Asian Journal of Chemistry Vol. 21, No. 10 (2009), S086-090

Transport and Magnetic Properties of $La_{0.85}Ca_{0.15}Mn_{1-x}Al_xO_3$ Manganites

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We present here the effect of Al doping on structural, electrical and magnetic properties in $La_{0.85}Ca_{0.15}Mn_{1-x}Al_xO_3$ (x = 0.0 and 0.1) manganites. Al has been doped on its Mn site because it has no magnetic moment and its atomic radius is smaller than that of Mn. X-ray diffraction (XRD) pattern confirms the single phase character of both the samples with orthorhombic symmetry and space group *Pnma*. No structural change has been observed due to Al doping up to x = 0.1 except the decrease in lattice parameters. Dc conductivity data have been analyzed using different conduction mechanisms. Theoretical models fitting show that the high temperature ($T>\Theta_D/2$, Θ_D being the Debye temperature) dc conductivity (σ_{dc}) of these samples is due to adiabatic large polaron-hopping conduction. The value of polaron coupling constant, which is a measure of electron-phonon (e-ph) interaction, suggests the presence of strong e-ph interaction in x = 0.1 sample. It is observed that ferromagnetism (FM) decreases with Al doping. Minimum value of magnetization is obtained for x = 0.1 sample.

Key Words: Electrical Properties, Magnetic materials

INTRODUCTION

Observation of colossal magnetoresistance (CMR) in the perovskite manganite system of the form $R_{1-x}A_xMnO_3$ (R= rare earth, A= Ca, Sr, Ba, Pb, etc) has spurred considerable interest in the study of these compounds among the scientific community.[1] These materials show a close interplay among the spin, charge and orbital ordering.[2] Nature of ferromagnetic insulating (FMI) state in lightly doped $R_{1-x}A_xMnO_3$ (x = 0.1 – 0.2) rare earth manganite perovskite system continues to pose a complex problem.[3] Particularly, FMI $Ln_{0.85}Ca_{0.15}MnO_3$ perovskite has been studied extensively because of its complex Mn^{3+}-O-Mn^{4+} network.[3] Despite the exhaustive study of the effect of the rare earth replacement in these manganites, very little is known about FMI state.[4] The present article puts forward the structural, dc conductivity and magnetization studies of the Al substituted $La_{0.85}Ca_{0.15}Mn_{1-x}Al_xO_3$ (x = 0.0 and 0.1) samples.

EXPERIMENTAL

Polycrystalline bulk samples of $La_{0.85}Ca_{0.15}Mn_{1-x}Al_xO_3$ (LCMAO) (x = 0.0 and 0.1) were prepared by standard solid-state reaction route using La_2O_3, $CaCO_3$, MnO_2, and Al_2O_3. The stoichiometric mixture was heated at 500 ^oC for 2 h, at 800 ^oC for 24 h and at 900 ^oC for 12 h in a closed Muffle furnace. Then it is pelletized and sintered at 1150 ^oC for 24 h. Powder x-ray diffraction (XRD) are performed using Bruker D8 X-ray diffractometer with CuK_α radiation at room temperature. DC resistivity of the samples is measured by conventional four-probe method in the temperature range 80-300 K. Magnetization as a function of applied magnetic field (0-8T) at fixed temperature is measured using PPMS-Vibrating Sample Magnetometer (VSM) of Quantum Design.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of $La_{0.85}Ca_{0.15}Mn_{1-x}Al_xO_3$ (x = 0.0 and 0.1) samples which show the clean and single phase. The lattice parameters were calculated using the PowderX software. It is found that the lattice parameter *a*

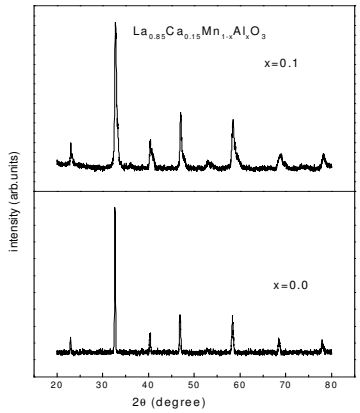

Fig.1. Room temperature x-ray diffraction (XRD) pattern for $La_{0.85}Ca_{0.15}Mn_{1-x}Al_xO_3$ (x = 0.0 and 0.1) samples.decreases from 5.477 to 5.425 Å, *b* from 7.754 to 7.730 Å and *c* from 5.511 to 5.491 Å with Al substitution at Mn site. The unit cell volume decreases from 234.065 to 231.412 $Å^3$ due to Al doping and is consistent with the lower size of Al^{3+} (0.5 Å) compared to that of Mn^{3+} (0.6 Å). Figure 2 shows the resistivity (ρ) of $La_{0.85}Ca_{0.15}Mn_{1-x}Al_xO_3$ samples as a function of temperature (80-300K). Room temperature (~300 K) resistivity for $La_{0.85}Ca_{0.15}MnO_3$ sample is ~ 0.62 Ω cm, whereas that for Al doped samples with x = 0.1, is ~ 105 Ω cm. The metal-insulator (MI) transition at ~ 200 K for the parent compound completely disappears for x = 0.1. At low temperatures, the resistivity value is about five orders of magnitude higher for x = 0.1 than that of

the parent (x = 0.0) compound. The σ_{dc} of these samples is explained using polaron hopping conduction mechanism[5] with an expression of the form

$$\sigma_{dc} = (\sigma_0/T)\exp(-W/k_BT) \quad (1)$$

where σ_o is a pre-exponential factor, W is the activation energy, k_B is the Boltzmann constant and T is the absolute measuring temperature. The Debye temperature (θ_D) of the samples decrease from 473 to 287 K with the increase of x. Density of states (DOS) at the Fermi level ($N(E_F)$) is too observed to decrease from 8.74 x 10^{21} to 2.20 x 10^{20} $eV^{-1}cm^{-3}$ with the increase of Al doping and is temperature (θ_D) of the samples decrease from 473 to 287 K with the increase of x. Density of states (DOS) at the Fermi level ($N(E_F)$) is too observed to decrease from 8.74 x 10^{21} to 2.20 x 10^{20} $eV^{-1}cm^{-3}$ with the increase of Al doping and

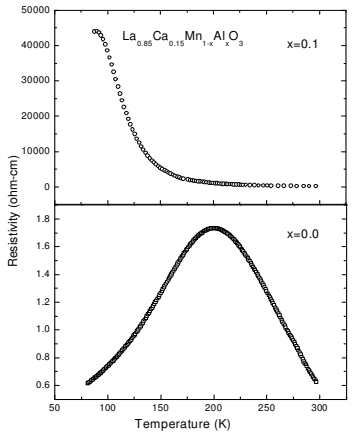

Fig. 2. Temperature dependence of resistivity of $La_{0.85}Ca_{0.15}Mn_{1-x}Al_xO_3$ (x = 0.0 and 0.1) samples.is consistent with the increase of resistivity data. Activation energy (W) determined from the slope of $\log_{10}(\sigma_{dc}T)$ vs. $10^3/T$ curve above the temperature of $\theta_D/2$ is ~ 45meV for undoped sample and 63meV for x=0.1 sample. Polaron-hopping energy (W_h) is calculated from the relation[5]

$$W = W_h + W_d/2 \text{ for } T > \theta_D/2 \quad (2)$$

where W_d is the disorder energy arising due to the energy difference of the neighboring sites and is significant at very low temperature ($T < \theta_D/4$). At high temperature, the activation energy is mainly contributed by W_h. The values of W_h calculated at a temperature of 290 K are 45 and 50 meV for x = 0.0 and 0.1 samples respectively. These findings are in accordance with the reported literature.[6] From Holstein's relation[7], the polaron bandwidth is given by

$$J \approx 0.67\, h\nu_{ph}\,(T/\theta_D)^{1/4}, \quad (3)$$

$$\text{where, } H = (2k_BTW_h/\pi)^{1/4}(h\nu_{ph}/\pi)^{1/2} \quad (4)$$

ν_{ph} is taken as 10^{13} Hz for both the samples. The values obtained at 290K for H are 18.60 and 14.89 meV, J ~ 23.89 and 27.00 meV, $W_h/3$ ~ 15.00 and 16.93 for x = 0.0 and 0.1 samples respectively. Since the value of $J > W_h/3$, it indicates the presence of large polaron hopping (LPH) in the LCMAO samples. The values of

polaron coupling constant (γ_P), which is a measure of electron-phonon (e–ph) interaction in these manganites[5] varies from 2.22 for undoped sample to 4.15 in Al doped sample. Hence, the e–ph interaction seems to be weak in undoped sample, however strong coupling is observed in case of doped sample. This fact is further confirmed using the relation[5]

$$m_p = m^* \exp(\gamma_P) \quad (5)$$

where, m_p is the polaron mass and m* is the rigid lattice effective mass. From the calculated values of exp (γ_P) (9.20 for undoped and 64.00 for doped sample), it is clear that strong e–ph interaction is present in Al doped sample. Therefore, it may be concluded that adiabatic large polaron hopping conduction of carriers with strong e–ph interaction is responsible for the dc conductivity of Al substituted LCMAO sample.

Figure 3 shows the M-H curves of $La_{0.85}Ca_{0.15}Mn_{1-x}Al_xO_3$ (x = 0.0 and 0.1) samples. The decrease of magnetization with Al doping concentration is

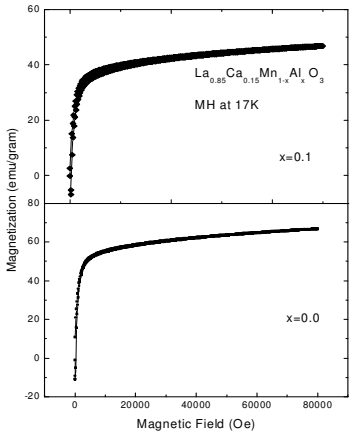

Fig.3. Magnetization versus magnetic field *(*M-H*)* curve for Al doped $La_{0.85}Ca_{0.15}Mn_{1-x}Al_xO_3$ (x = 0.0 and 0.1) at a temperature of 17K.

confirmed by the field dependent magnetization at a constant temperature of 17 K. Both of the samples show ferromagnetic behavior. The decrease in magnetization in Al substituted sample can be understood taking into account the fact that Al will increase the distance between the Mn ions causing certain degree of distortion in Mn sublattice, responsible for ferromagnetic interactions.

Conclusions

This study shows that Al doping increases the resistivity in LCMAO sample suppressing the metal insulator transition of $La_{0.85}Ca_{0.15}MnO_3$ (undoped) compound. Conduction in Al substituted sample takes place by large polarons in adiabatic region with strong e-ph coupling. Magnetization decreases with the increase of Al ion which is consistent with non magnetic nature of Al^{3+}.

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