Magnetotransport and thermoelectric power of \( \text{La}_{2/3}\text{Ba}_{1/3}\text{Mn}_{1-x}\text{Sb}_{x}\text{O}_3 \) \((x = 0–0.05)\) manganite perovskites

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Abstract

The effect of \( \text{Sb}^{+5} \)-doping on the magnetotransport and thermoelectric power of \( \text{La}_{2/3}\text{Ba}_{1/3}\text{Mn}_{1-x}\text{Sb}_{x}\text{O}_3 \) \((x = 0–0.05)\) perovskite manganites is reported here. Two insulator–metal (I–M) transitions have been observed in the electrical resistivity–temperature \( \rho(T) \) behavior of the undoped sample \( \text{La}_{2/3}\text{Ba}_{1/3}\text{Mn}_3\text{O}_3 \). Both the transitions (at \( T_{P1} \) and \( T_{P2} \)) shift to lower temperatures with doping but to a different extent. \( T_{P1} \) decreases faster while \( T_{P2} \) remains almost invariant up to 3\% of doping and then decreases. With increasing \( \text{Sb}^{+5} \) content, the intrinsic magnetoresistance (MR at \( T_{P1} \)) gets suppressed whereas the extrinsic magnetoresistance at lower temperatures gets enhanced. The thermoelectric behavior \( S(T) \) of the pristine sample shows a peak at \( T_{P1} \) while for the doped samples the peak gets suppressed. All the samples exhibit a crossover in their \( S(T) \) behavior from positive to negative at a temperature \( T^* \), indicating that the dominant carrier in these compounds changes from hole to electron above \( T^* \). Transport behavior above \( T_{P1} \) (the paramagnetic insulating region) is explained on the basis of the small polaron hopping model while the electron–magnon scattering process has been invoked to explain the thermoelectric power and electrical resistivity behavior in the ferromagnetic regime.

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1. Introduction

Mixed valence perovskite manganites with the general formula \( \text{L}_{1-x}\text{D}_x\text{MnO}_3 \) (where \( \text{L} \) is a trivalent rare-earth ion, e.g. \( \text{La}^{+3}, \text{Nd}^{+3}, \text{Pr}^{+3} \) etc., and \( \text{D} \) is divalent alkaline earth ion, e.g. \( \text{Ca}^{+2}, \text{Sr}^{+2}, \text{Ba}^{+2}, \text{Pb}^{+2} \) etc.) have been intensely studied during the last decade because of their interesting physical properties such as coupling of orbital, spin and lattice degrees of freedom, charge ordering, complex magnetic phase diagram and insulator–metal (I–M) transition (and corresponding paramagnetic–ferromagnetic transition) besides showing very high magnetoresistance (MR) \([1–5]\). The occurrence of ferromagnetic and metallic states simultaneously (in the vicinity of 33\% doping) has been qualitatively explained by the double-exchange (DE) mechanism \([6]\), which considers the magnetic coupling between \( \text{Mn}^{+3} \) and \( \text{Mn}^{+4} \) resulting from the hopping of an electron between the two partially filled d-shells. This mechanism, however, is found to be insufficient in explaining some phenomena like the ferromagnetic insulator (FMI) and the magnitude of MR, etc. \([7]\). A suitable theoretical analysis explaining all the observed phenomena is still elusive.

Most of the substitutional studies carried out \([8,9]\) have shown that I–M transition, Curie temperature \( (T_C) \), etc., depend upon the ions present at the rare-earth site and, by changing the carrier density (through \( \text{Mn}^{+3}/\text{Mn}^{+4} \) ratio) and the lattice distortion (through Mn–O–Mn bond angle and length), one can
always tailor these properties. In contrast, Mn-site substitution plays a more important role as it is directly involved in the DE interaction. Many researchers have substituted different d-group elements at the Mn-site [10–15]. It is found that for the lower concentration of substituents, they all suppress the transition temperature. But there are a few exceptions, like Ru-doped Pr$_{0.5}$Sr$_{0.5}$MnO$_3$, where $T_C$ increases [16]. Only a few studies exist where a higher valent ion has been substituted at the Mn-site and its effect on various properties studied in detail [14–18]. Among these, thermopower is the least studied property. Here we have attempted to study the magnetotransport and thermoelectric power of the pentavalent Sb ion at the Mn-site of the LBMO system and to examine the results vis-à-vis the other d-group substituted manganites. Thermoelectric power measurement is of great importance because it provides valuable information about the nature of carriers in manganites, which can be helpful in understanding the mechanism operative in these materials.

2. Experimental details

Polycrystalline samples of the series La$_{2/3}$Ba$_{1/3}$Mn$_{1-x}$Sb$_x$O$_3$ ($x = 0–0.05$) have been synthesized using the conventional solid-state reaction route. The detailed synthesis procedure has been reported elsewhere [17]. All the samples in the present investigations are single-phase material as checked through x-ray diffractometry. The resistivity was measured using the conventional four-probe method. The magnetic field was applied parallel to the current direction and the magnetoresistance is evaluated through the relation

$$\text{MR}(\%) = \left[ \frac{\rho(T, H = 0) - \rho(T, H)}{\rho(T, H = 0)} \right] \times 100$$

where $\rho(T, H)$ and $\rho(T, H = 0)$ are the electrical resistivities measured with and without magnetic field respectively at a temperature $T$. Seebeck coefficient or thermoelectric power measurements have been carried out with a heat pulse technique in a closed cycle refrigerator from 50–400 K [19]. Samples were cut in a rectangular parallelepiped shape of typical size $1.5 \times 1.5 \times 5.0$ mm$^3$ with one end glued (with thermal epoxy) to a copper block that served as a heat sink, while a calibrated chip resistor as a heat source was glued at the other end. The temperature difference was measured using an E-type differential thermocouple with junctions thermally attached to well-separated positions along the longest axis of the sample. The temperature gradient was controlled to be less than 1 K. Seebeck voltages were detected using a pair of thin Cu wires electrically connected to the sample with silver paint at the same position as the junctions of the thermocouple. The stray thermal emfs are eliminated by applying long current pulses (∼100 s) to the chip resistor, where the pulses appear in an off–on–off sequence. The experiments were performed during the warming cycle with a slow rate of ≤20 K/h. The reproducibility of the $S(T)$ measurement is better than 2%.

3. Results and discussion

All the samples under investigation possess a cubic structure with the lattice parameter increasing successively with Sb doping. The electrical resistivity versus temperature, $\rho(T)$, shows two I–M transitions, a higher temperature transition ($T_{P1}$) followed by a hump at $T_{P2}$ (Fig. 1). The subsequent doping of Sb$^{5+}$ ions at the Mn-site results in a movement of both the transitions to lower temperatures with $T_{P1}$ decreasing at a faster rate than $T_{P2}$. $T_{P1}$ results from the competition between double-exchange and superexchange mechanisms inside the grain whereas $T_{P2}$ arises due to the grain boundary effects that in turn are due to the larger ionic size mismatch of the ions present at the rare-earth site. The two transitions have previously been obtained in other Ba-based manganites also [20,21]. The reason for the decrease of both transition temperatures with Sb$^{5+}$ doping has been dealt with in our earlier paper [17]. Significantly, the grain size was found to increase with Sb$^{5+}$ doping. The magnetoresistance (Fig. 2) depicts a sharp peak near $T_{P1}$ in all the samples and then increases below it, reflecting the higher grain boundary effects in this class of manganites. At 77 K, the MR versus $H$ plot

Fig. 1a. $\rho$–$T$ variation of the La$_{2/3}$Ba$_{1/3}$Mn$_{1-x}$Sb$_x$O$_3$ series. The solid line represents the fitting with Eq. (4).

Fig. 1b. Fitting of $\rho$–$T$ data with Eq. (1) for various samples. (The right-hand and top axes refer to a 5% Sb sample).
The conduction mechanism of the manganites at higher temperature \( (T \geq T_P) \) is governed either by variable range hopping (VRH) or by small polaron hopping (SPH) depending on the Debye temperature \( (\theta_D) \) \[23\]. If \( T > \theta_D/2 \), the conduction mechanism is governed by small polarons and these polaronic models can be either adiabatic or non-adiabatic. Since the Debye temperature of the LBMO system is \( \sim 400 \) K \[24\] so the polaronic model can be applied to the insulating region above \( T_{P1} \).

The equations for the two processes are given by

\[
\rho = \rho_a T \exp(E_\rho/k_B T) \quad \text{adiabatic} \tag{1}
\]

\[
\rho = \rho_a T^{3/2} \exp(E_\rho/k_B T) \quad \text{non adiabatic} \tag{2}
\]

where \( \rho_a \) is the residual electrical resistivity, \( E_\rho \) is the activation energy and \( k_B \) is Boltzmann’s constant. Since the value of the density of states at the Fermi level \( N(E_F) \) is very high in pristine sample LBMO, only the adiabatic process is applicable in the present case. Values of \( E_\rho \) calculated using Eq. (1) [Fig. 1b] are given in Table 1.

The thermoelectric power data is shown in Fig. 3. Only the pristine LBMO sample shows a peak at the I–M transition \( T_{P1} \) (337 K), which gets suppressed with Sb-doping. It is clear that each sample \( (x = 0–0.5) \) shows a crossover of thermopower from positive to negative at temperature \( T^* = 264, 258, 250, 241 \) and 210 K respectively with increasing \( x \), suggesting the dominance of the electrons in the thermoelectric transport above these values. In the ferromagnetic state, the magnitude of the observed thermoelectric power in the range of a few \( \mu \text{V/K} \) seems to be reminiscent of the metallic system. It is also noted that the value of room-temperature thermoelectric power in these compounds becomes more and more negative with increasing Sb\(^{5+} \) content. This result is, however, different from the doped La\(_{0.5}\)Pb\(_{0.5}\)(Mn\(_{1−x}\)Cr\(_x\))O\(_3\) system \[25\], where \( S(T) \) was found to be more and more positive with Cr\(^{5+} \) substitution. Electrical resistivity increases with Cr and decreases with Ru. Such a difference in the measured \( S(T) \) can be understood considering the closed shell configuration (4d\(^{10} \)) of Sb\(^{5+} \) that weakens the double-exchange mechanism between Mn\(^{3+} \) and Mn\(^{4+} \) ions. This produces localization of the \( e_g \) electron and hence the increase in the electrical resistivity. But on Sb\(^{5+} \) doping the average valency at the Mn-site increases, which means that it acts like an electron-doped material and hence the Seebeck coefficient decreases with temperature on Sb\(^{5+} \) doping. The results at the same time are found to be in agreement with those of the Ni\(^{3+} \)-doped La\(_{0.7}\)Pb\(_{0.3}\)MnO\(_3\) \[26\] and Cu-doped La\(_{0.88}\)Te\(_{0.15}\)MnO\(_3\) \[27\] manganites where Ni\(^{3+} \) and Cu\(^{2+} \) dopings also act as n-type materials.

In order to explain the change of sign of thermopower from hole-like behavior to electron-like behavior in the metallic ferromagnetic (FMM) state we adopt the model given by Asamitsu et al. \[28\] that is based on the vanishing of the exchange interaction \( J \). This interaction arises due to the excitation of the electrons from the valence band (VB) \( t_{2g} \) to the conduction band (CB) \( e_g \). The mobility of electrons in the conduction band is high, leading to a negative thermopower. The degeneracy of the \( e_g \) band seems to be gradually lifted as the temperature is lowered below \( T^* \) and the thermopower changes its sign from negative to positive with the increase of spin polarization which is supported by the nature of the MR versus \( H \) data taken at 77 K (inset of Fig. 2).

The temperature dependence of the thermoelectric power \( (S) \) of the present series in the insulating regime (above \( T_{P1} \))

![Fig. 2. MR variation with \( T \) of the La\(_{2/3}\)Ba\(_{1/3}\)Mn\(_{1−x}\)Sb\(_x\)O\(_3\) series. The inset shows MR versus \( H \) at 77 K.](image1)

![Fig. 3. Thermopower variation with temperature for La\(_{2/3}\)Ba\(_{1/3}\)Mn\(_{1−x}\)Sb\(_x\)O\(_3\). The solid line represents the fitting with Eq. (5).](image2)

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_\rho ) (meV)</th>
<th>( E_S ) (meV)</th>
<th>( \alpha )</th>
<th>( W_H ) (meV)</th>
</tr>
</thead>
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<tr>
<td>( x = 0 )</td>
<td>91.2</td>
<td>21.693</td>
<td>89.507</td>
<td></td>
</tr>
<tr>
<td>( x = 0.01 )</td>
<td>98.02</td>
<td>14.016</td>
<td>84.004</td>
<td></td>
</tr>
<tr>
<td>( x = 0.02 )</td>
<td>112.92</td>
<td>7.903</td>
<td>105.001</td>
<td></td>
</tr>
<tr>
<td>( x = 0.03 )</td>
<td>126.15</td>
<td>5.869</td>
<td>120.281</td>
<td></td>
</tr>
<tr>
<td>( x = 0.05 )</td>
<td>152.98</td>
<td>5.316</td>
<td>147.664</td>
<td></td>
</tr>
</tbody>
</table>

\( W_H \) (\( E_\rho - E_S \)) corresponds to polaron binding energies.

(inset Fig. 2) shows the behavior of spin polarized tunneling proposed by Hwang et al. \[22\].
is well described by the following expression:

\[ S(T) = \frac{k_B}{e}(E_S/k_B T) + \alpha \]  

(3)

where \( e \) is the electronic charge; \( E_S \) is the activation energy obtained from thermoelectric power data and \( \alpha \) is a constant. \( \alpha < 1 \) implies the applicability of small polaron hopping model whereas \( \alpha > 2 \) is for large polaron hopping. On evaluating the resistivity activation energy \( \rho_0 \) [Fig. 1b] and the thermopower activation energy \( E_S \) (Table 1 and shown in Fig. 4) it is found that \( \rho_0 \) is much higher than \( E_S \).

Such a large difference in the activation energy is the indication of the applicability of the small polaron hopping (SPH) model in the insulating region above \( T_{P1} \) (the value of \( \alpha \) is also less than 1). The polaron hopping energy \( (W_H) \), deduced from the difference of \( \rho_0 \) and \( E_S \) (Table 1), increases with Sb-doping, which is corroborated by the resistivity data (Fig. 1). In the metallic regime \( (T < T_{P2}) \), the electron–magnon scattering equation fits the electrical resistivity data.

\[ \rho = \rho_0 + \rho_{2.5}T^{2.5} \]  

(4)

where \( \rho_0 \) is the electrical resistivity due to the grain boundary, domain boundary and other temperature independent processes and \( \rho_{2.5} \) represents the electrical resistivity due to electron–magnon scattering in the FM phase. Fig. 1 shows the fitting of the above Eq. (4). Similar to \( \rho(T) \) data, several factors, such as impurity, band structure, electron–electron and electron–magnon scattering, etc., also affect the \( S(T) \) data in the FM regime. \( S(T) \) data in this region has been analyzed by the following equation:

\[ S = S_0 + S_{3/2}T^{3/2} + S_4T^4. \]  

(5)

Here \( S_0 \), \( S_{3/2} \), and \( S_4 \) are fitting parameters. While the parameter \( S_0 \) seemingly has no physical origin, \( S_{3/2} \) has been related to the electron–magnon scattering [25,29]. The origin of \( S_4 \), though not clear, has been ascribed to spin–wave fluctuations in the FM metallic phase in the literature [25,29]. The increasing trend of the magnitude of \( S_4 \) (cf. Table 2) also substantiates this view point [25,29,30]. In the FM phase (i.e. at \( T < T_{P1} \) for the respective samples with \( x = 0.0–0.05 \)), \( S(T) \) data can well be described according to Eq. (5), i.e. electron–magnon scattering, dominates the transport mechanism in the FM metallic regime. The hole-like to electron-like crossover in thermoelectric power in Eq. (5) arises due to the fact that \( S_4 < 0 \) (Table 2). However, due to higher power of \( T \), the term \( S_4T^4 \) will dominate for large \( T \), making the thermoelectric power negative at \( T^* \). It would be prudent to mention here that \( S(T) \) fitting (with Eq. (5)) has been carried out in the FM region (i.e. below \( T_{P1} \)) whereas \( \rho(T) \) fitting (with Eq. (1)) refers to temperature regime below \( T_{P2} \). The dominance of the \( S_4 \) term would be in the temperature regime between \( T^* \) and \( T_{P1} \). Since \( T_{P2} \) is lower than the crossover temperature \( T^* \), the effect of \( S_4 \) would not therefore be reflected in the resistivity fitting.

### 4. Conclusions

The effect of Sb\(^{15} \) doping on the magneto-transport and thermoelectric power of La\(_{2/3}\)Ba\(_{1/3}\)Mn\(_{1-x}\)Sb\(_x\)O\(_3\) has been investigated. It is found that both the I–M transition temperatures \( T_{P1} \) and \( T_{P2} \) shifted to lower temperatures, and the electrical resistivity of the samples increases with Sb content. On the other hand, MR measurements show that intrinsic MR gets suppressed while the extrinsic MR enhances with the doping. The thermoelectric power data shows the change of sign from positive to negative at \( T^* \) with increasing temperature, indicating the change of dominant carrier from holes to electrons above such a temperature. Our present study suggests that the electron–magnon scattering dominates in the FM metallic region in the electric as well as thermoelectric power transport, whereas small polaron hopping is found to be applicable in the PM insulating region.

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