Study of low band width manganites with equal average ionic radii and manganese valence ratio

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Abstract

The reason for the interesting properties observed in CMR materials, other than average ionic radii ($< r_A >$) and Mn valence ratio (Mn^{3+}/Mn^{4+}), has been tried to find out by investigating the transport and magnetic properties of $Pr_{0.65}(Ca_{0.7}Sr_{0.3})_{0.35}MnO_3$, $Pr_{0.527}La_{0.123}(Ca_{0.8}Sr_{0.2})_{0.35}MnO_3$ and $Pr_{0.65}(Ca_{0.866}Ba_{0.134})_{0.35}MnO_3$. The $< r_A >$ and valence ratio of all three samples have been kept equal. The out come of the investigation indicates more intense role of the nature of individual A-site cation and the lattice mismatch.

Key words: CMR, Lattice Mismatch, Phase Separation

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1. Introduction

In the recent years, rare earth manganites have been extensively studied not only for their colossal magnetoresistance property but also for the novel and rich electrical and magnetic phases. [1–3] In the rare earth manganite systems CO antiferromagnetic phase is equally important like the ferromagnetic one, since melting of CO state by applied magnetic field can produce large colossal magnetoresistance. [4] In case of low bandwidth manganite $Pr_{1-X}Ca_xMnO_3$, for a broad range of doping ($0.3 \leq x \leq 0.75$) an antiferromagnetic charge ordered state is stabilized. [5] Interestingly the CO state of $Pr_{0.65}Ca_{0.35}MnO_3$ can be destroyed by application of magnetic field. [6] Also when Sr is doped in the Ca site of $Pr_{0.65}Ca_{0.35}MnO_3$ metal-insulator (M-I) transition appears and as doping of Sr increases to 50% CO completely disappears. [7]

It is well known that average A-site ionic radii $< r_A >$ and Mn^{3+}/Mn^{4+} artio are the crucial factor in the transport properties of rare earth manganites.[8,4]Recently, it is also found that the disorder introduced by the random substitution of the ionic radii at A site strongly affects the magnetism and conductivity of the manganites. [9,10] Thus, in this report we have chosen $Pr_{0.65}(Ca_{0.7}Sr_{0.3})_{0.35}MnO_3$ (PCSMO) as reference sample and doped this sample systematically in trivalent and divalent A-site with appropriate cations in such a way that both the $< r_A >$ and Mn oxidation state remain same for all these three samples. The other two doped samples are $Pr_{0.527}La_{0.123}(Ca_{0.8}Sr_{0.2})_{0.35}MnO_3$ (PLCSMO) and $Pr_{0.65}(Ca_{0.866}Ba_{0.134})_{0.35}MnO_3$.(PCBMO). The calculated value of $< r_A >$ for all these samples is 1.193$\mathring{A}$.

2. Experimental details

All the polycrystalline samples are prepared by standard ceramic method. The structure and phase purity of the samples were checked by powder x-ray diffraction (XRD) using CuKα radiation at room temperature. Compositional analyses were confirmed by energy disperssive x-ray analysis (EDX), which indicated that the obtained samples exhibited compositions nearly identical to nominal one. The value of Mn^{3+}/Mn^{4+} ratio is deduced from iodometric titration and it come out 1.78 ± 0.03 instead of 1.86 since some oxygen deficiency is there, which is originated due to sintering in air.

3. Results and discussion

In Fig. 1(a) the magnetization of (PCSMO) at 20 mT magnetic field. shows maxima around 210 K which is the characteristic of antiferromagnetic (AFM) ordering. With further decrease of temperature it shows a ferromagnetic (FM) transition around 90 K. In the resistivity curve at around 210 K the observed change in the slope of resistivity due to the charge ordering is consistent with the magnetization data. The insulator-metal transition at 90 K is accompanied with the FM transition. The magnetization and resistivity results suggest that Neel temperature T_N and Curie temperature T_C are correlated, respectively, with the charge ordering T_{CO} and insulator-metal T_{IM} transition temperatures. Our data is similar to those, earlier studied by Tomioka et.al. [7]

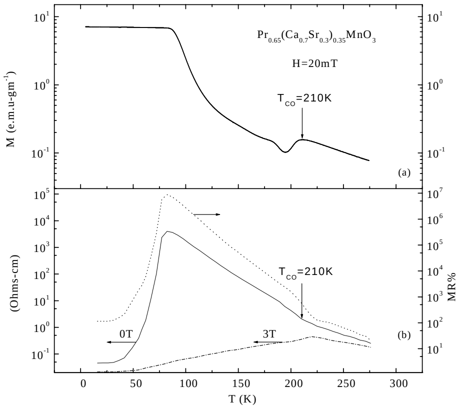

Fig. 1. Fig.1. (a)Variation of magnetization with temperature for $Pr_{0.65}(Ca_{0.7}Sr_{0.3})_{0.35}MnO_3$ sample in 20mT. (b) Temperature variation of resistivity and magnetoresistance.

In Fig. 2(a) the magnetization data of PLCSMO reveals a cusp at 182 K, which indicates the antiferromagnetic transition. At low temperature the magnetization attains a saturation value which corresponds to the FM phase. The variation of resistivity at zero and 3 T magnetic field is depicted in Fig. 2(b). An upturn in resistivity observed at about 182 K suggests the formation of CO state. The broad M-I transition occurs around 150 K while for PCSMO the resistivity decreases sharply. Both PCSMO and PLCSMO are metallic at low temperature but the resistivity of former is almost one order of magnitude lower than that of latter. The application of 3T magnetic field melts CO completely and the resistivity peak shifts to 185 K.

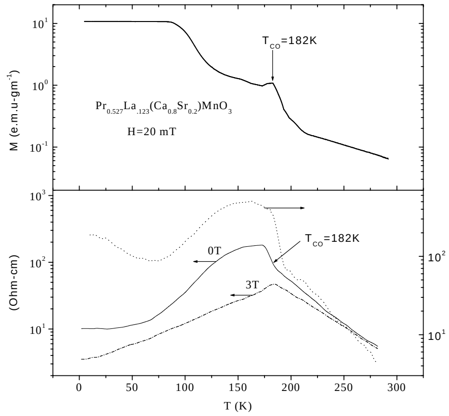

Fig. 2. Fig.2. (a)Variation of magnetization with temperature for $Pr_{0.527}La_{0.123}(Ca_{0.8}Sr_{0.2})_{0.35}MnO_3$ sample in 20mT. (b) Temperature variation of resistivity and magnetoresistance

The temperature dependence of magnetization of (PCBMO) at 20mT magnetic field and resistivity in absence of magnetic field and in presence of 3 T magnetic field are depicted in Figs 3(a) and 3(b) respectively. At around 145 K, the magnetization shows a small peak which indicates antiferromagnetic transition. The resistivity data exhibit a distinct discontinuity at 145 K, which corresponds to the onset of the charge ordering. The noticeable feature is that the I-M transition does not appear down to 50 K. The magnetic field of 3T induces FM state with $T_C = 145$ K as shown in the inset of Fig. 4(a) which confirms the MI transition of resistivity curve. The most fascinating fact is that although the $< r_A >$ and doping concentration of PCBMO is equal to those of PCSMO and PLCSMO a quite different behavior in transport and magnetic properties is found.

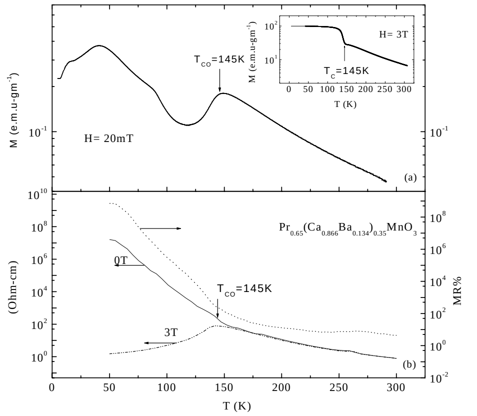

Fig. 3. Fig.3. (a)Variation of magnetization with temperature for $Pr_{0.65}(Ca_{0.866}Ba_{0.134})_{0.35}MnO_3$ sample in 20mT. (inset) Variation of magnetization with temperature in 3T magnetic field (b) Temperature variation of resistivity and magnetoresistance.

The variance in the distribution of $< r_A >$ has been used to quantify the lattice mismatch by the following relation [10],

$$\sigma^2 = \sum(x_i r_i^2) - < r_A >^2, \qquad (1)$$

where x_i is the fractional occupancy of A-site cations and r_i is the corresponding ionic radii. The calculated values of σ^2 for the samples PCSMO, PLCMO and PCBMO are $.0016\AA^2$, $.0011\AA^2$ and $.0037\AA^2$ respectively. It has also been mentioned that for PCSMO the T_{CO} is at 210 K (derived from the 1/M(T) vs T(K) plot), whereas for PLCMO and PCBMO, the T_{CO} are 182K and 145K respectively. The σ^2 values and the CO temperature (T_{CO}) for the respective samples clearly indicate that no specific correlation exist between them. [11] Excluding the direct possible explanation of this phenomena (change of T_{CO} with σ^2) with lattice mismatch effect, it is evident that not only $< r_A >$ and Mn- valence ratio, but also the interaction between Mn ion and Lanthanide ion plays important role which is consistent with the observation, obtained by S. Chatterjee et.al for layered perovskites. [12]

The substitution of Pr by La leads to the increase of T_{MI} and the width of the M-I transition. The increase of T_{MI} suggests the enhancement of DE interaction by La. When Sr is completely substituted by Ba the sample PCBMO becomes insulating down to lowest temperature and its T_{CO} is around 145K. The zero field data shows insulating behavior through out the whole temperature region, which may be due to the fact that substitution of Ba weakens the DE interaction.

The ground state of all the three studied samples in the present investigation is ferromagnetic. Thus there is a competition between FM and CO-AFM, which favors for the stabilization of phase separation (cluster formation). [13] The size of the cluster depends on the nature of disorder. The insulator-metal transition and the large MR may be due to the percolative effect through the clusters. [14]

4. Conclusion

Systematic doping of cation in the trivalent rare earth La and divalent A-site of the reference sample $Pr_{0.65}(Ca_{0.35}MnO_3$ has revealed the fact that nature of the cation is a key factor in the magnetotransport properties of low band width manganites. The resistivity behavior and the value of magnetoresistance of different samples support that La doping at Pr site weakens DE interaction while Ba doping at divalent cation site assists the DE interaction. The huge magnetoresistance observed in Ba doped systems may originate due to the disorder induced phase separation.

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