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Hopping conduction in double layered $La_{2-2x}Ca_{1+2x}Mn_2O_7$ manganite

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Abstract

Double layered $La_{2-2x}Ca_{1+2x}Mn_2O_7$ manganite has been synthesized using solid state reaction method for different dopant concentration $x = 0.0-0.5$. Their temperature dependence of resistivity ($\rho - T$) has been studied in the semiconducting region. The experimental observations were compared with the theoretically simulated temperature dependence of resistivity curves based on nearest neighbour hopping, Efros−Shklovskii variable range hopping, and Mott's 2D and 3D variable range hopping models. From the analysis of these results, Mott's 3D variable range hopping mechanism seemed to be most suitable mechanism describing the semiconducting behaviour of these double layered manganites. Temperature dependent activation energy also supported the Mott's 3D variable range hopping model. The Mott's activation energy was found to vary with the dopant concentration x and it showed a minimum value for $x = 0.3$.

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Keywords: Layered manganites; Colossal magnetoresistance; Hopping

1. Introduction

The doped rare earth perovskite manganites $R_{1-x}A_xMnO_3$ (R ≡ La, Pr, Gd…trivalent rare earth cations and A ≡ Ca, Ba, Sr divalent alkaline earth cations) have attracted a lot of interest by virtue of their unusual magnetic and electronic properties including colossal magnetoresistance (CMR) [1−4]. The metallic ferromagnetism in moderately doped rare earth manganite can be understood within double exchange model [5]. The observed polaronic behaviour at high temperatures required the inclusion of other interactions such as strong electron−phonon coupling [6] for understanding the CMR phenomenon. The recent studies attributed the existence of magnetic clusters in the insulating paramagnetic state of doped manganite to the origin of CMR [7−12]. More recently, intensive studies have also been performed on the double layered manganite $R_{2-2x}A_{1+2x}Mn_2O_7$ which is found to exhibit CMR [13,14]. Their crystal structure comprises ferromagnetic metallic MnO_2 bilayers separated by non-magnetic insulating rock salt type $(La,Ca)_2O_2$ layers. The double layered manganites have quasi-2D layered structure and display anisotropic magnetotransport properties [15−17]. The observation of 2D short range ferromagnetic ordering at temperatures much higher than the 3D ferromagnetic transition temperature is very interesting feature of double layered manganites [18,19]. Study of temperature dependence of resistivity of doped layered manganite has been the subject of considerable research interest due to observation of rich variety of transport properties [9−11]. Various transport mechanisms such as polaron hopping [20−23], bipolaron hopping [24], variable range hopping [25−27] or activated type of transport [7] mechanism are proposed for the semiconducting behaviour of the infinite

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layered doped manganites at higher temperatures above the metal insulator transition temperature. There were only few studies on the transport mechanism of the doped double layered manganite at higher temperatures. Moritomo et al. [15] suggested that the semiconducting behaviour is due to thermally activated process whereas Wagner et al. [28] attributed the spin dependent hopping in the paramagnetic state as a cause of the semiconducting behaviour of resistivity of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$. Chen et al. [29] proposed the variable range hopping conduction in the presence of coulomb gap (Efros–Shklovskii's variable range hopping mechanism) for the semiconducting behaviour of $LaSr_2Mn_2O_7$. Conduction mechanism of small polaron hopping [30], Mott's 2D variable range hopping [31,32] and Mott's 3D variable range hopping [33–36] has also been proposed for semiconducting behaviour of double layered manganite. A detailed quantitative understanding of these properties has not yet been achieved although much qualitative knowledge has been obtained through transport studies. This paper reports a detailed investigation of high temperature electrical transport properties of double layered manganite $La_{2-2x}Ca_{1+2x}Mn_2O_7$ ('x' = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5).

2. Experimental

The bulk samples of double layered manganite $La_{2-2x}Ca_{1+2x}Mn_2O_7$ for different compositions 'x' = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 were prepared by solid state reaction method. Stoichiometric proportions of La_2O_3, $CaCO_3$, and MnO_2 were thoroughly mixed and ground. The resultant powder was calcined at temperature 950 °C for 96 h. After calcination, pellets were prepared and sintered at temperature 1250 °C for 48 h. All the samples were found to be of single phase with tetragonal perovskite structure. As the composition 'x' is varied from 'x' = 0.0 to $x = 0.5$, lattice parameters 'a', 'c' and cell volume were found to decrease [42]. Electrical contacts were made by silver paste and the temperature dependence of electrical resistivity was measured by standard four probe method. The magnetoresistance studies have been done by using an electromagnet. The magnetoresistance (MR) has been calculated by using the expression

$$\mathrm{MR} = \frac{\rho(0) - \rho(H)}{\rho(0)} \times 100\%$$

where $\rho(H)$and $\rho(0)$ are the resistivity of the sample in the presence and in the absence of magnetic field, respectively.

3. Results and discussion

Fig. 1 shows the variation of resistivity of double layered manganite $La_{2-2x}Ca_{1+2x}Mn_2O_7$ ('x' = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) in the higher temperature range from 110 K to 300 K. The samples with compositions 'x' = 0.0, 0.1, 0.2 and 0.5 show the semiconducting behaviour in this temperature range whereas samples with compositions 'x' = 0.3 and 0.4 show semiconducting behaviour at temperatures above 127 K and 119 K, respectively. Fig. 2 shows the temperature dependence

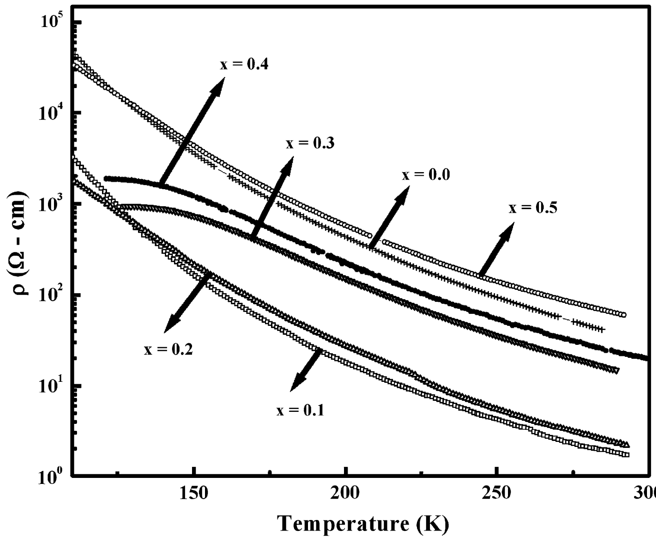

Fig. 1. Temperature dependence of resistivity (ρ) of double layered $La_{2-2x}Ca_{1+2x}Mn_2O_7$ manganite for 'x' = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 in the temperature range from 110 K to 300 K.

of magnetoresistance (MR) of double layered manganite $La_{2-2x}Ca_{1+2x}Mn_2O_7$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) in the presence of 1.5 kOe magnetic field in the temperature range from 110 K to 300 K. The inset shows the variation of magnetoresistance with composition 'x' at constant temperature T = 150 K. In this temperature range long range ferromagnetic ordering was not observed [42]. Appreciable magnetoresistance was not observed in the high temperature semiconducting region (T > 160 K) for all compositions $x = 0.0$ to $x = 0.5$ of double layered $La_{2-2x}Ca_{1+2x}Mn_2O_7$ manganite.

For analyzing the resistivity data, a temperature range from 171 K to 300 K has been chosen. In this temperature range, all the six compositions show the semiconducting behaviour.

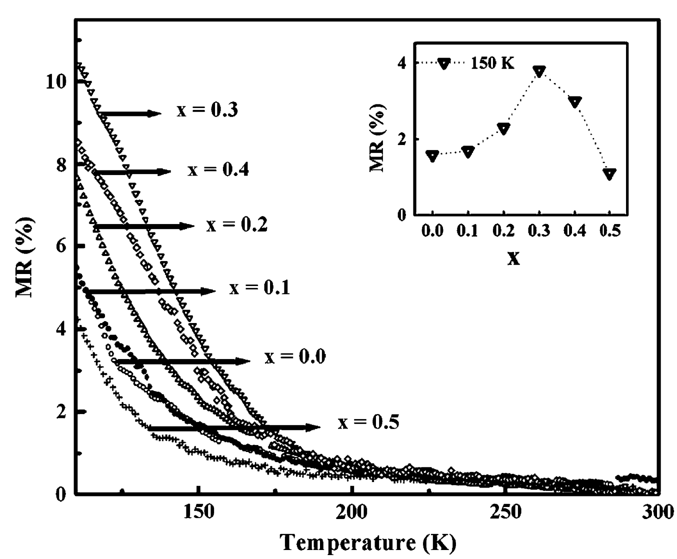

Fig. 2. Temperature dependence of magnetoresistance (MR) of double layered manganite $La_{2-2x}Ca_{1+2x}Mn_2O_7$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) at magnetic field H_{dc} = 1.5 kOe in the temperature range from 110 K to 300 K. The inset shows the variation of magnetoresistance with composition 'x' at constant temperature T = 150 K.