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Letter to the editor

Search for room temperature high-TCR manganite/silver composites

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Abstract

We have synthesized $La_{0.7}Ba_{0.3}MnO_3$ (LBMO):wt%Ag_x and $La_{0.7}Sr_{0.3}MnO_3$ (LSMO):wt%Ag_x composites with $x = 0.0$, 0.1, 0.2, 0.3 and 0.4 at different sintering temperatures of 1300 and 1400 °C by solid-state reaction route. In our previous work [Awana et al. Solid State Commun. 140 (2006) 410] on $La_{2/3}Ca_{1/3}MnO_3$ (LCMO):Ag_x ($x = 0.0$, 0.1, 0.2, 0.3, 0.4) composites, we reported about 12% temperature coefficient of resistance (TCR) for $Ag_{0.4}$ samples near metal–insulator (MI) transition, which was explained on the basis of better grains connectivity. A sharp MI transition results in high TCR. Such high-TCR material can be used as a bolometer or infrared detector at room temperature. In the present work, it is shown that the TCR is improved with Ag addition for both LBMO:wt%Ag_x and LSMO:wt%Ag_x composites. In addition to improvement in TCR, high MR is also achieved in the vicinity of room temperature.

Keywords: Manganites; Magneto-resistance; Ferromagnetism; MR; TCR

1. Introduction

Since after their invention [1,2], the magneto-resistive manganites with general formula $RE_{1-x}AE_xMnO_3$ (RE = La, Nd, Pr etc. and AE = Ca, Ba, Sr etc.) have been a topic of great interest. The rich electronic phase diagram showing a variety of unusual transport properties has been discussed previously by several researchers [1–6]. The most striking feature of these manganites that stimulated intense research activity is colossal magneto-resistance (CMR) effect observed around the metal–insulator (MI)/ferromagnetic–paramagnetic (FM–PM) transition [4,5]. CMR effect is known to depend crucially on the Mn^{4+}/Mn^{3+} ratio, which is controlled by the doping level (x) and the oxygen content of these compounds [4–6]. These compounds have many technological applications, one of them being as infrared (IR) detectors. In case of IR detectors, significantly large temperature coefficient of resistivity (TCR) in the vicinity of room temperature is pre-requisite [7–10]. Unfortunately, many of these manganites do not have such required characteristics. In search for room temperature TCR by tailoring the material's characteristics, we have explored manganite–silver (Ag) composites. In our previous work on $La_{0.7}Ca_{0.3}MnO_3$ (LCMO):Ag_x, we had reported a high TCR of 12% near its metal–insulator transition temperature (T_{MI}) at around 266 K [11]. In LCMO:Ag_x composites, though high TCR is achieved around transition temperature (266 K), it is below room temperature (300 K). In the present study, we have extended a similar work to two other mangnites, namely $La_{0.7}Ba_{0.3}MnO_3$ (LBMO) and $La_{0.7}Sr_{0.3}MnO_3$ (LSMO). We have synthesized and investigated the physical properties of $La_{0.7}A_{0.3}MnO_3$:Ag_x (A = Ca, Ba, and Sr) composites. It is observed that TCR is improved with Ag addition for both LBMO:wt%Ag_x and LSMO:wt%Ag_x composites. In addition to improvement in TCR, high MR is also achieved in the vicinity of room temperature.

2. Experimental details

$La_{0.7}A_{0.3}MnO_3$:wt%Ag_x (A = Ba, Ca, Sr, and $x = 0.0$, 0.1, 0.2, 0.3, 0.4) composites were synthesized by solid-state reaction route using high-purity powders of La_2O_3, $BaCO_3$, $SrCO_3$, MnO_2, and Ag in stoichiometric ratio and grounded thoroughly. All the mixed powders were calcined

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at 1000, 1100 °C till 1200 °C for 24 h with intermediate grinding. These calcined powders were palletized and finally palletized ceramics were annealed in air for 48 h in two batches: one at 1300 °C and the other at 1400 °C, respectively. In the end, these final pellets were annealed in the flow of oxygen at 800 °C for 48 h and subsequently cooled to room temperature. The structure and phase purity of $La_{0.7}A_{0.3}MnO_3$:wt%Ag_x composites were checked by powder X-ray diffraction (XRD) using Ni-filtered CuK_α radiation. Isothermal magnetization curves were obtained with applied fields of up to ± 50 kOe at different temperatures ($T = 100$, 200, and 300 K). The transport and magneto-transport measurements were carried out in a commercial apparatus (PPMS-6600, Quantum Design) between 5 and 400 K in magnetic fields up to 70 kOe.

3. Results and discussion

Fig. 1 depicts the room temperature XRD patterns of LSMO:wt%Ag_x, and LBMO: wt%Ag_x for $x = 0.0$ and 0.4. Both samples are polycrystalline single phase. The lattice parameters do not show any significant change with Ag addition. Detailed studies related to lattice parameter variation, magnetization, and magneto-transport of LBMO:wt%Ag_x are reported elsewhere [12]. In the present report, our aim is to directly inter-compare the best characteristic (room temperature TCR and MR) samples of LCMO:wt%Ag_x [11], LBMO wt%Ag_x [12] and LSMO:wt%Ag_x.

Temperature dependence of resistivity of the pure and Ag (0.4) samples of LCMO, LBMO, and LSMO is plotted in Fig. 2. For the sake of convenience we have plotted the normalized resistivity. Pristine samples of LCMO, LBMO, and LSMO exhibited the usual MI transition at T_{MI}~266, 331 and 398 K, respectively. These T_{MI} values are in general agreement with reported literature [4,5]. The resistivity curve of LBMO shows some anomaly. It has two MI transitions, one being the intrinsic one at 331 K, followed by a broad one at T~270 K. In case of LBMO:$Ag_{0.4}$ only one T_{MI} is observed at around T~270 K. Further, it is seen that in general the T_{MI} decreases with increase in x for LBMO:wt%Ag_x [12]. On the other hand, the transition temperature remains nearly invariant for LSMO:Ag_x; this is also true for LCMO:Ag_x [11]. This suggests that Ag addition induces modification in the grain boundary features in LBMO, but has no such effect in LSMO and LCMO. Thus, we conjecture that the Ag addition may play different roles in different manganites.

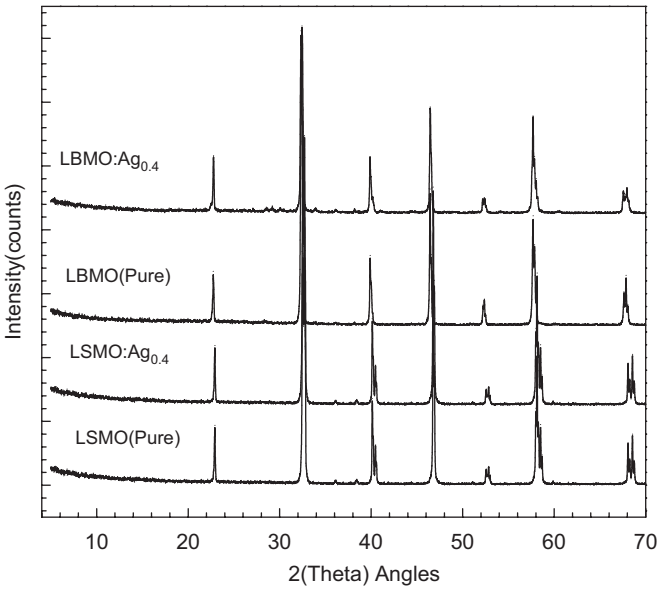

Fig. 1. X-ray diffraction patterns of $La_{0.7}Sr_{0.3}MnO_3$(LSMO), $La_{0.7}Sr_{0.3}MnO_3$:$Ag_{0.4}$, $La_{0.7}Ba_{0.3}MnO_3$(LBMO) and $La_{0.7}Ba_{0.3}MnO_3$:$Ag_{0.4}$.

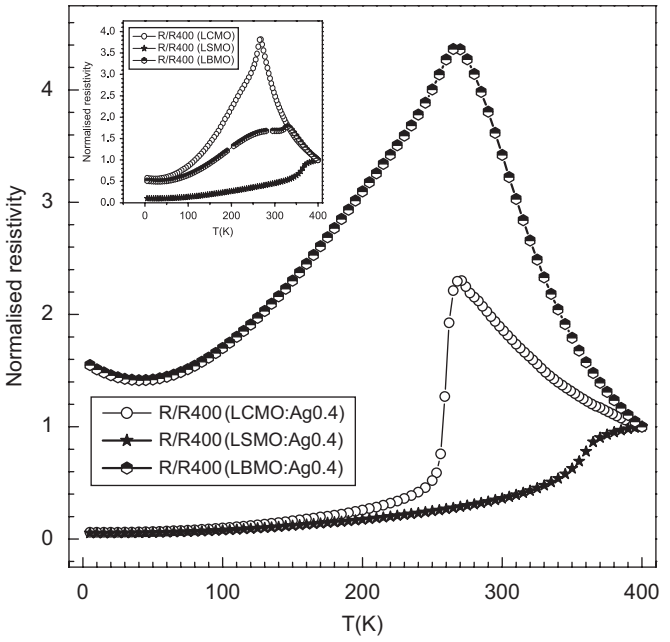

Fig. 2. Normalized resistivity versus temperature (R–T) curves of LCMO:$Ag_{0.4}$, LSMO:$Ag_{0.4}$, LBMO:$Ag_{0.4}$; inset shows R–T curves of LCMO, LSMO, and LBMO.

TCR (%), defined as $1/R[(d(R)/dT)] \times 100$ (R stands for resistance and T stands for temperature), of some of the LBMO, LCMO, and LSMO:wt%Ag_x composites is presented in Fig. 3. The maximum TCR shows a dramatic enhancement due to Ag addition and in fact it increases from 1.5% for LCMO to 12% for LCMO:$Ag_{0.4}$. Interestingly, this is not the case with LBMO and LSMO. In pristine LBMO and LSMO the maximum value of TCR is 0.41% and 1.8%, respectively, and this increases to 1.8% for LBMO:$Ag_{0.3}$ and 2.24% for LSMO:$Ag_{0.4}$. The TCR maximum decreased substantially for LBMO:Ag_x and LSMO:Ag_x. Further, these values are still too low in comparison with the TCR of LCMO:$Ag_{0.4}$ sample. The improved TCR value for silver-added samples may have its origin in better grain connectivity and growth, which is somehow enhanced by silver addition [10–12]. Interestingly, though the TCR is low for silver composites of LBMO and LSMO in comparison with LCMO, the