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Transport properties of Cs doped $Pr_{2/3}(Ba_{1-x}Cs_x)_{1/3}MnO_3$ manganites

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Abstract

Magneto-transport behaviour of $Pr_{2/3}Ba_{1/3}MnO_3$ manganite (PBMO) doped with Cs at Ba-site is reported here. The observed decrease in the Curie temperature T_C and the two insulator–metal like transitions (at T_{P1} and T_{P2}) in PBMO with Cs doping have been discussed in the light of the decrease in the carrier concentration emanating due to the change in the Mn^{3+}/Mn^{4+} ratio. While the peak magnetoresistance (MR) value at T_{P1} (reminiscent of the intra-granular behaviour) remains nearly invariant, the inter-granular (grain boundary) behaviour is clearly reflected through a substantial higher value of MR below T_{P2}. The insulating behaviour above T_{P1} has been co-related to the decrease in the density of states at the Fermi level and is substantiated by the observed decrease in the resistivity with magnetic field. Electron–magnon scattering process has been invoked to consider the ferromagnetic metallic state below T_{P2}.

Keywords: Magnetoresistance; Variable range hopping; Grain boundaries; Magnetic measurements

1. Introduction

Following the discovery of the colossal magnetoresistance (CMR) effect in manganites perovskites, good deal of research has been focused on the theoretical and experimental work to explore the physical mechanism responsible for this effect and the potential applications in transducers and magnetic sensors [1–4]. A distinct advantage of the manganites is the nearly 100% spin polarization [5] of Mn ions that may induce a large spin dependent magnetoresistance effect. The magnetic and electrical properties have been explained within the framework of the double-exchange (DE) model, which considers the magnetic coupling between Mn^{3+} and Mn^{4+} ions mediated by oxygen anions. Ferromagnetism facilitates the motion of the conduction electrons and lowers the kinetic energy [6]. However, Millis [7] has argued that the DE model alone could not quantitatively account for some of the features of the CMR effect in manganites, such as the magnitude of the resistivity. In polycrystalline samples, a good amount of magnetoresistance down to low temperatures has been observed in contrast to the epitaxial films and the single crystals, where it is higher near the transition temperature and tends to zero at the lower temperatures [8,9]. Effect of ionic radius $\langle r_A \rangle$ of the ions present at the rare-earth site [10], cationic disorder [11], grain boundaries [12,13], grain size [14], oxygen stochiometry [15] has been extensively studied. Several approaches and ideas had been suggested to understand the origin of the magnetoresistance in these manganites. Coey et al. [16] proposed that the charge transport in the manganites arises from the tunneling of the carriers between spin clusters. Ju et al. [17] suggested that the role of the spin polarized tunneling at the polycrystalline grain boundaries should be important in the observed MR behaviour at temperatures below the Curie temperature T_C. Wagner et al. [18] proposed a model where the negative MR scales with the Brillouin function (B) in the ferromagnetic state and square of it in the paramagnetic state of the manganites. De Andres et al. [9] proposed a macroscopic model that assumes the electrical transport is dominated by the evolution with temperature and magnetic field of different kinds of parallely connected channels. Besides these approaches and models, other theories like spin dependent scattering at the grain boundaries [5], in terms of chemical potential [19], electrical and magnetic phase separation [20], magnetic inhomogeneity [21] and percolation

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theory [22] are all reported to understand the MR behaviour and to get higher percentage of MR, in a broad temperature range and under the application of low magnetic field. So far, most of the studies have been focused towards the divalent alkaline-earth ion doped compounds. In contrast, there are few reports on the studies of monovalent alkali-metal doped samples [23–31]. These compounds were synthesized many years ago and tested as oxidation catalysts for exhausts gases for the internal combustion engines [32]. Since their valence state is +1, substitutions with these ions is expected to affect the ratio of the Mn^{3+} (t_{2g}^3 e_g^1: $S=2$) and Mn^{4+} (t_{2g}^3 e_g^0: $S=3/2$), which ultimately would affect the double exchange mechanism and hence, the MR behaviour in a way different from that of the divalent cation-substituted manganites. Boudaya et al. [23] have studied the effect of the monovalent potassium substitution into the lanthanide sites in $La_{1-x}K_xMnO_3$ ($0.05<x<0.2$) and observed that with K doping in $LaMnO_3$, which is antiferromagnetic insulator develops a paramagnetic insulator–ferromagnetic metallic transition which further increases with K doping. On the contrary, Wang et al. [24] found that the I–M transition and Curie temperature both decrease with Li^{1+} doping in $La_{1-x}Li_xMnO_3$ ($0<x<0.3$). They also noticed two insulator–metal transitions in the ρ–T behaviour. They argued that smaller size of Li^{1+} (0.78 Å) is responsible for the peculiar behaviour of resistivity. Bhattacharya et al. [25] noticed a decrease in T_C and T_P with Li doping in $La_{0.7}Ca_{0.3-y}Li_yMnO_3$ and their findings were similar to that of Wang et al. [24]. Roy et al. [26] reported the behaviour of Na^{1+} doped $La_{1-x}Na_xMnO_3$ ($0.07<x<0.20$). They also clearly noticed I–M transition in all Na doped samples which further increases (followed by a drop in the resistivity) to higher temperatures with Na doping. Abdelmoula et al. [27] studied the Na ion doping effect in $La_{0.7}Sr_{0.3-x}Na_xMnO_3$ manganites and noticed that T_C and T_P both systematically shift to lower temperatures with Na content. This behaviour was explained on the basis of the increase in the Mn^{4+} content and decrease in the average size of the A-site cations with alkali substitutions. In contrast to this, Bhattacharya et al. [28] found an increase in the conductivity and corresponding increase in electric and magnetic transitions with Na substitution in $La_{0.7}Ca_{0.3-y}Na_yMnO_3$ ($0<y<0.15$) and attributed to the increase in the Mn^{4+}/Mn^{3+} ratio with increasing Na content. Recently, Das and Dey [30] reported the enhancement of T_C in $La_{1-x}K_xMnO_3$ ($0.05<x<0.15$) prepared by the pyrophoric method. The explanation was based on the phase separation theory assuming the system consisting of regions of FMM and PMI states. The lower temperature upturn in the resistivity was referred to the spin polarized tunneling at the grain boundaries. Therefore, the studies so far have been confined to the doping of smaller ions like Na^{1+}, K^{1+}, Li^{1+} at the rare-earth site and no study, to our knowledge, have been carried out to observe the effect of higher ionic size cations like Cs^{1+} (1.71 Å) in such manganites. We report here, the effect of Cs^{1+} ion doping at Ba-site in $Pr_{2/3}(Ba_{1-x}Cs_x)_{1/3}MnO_3$. The parent compound $Pr_{2/3}Ba_{1/3}MnO_3$ (PBMO) has been chosen as it shows two I–M transitions in the ρ–T behaviour and it would be worthwhile to explore the effect of Cs^{1+} ion doping on these transitions.

2. Experimental procedure

Ceramic samples of $Pr_{2/3}(Ba_{1-x}Cs_x)_{1/3}MnO_3$ ($x=0.0$–0.05) were synthesized from the high purity powders following the conventional solid-state reaction route. The detailed synthesis procedure has been reported elsewhere [12]. It would be appropriate to mention here that x represents only the nominal amount of Cs at Ba-site in the various samples synthesized. X-ray diffraction patterns were obtained using the Philips X-ray diffractometer with Cu Kα radiation ($\lambda=1.54$ Å). The magnetic transition with temperature was recorded through complex susceptibility χ $(=\chi'+i\chi'')$ using AC susceptometer (Lakeshore Model 7000). DC resistance was measured by the standard four-probe technique in the temperature range of 4.2–300 K. The magnetoresistance measurements were carried out using an electromagnet with 0.6 T magnetic field (applied parallel to the direction of the current).

3. Results and discussion

X-ray diffractograms of $Pr_{2/3}(Ba_{1-x}Cs_x)_{1/3}MnO_3$ (PBCMO) exhibit the single-phase nature upto 25% Cs doping, however, small peaks of $BaMnO_3$ appear in the sample with 50% Cs doping. All the samples crystallize in the orthorhombically distorted perovskite structure. The values of the tolerance factor t also confirm this [3] (tolerance factor is measure of the distortion from the cubic structure and defined by $t=d_{A-O}/(\sqrt{2}\,d_{Mn-O})$ where d_{A-O} is the distance between the A-site and the nearest oxygen, if t is less than 0.96, then the structure is orthorhombic which is the case here). Fig. 1 shows the ρ–T behaviour of PBCMO series. The prestine compound PBMO exhibits two insulator–metal like transitions: the sharp transition at 194 K (T_{P1}) followed by a broad transition at 160 K (T_{P2}). The sample also shows the reentrant insulating behaviour at temperatures below 35 K. With Cs^{1+} ion doping there is a systematic decrease in both the transitions, with the corresponding increase in the resistivity. There is an almost disappearance of two transitions with Cs 50% doping which shows only an indication of transition (change of slope) at 145 K. It is conjectured that this may correspond to the higher temperature transition $T_{P1.}$ The average ionic radius $\langle r_A \rangle$ increases with the Cs^{1+} doping in PBMO which implies that the Mn–O–Mn bond angle θ should increase towards 180° resulting in an decrease of the resistivity. However, a reverse trend is observed here as there is a total increase in the resistivity with the Cs^{1+} doping. This indicates that the reduction of the both the transition temperatures and increase in the resistivity cannot be explained on the basis of $\langle r_A \rangle$ alone. Taking the charge neutrality in account, monovalent Cs is expected to strongly shift the average valence state of Mn towards +4, according to ${Pr^{3+}}_{2/3}({Ba_{1-x}}^{2+}{Cs_x}^{1+})_{1/3}{Mn_{(1-x)/3}}^{3+}{Mn_{(1+x)/3}}^{4+}O_3$. Therefore, with every x of Cs^{1+} doping, an amount x of Mn^{3+} will be converted into Mn^{4+} ions, further depleting the e_g band from the charge carriers. As a result, the double exchange mechanism (which is most effective when the Mn^{3+}/Mn^{4+} ratio is 0.67:0.33) gets weakened and consequently, the two transitions shift to lower temperatures. The other factor which seems to account for the observed resistivity temperature behaviour is the larger ionic size mismatch [12] between the ions present at the rare-earth site viz. Pr^{3+}(1.179 Å)/Ba^{2+}(1.47 Å)/Cs^{1+}(1.71 Å). Due to this mismatch, there is a natural strain at the grain boundary that results in two transitions in the undoped compound PBMO [13]. This strain resulting grain boundary effect further gets enhanced