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Bi-doping effects on the transport properties in $La_{0.7-x}Bi_xSr_{0.3}MnO_y$

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Abstract

DC electrical resistivity (ρ) and thermoelectric power (TEP) of $La_{0.7-x}Bi_xSr_{0.3}MnO_y$ ($x=0$, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 at%) manganites have been studied. The resistivity of the samples shows a metal–semiconductor (insulator) transition for $x \geqslant 0.2$. For $x=0.25$ and 0.3 at%, the compounds exhibit semiconducting behavior down to $T=83$ K. The TEP for $x \leqslant 0.2$ at% is of positive sign above the transition temperature (T_m); it decreases below T_m and has changed sign for $T>300$ K. The replacement of the La ion by Bi ion results in a reduction of transition temperature (T_m) (M–S transition) and increasing the value of both ρ and TEP. The value of resistivity activation energy (E_ρ) and TEP activation energy (E_s) calculated above T_m.

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Keywords: Metal–semiconductor transition; Thermoelectric power; Electrical resistivity

1. Introduction

Recent investigations of the phenomenon of giant magnetoresistance (GMR) in perovskite of the type have clearly established that these pervoskite oxides undergo an insulator to metal like (I–M) transition at a temperature T_m which is close to the ferromagnetic transition temperature T_c [1–8]. Doping holes to $LaMnO_3$ makes it a ferromagnetic metal and a structural phase transition from the orthorhombic to the rhombohedral structure takes place [9]. The transition to the ferromagnetic metal is thought to be due to the double exchange interaction between Mn^{3+} and Mn^{4+} through the doped holes. It is known that by doping the Bismuth to this system the electrical resistivity and magneto-optical effect change [10], but the details are not clear.

In order to reveal the mechanism of magneto-transport, Righi et al. [11] have investigated the Bi-doping effects on the structural, transport and

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magnetic properties of $La_{0.7-x}Bi_xCa_{0.3}MnO_x$, and have found that the dopant Bi causes structure change and decreases the T_m. As we know, there are many different properties in $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xMnO_3$, such as metal–insulator transition temperature at optimal doping and the critical doping concentration for the presence of ferromagnetism [12,13]. So we have investigated systematically the Bi-doping effect on transport in $La_{0.7-x}Bi_xSr_{0.3}MnO_3$ with the expectation that it will provide new insight and interesting physics.

2. Experimental

All samples reported in the present study were synthesized by a standard solid-state reaction procedure. Stoichiometric compositions of $La_{0.7-x}Bi_xSr_{0.3}MnO_y$ ($x=0$, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 at%) were prepared by mixing equimolar amounts of La_2O_3, Bi_2O_3, SrO and $MnCO_3$ respectively (all having greater than 99.99% purity). The powders of these oxides and the carbonate were mixed and were finely ground in an electric grinder for 30 min. After grinding, the powders were pressed into pellets with a pressure of 2 tonnes cm^{-2} and calcined at 1173 K for 8 h. Followed by cooling to room temperature, they were reground and again pressed into pellets with a pressure of 7 tonnes cm^{-2} and subsequently annealed at 1373 K for 6 h. Samples with $x\leqslant 0.2$ were checked by X-ray powder diffraction analysis indicating the presence of a unique phase with perovskite-type structure.

Resistivity measurements were performed in a commercial variable temperature liquid nitrogen cryostat. The electrical resistance was measured by using the stand four-probe technique using an air-drying conducting silver paste. The sample temperature was monitored by calibrated Pt-100 thermocouple in the range 83–373 K. The temperature accuracy was 0.5 K. A constant current in the range of 100 μA–10 mA was supplied by the current source and voltage across the sample was measured with a digital voltmeter. The thermoelectric power measurements were carried out using the sample two-heater method with copper electrodes. The difference in temperature between the two opposite surfaces of the sample was adjusted to be equal to 3 K during the entire measurement. The thermoelectric voltage was measured by a digital voltmeter with sensitivity 1 μV.

3. Results and discussion

In Fig. 1, the X-ray diffraction patterns for the series of compounds ($La_{0.7-x}Bi_xSr_{0.3}MnO_y$ with $x\leqslant 0.2$) are shown. A remarkable fact from the comparison of these patterns is that the systematic substitution of La by Bi does not produce relevant effect on them. In general, all the peaks for five samples satisfy the La–Sr–Mn–O phase. In addition, some weak impurity peaks from SrMnO, BiSrMnO and BiO phases were observed as marked in Fig. 1. The crystal structure for the compositions $La_{0.7-x}Bi_xSr_{0.3}MnO_y$ was found to be rhombohedral structure [14–16]. Lattice parameter were calculated and tabulated in Table 1. As seen in Table 1, by increasing the amount of Bi, a very slight increase of the cell parameters a and b were observed for $x\geqslant 0.15$, but the cell parameter c decreases slightly for $x>0.15$. This almost perfect match can be explained considering the similar

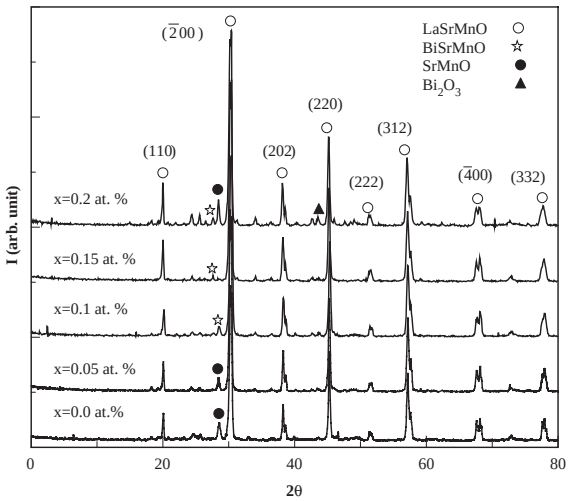

Fig. 1. X-ray diffraction patterns of $La_{0.7-x}Bi_xSr_{0.3}MnO_y$ ($x\leqslant 0.2$).

Table 1
The lattice parameters

Bi content	0.0	0.05	0.1	0.15	0.2
a (Å)	6.034	6.043	6.05	6.052	6.051
b (Å)	6.034	6.044	6.051	6.052	6.051
c (Å)	7.744	7.76	7.76	7.748	7.74

dimension of the two cations La^{3+}(ionic radius = 1.302 Å) and Bi^{3+}(ionic radius = 1.30 Å) [17].

Fig. 2 shows the variation of resistivity with temperature for $La_{0.7-x}Bi_xSr_{0.3}MnO_y$. Obviously, the resistivity increases with Bi doping. However, we can expect that the Bi content increase does not only decrease the La content, but also the charge carrier density [18]. Therefore, the La/Bi mixture ions play a prominent role in controlling the resistivity. On other hand, the figure shows that the peak transition (M–S) for Bi $\leqslant$ 0.2 at%, decreases with the increase of Bi. These compounds have a distinct metallic phase below the transition temperature (T_m) and above this temperature they become semiconducting. The (M–S) transition is believed to arise from the increase of Mn–O–Mn bonding angle [19]. Within the semiconducting region (above T_m) an Arrhenius equation was applied in order to determine the small thermal activation energy E_ρ of the electrical resistivity then, omit (E_ρ is the activation energy for conduction) where

$$\rho = \rho_0 \exp(-E_\rho/kT), \quad (1)$$

E_ρ is the activation energy for conduction, k is the Boltzmann's constant.

Using Eq. (1), we calculated E_ρ and plotted in Fig. 3. Fig. 3 shows that the values of E_ρ decrease with increasing Bi content; the larger values of E_ρ agree with previous work [20–22].

Fig. 4 shows the dependence of Seebeck coefficient (S) on the temperature for $x \leqslant 0.2$ at%. The TEP of these samples, depicted in Fig. 4, is positive at low temperatures, suggesting hole conduction, but becomes negative at high temperatures ($T > 300$ K). The transition from metallic to semiconducting behaviour (M–S) is clearly seen in the figure. Above the M–S transition temperature, the value of S increases with increasing Bi

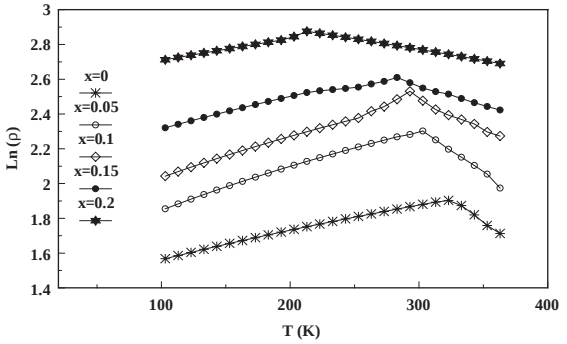

Fig. 2. Ln (ρ) versus temperature for $La_{0.7-x}Bi_xSr_{0.3}MnO_y$.

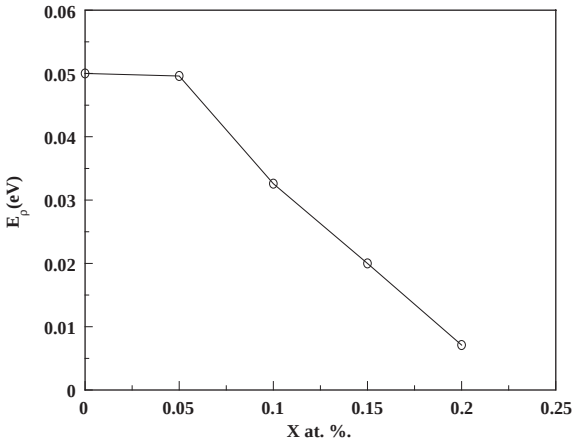

Fig. 3. The dependence of E_ρ (eV) on the composition ($x \leqslant 0.2$ at%).

doping, below the transition this is also true except for $x = 0.15$ at%. In addition, below the transition S decreases rapidly. When the resistivity is thermally activated, the thermopower may also be expected to show semiconducting-like behavior. The values of activation energy E_s of Seebeck coefficient for the semiconductor behavior were

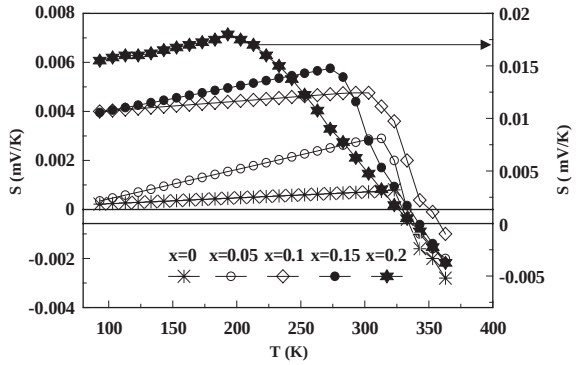

Fig. 4. Thermoelectric Power $S(T)$ of $La_{0.7-x}Bi_xSr_{0.3}MnO_y$ ($x \leqslant 0.2$).

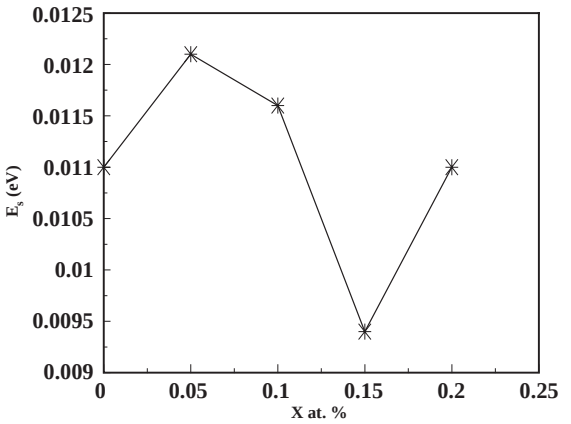

Fig. 5. The dependence of E_s (eV) on the composition ($x \leqslant 0.2$ at%).

calculated from the formula

$$S = \pm \frac{k}{e}\left(\frac{\Delta E_s}{kT} + B\right), \tag{2}$$

and plotted in Fig. 5.

As can be seen in Fig. 5, the values of E_s are very small and have a maximum value at $x = 0.1$ at% and has a minimum value at $x = 0.15$ at%. As shown in Figs. 3 and 5, we notice that the values of E_s are of the order of E_ρ for all samples except the highest Bi doping, this is the general trend in crystalline semiconductors.

If conduction in GMR materials is by small polarons, as suggested by Millis et al. [23], the charge carriers move by hopping between neighboring sites [24]. At high T hopping is *thermally activated* and the mobility μ obeys the relation $\mu \sim \exp(-W_H/kT)$, where W_H is the hopping energy and measures one half of the polaron formation energy [25]. This leads us to consider variable range hopping (VRH) conduction, where

$$\rho \sim \exp[(T_0/T)^{-1/4}], \tag{3}$$

and the thermopower varies as $S_{VRH} \sim T^{1/2}$, tending to zero as $T \to 0$. This behavior is to be expected only at low temperature. For hopping to nearest neighbors, on the other hand, S_{VRH} should behave again as $1/T$.

The results obtained from DC resistivity and TEP of $x \leqslant 0.2$ at% are shown in Fig. 6. As it is seen in Fig. 6, the effect of substitution of La

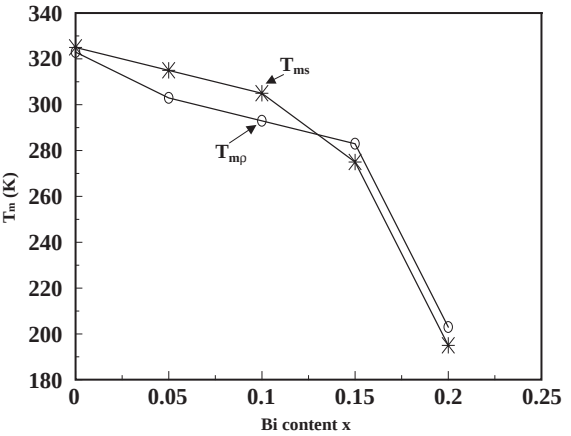

Fig. 6. Variation of metallic-semiconductor transition for ρ ($T_{m\rho}$) and for TEP (T_{ms}) with Bi content for $x \leqslant 0.2$ at%.

atoms by Bi is a continuous decrease in the MST temperature ($T_{m\rho}$ and T_{ms}). The values of transition temperature in ρ–T and S–T measurements are close; this confirms both measurements. The decrease in transition temperature corresponds to the extension of antiferromagnetic semiconducting phase of the compounds and is explained. The Bi atom seems to be in a 3+state and is fully equivalent to the La ions. However, the Bi weakens the ferromagnetic character of these compositions [18].

For the hole-doped perovskite manganite $R_{1-x}A_xMnO_3$, (R is the trivalent rare earth ions

and A is the divalent alkaline earth ions) $x=0.31$ is supposed to be the optimal doping level for the double-exchange interaction that favors ferromagnetism and metallic conductivity [26]. Usually, one observes the highest Curie temperature at $x\sim0.3$ in $R_{1-x}A_xMnO_3$ with a fixed combination of R and A atoms. Assuming a random distribution of Mn^{3+} and Mn^{4+} ions over the Mn sites, the optimal doping level corresponds to a situation which has the largest number of Mn^{3+} ions with one, and only one, Mn^{4+} nearest neighbor in a disordered perovskite structure [26]. To understand the effect of Bi substitution for La on the transport properties, as Rao et al. [18], we propose cluster model. The first effect is usually related to Zener bond blocking. The Bi^{3+} ions replace the La^{3+} ions, so according to Rao et al. [18] $T_c/T_{c(x=0)}=1-ax$ (where T_c is the Curie temperature and a is 1, 2).

One expects one Zener bond to be broken if, instead of La^{3+} a Bi^{3+} is located close to the next nearest environment of a qualified Zener bond. This data suggest rather a quadratic dependence on x. That looks very much as if one Bi^{+3} close to the Zener bond is ideally replacing La^{3+}, but that two Bi^{3+} at the same Zener bond is blocking that bond and so $T_c/T_{c0}=1–10xx$. There are 11 NN-octahedra where we can place one Bi close. If there is to be placed one other Bi close, only 10 possibilities remain. The probability of getting a pair together is of course xx. If x gets large enough, the metallic state ceases to exist because the (few) intact Zener bonds do not percolate any more.

The variation of the DC electrical resistivity with the ambient temperature (T) for the considered range of T (83–373 K) for $x=0.25$ and 0.3 at% are shown in Fig. 7. It was found that ρ always decreases with increasing T for the two compositions. Hence, the investigated compositions behave as semiconducting material (no transition). Besides, the results indicate that in general the resistivity for $x=0.3$ at% is larger than that of $x=0.25$ at% and that of former compositions ($x\leqslant0.2$). As shown in this figure the plots of Ln ρ vs. $1/T$ indicate two segments which correspond to two values of the activation energy. The relatively low-temperature range, is characterized by a weak temperature dependence, which eventually relates to hopping conduction mechanism. In contrast, the relatively high-temperature range is characterized by relatively stronger dependence on temperature, which possibly reveals conduction based on extended states. Therefore, the temperature dependence of the resistivity within the temperature range can be described by Eq. (1). The values of E_ρ obtained by the least-square fits to experimental data of Fig. 7 are listed in Table 2.

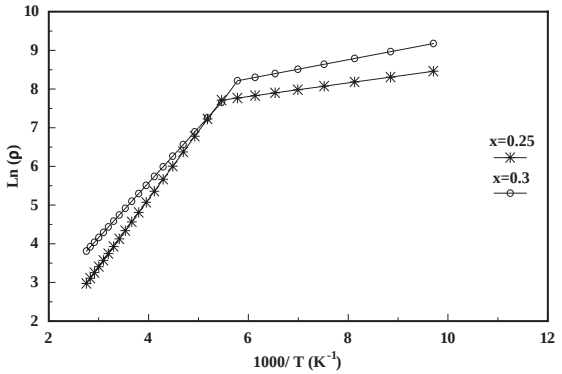

Fig. 7. The temperature dependence of the electrical resistivity of $La_{0.45}Bi_{0.25}Sr_{0.3}MnO_y$ and $La_{0.4}Bi_{0.3}Sr_{0.3}MnO_y$.

Table 2
Values of E_ρ of $x=0.25$ and 0.3 at%

X	0.25	0.3
E_ρ (eV)	0.151	0.1224

As it is seen in Fig. 8, the plots between Seebeck coefficient (S) and $1/T$ for the last two compositions ($x=0.25$ and 3 at%) are kinked linear. The samples at high temperatures, but below 300 K exhibit a positive TEP, proving that these materials are of p-type behavior; this agrees with the former compositions ($x\leqslant0.2$). The increase of the negative TEP suggests a contribution of electrons at increased temperatures. Above 300 K the electrons become more significant. Besides, values of the activation energy in the low range of T (E_{s1}) and the high range of T (E_{s2}) are calculated using Eq. (2) and tabulated in Table 3.

As it is seen, the values of E_{s1} are very small, a matter that possibly reflects mixed conduction. In

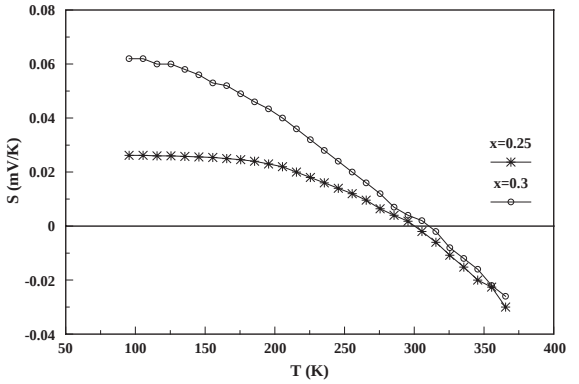

Fig. 8. The temperature dependence of TEP for $La_{0.7-x}Bi_xSr_{0.3}MnO_y$ ($x=0.25$ and 0.3 at%).

Table 3
Values of E_s of $x=0.25$ and 0.3 at%

X	0.25	0.3
E_{s1} (eV)	6.2×10^{-4}	2.7×10^{-3}
E_{s2} (eV)	0.023	0.025

particular $E_{s1}<E_{s2}$, which emphasizes that the contribution of electrons becomes more dominant in the relatively high range of temperatures.

4. Conclusions

In the light of our experimental work, we can affirm that doping $La_{0.7}Sr_{0.3}MnO_y$ with a low amount of Bi atoms gives rise to increasing values of ρ and TEP and reduces the M–S transition temperature. Bi^{3+} is expected to substitute La^{3+} almost perfectly composition $LaMnO_3$ pervoskite because of its valence and ionic radius. However, the magnetic and electrical properties are rather different from La-manganite ones. The increase of the Bi-content to 0.25 at% reduces the M–S transition temperature, at least inside our temperature range of measurement.

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