HOPPING CONDUCTION IN La$_{1/2}$Ba$_{1/2}$(Mn$_{1-x}$Al$_x$)O$_3$

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ABSTRACT

Electrical resistivity behaviour of La$_{1/2}$Ba$_{1/2}$(Mn$_{1-x}$Al$_x$)O$_3$ compounds, prepared by the solid state reaction, have been investigated below the charge-ordering temperature to understand the mechanism of conduction. On analyzing the data by using several theoretical models, it is found that the metallic (ferromagnetic) part of the resistivity ($\rho$) (below $T_p$) fits well with the equation $\rho = \rho_0 + \rho_2 T^2$, where $\rho_0$ is due to the importance of grain/domain boundary effects, a second term $\sim \rho_2 T^2$ appears that might be attributed to the electron–electron scattering. In high temperature ($T_p < T < \theta_D/2$) paramagnetic insulating regime, the resistivity of samples obey the $T^{-1/4}$ law, characteristic of variable range hopping (VRH) model.

INTRODUCTION

La-\textit{A}-Mn-O (\textit{A} = a diavalent element; such as Ca, Ba, Sr, etc) is the one of widely studied materials of current interest showing semiconductor to metal transition [1]. However, the conduction mechanism in such mixed valence materials is a complex interplay between magnetic spin, charge ordering and also structure change. The Zener proposed that mechanism caused by a double exchange (DE) [2]. The basic process in DE is the hopping of d hole from Mn$^{4+}$ to Mn$^{3+}$ via oxygen. Therefore, polaronic hopping conduction mechanism is responsible for the conducting behaviour in this system. Since lattice interaction is also involved, there is strong electron (hole) – phonon interaction is such compounds above the metal-insulator trasition (MIT). In addition, hopping mechanism of conduction corresponds to a very low mobility, since the electron jumps are associated with a weak overlap of wave-function tails from the neighboring. The variable range hopping theory has been widely used to explain the electric conduction process in manganites in the high-temperature regime is involved also equally semiconductor-like region. In this paper, we have studied the Al doping in place of Mn. The compounds La$_{1/2}$Ba$_{1/2}$(Mn$_{1-x}$Al$_x$)O$_3$ were prepared in single-phase form.
EXPERIMENTAL DETAILS

Polycrystalline of La$_{1/2}$Ba$_{1/2}$(Mn$_{1-x}$Al$_x$)O$_3$ ($x = 0.0$, 0.1, 0.2 and 0.3), were prepared via conventional solid-state reaction method. A well-mixed stoichiometric mixture of La$_2$O$_3$, Al$_2$O$_3$, BaCO$_3$ and MnCO$_3$ of 99.9% purities was mixed and grinded for 2 hours. The dried powder was heated at 900°C in air for 12 hours to produce a highly reactive powder. After calcinations, the black powdery mixture was reground, palletized, and sintered in air at 1300°C for 24 hours. DC four probe method with closed cycle helium refrigerator in the temperature range of 30 to 300 K was used to investigate the electrical properties.

RESULTS AND DISCUSSION

Electrical resistivity of La$_{1/2}$Ba$_{1/2}$(Mn$_{1-x}$Al$_x$)O$_3$ samples was measured in the temperature range 30 - 300K. Resistivity ($\rho$) versus temperature (T) plots for these samples are shown in Figure 1. All samples exhibit metal-insulator transition (MIT) with a maximum peak in the resistivity at a temperature defined as $T_p$. The values of $T_p$ for each plot have been state in Table 2. $T_p$ shifted to lower temperature as Al doping increases. This decrease, as expected, indicates that Al$^{3+}$ does not take part in the double exchange mechanism. Therefore, the magnetic ordering takes place at lower temperature as $x$ increases. The resistivity at $T_p$ increases with Al concentration. For $x = 0.3$, the increment of resistivity is large. This is obvious because the replacing conducting regions of a conducting matrix by insulating regions.

To understand electronic conduction in La$_{1/2}$Ba$_{1/2}$(Mn$_{1-x}$Al$_x$)O$_3$ samples, at low temperature ($T < T_p$) the metallic behavior, we fitted the resistivity data to Zener Double Exchange (ZDE) conduction law, given by;

$$\rho = \rho_0 + \rho_2 T^2$$

(1)

where the first term $\rho_0$ corresponds to the resistivity arising due to domain, grain boundary and other temperature independent scattering mechanism. The second term $\rho_2 T^2$ appears as a result of electron-electron scattering and electron–magnon scattering. Thus, the spin scattering cannot be neglected in the low temperature ($T < T_p$) regime as the measured data can be best explained by electron–magnon scattering.
Figure 1 (a)(b): The temperature variation resistance of La$_{1/2}$Ba$_{1/2}$(Mn$_{1-x}$Al$_x$)$_3$O$_3$ samples.
Figure 2: Replotted resistivity data showing $T^2$ dependence for La$_{1/2}$Ba$_{1/2}$(Mn$_{1-x}$Al$_x$)O$_3$ system below the respective $T_p$. Solid lines are the best fit to the equation $\rho = \rho_0 + \rho_2 T^2$.

The best fitted parameters are given in Table 1. It is noted that the values of both $\rho_0$ and $\rho_2$ increase with the increase of $x$. The increase of $\rho_0$ with $x$ is suggested the increasing the grain boundary region. While, by the increase of $\rho_2$ with $x$ is suggested due to the increment of the spin fluctuation. The spin fluctuation is caused by one-magnon scattering. Therefore, grain boundary plays a dominant role in the conduction process and it acts as the region of enhanced scattering center for conduction electron (A. Banerjee, 2002).
Table 1: Best fitted parameters obtained from the fitting of the low temperature resistivity data in the metallic regime of La$_{1/2}$Ba$_{1/2}$(Mn$_{1-x}$Al$_x$)O$_3$ manganites with $\rho = \rho_0 + \rho_2T^2$.

<table>
<thead>
<tr>
<th>concentration, x</th>
<th>$\rho_0$ (Ω-cm)</th>
<th>$\rho_2$ (Ω cm K$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.04</td>
<td>1.50E-06</td>
</tr>
<tr>
<td>0.10</td>
<td>0.34</td>
<td>1.40E-05</td>
</tr>
<tr>
<td>0.20</td>
<td>2.32</td>
<td>1.50E-04</td>
</tr>
<tr>
<td>0.30</td>
<td>10.7</td>
<td>4.80E-04</td>
</tr>
</tbody>
</table>

It is well known that transport in semiconductor region ($T_p < T < \theta_D/2$) can be described by Variable Range Hopping (VRH) of charge carriers. Recently Jaime (1996) and Viret (1997) also applied VRH conduction mechanism in systems like Nd-(Sr,Pb)-Mn-O, La-Ca-Mn-O, etc [1]. The Mott mechanism of the variable range hopping (VRH) conductivity was obtained and has been utilized, given:

$$\sigma_{dc}=\sigma \exp \left(-\frac{T_0}{T}\right)^{1/4}, \quad (2)$$

where, $T_0$ is a constant [$= 16\alpha^2/K_B N(E_F)$] and $N(E_F)$ is the density of states at the Fermi level which can be calculated from the slope of the plot $\log(\sigma)$ versus $T^{-1/4}$ curves as shown in Figure 3. Parameter $\alpha$ is the electron wave function constant, where considered as 2.22 nm$^{-1}$ for the purpose of calculation. These also been used by Sayani et al. (2004) and Pal et al. (2001). $\theta_D/2$ values are also estimated, based on the graph $\theta_D/2 \approx T^{-1/4}$ where deviation from linearity occurs in the temperature region above $T_p$. The $\theta_D/2$ values are found to decrease systematically with increasing concentration, are given in Table 2.

Table 2: Values of $T_p$, $T_0$, $\theta_D/2$ and the density of states, $N(E_F)$ at Fermi level, from resistivity.

<table>
<thead>
<tr>
<th>Content, x</th>
<th>$T_p$ (K)</th>
<th>$\theta_D/2$ (K)</th>
<th>$T_0$</th>
<th>$N(E_F)$ (eV$^{-1}$cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>252</td>
<td>262.237</td>
<td>6.176</td>
<td>5.015E+22</td>
</tr>
<tr>
<td>0.10</td>
<td>240</td>
<td>256.000</td>
<td>0.806</td>
<td>3.844E+22</td>
</tr>
<tr>
<td>0.20</td>
<td>198</td>
<td>218.024</td>
<td>0.258</td>
<td>3.989E+22</td>
</tr>
<tr>
<td>0.30</td>
<td>190</td>
<td>216.025</td>
<td>0.655</td>
<td>1.310E+22</td>
</tr>
</tbody>
</table>
Figure 3: The fitting plot of $\sigma(T)$ curves of La$_{1/2}$Ba$_{1/2}$(Mn$_{1-x}$Al$_x$)O$_3$ according to the VRH model. The dashed lines represent the experimental data.

Further $T_0$ values for each sample were calculated from the slopes of log ($\sigma$) vs. $T^{-1/4}$ plot. By using the $T_0$ values and the equation (3), $N(E_F)$, the density of states at the Fermi level for each material was also obtained. All the estimated parameters such as
$N(E_F)$, $T_0$ are found to be in agreement with, those reported in the literature for other manganites materials. $T_0$ values are found to increase enormously and continuously with increasing the concentration of Al. $N(E_F)$ are found to be decreasing continuously with the increasing the concentration. If the mobility of carrier reduces, this was suggested that the conduction of $e_g$ band were decreased due to a strong electron-phonon coupling due to slowly fluctuating local Jahn-Teller distortion, permitting the formation of metallic state.

**CONCLUSION**

All samples show metal to insulator transition (MIT) at phase transition temperature ($T_p$). With the increase of Al content, $T_p$ shifted to lower temperatures. The resistivity data (below $T_p$) fits well with the equation $\rho = \rho_0 + \rho_2 T^2$, where $\rho_0$ is due to the importance of grain/domain boundary effects, a second term $\sim \rho_2 T^2$ appears that might be attributed to the electron–electron scattering. The low temperature resistivity signifies the importance of electron-electron scattering and electron-magnon scattering; whereas the high temperature transport properties are mainly governed by the Variable Range Hopping (VRH) model. As the Al content is increased, the effective number density of electrons decreases due to the narrowing of the bandwidth. This will cause the reduction of conduction electron to hop to the neighboring sites.

**ACKNOWLEDGEMENT**

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**REFERENCES**


