PRAMANA
— journal of
physics

© Indian Academy of Sciences

Vol. 58, Nos 5 & 6
May & June 2002
pp. 1035–1039

Effect of Pr–Ca substitution on the transport and magnetic behavior of $LaMnO_3$ perovskite

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Abstract. The effect of simultaneous substitution of a fluctuating cation and a divalent cation in $LaMnO_3$ perovskite modifies the properties of the material to exhibit large valence colossal magnetoresistance (CMR) effect. A good example of these properties is $(La_{1-2x}Pr_xCa_x)MnO_3$ (LPCMO) type CMR material. In this communication it is reported that, with the increase in x (for $x = 0.1$, 0.15, 0.2), the T_c varies between 100 and 120 K with improvisation in metal–insulator transition. Interestingly, resistance increases with x from few hundred ohms to few kilo ohms with corresponding decrease in the unit cell volume. The results of the studies using X-ray diffraction (XRD), electrical resistivity, magnetoresistance and ac susceptibility measurements on LPCMO samples for understanding the structural, transport and magnetic properties are discussed in detail.

Keywords. Colossal magnetoresistance (CMR); $LaMnO_3$ perovskite; Pr–Ca substitution; transport properties; magnetic properties.

PACS No. 75.30.Vn

1. Introduction

The $ReMnO_3$-type perovskite colossal magnetoresistive (CMR) material exhibits transport and magnetic properties due to divalent cation substitution at rare earth site. Several such studies have been reported on $La_{1-x}A_xMnO_3$ and $Pr_{1-x}A_xMnO_3$ manganite systems (A = Ca, Sr, Ba etc.). The structure of these ABO_3 perovskite systems is dependent upon the size of A and B cations [1,2]. The $La_{1-x}Ca_xMnO_3$ (LCMO) system exhibits prominent transport, magnetic transitions for $x = 0.1$ to 0.5. For $x > 0.5$ charge order state is predominant. CMR effect is reported under different fields around T_c. The dopant concentration also induces the structural transitions [1–3]. The other rare earth manganite system $Pr_{1-x}Ca_xMnO_3$ does not show high conductivity associated with ferromagnetism in a cubic or rhombohedral phase. $Pr_{1-x}Ca_xMnO_3$ (PCMO) shows insulator–metal (I–M) transition under applied magnetic field [4–6]. The insulating nature of $Pr_{1-x}Ca_xMnO_3$ perovskite is due to smaller size of Pr as compared to La which reflects the importance of structural details such as Mn–O–Mn bond angle for the double exchange mechanism. The smaller size of Pr reduces the bond angle making super exchange competitive with the Zener double exchange [7]. Though there are no transport properties, the system exhibits ferromagnetic properties for $x = 0.2$ to 0.3 [5]. The ferromagnetism appears due to the high intrinsic magnetic moment of Pr. These observations prompted us to study the effect of simultaneous Pr and Ca substitution for La site in $LaMnO_3$. For this purpose, the mixed manganite system with the stoichiometric composition $La_{1-2x}Pr_xCa_xMnO_3$ was studied for its transport and magnetic properties with a view that it will show the best transport properties of LCMO and magnetic properties of PCMO. Also, fluctuating valency of $Pr^{3+/4+}$ plays an important role in modifying the transport properties of LPCMO manganite system. In this paper the results of structural, transport and magnetic property measurements on $La_{1-2x}Pr_xCa_xMnO_3$ ($x = 0.10$–0.20) have been discussed in the light of size of cation and valency of dopant.

2. Experimental

A series of samples of $La_{1-2x}Pr_xCa_xMnO_3$ with $x = 0.10$, 0.15, 0.20 were synthesized by mixing thoroughly the high purity (99.99%) stoichiometric amounts of La_2O_3, Pr_6O_{11}, $CaCO_3$ and MnO_2. The mixed powders were ground thoroughly and heated at 1000°C for 24 h. The samples were reground, palletized and heated up to 1100°C. Structural studies were done using X-ray diffractometer with Cu-K_α radiation. The R–T measurements were carried out by standard four-probe method. Magnetic properties were studied by low temperature ac susceptibility measurements. Colossal magnetoresistance effect was observed under 1 T field.

3. Results and discussion

Figures 1–3 show the R–T measurements without applied field (R_0), under 1 T field (R_H) and magnetoresistance (MR%) for the stoichiometric composition $La_{1-2x}Pr_xCa_xMnO_3$, $x = 0.10$, 0.15 and 0.20 respectively. The MR% increases with the increase in dopant

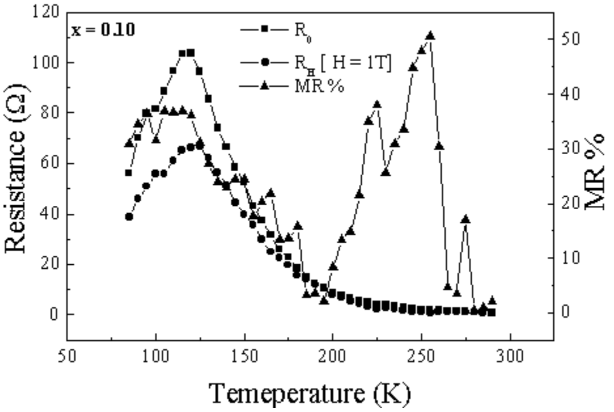

Figure 1. Temperature dependence of resistance (R_0 and R_H) and MR% for $La_{0.8}Pr_{0.1}Ca_{0.1}MnO_3$ sample.

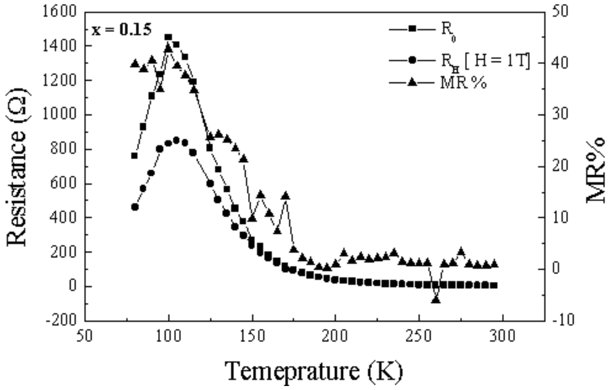

Figure 2. Temperature dependence of resistance (R_0 and R_H) and MR% for $La_{0.7}Pr_{0.15}Ca_{0.15}MnO_3$ sample.

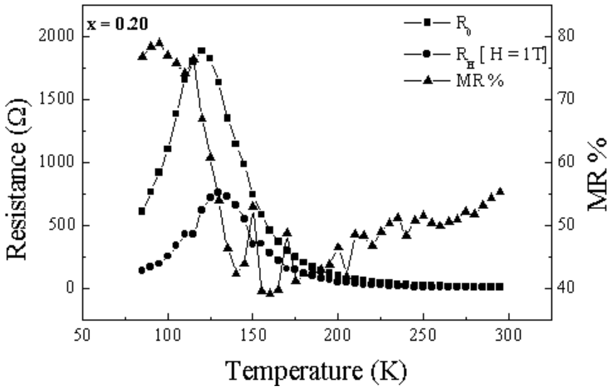

Figure 3. Temperature dependence of resistance (R_0 and R_H) and MR% for $La_{0.6}Pr_{0.2}Ca_{0.2}MnO_3$ sample.

concentration (x). Figure 4 shows the ac susceptibility curves for all the samples studied. Figure 4 reveals that transition temperature from ferromagnetic to antiferromagnetic state decreases with increase in x.

The XRD patterns confirm the single-phase nature of all the samples. Generally the orthorhombic distortion ($b > a > c/\sqrt{2}$, Pbnm) observed in case of undoped LaMnO$_3$ [8] was also observed in these samples. The substitutions of smaller size cations ($Pr^{3+/4+}$ and Ca^{2+}) at larger cation (La^{3+}) results into the reduction of the unit cell volume (table 1).

The transport properties studied for R–T measurement for different stoichiometric compositions showed I–M transitions in the range of 100–120 K. With the increase in dopant concentrations, the system exhibits insulator–metal transition with greater resistivity drop. It is observed that there is no systematics in T_c variation as a function of Pr–Ca doping concentration possibly due to the fluctuating valence of $Pr^{3+/4+}$ and divalent nature of Ca^{2+}. Magnetoresistance effect observed under 1 T field shows remarkable results. A significant drop in resistance is observed around T_c and peak shifts to higher temperature by small

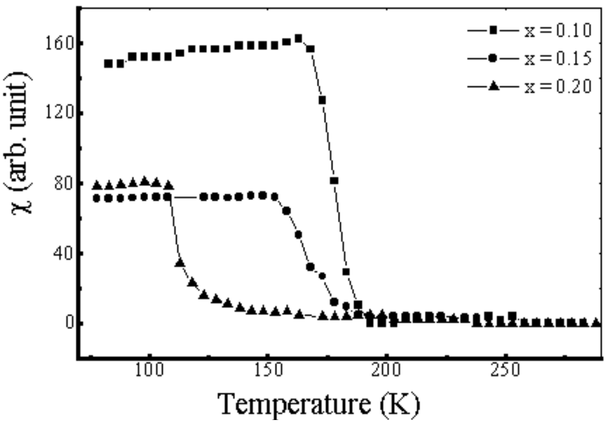

Figure 4. Temperature dependence of ac susceptibility for $La_{1-2x}Pr_x Ca_xMnO_3$ ($x = 0.1, 0.15$ and 0.2) system.

Table 1. Lattice parameters, unit cell volume and T_c for $La_{1-2x}Pr_xCa_xMnO_3$ system.

x	a (Å)	b (Å)	c (Å)	Volume (Å^3)	T_c (K) (I–M)
0.10	5.5282(3)	5.7418(3)	7.7143(3)	244.8659(9)	119
0.15	5.4801(3)	5.7429(3)	7.7211(3)	242.9958(9)	101
0.20	5.4879(3)	5.7379(3)	7.6917(3)	241.5743(9)	120

margin. MR effect of 20% to 80% is observed with the increase in substitution of Pr and Ca at La site (figures 1–3).

The magnetic behavior of Pr–Ca-doped LPCMO samples using low temperature ac susceptibility studies show that the magnetic transition temperature from antiferromagnetic to ferromagnetic state decreases with increase in doping concentration. A nearly saturated ferromagnetic region is observed below T_c (figure 4). These saturated magnetization curves as well as resistivity vs. temperature plots show that these compounds exhibit ferromagnetic properties coupled with metallic conductivity. The sharp magnetic transition also favors the CMR effect at T_c possibly due to the fact that an increase in the Mn–O–Mn bond angle along with the parallel alignment of spins causing an increase in Zener double exchange. The increase in resistance and magnetoresistance may also be attributed to the grain boundary effect on the conduction of electrons [9]. The grain boundaries act as regions of enhanced scattering for conduction of electrons and the application of relatively low fields can align the canted spins of electrons in the magnetically disordered region near grain boundaries.

4. Conclusion

The mixed valent manganite LPCMO system exhibits transport and magnetic properties with sharp electrical and magnetic transitions. The fluctuating valency of $Pr^{3+/4+}$ and larger magnetic moment of Pr play a significant role in modifying the transport and magnetic properties of LCMO system. The above stoichiometric compositions show remarkable sensitivity to the applied magnetic field. Simultaneous substitution of Pr with Ca increases the MR% that gives us a better understanding of the role played by the size of the cations in the structural, electrical and magnetic transitions. The interesting feature of the simultaneous substitution of Pr and Ca in $LaMnO_3$ system is that, though it decreases the transition temperature as compared to LCMO system, it increases the magnetoresistance (CMR effect).

Acknowledgements

This work is supported by UGC (New Delhi) research project of Dr. D G Kuberkar. One of the authors C M Thaker, is thankful to UGC for teacher fellowship. D S Rana is thankful to UGC for project fellowship.

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