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Intrinsic and extrinsic transport properties of $Pr_{0.67}Ba_{0.33}MnO_3$:Ag_2O composites

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ABSTRACT

We have studied the electrical resistivity, magnetoresistance (MR), and specific heat of $(1-x)$ $Pr_{0.67}Ba_{0.33}MnO_3$:xAg_2O (x = 0–30 mol% Ag_2O) composite manganites. Two insulator–metal-like transitions ($T_{P1} \sim 194$ K and $T_{P2} \sim 160$ K) are observed in the electrical resistivity behaviour of the pristine material $Pr_{0.67}Ba_{0.33}Mn_{O3}$ (PBMO). With Ag_2O addition, T_{P1} becomes sharper whereas T_{P2} disappears beyond 25 mol% Ag_2O addition. Electrical resistivity also decreases in the composites in the whole temperature range of measurement. Intrinsic MR (due to grain) gets enhanced from 22% for the pure sample to ~40% for 30% Ag_2O sample with 0.6 T field. Extrinsic MR (due to grain boundary), however, is found to decrease with Ag_2O addition. Peak MR enhances in composite at the same temperature and at low temperature, beyond the peak, it is almost constant in a large temperature window. Anomaly observed in the specific heat (C_P) near the high temperature insulator–metal transition temperature for various samples signifies the onset of magnetic ordering. Also C_P vs T trend is similar in all the samples indicating that Ag_2O addition does not produce any magnetic inhomogeneity.

1. Introduction

Considerable attention in the past has been paid worldwide to the perovskite manganites studies owing to their exhibition of colossal magnetoresistance (CMR) and other novel properties [1–4]. Generally, a large magnetoresistance (MR) value is often obtained at low temperatures with high magnetic field up to several teslas, which restricts their practical applications. Higher MR at low magnetic field with low electrical resistivity is the requirement of any magnetic device fabricated from these materials. While high MR at low magnetic field would help in reducing the bit size on the recording media (thereby increasing the data storage capacity), at the same time the good electrical conductivity will ensure the better connectivity of the device with external circuitry. Recently, several reports indicated that the metal doping/addition or its oxide addition in manganites was helpful in observing improved peak magnetoresistance at low fields with better electrical resistivity [5–14]. Xiong et al. carried out the addition of Pd in $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ and reported that Pd addition had a little influence on the Curie temperature (T_C) whereas it decreased the electrical resistivity dramatically and shifted the insulator–metal transition temperature (T_P) towards a higher value substantially [5]. They also observed enhanced value of MR near room temperature. Lakshmi and Reddy found that the insulator–metal and para-ferromagnetic transitions in $La_{1-x}Ag_xMnO_3$ (x = 0.05–0.3) systems increased up to x = 0.20 and saturated thereafter [6]. The sample with x = 0.10 was found to exhibit insulating behaviour in the whole temperature range of measurement while the sample with x = 0.20 exhibited two peaks, and the observed behaviour was explained on the basis of phase separation model. Tang et al. investigated the effect of Ag substitution in $NdMnO_3$ manganite and observed that low field MR was enhanced with increasing silver content [7]. Phong et al. [8] and Khiem et al. [9] studied the effect of Ag addition on low-field magnetotransport properties of $La_{2/3}Ca_{1/3}MnO_3$ (LCMO). They observed that with the increasing Ag content, paramagnetic–ferromagnetic (PM–FM) transition temperature remained almost constant and the insulator–metal transition temperature shifted towards higher temperatures. The low field magnetoresistance (LFMR) also increased and was attributed to enhanced spin-polarized tunneling behaviour at low temperatures in the composites. Tripathi et al. compared the results of Ag addition in $La_{0.67}Ca_{0.33}MnO_3$, $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) and $La_{0.67}Ba_{0.33}MnO_3$ (LBMO) and reported that T_P and T_C remained unchanged in case of LSMO and LCMO, while a large suppression was seen in T_C/T_P for LBMO/Ag [10]. About 12% temperature coefficient of resistance (TCR) was observed for 40% Ag added LCMO composite sample near insulator–metal (IM) transition due to better connectivity among grains. Pal et al. [11] reported the

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$La_{0.7}Pb_{0.3}MnO_3$/Ag composites and their study showed that both electrical resistivity and magnetization decreased with Ag addition, particularly for lower concentration of Ag (<10 wt%). Curie temperature increased with Ag addition. A shoulder like nature of the resistivity curve appeared little below T_P for 10 wt% Ag added samples due to the interfacial tunneling in the grains. Similar studies have been reported elsewhere also [12–14]. All such studies as discussed have been carried out in manganite materials which exhibit only single insulator–metal transition in the electrical resistivity. In such materials only intrinsic properties are important. However, PBMO is such a material that exhibits two insulator–metal transitions (due to large grain boundary effects) and it would be interesting to examine how the metal oxide addition affects both the intrinsic and extrinsic properties and the ensuing low field magnetoresistance of PBMO manganite [15]. For this purpose Ag_2O addition has been attempted in PBMO and its effect on intrinsic and extrinsic transport properties are presented here.

2. Experimental details

$(1-x)$PBMO + $x$$Ag_2O$ (x = 0, 5 10, 20, 25, 27 and 30 mol%) polycrystalline composites have been synthesized in two steps using the conventional solid-state reaction method. First, the polycrystalline powder of PBMO was obtained through several calcinations with intermediate grindings and final sintering at 1260 °C for 25 h. Later, Ag_2O was added to the calcined PBMO powder in different mole ratios and the grounded mixtures were again heat treated at 1260 °C for about 2 h to avoid any diffusion of Ag inside PBMO matrix. Electrical resistivity with and without magnetic field (0.6 T) was recorded using four-probe method from 300 to 77 K with field applied parallel to the current direction. Heat capacity measurements have been carried out on physical properties measurement system (PPMS) (Quantum Design, USA) from 300 K down to 5 K.

3. Results and discussion

Fig. 1 shows the XRD patterns of the pristine and 30 mol% Ag_2O added PBMO manganite. The pristine sample PBMO is single phase and has been indexed having the orthorhombic structure with *Pbnm* space group. In the composite manganite material, besides all the characteristics peaks of pure sample, peaks related to metallic silver are also observed. Due to low dissociation temperature of Ag_2O (350 °C) it gets converted into metallic silver during sintering of the composite system and the XRD pattern confirms this. The electrical resistivity variation with temperature is shown in Fig. 2. There is a large ionic size difference between Pr^{+3}(1.179 Å) and Ba^{+2} (1.47 Å) of the PBMO material due to which the lattices inside the grain feel a good deal of strain. However, this strain is transferred to the grain boundaries to achieve the minimum energy configuration for equilibrium. The transferred strain at the

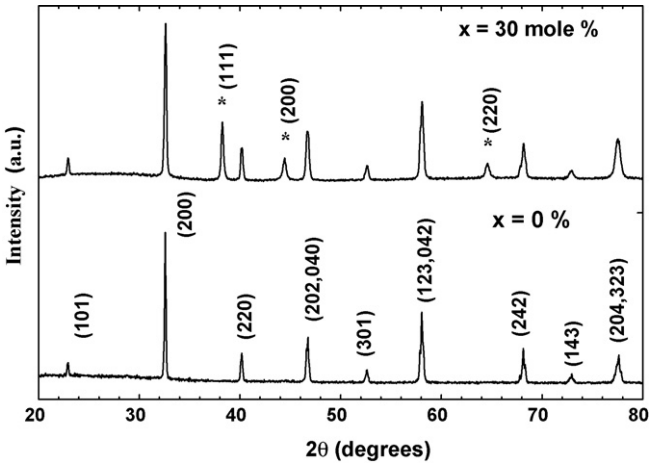

Fig. 1. XRD patterns of pure and 30 mol% Ag_2O added PBMO manganite materials.

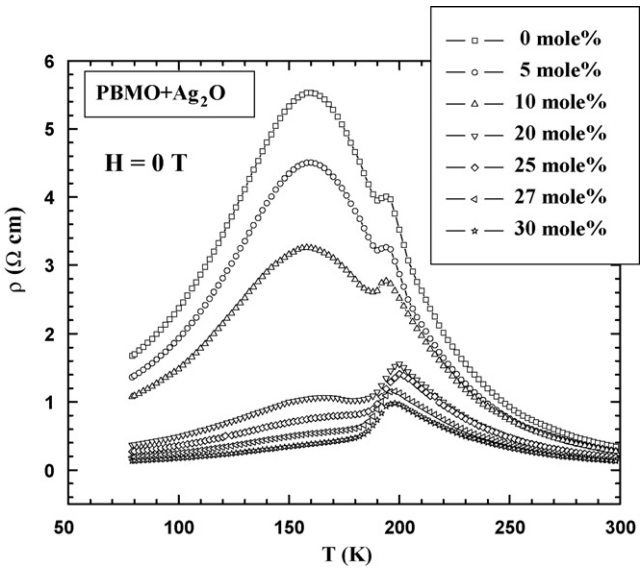

Fig. 2. Electrical resistivity variation with temperature of the composites.

grain boundary tilts the MnO_6 octahedron randomly rendering the electron transfer more difficult from Mn site to the other in the grain boundary region. Thus, the transitions: one from the grain and other from the grain boundary separate out resulting in two insulator–metal transitions in PBMO [16]. T_{P1} (∼194 K) of the pristine PBMO sample remains almost unchanged with Ag_2O addition from which we can infer that Ag has not substituted at the Pr/Ba-site in PBMO and remains at the grain boundary only. On the other hand, T_{P2} disappears in the samples with more than 25 mol% Ag_2O. Significantly, the electrical resistivity is also seen to decrease in the whole temperature range. Therefore, the presence of metallic silver at the grain boundary makes it conducting leading to a decrease in the total resistivity (sum of grain and grain boundary resistivities) in the composite manganites. In some reports decrease of electrical resistivity has been noticed only up to 27% Ag_2O and increasing thereafter [17,18]. It would appear to be a safe conjecture to assume that in the present system Ag is probably more tightly bound and does not volatilize even up to 30 mol% addition. There are two factors responsible for the observed resistivity behaviour of the composite samples. Firstly, oxygen liberated from the breaking of Ag–O bond is likely to move inside the grains, compensating the oxygen loss there, if any, by filling the oxygen vacancy in the bond between Mn^{+3} and Mn^{+4} ions. This would make the electron transfer easier, resulting in the decrease of electrical resistivity. Secondly, presence of Ag will make the grain boundary (GB) more conducting, by opening the new conducting channels among the PBMO grains and thus leading to a decrease in the spin dependent/independent scattering. The barrier formed by the disorder/strain at the grain boundary decreases or rather disappears with higher concentration of Ag_2O.

Fig. 3 shows the magnetoresistance behaviour of the composite samples under 0.6 T applied magnetic field. It is evident that the intrinsic MR (related to grain) is a peaked function of temperature and gets enhanced from 22% for pristine PBMO to 40% for 30%Ag_2O added sample. The extrinsic MR (MR related to grain boundary and generally occurs at low temperatures) decreases in composites. This behaviour can be understood from the fact that spin dependent scattering at the grain boundary decreases in the composites, which is responsible for the extrinsic MR in polycrystalline manganites. The MR behaviour below the peak is constant in a large temperature window which is good from the application point of view. It is also worthwhile to note that intrinsic MR

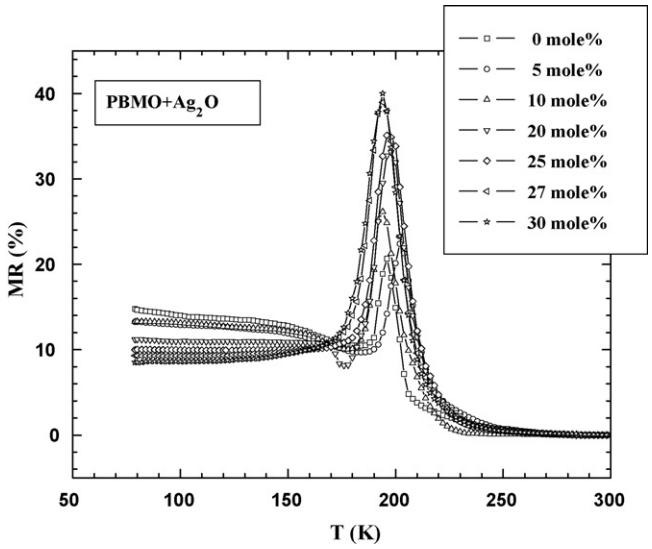

Fig. 3. Magnetoresistance variation with temperature of the composites.

has increased near the I–M transition temperature and the Ag_2O addition has not shifted the peak of I–M towards low temperatures as is generally observed in the case of insulating oxides/manganite composites [19–22]. Thus, enhancement of peak MR in a very narrow temperature window (though the temperature is lower than the room temperature) and the constant value of MR below the MR peak are the salient features of these particular composites systems.

In order to investigate the effect of Ag_2O addition on the thermal properties especially specific heat we carried out the heat capacity (C_P) measurement on the composite materials and the results are shown in Fig. 4. The behaviour of all the samples is nearly similar. A lamda-like peak is observed in all the samples at ~186 K which is close to T_{P1}. This indicates that the peak is due to the onset of magnetic ordering in the samples because there is a drastic change in the value of spontaneous magnetization in passing through the paramagnetic state to the ferromagnetic state. From the anomaly in specific heat, it is also clear that paramagnetic-ferromagnetic transition in such manganites is second order type phase transition. Further, no anomaly corresponding to T_{P2} is observed in C_P vs T measurement which can be understood on the basis that thermal

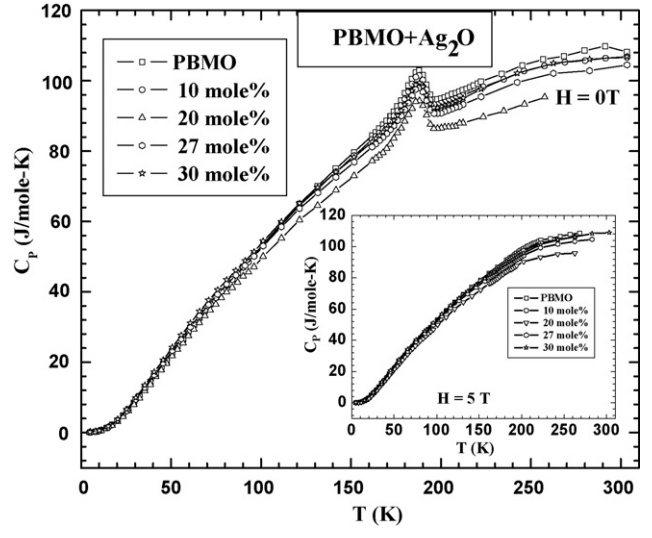

Fig. 4. Specific heat variation with temperature of the composites. Inset shows the variation under 5 T magnetic field.

measurements being volume averaged mask the grain boundary effects here which otherwise are observed in electrical properties. The area under the peak does not change significantly in the composites implying that presence of silver does not disturb the magnetic nature of the sample and also does not produce any magnetic inhomogeneity [23]. Inset of Fig. 4 depicts the effect of 5 T magnetic field application on the specific heat variation of the composites. It can be observed that with the magnetic field application the anomaly near the transition temperature is almost suppressed with a shift towards high temperature side. In rest of the temperature range the specific heat behaviour is identical to the zero magnetic field data. These materials with such thermal behaviour and with proper substitutions can be made suitable candidates for magnetocaloric applications.

4. Conclusions

Effect of Ag_2O addition on the intrinsic and extrinsic transport properties of $Pr_{0.67}Ba_{0.33}MnO_3$ manganite has been investigated. Two insulator–metal-like transitions ($T_{P1} \sim 194$ K and $T_{P2} \sim 160$ K) are observed in the electrical resistivity behaviour of the pristine sample $Pr_{0.67}Ba_{0.33}MnO_3$ (PBMO). With Ag_2O addition, T_{P1} becomes sharper whereas T_{P2} disappears beyond 25 mol% Ag_2O addition. The observed electrical resistivity decreases in the composites in the whole temperature range of measurement has been viewed in terms of the easier electron transfer by virtue of the release of oxygen from Ag–O bond and opening of the new conducting channels among the PBMO grains with metallic silver. While intrinsic MR enhances up to ~40% in the composites, extrinsic MR decreases. Intrinsic MR peak did not shift to low temperatures in the composites as has earlier been observed in manganite composites with insulating oxides. Extrinsic MR remained constant with temperature variation which is good from the application point of view. Specific heat measurement on the composites revealed that the nature of C_P vs T is almost immune to Ag_2O addition and no signature of extrinsic effects was observed.

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