World Journal of Condensed Matter Physics, **2011, 1, 153-156**
doi:10.4236/wjcmp.2011.14022 Published Online November 2011 (http://www.SciRP.org/journal/wjcmp)

Transport Properties of the Layer Manganite $La_{1.5}Ca_{1.5}Mn_{2-x}Fe_xO_7$

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Received June 20th, 2011; revised August 9th, 2011; accepted August 20th, 2011.

ABSTRACT

Layered perovskite manganite ceramics with a nominal chemistry $La_{1.5}Ca_{1.5}Mn_{2-x}Fe_xO_7$ (x = 0.0, 0.05, 0.1, 0.3, 0.5) *were prepared using sol-gel method. The manganese ions are highly mixed states of* Mn^{3+} *and* Mn^{4+}. *It is found that the* Mn^{3+}/Mn^{4+} *ratio decreases with the Fe doping content increasing. The conductivity and magnetoresistance* (*MR*) *were studied. The sample of* x = 0.05 *shows metal insulator transition* (*MIT*) *at* 135 *K. The MIT peak temperature* (T_p) *shifts towards higher temperature with increasing applied magnetic field. All the samples can be well fitted to the variable-range hopping* (*VRH*) *model. The maximum value of MR* (%) $[\rho(0) - \rho(H)]/\rho(0) \times 100$ *for* x = 0.05 *is* 34% (105 *K*, 7 *kOe*).

***Keywords*:** *Layered Perovskite*, *M-I Transition*, *GMR*

1. Introduction

The hole-doped ABO_3-type perovskite manganites (Ln, M)MnO_3 (Ln is lanthanide ion, and M is divalent cation) have attracted much attention owing to the colossal magnetoresistance (CMR) exhibited by them [e.g., 1-3]. Substitution of M^{2+} ions for Ln^{3+} leads to ferromagnetism and also metallic conduction. This has been explained as arising due to double exchange (DE) interaction and electron hopping between Mn^{3+} and Mn^{4+} cations (Mn^{4+} arising due to replacement of Ln^{3+} by M^{2+}) via Mn-O-Mn path [4,5]. In the three dimensional perovskites, the Mn^{3+}/Mn^{4+} ratio and the microstructure of the Mn–O network are two key parameters controlling the DE interaction, and magnetic properties. $La_3Mn_2O_7$ like bi-layer manganites also exhibit magneto-resistive behaviour [6] but these are much less studied. In the present paper, the result of temperature and field dependent resistivity measurements on substituting Fe ion for Mn site in calcium substituted bi-layer system $La_{1.5}Ca_{1.5}Mn_2O_7$.

2. Experimental Details

Polycrystalline samples of $La_{1.5}Ca_{1.5}Mn_{2-x}Fe_xO_7$ (x = 0.0, 0.05, 0.1, 0.3, 0.5) were prepared by sol-gel method. The method consisted of adequate citric acid and stoichiometric amounts of the starting materials $La(NO_3)_2{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}6H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$ and $Fe(NO_3)_3{\cdot}6H_2O$, which were dissolved in distilled water, and the pH was adjusted to about 3 to 4 with ammonia solution. First it was heated at 80˚C until a forming the powder. The powder was pressed into thin plates and calcined in air at 1200˚C for 24 h and 1350˚C for 24 h with intermediate grindings between each heating step. To characterize the samples, X-ray diffraction (XRD) measurements were carried [7]. The electrical resistivity was measured at zero field and 7 kOe field by a standard four-point technique. The magnetoresistance (MR) ratio is defined here as $\Delta\rho/\rho(0) = [\rho(0) - \rho(H)]/\rho(0)$, where $\rho(0)$ and $\rho(H)$ denote resistivity at zero field and an applied field, respectively.

3. Results and Discussion

Figure 1 shows resistivity versus temperature plots for the $La_{1.5}Ca_{1.5}Mn_{2-x}Fe_xO_7$ (x = 0.0, 0.05, 0.1, 0.3 and 0.5) samples at zero field. It is clear from the plots that resistivity enhances with increasing x. It is due to the Mn^{3+}/Mn^{4+} ratio reducing with increasing x. This results in the e_g electrons decreasing, which in turn weakens double-exchange mechanism.

For the samples of x = 0.0 and 0.05, resistivity first rises with increase in temperature, and then exhibits peak around the metal-insulator transition (MIT) temperature denoted by T_p, with the peak temperature T_p about 150 K and 140 K respectively.

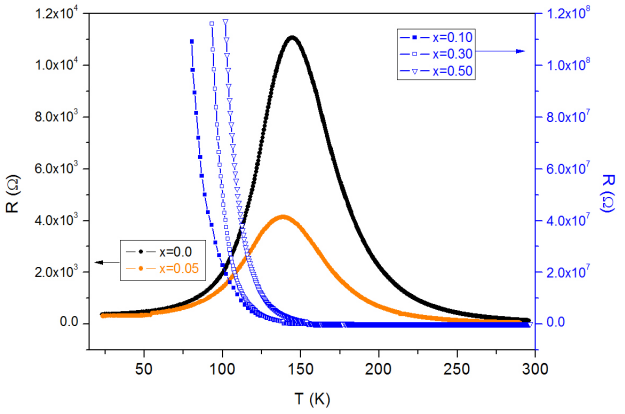

Figure 1. Temperature dependence of resistance for the $La_{1.5}Ca_{1.5}Mn_{2-x}Fe_xO_7$ (x = 0.0, 0.05, 0.10, 0.30, 0.50).

For $T > T_p$, resistivity decreases with increase of temperature. Concentrating on the behavior of temperature dependent resistivity curve, it is noted that $d\rho/dT < 0$ for $T > T_p$, which is a characteristic of semiconducting behavior. However for $T < T_p$, the sample showed metallic character with $d\rho/dT > 0$. For higher values of x, the samples show semiconducting behavior and no metal-insulator transition is observed. Usually, the conduction behavior can be described by the a band-gap model, variable range hopping (VRH) mechanism [8-11], or can be described by the adiabatic nearest neighbor hopping model of small polaron conduction (NSPH) [12-14]. An Arrhenius law $\rho = \rho_0 \exp(E/kT)$ is used to account for thermal activation process due to a band gap or a mobility edge. In Mott's VRH model, the resistivity is expressed in the form of $\rho = \rho_0 \exp(T_0/T)^{1/4}$, where ρ_0 is the pre-factor and T_0 represents the characteristic temperature. In the nearest-neighbor hopping model of small polaron conduction (NSPH), the resistivity of the sample is given by $\rho = \rho_0 T \exp(E/K_B T)$, where E is the characteristic energy of small polaron hopping. To understand the nature of electronic conduction in the samples, we tried to fit the resistivity to all the three samples. The increasing size disorder with increasing x produces random spin and Coulombic potential fluctuations. So, the carriers find some potential difference beyond the Mn–O distances to hop at farther distances and hence conduct through the Mott's type of Variable Range Hopping. The T_0 occurring in the VRH relation can be related to the carrier localization length by the expression $kT_0 = 24/L^3\pi N(E)$, where k is the Boltzmann constant, L the carrier localization length and N(E) is the density of states [8,15]. The values of the localization length should be comparable to Mn-O distances for the VRH type of conduction, here $L = 10^{-10}$ m [16].

Figure 2 displays the fitting results using the three different functions, a band-gap model, nearest-neighbor hopping model of small polaron conduction (NSPH) and variable-range hopping (VRH) respectively. It can be seen that the fitting results of VRH are better than the other two models *i.e.* band-gap model and NSPH. This leads us to conclude that the VRH process dominates the conduction mechanism at T > 170 K in these layered manganites. We show the fitting results of VRH model in **Figure 3**. The fitting parameters T_0, N(E) and chi-square are given in **Table 1**.

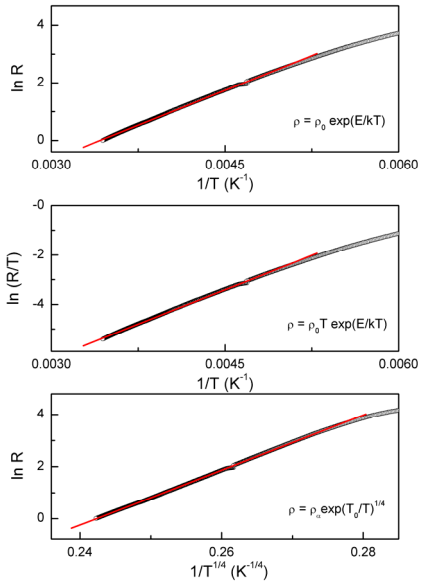

Figure 2. Fitting of three different functions in R-T data for $La_{1.5}Ca_{1.5}Mn_{1.95}Fe_{0.05}O_7$.

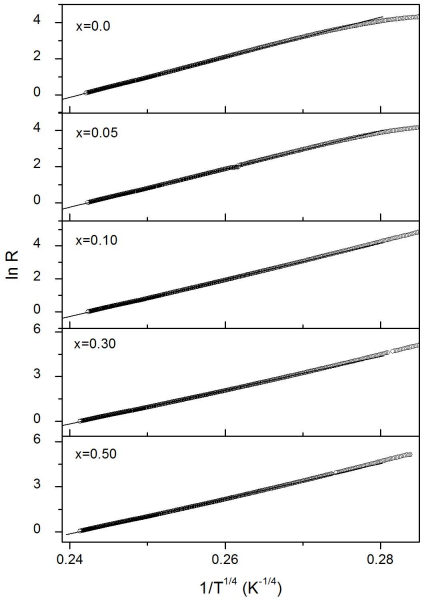

Figure 3. ln(R) shown as a function of $1/T^{1/4}$ for $La_{1.5}Ca_{1.5}Mn_{2-x}Fe_xO_7$ (x = 0, 0.05, 0.1, 0.3, 0.5). Solid line show Mott's VRH model fitting.

From **Table 1** one finds that the value of N(E) decreases with the *x* increasing, which indicates that the capacity to conduct reduces with the Fe ion doping. N(E) is also two orders of magnitude higher in these manganites than those of usual oxide semiconductors. Such a higher value of N(E) also estimated by other researchers [8,17], is due to the higher conductivity of these oxides than those of the usual transition-metal-oxide semiconductors [18] and this large value of N(E) is also an indication of adiabatic hopping behavior of the carriers in these manganites as pointed out by Jung [17]. For the NSPH model, the value of E_P augments with the *x* increasing. It is based on that the amount of e_g electrons reduces with the Fe ion increasing. This results in the resistivity increasing and accordingly the hopping energy increases.

From **Figure 4** one finds that for the samples of x = 0.05, the resistivity decreases but T_p shifts to higher temperature with the application of magnetic field. This is due to charge carrier delocalization is induced by the magnetic field, which suppresses the resistivity. The application of the magnetic field, also causes the local ordering of magnetic spin and due to this ordering, the ferromagnetic metallic (FMM) state suppresses the paramagnetic insulating (PMI) state. So, the peak temperature (T_p) shifts to the high temperature regime with application of magnetic field.

Table 1. Values of T_0, density of states at Fermi energies and chi-square obtained from fitted of resistivity—temperature data of the samples in the series $La_{1.5}Ca_{1.5}Mn_{2-x}Fe_xO_7$.

x	T_0 (10^6 K)	$N(E_F)$ ($eV^{-1}\cdot cm^{-3}$)	χ^2
0.0	146.4	1.3871×10^{19}	99.986
0.05	124.2	1.6356×10^{19}	99.991
0.10	151.3	1.3416×10^{19}	99.985
0.30	161.6	1.2566×10^{19}	99.973
0.50	187.0	1.0863×10^{19}	99.968

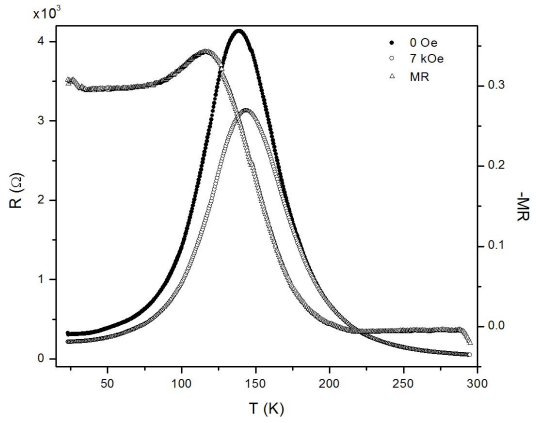

Figure 4. The temperature dependence resistance and MR for $La_{1.5}Ca_{1.5}Mn_{1.95}Fe_{0.05}O_7$.

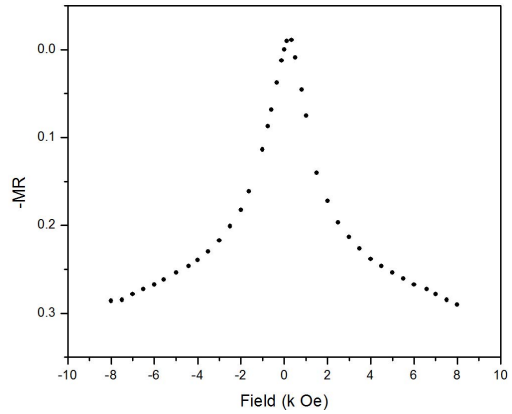

Figure 5. The field dependence of MR for $La_{1.5}Ca_{1.5}Mn_{1.95}Fe_{0.05}O_7$ at 20 K.

We discuss below, about magnetoresistance (MR) of the samples of our present investigation. **Figure 4** indicates the thermal variation of MR ($\rho/\rho(0)$ (%) = $\rho(0) - \rho(H)/\rho(0) \times 100$, where $\rho(H)$ = resistance in a field of 7 kOe, $\rho(0)$ = resistance at zero field) of two samples. The maximum value of MR for x = 0.05 is 34% (105 K, 7 kOe). The pronounced MR ratio for x = 0.0 and 0.05 is stable in a wide temperature region below T_p. This low temperature MR effect is popular in many n = 2 layered perovskites [6]. **Figure 5** show the field variation of MR at 20 K for x = 0.05. As for the heavily doped samples with x = 0.1, 0.3 and 0.5, they present the other kind of ρ-T curves, which are quite different from those of the lightly doped samples.

4. Conclusions

Single-phase rare-earth manganites $La_{1.5}Ca_{1.5}Mn_{2-x}Fe_xO_7$ (x = 0.0, 0.05, 0.1, 0.3 and 0.5) were prepared to study the effect of doping content on the metal-insulator transition and electrical resistivity. It is found that the ratio of Mn^{3+}/Mn^{4+} reduces with the x increasing. The metal-insulator transition is observed with the lower values of x (x = 0.0, 0.05) and the T_p shifts to higher temperature with the application of magnetic field. The conductivity also depends on the Fe concentration and shows obvious decrease with the increase of Fe content in the samples. It is due to the e_g electrons decrease which in turn weakens double-exchange mechanism. All the ρ-T curves in T > 170K are fitted quite well in the VRH mechanism. The density of states N(E) is two orders of magnitude higher than those of many transition-metal-oxide semiconductors. The value of N(E) decreases with the x increase, which indicates that the capacity to conduct reduces with the Fe ion doping.

5. Acknowledgements

MPS thanks to Council of Scientific and Industrial Re-

search (CSIR), New Delhi, for the award of fellowship.

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