Influence of Ce doping on Structural, Magnetic and Transport Properties of $CaMnO_3$ Perovskite

Irfan Mansuri[1, 4, *], Dinesh Choudhary[2,4] Sonu Sen[4,5] and Mohammed Wasim Shaikh[3, 4, *]

[1]*Department of Physics, Indore Institute of Science and Technology, Indore 453331, India.*
[2]*Department of Physics, Govt. Post Graduate College, Khargone 451001, India.*
[3]*Department of Physics, Acropolis Technical Campus, Tillore Khurd, Indore 452020, India.*
[4]*School of Physics, Vigyan Bhavan, Devi Ahilya University, Khandwa Road Campus, Indore 452001, India.*
[5]*School of Automobile and Manufacturing Engineering, Symbiosis University of Applied Sciences, Indore 453112.*

[*]*Corresponding author: drmwshaikh@gmail.com; dr.irfan.mansuri@gmail.com*

Abstract. We have systematically investigated the structural, magnetic, and transport properties of the $Ca_{0.4}Ce_{0.6}MnO_3$ perovskite as functions of temperature. For Ce doped $CaMnO_3$ sample, the *dc* electrical resistivity is large (~ M Ω cm) and shows increasing trend on lowering the temperature. A small-polaron hopping conduction approach is employed to explain the temperature dependence of resistivity in the intermediate temperature range. From the best fit, the activation energy, the optical phonon frequency and the polaron diffusion constant are estimated. The temperature dependence of thermopower of $Ca_{0.4}Ce_{0.6}MnO_3$ perovskite increases on lowering the temperature; confirm the paramagnetic insulating state following the small polaron model. The *ac*-susceptibility data infers the paramagnetic phase up to $T = 80$ K.

INTRODUCTION

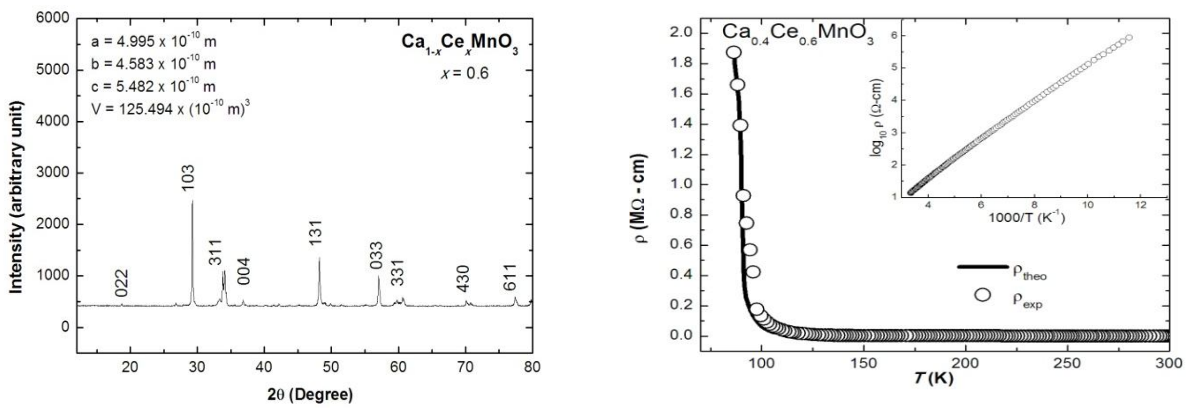
In the recent past, $CaMnO_3$ perovskite have been focused because of their interesting magnetic and ferroelectric properties. The ground-state crystal structure of $CaMnO_3$ is orthorhombic with space group *Pnma*. The structure can be regarded as a distorted perovskite structure having four formula units. It is an insulator with an energy gap of about 3 eV [1, 2], and the magnetic structure is antiferromagnetic and the observed Neel temperature is about 130 K [3]. In the present investigations we aimed at measuring the temperature dependence of the *dc* electrical resistivity (ρ), thermopower (S) and *ac*-susceptibility (χ) of polycrystalline Cerium doped manganites: $Ca_{0.4}Ce_{0.6}MnO_3$. The x-ray diffraction patterns are well indexed and are in crystalline phase with orthorhombic crystal structure. Later on, we shall use small polaron hopping model to fit the experimental data for resistivity and thermopower.

EXPERIMENTAL DETAILS

The samples were prepared by solid-state synthesis. Stoichiometric amounts of CeO_2, $CaCO_3$, and MnO_2 were mixed and heated at 1350 ^{o}C in air for 24 h with intermediate grindings. The pellets were finally annealed at 1000 ^{o}C in oxygen atmosphere. The powder x-ray patterns were recorded using a Rigaku diffractometer with Cu Kα radiation and scanning over the angular range 10^{o} – 80^{o}. Electrical resistivity measurements were carried out by standard four-probe method in the temperature range 10-300 K. The thermopower measurements have been made down to 77 K using a two-stage closed cycle refrigerator. The *ac* susceptibility measurements were carried out using vibrating sample magnetometer set-up.

RESULTS AND DISCUSSION

The XRD pattern could be indexed in the orthorhombic systems shown in Fig. 1(a). The substitution of Ca ions with Ce ions in $CaMnO_3$ manganites will cause the distortion of lattice, which has been confirmed by the XRD pattern. The variation of resistivity with temperature is illustrated in Fig. 1 (b) for $Ca_{0.4}Ce_{0.6}MnO_3$. The inset shows the plot in ($\log_{10}\rho$) the natural log scale as functions of $1000/T$. A nearly straight line is traced that indicates that prepared compound is in purely insulating phase. Such an insulating state is in agreement with reported data for the lightly electron doped compounds [4]. We find that the small polaron hopping conduction model [5] successfully fits the measured resistivity data as depicted in Fig. 1 (b). The calculated parameters are listed in Table 1. The Polaron binding energy deduced is consistent with earlier reports on $Ca_{1-x}Ce_xMnO_3$ [4]. The choice of resistivity interpretation with small polaron hopping conduction has an advantage that it incorporates naturally the electron-lattice interactions, which stem from dynamic Jahn-Teller (JT) effect in the insulating samples.



(a) (b)

Figure 1.(a) The x-ray diffraction pattern of $Ca_{0.4}Ce_{0.6}MnO_3$ manganite. (b) The fitted temperature dependence of electrical resistivity for the $Ca_{0.4}Ce_{0.6}MnO_3$ manganite.

The variation of thermopower (*S*) with temperature is illustrated in Fig. 2 (a) for $Ca_{0.4}Ce_{0.6}MnO_3$ manganite. As the temperature decreases from 300 K the *S* increases slowly, reaches a maximum value in the temperature range 150 to 170 K. With a further decrease in temperature, *S* drops and further decreases. The *S* exhibits insulating behaviour throughout the temperature range. In the paramagnetic (PM) phase, on cooling, *S* increases with decreasing in temperature. Usually, the thermopower of metals and nonmetals differ not only in their magnitude but also in their temperature dependence. In the temperature range where diffusive thermopower dominates, the thermopower of metals, even disordered ones, is of the order of a few μV/K and is linear in temperature. The thermopower of semiconductors, in contrast, is typically several tens to hundreds of μV/K, and is governed by thermal activation of carriers thus increasing with decreasing temperature. The value of *S* is slightly negative at high temperature and then become positive on cooling and shows the hole as carriers for conduction. A phonon-drag-type anomaly is clearly visible at higher temperatures.

We have attempted to interpret the observed behaviour of thermopower following the small polaron conduction model [5]. The fitting parameters are illustrated in Table 1. The magnitude of activation energy E_S obtained by fitting of thermopower data is much smaller than activation energy E_ρ obtained by fitting of resitivity data, implying that SPC dominates the transport of the carriers in these Ce-doped manganites. In the framework of the SPC model, $E\rho$ is the sum of the activation energy required for the creation of the carriers and activating the hopping of the carriers and E_S is the energy required to activate the hopping of carriers only. Hence, E_S is expected to be smaller than E_ρ, as we indeed found. Additionally, based on E_ρ and E_S, both the polaronic energy W_H (= $E_\rho - E_S$) and the polaronic formation energy $E_P = 2W_H$ can be obtained. Therefore the present results provide strong evidence for the applicability of the SPC model in Ce-doped $Ca_{0.4}Ce_{0.6}MnO_3$ manganite.

We have also measured low field (0.5 Oe) *ac*-susceptibility to explore the magnetic phases. Fig. 2 (b) gives the temperature dependence of the real part (χ) of *ac*-susceptibility for $Ca_{0.4}Ce_{0.6}MnO_3$ manganite. It is noticed that the sample shows paramagnetic phase upto T = 80 K. The noteworthy coincidence of both the *ac*-susceptibility and thermopower seems to satisfying that the samples is in paramagnetic insulating states which is confirm from the earlier reports of Ca doped $SmMnO_3$ manganites [6].

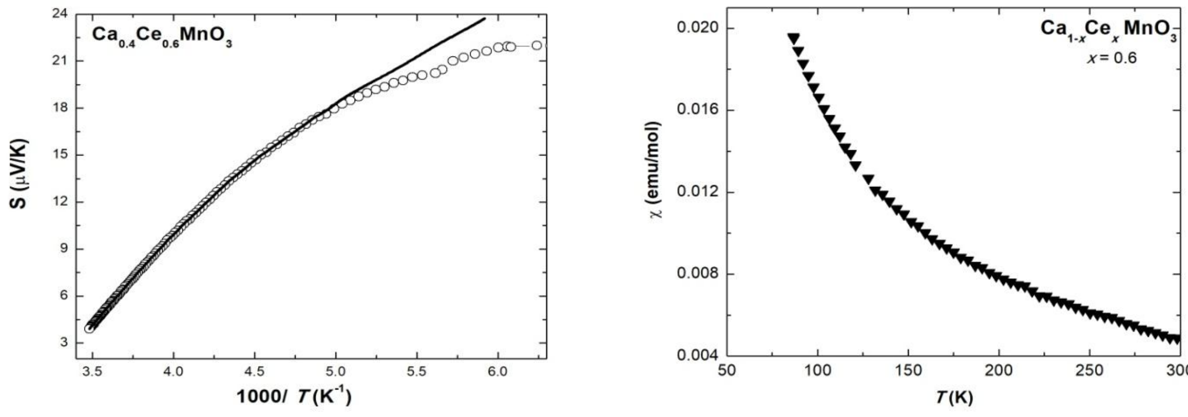


Figure 2.(a) The fitted thermopower as functions of temperature for $Ca_{0.4}Ce_{0.6}MnO_3$ manganite. (b) The *ac*-susceptibility as a function of temperature for the $Ca_{0.4}Ce_{0.6}MnO_3$ manganite.

TABLE 1. The fitting parameters obtained by fitting of resistivity and thermopower data of $Ca_{0.4}Ce_{0.6}MnO_3$ manganite.

Sample	Residual resistivity ρ_0 (Ω cm)	Carrier density n (10^{20} cm^{-3})	Polaron diffusion constant D (cm^2 s^{-1})	Polaron activation energy E_ρ (meV)	Polaron activation energy E_S (meV)	Polaron formation energy E_P (meV)
$Ca_{0.4}Ce_{0.6}MnO_3$	3.508	0.094	0.031	180	7	346

ACKNOWLEDGMENTS

Authors are thankful to UGC-DAE CSR, Indore for providing characterization facilities.

REFERENCES

1. S. F. Matar, Prog. Solid State Chem. **31,** 239 (2003).
2. J. H. Jung, K. H. Kim, D. J. Eom, T. W. Noh, E. J. Choi, J. Yu, Y. S. Kwon and Y. Chung, Phys. Rev. B **55,** 15489 (1997).
3. M. Nicastro and C. H. Patterson, Phys. Rev. B **65,** 205111 (2002).
4. Z. Zeng, M. Greenblatt and M. Croft, Phys. Rev. B. **63,** 224410 (2001).
5. N. F. Mott and E. A. Davis, in Electronics Process in Non Crystalline Materials Clarendon, Oxford, (1971).
6. J. Hejtmanek, Z. Jirak, M. Marysko, C. Martin, A. Maignan, M. Hervieu and B. Raveau, Phys. Rev. B **60,** 14057 (1999).