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Electrical, thermal and magnetic studies on Bi-substituted LSMO manganites

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ABSTRACT

In the present investigation detailed electrical, magnetic and thermoelectric measurements on Bi-doped $L_{0.6-x}Bi_xSr_{0.4}MnO_3$ $(0 \le x \le 0.3)$ manganites have been done. All the samples are single phased. The metal-insulator transition temperatures (T_{MI}) as well as the Curie temperature (T_C) are both found to decrease with Bi-content. Magneto-resistance (MR) data shows that MR (%) increases with Bi-content thereby showing it can be used in magnetic memory based devices. Resistivity data shows that small polaron hopping (SPH) model is valid in high temperature regime. Low temperature resistivity data depicts that electron–electron scattering is mainly responsible for the conduction mechanism. High temperature thermoelectric power (TEP) data reaffirms the validity of SPH model.

1. Introduction

Ever since the discovery of Colossal Magneto-resistance (CMR) in manganites with general formula $La_{1-x}A_xMnO_3$ (A=Sr, Ca Ba etc), lot of work has been done by various researchers with the aim to understand physics of these materials and to explore possible applications [1–5]. These compounds have pervoskite structure and display a variety of phases which depend on their stoichiometry. In particular, hole doped manganites $La_{1-x}Sr_xMnO_3$ (LSMO) are significant because, they have high transition temperatures (≈ 370 K) and exhibit large magneto-resistance (MR). Further, these compounds have attracted extra attention for doping levels $0.2 < x < 0.5$, as they have fascinating physical properties like metal-insulator transition, CMR effect and paramagnetic–ferromagnetic transition.

It is well-established that LSMO is a promising candidate for practical applications. Liu et al. [6] have shown that LSMO is a good material for non-volatile memory based applications. Recently Wu et al. [7] have reported that LSMO along with yttria-stablilized bismuth oxides can be used for intermediate-temperature solid oxide fuel cells. Liu et al. [8] have demonstrated the use of LSMO suspended micro-bridges for fabrication of un-cooled bolometers.

There are several reports on effect of substitution of La by various rare-earth elements like Pr, Eu etc. [9,10]. It is seen that Pr-doping at La site introduces local structural distortions which is attributed to large ionic size mismatch at the A-site [9]. Partial substitution of Eu at La-site increases temperature coefficient of resistance (TCR) as well as magneto-resistance which is attributed to enhancement of lattice distortion introduced by Eu-doping [10]. Of late, Bi-doped manganites have captivated researchers due to the observation of large MR and large magneto caloric effect (MCE) which make them potential candidates as refrigerant materials [11–17]. It well-known that there are two types of magnetic materials which demonstrate large MCE viz. those showing first order and second order phase transitions. The compounds investigated in this work belong to the latter type. It may be mentioned that magnetic materials showing second order transitions are more suitable for MCE applications than those showing first order transition.

Recently we have reported electrical, magnetic and thermal properties of Bi-doped $La_{0.7-x}Bi_xSr_{0.3}MnO_3$ compounds [14]. It is observed that the metal-insulator transition temperature T_{MI} and Curie temperature T_C decrease with Bi-content [14]. The magneto-resistance is found to increase with Bi-doping which demonstrates that Bi-doping enhances use of these compounds for MR based applications. It would thus be exciting to study electrical, thermal and magnetic properties of $La_{0.6-x}Bi_xSr_{0.4}MnO_3$ compounds. Such studies will give information about the behavior of dependence of MR with doping. In addition to this we can also see if Mn-doping can enhance *TCR* of these materials which can possibly make them potential candidates for TCR based applications. Keeping this in

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mind we report electrical, thermoelectric and magnetic properties of Bi-doped compounds $L_{0.6-x}Bi_xSr_{0.3}MnO_3$ ($0 \le x \le 0.3$).

2. Experimental details

The samples of $La_{0.6-x}Bi_xSr_{0.4}MnO_3$ ($0 \le x \le 0.3$) were prepared by standard ceramic method. High purity powders of La_2O_3, Bi_2O_3, $SrCO_3$, and Mn_2O_3 (99.9% purity) were mixed and calcinated at 900 °C for 12 h. This process was repeated three times to obtain homogenous mixture. Finally the calcined powder was pressed into rectangular pellets, heated at 1100 °C for 24 h and slowly cooled to room temperature. The samples were subjected to X-ray diffraction (XRD) at room temperature. For structural analysis, we have employed Rietveld refinement method and it is found that all the samples are single phased with rhombohedral structure with space group pertaining to R-3 C. The X-ray diffraction patterns along with the simulated plots for typical samples of $La_{0.6-x}Bi_xSr_{0.4}MnO_3$ are depicted in Fig. 1. The Rietveld refined structural parameters are listed in table 1.

Resistivity and magneto-resistance measurements were performed employing the usual four probe method in the temperature range 10–375 K using a superconducting magnetic system (Oxford Spectromag). Thermo-electric power (S) measurement was performed in the temperature range of 5–300 K, using differential dc method. The details are given elsewhere [18]. The magnetic studies were carried out using a SQUID VSM dc magnetometer.

3. Results and discussions

3.1. Resistivity measurement

The variation of resistivity with temperature for $La_{0.6-x}Bi_xSr_{0.4}MnO_3$ ($0 \le x \le 0.3$) manganites is shown in Fig. 2. The resistivity behavior for pristine sample is shown in the insets of Fig. 2. All the samples exhibit metal–insulator transition around a critical temperature T_{MI}. We observe that the metal–insulator transition temperature, T_{MI} decreases with increase in Bi-content. The pristine sample exhibits metal-insulating transition around 360 K. For the sample with $x=0.1$ the observed T_{MI} is 239 K, which reduces to 87 K for the sample with $x=0.3$ We now explain the cause for decrease in T_{MI} with Bi-concentration which is essentially due to reduction in Mn^{3+}–O–Mn^{4+} bond length with increase in Bi-content. This in turn reduces the double exchange coupling via the intermediate oxygen ion, thus the transition temperature is found to decrease with increase in Bi-content.

Temperature dependence of resistivity is generally classified into two regions, viz. low temperature ($T < T_{MI}$) and high temperature ($T > T_{MI}$) regimes. In order to understand the nature of conduction mechanism below T_{MI}, the experimental resistivity data in low temperature metallic region for $La_{0.7-x}Bi_xSr_{0.4}MnO_3$ samples are fitted to the well-known equation [19],

$$\rho = \rho_0 + \rho_2 T^2 + \rho_{4.5} T^{4.5} \tag{1}$$

where ρ_0 is the residual resistivity; the terms $\rho_2 T^2$, $\rho_{4.5} T^{4.5}$ are respectively due to electron–electron scattering and two magnon scattering processes in ferromagnetic (FM) state. In the present work, we have fitted the low temperature experimental data of resistivity to Eq.(1) and it is observed that the data fits well with the above equation which demonstrates the significance of electron–electron and electron–magnon scattering processes in explaining the phenomenon of electrical conduction [11]. From the fitting, it is observed that $\rho_o > \rho_2\ T^2 > \ \rho_{4.5}\ T^{4.5}$ which evidently demonstrates that electron–electron scattering processes play vital part in elucidating the conduction process. Table 2 shows the fitting parameters obtained using Eq. (1). One can see that ρ_0 increases with Bi-content which means that the residual resistivity is enhanced due to introduction of Bi-doping which is shows that Bi-doping is introducing scattering centers. One observes that ρ_2 increases with Bi-concentration, which demonstrates that electron–electron scattering also increases with doping. In a similar manner, $\rho_{4.5}$ also increases with Bi-content demonstrating that electron–magnon scattering increases with Bi-doping.

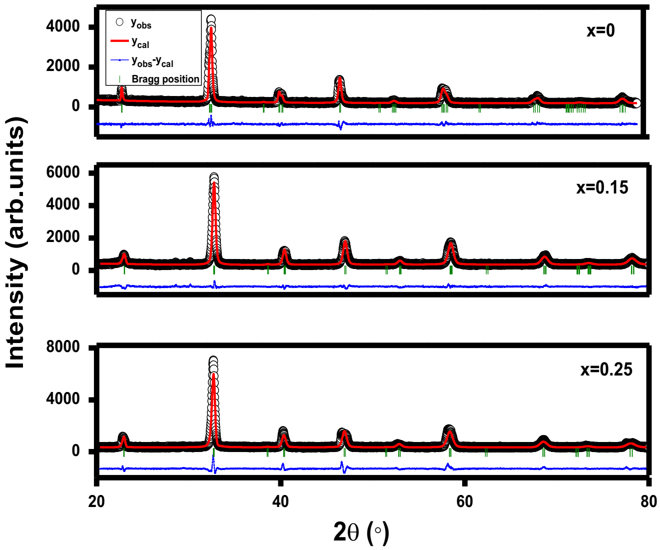

Fig. 1. Rietveld refined XRD for typical samples of $La_{0.6-x}Bi_xSr_{0.4}MnO_3$ ($x=0$, 0.15, and 0.25).

It is customary to describe the high temperature resistivity data (above T_{MI}) using small polaron hopping (SPH) model [20] which is given by,

$$\rho = \rho_0 T \exp\left(\frac{E_\rho}{k_B T}\right) \tag{2}$$

where ρ_0 is a constant, E_ρ is the activation energy, and k_B is the Boltzmann constant. The high temperature experimental data of electrical resistivity is fitted using Eq. 2. The estimated values of activation energy (E_ρ) are given in Table 2.

It is well-known that the parameter temperature coefficient of resistance (TCR) is defined as $TCR\% = 100 \times (d\rho/dT)/\rho$. TCR is an important factor specially for device applications for improving sensitivity of infrared bolometers. In this study *TCR* does not change significantly for small doping levels of bismuth ($x \le 0.2$); on contrary, for samples with $x=0.25$ and 0.3 a significant increase is seen near room temperatures as shown in Fig.3. In fact the TCR values for these samples are comparable to some common materials used for infrared detectors like vanadium oxide and amorphous silicon [21]. This demonstrates that Bi-doped LSMO manganites are good candidates for infrared detectors.

For the present work, we have used applied external magnetic field of 8 T and measured resistivity in the presence of magnetic field. Magneto-resistance is defined as the relative change in electrical resistivity by the application of external magnetic field and is given by $MR\ (\%) = [(\rho_o - \rho_H\ )/\rho_H\ ] \times 100$. We observe that application of magnetic field suppresses electrical resistivity for all the samples under present studies. Fig. 4 shows the temperature dependence of MR of the samples $La_{0.6-x}Bi_xSr_{0.4}MnO_3$ ($0 \le x \le 0.3$). It is seen that MR (%) decreases with increasing temperature; on contrary, MR (%) increases with Bi-content. In fact