was operated at 100 mA and 40 kV with anode of Cu. A graphite monochromator was used to select the  $\text{Cu-K}_\alpha$  radiation. Magnetic measurements were carried out from 5 K to 300 K. The resistance measurements were performed by standard four-probe method at the physical properties measurement systems (Q/D Model PPMS-9) with temperature range of 1.9 K to 300 K. All experimental results were characterized by good repeatability.

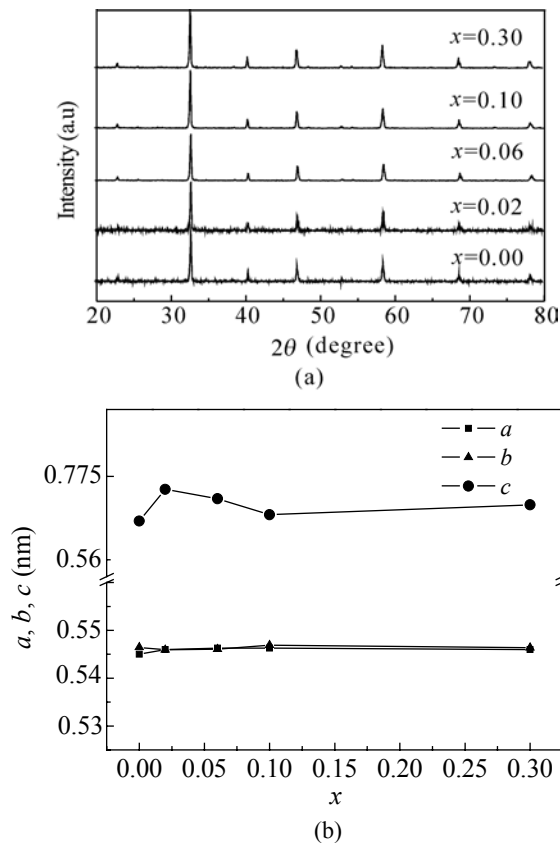
## RESULTS AND DISCUSSIONS

Fig.1 giving the typical results of XRD for experimental samples shows that all samples had good perovskite single-phase structure of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  in the whole doping range, indicating that Fe ion could reach into lattice well and substitute Mn effectively. This also means that the

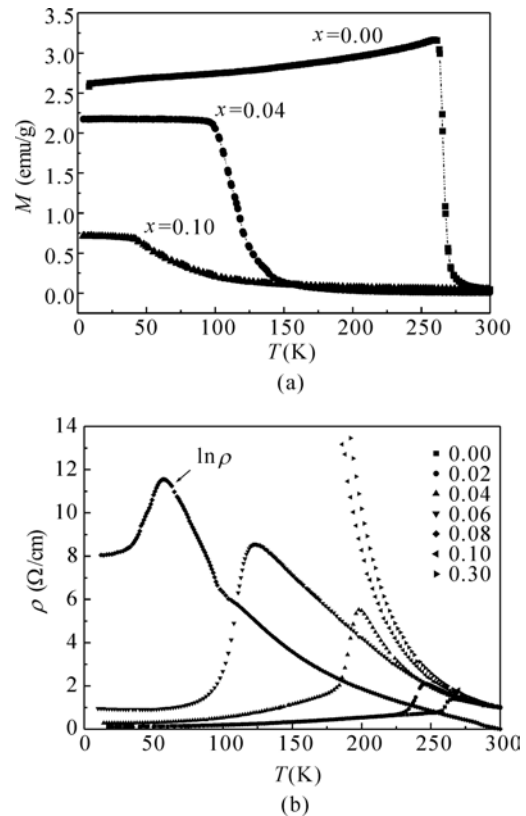
present samples had a good quality and reliability. Fig.1b shows the crystal cell parameter  $a$ ,  $b$  and  $c$  axes variation with the Fe doping amount  $x$ . From Fig.1b we can see that the cell parameters all had no obvious variation in range of doping content. The temperature dependence of the magnetization  $M$  at  $H=0.01$  T and the resistivity  $\rho$  for the  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  series are shown in Fig.2a and Fig.2b respectively. The undoped sample and samples with small doping content ( $x=0.02-0.08$ ) show a typical metal-insulator (M-I) transitional characteristic, accompanied simultaneously by a paramagnetic (PM) to FM transition, systematic lowering of the transition temperature  $T_{\text{IM}}$  and rapid increase of resistance peak value with increase of doping content  $x$ . For large doping content ( $x \geq 0.1$ ), the samples all showed semiconductor behavior in the range of selected temperature. In order to see direc-

tly the M-I transitional characteristics, Fig.3 gives the M-I transitional temperature  $T_{\text{IM}}$  variation with the doping amount for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ .

In the double-exchange model for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ,  $\text{Mn}^{4+}$  has three local electrons ( $3t_{2g}$ ), and  $\text{Mn}^{3+}$  has an itinerant electron ( $e_g$ ) and a  $3t_{2g}$  electron inducing local spin state  $S=3/2$ . They have the same spin direction because of their strong Hund's coupling with the itinerant electron, and the adjacent spins generate double-exchange action through  $\text{O}^{2-}$ . The itinerant electron hops between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ , with hopping probability proportional to  $\cos(\theta/2)$ , where  $\theta$  is the angle between the local spin direction of adjacent Mn ions. The double-exchange intensity of  $\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{4+}$  is related to its bond length and angle. The radius of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  are critical factors influencing the metal conductivity. In order to understand clearly the phy-

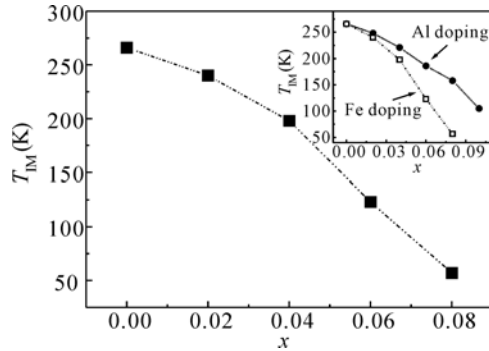


**Fig. 1** Structure of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  systems (a) Results of X-ray diffraction with different Fe ions doping content  $x$ ; (b) Lattice parameters as a function of Fe ions doping content  $x$



**Fig. 2** Magnetic and transport properties of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  samples

(a) Temperature vs magnetization for different Fe doping content  $x$ ; (b) Temperature vs resistivity for different Fe doping content  $x$



**Fig.3** Metal-insular transition temperature  $T_{IM}$  as a function of Fe doping content  $x$  (Inset is  $T_{IM}$  variation with Al and Fe doing content  $x$ )

sical mechanism of Fe dopings' influence on the transport properties, we fitted the curve of resistance variation with temperature at  $T < T_{IM}$  using metal transport model

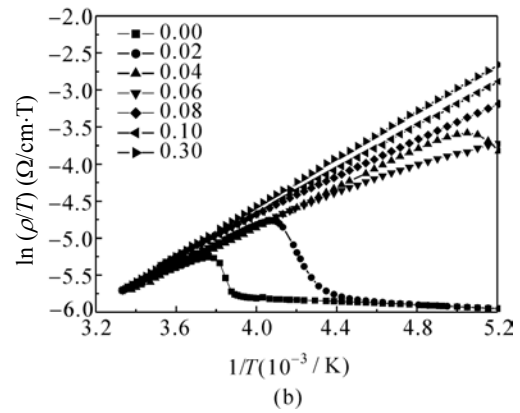
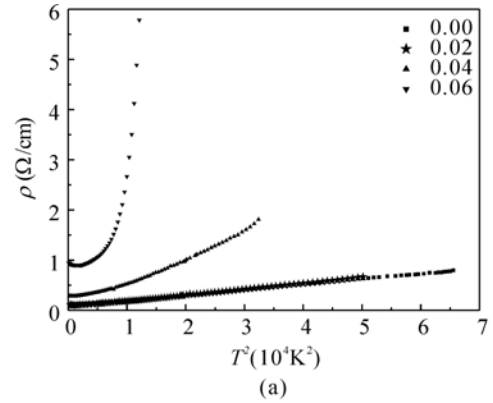
$$\rho = \rho_0 + AT^2$$

Here,  $A$  is a constant. Fig.4a shows the fitting curves of non Fe-doping and the doping amount  $x=0.02, 0.04,$  and  $0.06$  when  $T < T_{IM}$ . Fig.4a shows that the resistance variation with temperature satisfies the law of  $\rho \propto T^2$  in  $T < T_{IM}$  for samples without doping and with small doping content ( $x=0.02, 0.04$ ). But, for  $x > 0.06$ , it deviated badly from the  $T^2$  law. In the region of  $T > T_{IM}$ , the variation of resistance with temperature can be described very well by the small polaron model for Fe doping. Fig.4b presents the results of resistance variation with temperature according to the small polaron model. Fig.4b shows that in the range of Fe doping content  $x=0-0.30$ , the resistance variation with temperature can satisfy very well the small polaron model

$$\rho = \rho_0 T \exp(E_p / k_B T).$$

Here,  $\rho_0$  is constant,  $E_p$  is activating energy and  $k_B$  is Boltzmann constant.

In the perovskite oxides, the  $3d$  level of the Mn and Fe ions, in the order of increasing energy, are known to split into  $t_{2g\uparrow}, e_{g\uparrow}, t_{2g\downarrow},$  and  $e_{g\downarrow}$  due to the crystal field and the strong Hund's coupling. The electronic configurations are  $t_{2g\uparrow}^3 e_{g\uparrow}^2$  for  $Fe^{3+}$ ,  $t_{2g\uparrow}^3 e_{g\uparrow}^1$  for  $Fe^{4+}$  and  $Mn^{3+}$ , and  $t_{2g\uparrow}^3$  for  $Mn^{4+}$ , respective-



**Fig.4** The result of fitting resistance vs temperature (a) Temperature square dependence of resistivity at low temperature region of  $T < T_{IM}$ ; (b)  $\ln\rho/T$  vs  $1/T$ , at region of  $T > T_{IM}$

ly. For these ions, the  $t_{2g\uparrow}$  bands are fully occupied, the  $t_{2g\downarrow}$  and  $e_{g\downarrow}$  bands are empty, and the  $e_{g\uparrow}$  bands, which can accommodate a maximum of two electrons per ion, play a crucial role. In a mixed system of Fe and Mn, the widths and energies of their  $e_{g\uparrow}$  bands control the electron distribution of the Fe and Mn ions. Ahn *et al.*(1997) studied the effect of Fe-doping on the transport property of  $La_{1-x}Ca_xMn_{1-y}Fe_yO_3$  ( $x=0.37$  and  $0.53, y < 0.2$ ), and indicated that the Fermi surface of the system lies at  $0.14-0.29$  eV above the top of the Fe  $e_{g\uparrow}$  band. Electron hopping from Mn to Fe is energetically impossible even at room temperature. Consequently, electron hopping between  $Mn^{3+}$  and  $Mn^{4+}$  can occur only in the electronically active Mn  $e_{g\uparrow}$  band. Since  $Fe^{3+}$  replaces  $Mn^{3+}$ , doping with Fe causes a depletion of the  $Mn^{3+}/Mn^{4+}$  ratio, the population of the hopping electrons, and the number of available

hopping sites. Thus, double exchange is suppressed, resulting in the reduction of ferromagnetism and metallic conduction. However, the above experimental results showed that the decrease of the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio alone cannot sufficiently account for the resulting transport properties. Our studies on the effects of Al doping  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  on transport properties under the same condition as the Fe doping (Ref: Chinese Functional Material. 2004, 2. to be published) revealed that the range of Fe-doping ( $x$  from 0 to 0.08) was narrower than that of Al ( $x$  from 0 to 0.1), and that the M-I transition temperature  $T_{\text{IM}}$  drop with doping content  $x$  was very much steeper than that of Al doping (See inset in Fig.3), i.e., Fe-doping effect of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  on the transport properties was more serious than that of Al-doping. However, the effects of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  substitute  $\text{Mn}^{3+}$  on suppressing double exchange action were the same, so the emergent physical picture appears to converge on an association between carrier motion and local polarization effects of the magnetic lattice beyond the double exchange. Simopoulos *et al.* (1999) investigated the effect of Fe-doping on transport property of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  by Mössbauer spectroscopy and indicated that Fe couples antiferromagnetically with its Mn neighbors. Therefore, the large rise in resistivity due to Fe doping should be associated with the formation of local antiferromagnetic (AF) clusters of Fe ions. At low concentrations ( $x < 0.02$ ), where atoms of Fe are few, and the formation of Fe clusters is improbable, the rise of resistivity is due solely to reduction in quantity of  $\text{Mn}^{3+}$ . This decreases the channel of the charge carriers. In this range of concentration, the resistivity is not expected to increase significantly with Fe doping. In the regime of cluster formation ( $x > 0.04$ ), the Mn ion spins are somehow depolarized by the antiferromagnetic clusters of Fe. Therefore, the conduction, in this range of concentration, decreases mainly due to the AF clusters induced spin scattering of the Mn ions.

## CONCLUSION

In summary, the structural and transport pro-

perties were systematically studied for Fe doping  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  systems. The result showed that the crystal structure had no obvious variation with increasing Fe doping content. The resistances increased rapidly and the metal-insulator temperature  $T_{\text{IM}}$  moved to lower temperature region. At small Fe-doping content, the resistance satisfied metal transport properties in the regime  $T < T_{\text{IM}}$ ; and it satisfied the small polaron model in the region of  $T > T_{\text{IM}}$ . The characteristics of the transport behavior for Fe ion substitution can be explained by  $\text{Fe}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$  links suppressing the double exchange channel  $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$  and the Mn ions's spin scattering, induced by the AF clusters of Fe ions.

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