Electrical transport and magnetoresistance of double layered CMR manganites $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R = La, Pr, Sm$)

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Polycrystalline bulk samples of double layered (DL) colossal magnetoresistive (CMR) manganites $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R = La, Pr, Sm$) were prepared by sol-gel method to study the effect of size of lanthanide ion on their magnetotransport properties. The electrical resistivity of the samples was investigated in the temperature range of 70 K to 300 K at different magnetic fields. The samples LSMO and PSMO show insulator-to-metal transition (IMT) behavior, while SSMO sample exhibits insulating behavior in the entire temperature range with a very large value of resistivity. The insulator-to-metal transition temperature (T_{IM}) decreases from 123 K (LSMO) to 90 K (PSMO) and disappears in SSMO sample. To explain the electrical transport above T_{IM} , the temperature dependent resistivity data ($T > T_{IM}$) of all the samples were fitted to the equations of different conduction models. The results indicate that the conduction at $T > T_{IM}$ is due to Mott variable range hopping (VRH) mechanism in the LSMO and PSMO samples, while Efros-Shkloskii (ES) type of VRH model dominates the conduction process in the SSMO sample. All the three samples show increasing magnetoresistance (MR) even below T_{IM} and the maximum MR is shown by LSMO (39 % at 75 K, 3 T).

Keywords: *double layered manganites; electrical transport; magnetoresistance; variable range hopping; sol-gel process*

1. Introduction

The doped rare earth manganese perovskites with a general compositional formula $R_{1-x}A_xMnO_3$ (R is a rare earth element and A is a divalent alkaline earth metal) have been extensively investigated due to their CMR properties [1–5]. The CMR phenomena in this system are generally understood in terms of double-exchange mechanism and Jahn-Teller distortions of Mn^{3+} ions [6–8]. Although these materials show large magnetoresistance (MR) values, the requirement of high magnetic fields and MR at narrow temperature range put constraints on the practical usage of these materials. Hence, there has been a world-wide research activity to discover the materials which show high MR values at moderate magnetic fields and in a wide temperature range.

The La-based DL manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ have gained much importance since Moritomo et al. discovered CMR

in these materials [9]. These DL manganites belong to $n = 2$ members of the Ruddlesden-Popper series $(R,A)_{n+1}Mn_nO_{3n+1}$ [10]. These materials show large values of MR at moderate magnetic fields and proved to be promising materials for many technological applications. The reduced dimensionality and structural anisotropy of these materials are expected to result in anisotropic characteristics in charge-transport and magnetic properties. The crystal structure of $La_{1.2}Sr_{1.8}Mn_2O_7$ consists of double layers of corner shared ferromagnetic-metallic MnO_6 octahedra (perovskite structure-type) in the ab -plane of the crystal, separated by a single rock-salt-type nonmagnetic-insulating (La,Sr)O layer along the c -axis giving it 2D character. Hence, a natural array of ferromagnetic-insulator-ferromagnetic junctions is present in the structure of these materials which actually may lead to large CMR at low magnetic field, i.e. low field magnetoresistance (LFMR) [11–14]. The two important interactions between Mn ions, namely double exchange (DE) driven ferromagnetic (FM) interactions and superexchange (SE) driven antiferromagnetic (AFM)

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interactions, are responsible for the observed transport and magnetic properties of the manganites. Because of reduced dimensionality, the balance between FM DE and AFM SE interactions between Mn ions is more subtle [15, 16]. Therefore, one can expect that the slight changes in the size and/or concentration of (R,A) site ions can result in significant effect on bulk transport and magnetic properties. The overlap between the Mn 3d orbital and the O 2p is a crucial factor in promoting electronic conduction which is very sensitive to bond lengths and bond angles of Mn–O–Mn that result from the variation of the size of lanthanide ions. This implies that the chemical pressure not only affects the magnetic ground states through changing the effective transfer integral in the DE interaction but also the magnetotransport properties by varying the strength of carrier localization effect [12, 14, 17]. Further, the Mn–O–Mn bond angle is about 180° in the $(\text{La,A})_3\text{Mn}_2\text{O}_7$ system and about 155° to 170° in $(\text{La,A})\text{MnO}_3$ system. The bond length can be altered by the internal pressure, i.e. by changing the size and/or concentration of (R,A) site ions, however, the variation of the Mn–O–Mn bond-length in Mn_2O_7 system is different from that in MnO_3 system. Therefore, the study of lattice effects on the magnetotransport properties in the $(\text{R,A})_3\text{Mn}_2\text{O}_7$ system might be useful in understanding the fundamentals of the CMR and its related properties.

Earlier, the author reported the results of transport and elastic properties of some DL manganites [18–21]. It was observed that $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ has much lower IMT than $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. However, $\text{Pr}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ shows CMR over a wide temperature range and at relatively low magnetic field values. Hence, a systematic investigation was carried out to elucidate the effect of lanthanide ion size on the magnetotransport properties of DL manganites. In this paper, the magnetotransport results obtained for bulk samples of DL manganites $\text{R}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($\text{R} = \text{La, Pr, Sm}$) with a main focus on their electrical transport behavior are presented.

2. Experimental

The polycrystalline samples of $\text{R}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($\text{R} = \text{La, Pr, Sm}$) were synthesized by sol-gel method. This method is more preferable in the case of DL manganites, as they require very high processing temperatures and long reaction times. The detailed description of synthesizing these samples is given in the literature [18]. The structural characterization was done using powder X-ray diffraction (XRD) with a M/s PANalytical X-ray diffractometer giving $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) in 2θ range of 20° to 80° with a step size of 0.01° and a count time of 0.6 s per step.

The temperature dependent electrical resistivity measurements from 70 K to 300 K were made using four-probe method in absence and presence of applied magnetic field ($H = 1.5 \text{ T, } 3 \text{ T}$). A superconducting magnet system of OXFORD was used to produce the required magnetic fields.

3. Results and discussion

3.1. Crystal structure

The powder XRD patterns of DL manganites $\text{R}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($\text{R} = \text{La, Pr, Sm}$) are shown in Fig. 1 and they suggest that the samples are of single phase with $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type body-centered tetragonal perovskite structure with the space group $I4/mmm$ ($Z = 2$). The values of lattice parameters (a and c) and cell volume (V) decrease with the decrease of the size of lanthanide ion, as expected (Table 1). Here, Shannon ionic radii values of $1.216 \text{ \AA}$ (La^{3+}), $1.179 \text{ \AA}$ (Pr^{3+}) and $1.132 \text{ \AA}$ (Sm^{3+}) are taken for coordination number 9 [22]. The decreasing c/a ratio with the size of the lanthanide ion suggests that the lattice contracts preferably in the c -direction rather than in the a -direction [14]. Further, the lattice contraction on replacing the larger lanthanide ion with relatively smaller lanthanide ion may induce chemical pressure, and the distortion of MnO_6 octahedra in the perovskite block increases. This increases the electron-phonon coupling via the strengthening of the cooperative Jahn-Teller distortion which may have an appreciable effect on the transport and magnetic properties of the DL manganites.

Fig. 1. Powder XRD patterns of $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R = La, Pr, Sm$).

Table 1. Crystallographic data of $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R = La, Pr, Sm$).

Sample	a [Å]	c [Å]	c/a	V [Å ³]
LSMO	3.8803	20.1219	5.1857	302.97
PSMO	3.8766	20.0805	5.1800	301.76
SSMO	3.8689	19.7979	5.1172	296.35

3.2. Electrical resistivity and conduction mechanism at $T > T_{IM}$

The temperature dependent electrical resistivity ($H = 0$ T, 1.5 T, 3 T) plots are shown in Fig. 2. LSMO and PSMO samples show a resistivity peak (ρ_{IM}) at T_{IM} at which IMT takes place. The value of T_{IM} decreases with the size of the lanthanide ion, i.e. from LSMO (123 K) to PSMO (90 K), whereas the value of ρ_{IM} increases from LSMO to PSMO. However, in case of SSMO sample, the resistivity continuously increases largely with decreasing temperature and IMT disappears in this sample. When a lanthanide ion is replaced with a relatively smaller lanthanide ion, chemical pressure is induced which results in anisotropic lattice distortion and canting of ferromagnetic spins. As a consequence, the charge carriers suffer more scattering by Mn spins and as a result ρ_{IM} increases and T_{IM} decreases [12, 14]. In case of SSMO sample, such canting of ferromagnetic spins is very high and results in a very high resistivity and therefore IMT vanishes. The increasing resistivity of the samples with decreasing the size of the lanthanide ion suggests the weakening of FM-DE interactions.

The conduction mechanism in semiconducting/insulating region in manganites is usually

Fig. 2. Temperature dependent resistivity plots of $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R = La, Pr, Sm$)

explained by four models: They are: (i) semi-conduction (SC) model described by Arrhenius equation [23]:

$$\rho = \rho_0 \exp(E_a/k_B T) \quad (1)$$

(ii) nearest neighbor small polaron hopping (SPH) model described by:

$$\rho = \rho_0 T^n \exp(E_p/k_B T) \quad (2)$$

where $n = 1$ for adiabatic hopping [24] and $n = 1.5$ for non-adiabatic hopping [25], (iii) Mott type of variable range hopping (VRH) model described by:

$$\rho = \rho_{\infty} \exp(T_0/T)^p \quad (3)$$

where $p = 1/(d + 1)$ with d being the dimensionality of the system [26, 27] and (iv) Efros-Shkloskii (ES) type of VRH model [27, 28] described by:

$$\rho = \rho_{\infty} \exp(T_0/T)^{1/2} \quad (4)$$

Here, ρ_0 is a pre-factor in SC and SPH models and ρ_{∞} is a pre-factor in VRH models. E_a and E_p are the activation energies in SC model and SPH model, respectively. T_0 is a characteristic temperature in VRH models and its value in Mott VRH model is given by:

$$24/\pi L^d k_B N(E_F) \quad (5)$$

where L is localization length of trapped charge carriers (here, $L = 10^{-10}$ m), $N(E_F)$ is density of the localized states at Fermi level and d is the dimensionality of the system. The Coulomb interaction in hopping regime which produces a gap in electronic density of states (DOS) is responsible for ES VRH type of conduction mechanism, whereas Mott VRH arises, when such gap is filled. Each model predicts a different temperature dependence of resistivity and fits the resistivity data in different temperature ranges. Generally, electron hopping is of a variable range type at low temperatures, where the thermal energy is not great enough to allow electrons to hop to their nearest neighbors. In that case, electrons choose to hop farther to find a smaller potential difference. At high temperatures, conduction may be promoted by activation above the mobility edge or narrow band gap. In the intermediate temperature range, nearest neighbor (small polaron) hopping dominates.

In case of DL manganites, the conduction at $T > T_{IM}$ has been explained by Matsukawa et al. [29], Zhu et al. [30] and others [21, 31, 32] using Mott type VRH while Chatterjee et al. [12] and others [33, 34] suggested SPH model. Chen et al. [35] suggested ES VRH type of conduction in

similar DL manganites. However, the DL manganites, because of their quasi-2D nature, are expected to exhibit some complexity in their transport behavior, therefore, the presence of Coulomb gap and the dimensionality of the materials are to be considered in order to evaluate the nature of conduction mechanism.

In the present study, the ρ - T data above T_{IM} are analyzed by fitting the data to all the equations of the conduction models mentioned above. The fittings obtained are rather poor with SC and SPH models and the best fittings, for the three samples, are obtained with VRH models over a wide temperature range (Fig. 3). The Mott VRH model gives better fittings for LSMO and PSMO samples than ES VRH model in the temperature range given in Table 2, while ES VRH equation fits the resistivity data of SSMO better than Mott VRH model in the entire temperature range, i.e. 70 K to 300 K. For LSMO and PSMO samples, Mott 2D VRH and Mott 3D VRH models give almost indistinguishable fittings to draw any conclusion about the dimensionality dependence, but the results clearly indicate that the conduction at $T > T_{IM}$ in these two samples follows Mott VRH mechanism. The ES VRH mechanism is a dimensionality independent mechanism which arises due to strong electron-electron Coulomb interactions reducing the density of states near the Fermi level. The observed ES VRH mechanism in SSMO sample may be attributed to its very high resistivity, where electron-electron interactions are dominant in the conduction process. The best fit parameters obtained with all VRH models are listed in Table 2.

The variation of T_{IM} and ρ_{IM} with lanthanide ion can be explained in terms of characteristic temperature (T_0), obtained from the fitting of resistivity data to the Mott VRH model. As T_0 is inversely related to the extent of localized states, the increasing value of T_0 is due to the decrease of localization length and hence, the hopping distance. This leads to the decrease of whole mobility which, in turn, results in the increase of ρ_{IM} and decrease of T_{IM} . The decreasing value of $N(E_F)$ with the decrease of the size of lanthanide ion also indicates that the ability to conduct decreases from

Table 2. The best-fit parameters obtained from VRH model fittings for $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R = La, Pr, Sm$).

Sample	T_{range} [K]	Mott 3D VRH			Mott 2D VRH			ES VRH	
		T_0 [K]	ρ_∞ [$\Omega \cdot cm$]	$N(E_F)$ [$eV^{-1} \cdot cm^{-3}$]	T_0 [K]	ρ_∞ [$\Omega \cdot cm$]	$N(E_F)$ [$eV^{-1} \cdot cm^{-2}$]	T_0 [K]	ρ_∞ [$\Omega \cdot cm$]
LSMO	>210	1.77×10^7	2.17×10^{-6}	5.01×10^{21}	4.44×10^5	1.43×10^{-4}	1.99×10^{15}	1.64×10^4	7.93×10^{-3}
PSMO	>185	2.05×10^7	4.91×10^{-7}	4.32×10^{21}	5.05×10^5	3.54×10^{-5}	1.75×10^{15}	1.74×10^4	2.55×10^{-3}
SSMO	>70	1.99×10^8	5.23×10^{-12}	4.45×10^{20}	2.47×10^6	2.38×10^{-8}	3.58×10^{14}	4.28×10^4	1.08×10^{-4}

LSMO to SSMO. The obtained best fit parameters are in good agreement with the previous reports on similar DL manganites [21, 29–32, 36]. All the fitting parameters in Mott 2D and 3D VRH models vary in a similar manner with lanthanide ion and these results suggest the reliability of the performed fittings.

3.3. Magnetoresistance

MR is defined as:

$$MR\% = 100 \times (\rho_0 - \rho_H) / \rho_0 \quad (6)$$

where ρ_0 and ρ_H represent the resistivity in absence and in presence of applied magnetic field H , respectively. Temperature dependent MR ($H = 3$ T) plots are shown in Fig. 4. It is known that an applied magnetic field can suppress the magnetic frustration and spin scattering of electrons, reduce the resistivity which results in large MR effect at T_{IM} . However, it is interesting to note that in the present DL manganite system, no peak is seen in MR-T plots unlike the resistivity peak observed at T_{IM} in ρ -T plots (Fig. 2) and the MR increases even below T_{IM} , which is a typical characteristic of DL manganites [14, 21, 32]. The property of exhibiting CMR effect over a wide temperature range suggests potential applications for layered perovskites. Further, with the application of magnetic field ρ_{IM} decreases greatly and T_{IM} shifts to higher temperature. In the present system of DL manganites, the MR at T_{IM} (MR_{IM}) is maximum (32 %) for PSMO but, the maximum MR ($MR_{max} \approx 39$ %) in the given temperature range is shown by LSMO at 75 K.

In order to realize the field induced phenomena in CMR manganites, the change in T_{IM} and MR with an applied magnetic field can also

be considered. From Fig. 2, it can be seen that T_{IM} shifts in a higher degree to higher temperature with applied magnetic field in LSMO as compared to that in PSMO. For LSMO sample, the value of T_{IM} is 123 K, 137 K and 145 K at $H = 0$ T, 1.5 T and 3 T, respectively. For PSMO sample, the value of T_{IM} is 90 K, 92 K and 94 K at $H = 0$ T, 1.5 T and 3 T, respectively. This shows that T_{IM} of PSMO sample is not much sensitive to the applied magnetic field. The variation of MR with the applied magnetic field at 90 K is shown in Fig. 5. LSMO and PSMO samples show more rapid increase in MR at lower magnetic fields than at higher fields, while SSMO shows a linear increase in MR with the applied magnetic field. Although the MR-H data were taken at 90 K which is T_{IM} for PSMO sample, the increase in MR with the applied magnetic field is larger in LSMO than that in PSMO sample. This also indicates the pronounced magnetic field induced effects over a wide temperature range in LSMO sample.

4. Conclusions

Single phase DL manganites $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R = La, Pr, Sm$) were synthesized by the sol-gel method. The anisotropic lattice contraction is observed with decreasing the size of the lanthanide ion. LSMO and PSMO samples exhibit IMT at 123 K and 90 K, respectively while it vanishes in SSMO sample which suggests the weakening of FM-DE interactions with the decreasing size of the lanthanide ion. The conduction at $T > T_{IM}$ is due to Mott VRH mechanism in LSMO and PSMO samples. The observed ES VRH mechanism in SSMO sample may be attributed to its very high resistivity arising from electron-electron interactions. All the three samples exhibit CMR property over a wide

Fig. 3. Plots of $\ln \rho$ vs. $T^{-1/4}$ and $\ln \rho$ vs. $T^{-1/3}$ for LSMO and PSMO, and $\ln \rho$ vs. $T^{-1/2}$ for SSMO. The solid lines give the best fits to the VRH models.

Fig. 4. MR ($H = 3$ T) versus T plots for $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R = La, Pr, Sm$).

Fig. 5. MR versus H plots for $R_{1.2}Sr_{1.8}Mn_2O_7$ ($R = La, Pr, Sm$)

temperature range and LSMO sample is found to exhibit pronounced magnetic field induced effects much below its T_{IM} .

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