Crossover form dominant magnon drag to phonon drag in Bismuth rich La$_{0.85}$Na$_{0.15}$MnO$_3$ manganite

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Abstract. The thermoelectric power (TEP) or seebeck coefficient ($S$) characteristic of bismuth substituted La$_{0.85-x}$Bi$_x$Na$_{0.15}$MnO$_3$ manganites ($x=0$, 0.1, 0.2, 0.25, and 0.3) were studied to understand the effect of bismuth on influencing the conduction of charge carriers in large bandwidth manganite La$_{0.85}$Na$_{0.15}$MnO$_3$. A pragmatic equation $S = S_0 + S_1T + S_3/2T^3/2 + S_3T^3 + S_4T^4$ was exploited to obtain the contributions to thermopower at low temperature ferromagnetic state of the specimen. Both electrons and holes involve in conduction at different regime of temperature from 14K to 295K. A large increase of maximum TEP, $S_{\text{max}}$ changing from 3$\mu$V.K$^{-1}$ to 67$\mu$V.K$^{-1}$ was realized at 30% substitution of Bi. This large increase in the TEP value is due to the appearance of phonon drag effect at low temperature in Bismuth rich La$_{0.85}$Na$_{0.15}$MnO$_3$. The signature of both magnon drag and phonon drag is seen at low temperature. At high temperature small polarons are governing the conduction in the investigated specimen. Bismuth substitution in soft ferromagnetic manganites such as La$_{0.85}$Na$_{0.15}$MnO$_3$ increases the activation energy thereby improving the TEP.

INTRODUCTION

The manganites are known for about half a century owing to their correlation property. However, the real application-oriented attributes of these material are under study from recent years. The colossal magneto resistance, the magnetocaloric effect, and the large thermoelectric power are few examples in this regard. The correlation property of manganites is exploited to produce good thermoelectric (TE) material. Realizing a high-performance TE material is challenging as the requisites viz. large Seebeck coefficient ($S$), low electrical resistivity ($\rho$) and low thermal conductivity ($\kappa$) are conflicting with each other. Manganites provide a platform to accommodate the requisites by effectively reducing the $\kappa$ due to the incorporation of rare earth ions in the crystal system and displaying the large values of $S$ due to ordering phenomena. Recently few $e$ doped, and half doped systems have shown anomalous growth in $S$ owing to charge and orbital ordering. In contrast, bismuth substituted alkali metal based manganite La$_{0.7}$Li$_{0.3}$MnO$_3$, has shown TEP of magnitude 0.9 V.K$^{-1}$ and this colossal growth was credited to the $6s^2$ lone pair electrons of $Bi^{3+}$ leading to strong carrier localizations. With this motivation we have chosen a similar monovalent based manganite system, La$_{0.85}$Na$_{0.15}$MnO$_3$ with Bi substitution to La to investigate its TEP characteristics.

EXPERIMENTAL METHODS

The manganites La$_{0.85-x}$Bi$_x$Na$_{0.15}$MnO$_3$ ($x=0$, 0.1, 0.2, 0.25 and 0.3) viz. LB0, LB10, LB20, LB25 and LB30 are prepared using solid state route have crystallized in rhombohedral structure of $R3c$ space group. The samples have shown homogenous morphology and grain growth with improvement in Bi content. The samples are changing from soft ferromagnetic metal to canted ferromagnetic insulators with large inflection in resistivity at bismuth rich compositions. The temperature dependent variation of thermo-electric power ($S$) was probed in the range of 13-300K using differential dc method and the details can be seen elsewhere.

RESULTS AND DISCUSSION
Figure 1 shows the temperature dependence of $S(T)$ of LB0 to LB30 manganites between 14K and 295 K. As the temperature varies from 295K to 14K, the magnitude of $S$ shows a maxima at some temperature $T_S$ around 150K to 200K in each sample. Below $T_S$ the $S$ decreases slowly exhibiting a local minima and increases again. On the other hand, the effect of bismuth substitution manifest itself by increasing the magnitude of $S$ from 3 μV.K$^{-1}$ to 67 μV.K$^{-1}$ (LB0 to LB30) around the transition temperature region. In general, the magnitude of thermoelectric power varies inversely with the carrier concentrations$^{5,6}$. But in the present investigation, due to the same oxidation state of Bi and La, the carrier concentration ($\text{Mn}^{3+}$/Mn$^{4+}$: 70/30) is expected to remain same within the experimental limitations. Therefore, the variation in the magnitude of $S$ with bismuth substitution may be understood based on the electronic attributes of the Bi. From the previous reports$^3$, it has been established that due large electronegativity of Bi, its $6s$ orbital hybridizes with $O 2p$ orbital. This hybridization through polar covalent bond would hamper the movement of $e_g$ electron from one Mn site to the other resulting in electron localization around $\text{Bi}^{3+}$ ion. The formation of localizations state will reflect as distortions in bismuth substituted samples. these distortions cause hindrance to the motion of the charge carriers thereby enhancing the $S$ values$^7$. Further the sign of $S$ changes from negative to positive down the room temperature except LB30 which is indication of electrons and holes participating in the conduction mechanism.

In ferromagnetic materials magnon drag ($S_3/2 T^{3/2}$) and phonon drag ($S_3 T^3$) are two major mechanism deciding $S$ at low temperature. further the diffusion of carriers ($S_1 T$) as well as spin wave fluctuation ($S_4 T^4$) also contributes to $S$ in FM regime. In this regard a single empirical equation containing all the contributions is used quantify $S$ in low temperature ferromagnetic region (LT-FM) as stated in equation 1.
Here $S_0$ has no physical implications but is introduced to account the low temperature TEP data truncation. The experimental data is fitted to equation 1, and the fit is shown in figure 2(a) for LB0, LB20 and LB30. The fit parameters are summarized in table 1.

**Table 1.** The contributory terms of $S(T)$ at low temperature along with activation energy $E_S$ and $\alpha'$ tabulated with respect to Bi content.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>$S_0$ ($V.K^{-1}$)</th>
<th>$S_1$ ($V.K^{-2}$)</th>
<th>$S_{3/2}$ ($V.K^{-5/2}$)</th>
<th>$S_3$ ($V.K^{-4}$) x $10^{-6}$</th>
<th>$S_4$ ($V.K^{-5}$) x $10^{-8}$</th>
<th>$E_S$ (meV)</th>
<th>$\alpha'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB0</td>
<td>3.462</td>
<td>-0.186</td>
<td>0.017</td>
<td>-0.002</td>
<td>-0.850</td>
<td>9.199</td>
<td>-0.474</td>
</tr>
<tr>
<td>LB10</td>
<td>1.508</td>
<td>0.056</td>
<td>-0.010</td>
<td>10.900</td>
<td>-4.930</td>
<td>16.570</td>
<td>-0.772</td>
</tr>
<tr>
<td>LB20</td>
<td>1.759</td>
<td>-0.048</td>
<td>0.006</td>
<td>-1.370</td>
<td>0.122</td>
<td>11.328</td>
<td>-0.532</td>
</tr>
<tr>
<td>LB25</td>
<td>79.079</td>
<td>-6.554</td>
<td>0.787</td>
<td>-315.000</td>
<td>105.000</td>
<td>18.480</td>
<td>-0.755</td>
</tr>
<tr>
<td>LB30</td>
<td>-20493.6</td>
<td>1285.059</td>
<td>-139.111</td>
<td>44400.000</td>
<td>-13300.000</td>
<td>19.080</td>
<td>-0.380</td>
</tr>
</tbody>
</table>

Basically, the magnon drag effect ($S_{3/2}T^{3/2}$) is thought to be dominant mechanism at LT-FM region. However, in some composition of ABO$_3$ manganites both magnon and phonon drag effects can prevail at low temperature regime. By mere inspection of table 1, one can infer that electron-magnon interaction is dominant interaction in the present samples, because the magnitude of $S_{3/2}$ is greater than $S_3$ and $S_{3/2}$ is enhancing with Bi content. But the difference between $S_{3/2}$ and $S_3$ is found to reduce with improvement in Bi. This implies magnon drag and phonon drag are likely to be in force at LT-FM regime for higher concentrations. Figure 2(b) portrays the variation of $S_{1/2}T^{3/2}$ versus $T^{3/2}$ and $S_1T^3$ versus $T^3$ for LB0, LB20 and LB30. The Linear fit to experimental data at low and high $T$ indicates the contribution of magnon drag and phonon drag to the TEP respectively. Clearly $S_{3/2}T^{3/2}$ contribution seizes to exist in the entire ferromagnetic range. In all the samples the deviation occurs below 165K. As the phonon contributions are expected to be pronounced in relatively high temperature region, the high $T$ region of $S_{3/2}T^3 - T^3$ was given a linear fit and concluded that the phonon drag exists below $T_C$ and above the temperature where magnon drag effect seizes. But in LB30 the scenario is quite different, the phonon drag is existing even at lowest temperature of measurement. So, one can infer that the magnon drag and phonon drag contributing to TEP at different regions of LT-FM is true. But with large bismuth content both contributions become significant even at lowest measurement temperature. This is a direct consequence of large Bi-6s, O-2p hybridization where electrons are trapped at the sight of bismuth and is unavailable for conduction.

At high temperature paramagnetic regime, charges are not itinerant, but the transport is governed by the thermally activated polaron. Hence the TEP of the specimen is evaluated by the Mott’s polaron hopping equation.

$$S(T) = \frac{k_B}{e} \times \left[ \frac{E_S}{k_B T} + \alpha' \right]$$

(2)

Here $e$ is the electronic charge, $k_B$ is the Boltzmann’s constant, $E_S$ is the activation energy and $\alpha'$ is a constant of proportionality between the heat transfer and the kinetic energy of an electron. If $\alpha' < 1$, it signifies small polarons being responsible for observed thermopower, if $\alpha' > 2$, they are large polarons. Giving liner fit to $S$ verses $1/T$ (figure 2(a)), the activation energy is obtained from the slope. The values of $E_S$ and $\alpha'$ are tabulated in table1. From LB0 to LB30 the $E_S$ is increasing. This can be understood by considering the bandwidth of manganites. The improvement in bismuth continuously tends to reduce the bandwidth which in turn suggest the manifestation of distortions in the Bi rich compounds. The reduces the bandwidth, increases the effective mass of the charge carriers or in other words it increases in the bandgap causing the carrier to have greater deal of energy to overcome the gap. Further, the $\alpha'$ is found to be less than unity, which support the validity of using small polaron hopping mechanism to discuss the thermopower at high temperature insulating region.
CONCLUSION

The 6s lone pair characteristic of bismuth favors the improvement in the seebeck coefficient of the La_{0.85}Na_{0.15}MnO_3 and transforms it from a poor low temperature thermoelectric material to attractive high TEP candidate. The 6s lone governed hybridizations not only improve the distortion in the crystal lattice but also improves the effective mass of conduction electron interacting with the lattice. The reduced electron mobility manifest as phonon drag effect and improve the TEP. The existence of phonon drag even at low temperatures is beneficial trait of thermoelectric material for direct energy conversion applications.

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