

Metal–insulator transition in electron-doped $\text{Ba}_{1-x}\text{La}_x\text{MnO}_3$ compounds

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Abstract. Electron-doped $(\text{Ba}_{1-x}\text{La}_x)\text{MnO}_3$ compounds were prepared for $x = 0–0.5$. Measurements of X-ray diffraction (XRD) at room temperature and temperature variation of dc electrical resistivity down to 20 K were carried out. Samples with $x = 0.2–0.5$ exhibit metal–insulator (M–I) transition. The maximum M–I transition temperature (T_c) of 289 K was observed for 30% of La doping ($x = 0.3$). XRD patterns of these samples ($x = 0.2–0.5$) were analyzed using Rietveld refinement. These samples are found to be mostly in single-phase form with orthorhombic symmetry (space group Pbnm). We have found strong correlation between Mn–O–Mn bond angles and T_c of M–I transition. The resistivity data below T_c could be fitted to the expression $\rho = \rho_1 + \rho_2 T^2$ and this shows that double exchange interaction plays a major role even in Mn^{4+} -rich compound. Above T_c the resistivity data were fitted to variable range hopping and small polaron models.

Keywords. Colossal magnetoresistance; metal–insulator transition; electron-doped $\text{Ba}_{1-x}\text{La}_x\text{MnO}_3$.

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1. Introduction

Lanthanum and rare-earth manganites have drawn considerable interest recently, because they exhibit M–I transition and colossal magnetoresistivity (CMR) behavior [1–4]. These materials have very interesting electrical and magnetic properties and also have potential applications for magnetic recording, magnetic switches and magnetic sensors. There are several reports in literature on $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ compounds ($\text{R} = \text{La}, \text{Y}, \text{etc.}, \text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) where the structural, transport and magnetic properties are studied. These compounds are Mn^{3+} -rich, doping of divalent atoms introduce mixture of Mn^{3+} and Mn^{4+} ions. The mixed valency of Mn ions play a major role in double exchange (DE) ferromagnetic interaction coupled with metallic resistivity [5–7]. The optimum doping of divalent atoms in the above series is found to be 30% and in other words, Mn^{4+} replaces 30% of Mn^{3+} . There are very few reports on Mn^{4+} -rich AMnO_3 ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) compounds. Recently Yuan *et al* [8] have reported the M–I transition in $\text{Ba}_{0.7}\text{La}_{0.3}\text{MnO}_3$ compound at around 230 K. In the present work we have taken the Mn^{4+} -rich $(\text{Ba}_{1-x}\text{La}_x)\text{MnO}_3$ series with $x = 0–0.5$, for detailed structural and electrical resistivity studies.

2. Experimental details

$(\text{Ba}_{1-x}\text{La}_x)\text{MnO}_3$ compounds were prepared by solid state route. Stoichiometric amounts of high purity BaCO_3 , La_2O_3 , and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ compounds were weighed and ground under acetone. The mixed powder was made in pellet form and annealed at different temperatures in the range of 900 to 1100°C for over 40 h with intermediate grindings and repelletizing. The final sintering was performed at 1150 to 1200°C for 35 h. X-ray diffraction patterns were recorded at room temperature using SEIFERT XRD machine with Cu K_α radiation. Electrical resistivity as a function of temperature was measured by employing four probe technique and by using a constant current source and nanovoltmeter. Temperature variation down to 20 K was achieved using a closed cycle helium refrigerator cryostat equipped with a temperature controller. The accuracy of the temperature measurement is ± 1 K.

3. Results and discussion

Typical XRD patterns of $\text{Ba}_{0.7}\text{La}_{0.3}\text{MnO}_3$ ($x = 0.3$) and $\text{Ba}_{0.5}\text{La}_{0.5}\text{MnO}_3$ ($x = 0.5$) compounds are shown in figure 1. XRD patterns of the samples for $x = 0.2$ – 0.5 were analyzed using fullprof program by employing Rietveld refinement. These patterns could be fitted by taking the Pbnm space group. The fitted data are shown as solid lines in figure 1. We can see that almost all the observed peaks could be fitted and the samples are essentially in single-phase form. The lattice parameters, atomic positions, occupancy of Ba and La, etc. were taken as free parameters of the fit. The refined lattice parameters, Mn–O–Mn bond angles and occupancy are given in table 1. The refined occupancy values are comparable to the fractional substitutions and minimum bond angle is obtained for $x = 0.3$ sample.

Typical plots of temperature variation of electrical resistivity are shown in figure 2 for samples with $x = 0.2$ and 0.3. The M–I transition temperature T_c for different samples are

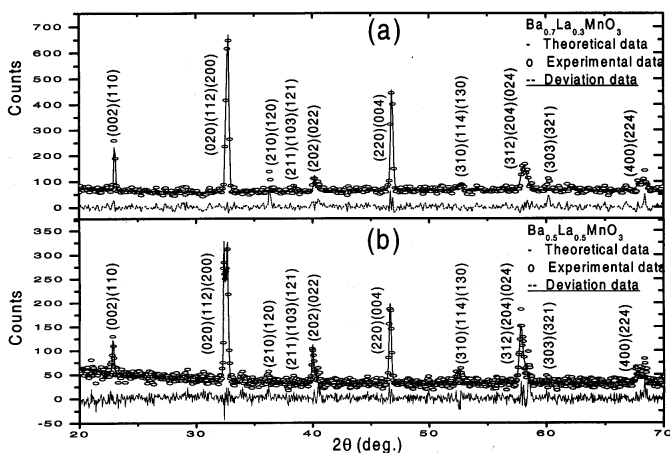


Figure 1. XRD patterns of (a) $\text{Ba}_{0.7}\text{La}_{0.3}\text{MnO}_3$ and (b) $\text{Ba}_{0.5}\text{La}_{0.5}\text{MnO}_3$ compounds along with theoretical fit.

given in table 1. The metallic resistivity data below T_c could be fitted to the expression

$$\rho = \rho_1 + \rho_2 T^n \tag{1}$$

with $n=2$. Here ρ_1 and ρ_2 are constants. Attempt to fit these data for $n=2.5$ and 3 was not successful. The above fit shows that double exchange interaction plays a major role on the CMR behavior of the above samples. The fitted data are shown as dashed lines in figure 2. The typical values of ρ_1 and ρ_2 for $x=0.3$ samples are $0.671 \Omega \text{ cm}$ and $20 \mu\Omega \text{ cm/K}^2$ respectively. The resistivity data of $x=0.5$ sample was not fitted, because this sample exhibits M-I transition at high temperature followed by re-established semiconducting behavior at low temperature. This could be due to the domination of charge ordered state for the equal concentration of Mn^{3+} and Mn^{4+} ions. The resistivity data above T_c were fitted to variable range hopping (VRH) and small polaron hopping models using the following expressions:

$$\rho = \rho_{oh} \exp(T_0/T)^{1/4}, \tag{2}$$

$$\rho = \rho_{op} T \exp(E_a/k_B T). \tag{3}$$

Table 1. Parameters determined from XRD analysis and resistivity measurements.

No.	Sample name	a, b, c (Å)	$\frac{Mn-O-Mn}{(^\circ)}$	Occupancy		T_c (K)
				Ba	La	
1	$Ba_{0.8}La_{0.2}MnO_3$	5.504, 5.480, 7.754	166.3	0.801	0.200	254
2	$Ba_{0.75}La_{0.25}MnO_3$	5.508, 5.476, 7.759	156.1	0.744	0.258	256
3	$Ba_{0.7}La_{0.3}MnO_3$	5.523, 5.476, 7.767	151.1	0.697	0.292	289
4	$Ba_{0.6}La_{0.4}MnO_3$	5.518, 5.474, 7.770	159.9	0.607	0.402	280
5	$Ba_{0.5}La_{0.5}MnO_3$	5.525, 5.476, 7.775	154.7	0.505	0.500	242

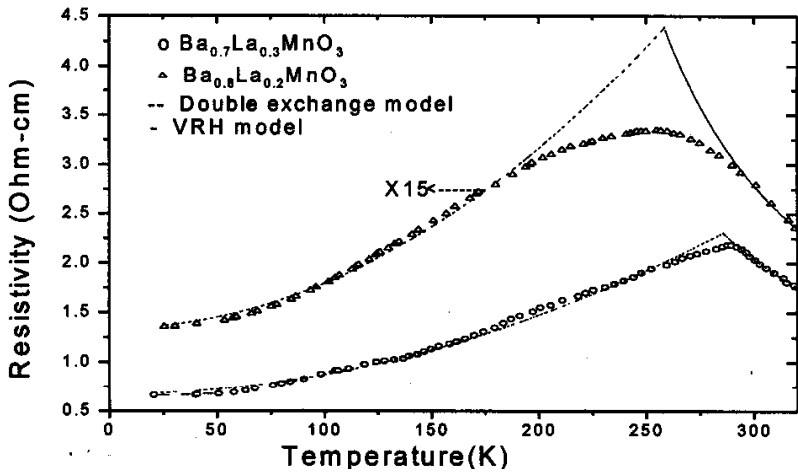


Figure 2. Resistivity vs. temperature plots of $Ba_{0.8}La_{0.2}MnO_3$ and $Ba_{0.7}La_{0.3}MnO_3$ compounds along with theoretical data. For clarity resistivity data of $Ba_{0.8}La_{0.2}MnO_3$ compound is shown by dividing the data by a factor 15.

Here, T_0 is the characteristic temperature which is related to the density of states in the vicinity of the Fermi energy and localization length, E_a is the polaron hopping energy and ρ_{oh} , ρ_{op} are constants.

We have found that both of these models fit the experimental data above T_c . We could not unequivocally determine the appropriate model for the present samples due to the limitation of 350 K as the maximum temperature, in our experimental set up. The root mean square deviation of VRH model fit is marginally smaller than that of small polaron model. We can see from table 1 that there is a correlation between T_c and Mn–O–Mn bond angles. The maximum T_c is obtained for $x = 0.3$ and it corresponds to minimum Mn–O–Mn bond angles. Thus for $x = 0.3$, the maximum deviation in Mn–O–Mn bond angles from 180° is observed. Such a large deviation of bond angle from 180° enhances the double exchange interaction and the sample with $x = 0.3$ exhibits highest T_c .

To cross check the presence of mixed valency in the above materials, we have performed chemical titration for some of the above samples using the method described in [9]. The oxidation state of Mn is found to be a mixture of Mn^{3+} and Mn^{4+} as expected.

4. Conclusions

Electron-doped $(Ba_{1-x}La_x)MnO_3$ compounds were prepared in single-phase form for $x = 0.2$ – 0.5 . All these samples exhibit M–I transition. The sample with $x = 0.5$ exhibits M–I transition at high temperature followed by low temperature semiconducting behavior. The highest T_c was observed for $x = 0.3$ among the above prepared samples, which is in correlation with lowest Mn–O–Mn bond angles estimated from XRD analysis. The metallic resistivity data could be fitted to double exchange model. The high temperature resistivity is fitted to both VRH and small polaron models.

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