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Magnetic and electrical response of Co-doped $La_{0.7}Ca_{0.3}MnO_3$ manganites/insulator system

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ABSTRACT

We present a systematic study of the structural, magnetic and electrical properties of $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) and $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$ (LCMCO0 perovskite manganites. Most of the work is devoted to the electrical properties with a thorough discussion about different models for both the metallic and insulator states. With a view to understand the conduction mechanism in these materials, the resistivity of both materials was measured over a temperature range 5–300 K and in a magnetic field up to 1 T and the data were analysed by using several theoretical models. It has been observed that the metallic part of the temperature dependent resistivity (ρ) curve fits well with $\rho=\rho_0+\rho_{2\square 5}T^{2\square 5}$, indicating the electron–magnon scattering processes in the conduction of these materials. On the other hand, in the high temperature paramagnetic insulating regime, the adiabatic small polaron and VRH models fit well, thereby indicating that polaron hopping might be responsible for the conduction mechanism.

1. Introduction

The researches on rare earth manganites have generated a considerable interest because of their unusual magnetic and electronic properties especially for two phenomena. The first is to decipher the underlying mechanisms of intricate phenomena like colossal magnetoresistance (CMR) [1–4] and the second is synthesis of materials suitable for meaningful uses such as the temperature coefficient of resistance (TCR) which can be useful in bolometric applications [5,6]. The microscopic mechanism underlying the electronic, structural and magnetic properties in these materials can be characterized by a delicate interplay of spin, charge and lattice degrees of freedom [7,8].

Colossal magnetoresistance (CMR) phenomena were observed in the hole-doped perovskite manganites. They were explained by double-exchange (DE) model, phase separation and spin-polarized tunnelling effect [9–11]. Double exchange (DE) has been featured prominently in the discussion of the fascinating properties of CMR materials. Doping the insulating $LaMnO_3$ material, in which only Mn^{3+} exists, with the divalent ions (Ca, Ba, etc.) causes the conversion of a proportional number of Mn^{3+} to Mn^{4+}. Because of the strong Hund's coupling, the electronic configurations are $Mn^{3+}(3d^4, t_{2g}^3\uparrow e_g^1\uparrow$, S=2) and $Mn^{4+}(3d^3, t_{2g}^3\uparrow e_g^0\uparrow$, S=3/2). The presence of Mn^{4+}, due to the doping, enables the e_g electron of Mn^{3+} ion to hop to the neighbouring Mn^{4+} ion via DE, which mediates ferromagnetism and conduction. The magnetic properties of the perovskite manganite phase are strongly affected by the Mn-O-Mn bond angle and Mn-O bond length controlled by the ionic radii of A and B site ions and Mn^{3+}/ Mn^{4+} ratio which modifies the double exchange and superexchange (SE) interactions [12]. The $La_{1-x}Ca_xMnO_3$ in the doping levels $0.25 < x < 0.33$ shows a CMR characteristics combining simultaneous metal-insulator (MI) and ferromagnetic paramagnetic (FM-PM) transition [13,14] in temperature 200 K < T_P < 300 K (where T_P is the transition temperature).

One crucial parameter for bolometric applications is temperature coefficient of resistance (TCR) which is found to be large in manganites [15–17]. The TCR of a material depends on the rate of change of resistance with respect to temperature. Generally, the undoped manganites ($RMnO_3$, R is trivalent ion) show insulating properties. In contrast to that insulator to metal transition takes place in the doped manganites, with general formula: $R_{1-x}B_xMnO_3$, where "B" is a bivalent ion (Ca^{2+}, Ba^{2+}, Sr^{2+}, etc.). The insulator-metal transition frequently appears at low doping range ($x < 0.5$) and the resistivity rapidly drops with the lowering of temperature stabilizing a metallic ground state. So a sharp drop in resistivity towards lower temperature gives rise to high value of temperature coefficient of resistance (TCR) which can be useful in bolometric applications.

Electron transfer with spin memory is an essential ingredient for an understanding of the transport properties of mixed-valence manganites, but something more is needed to account for the metal-insulator

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transition near the Curie point [7]. The change of conduction regime below T_C appears to be brought about by the onset of ferromagnetism. As temperature decreases, the magnetization increases and the resistivity drops.

Interest in lanthanum manganite has been rekindled in the last few years due to the observation of large MR and TCR [18–25]. Most of the results on rare-earth manganites reported so far, have concentrated on the divalent-ion-doped $R_{1-x}B_xMnO_3$ (B = Ca, Ba, Sr, etc.) compounds. As per our knowledge, no study has been reported for the description of conduction mechanism by using various theoretical approaches on Co doped $La_{0.7}Ca_{0.3}MnO_3$.

In this letter we would like to explain the electrical behaviour of $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$ perovskite manganites over the whole temperature range by using the idea of magnetic potential barriers to electron transport. The temperature dependence of the resistivity ρ (T) has been fitted using various theoretical approaches. Below the transition temperature (T_P) the ρ (T) graphs were well fitted using the $\rho(T) = \rho_0 + AT^{\alpha}$ formula. Above T_P, the ρ(T) graphs were found to be well fitted with the variable Range hopping (VRH) model and the small polaron models. And finally the TCR values were calculated.

2. Experimental procedures

The manganites $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) and $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$ (LCMCO) were prepared by the conventional solid state reaction method. Stoichiometric proportions of La_2O_3, $CaCO_3$, MnO_2, and Co_3O_4 were mixed and first fired at 700 °C for 12 h. Then the mixture was reground and again fired at 900 °C for 12 h. Then the mixture was ground for a third time, pressed into pellets and fired at 1100 °C for 12 h to obtain better crystallization. Finally, the sample was again reground, pressed into pellets, and sintered at 1350 °C for 24 h. Powder X-ray diffraction (XRD) patterns, obtained with Cu Kα radiation at room temperature, revealed the single-phase orthorhombic perovskite structure. The results show very good single phase samples. The magnetization and resistivity measurements were performed using a physical properties measurement system (PPMS) 14 T magnetometer in the temperature range from 5 to 300 K and magnetic fields up to 1 T.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) and $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$ (LCMCO) samples. The X-ray diffraction analysis shows that the perovskites are of single phase with orthorhombic structure (Pbnm space group). The lattice parameters of the samples were estimated to be *a* (Å)=5.4815, *b* (Å)=5.4756 and *c* (Å) =7.7334, V ($Å^3$)=232.19 for $La_{0.7}Ca_{0.3}MnO_3$ and *a* (Å)=5.4798, *b* (Å) =5.475 and *c* (Å)=7.728, V ($Å^3$)=231.89 for $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$ respectively. It is shown that with Co doping the lattice parameters decrease slightly, which can be easily understood in terms of the difference of Co and Mn ionic radii. And based on the composition dependence of lattice parameters in these systems, it had been concluded that, there exists a random distribution of Mn and Co ions in the lattice, i.e. no long range Co/Mn order [26].

Fig. 2 shows the temperature dependence of magnetization, M (T), for $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$ at a 100 Oe magnetic field, where, the ferromagnetic paramagnetic (FM-PM) transition characterizes both composites at T_C. The sharp drop of the magnetization at the magnetic transitions of both samples confirms its high homogeneity as observed in XRD. Co doping is found to decrease the system magnetization due to the decrease in LCMO ferromagnetic ratio. The magnetic transition temperatures, T_C, were determined from the minimum of dM/dT curves which is presented as an inset in Fig. 2 and these are 245 and 190 K for $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$ respectively. We know that in $La_{1-x}Ca_xMnO_3$ perovskite, the Curie temperature is determined by the double exchange interaction between Mn^{3+} and Mn^{4+} ions. The significant decrease of T_C for Co doped sample can be easily understood, where, the small partial substitution of Mn^{3+} by Co weakens the intrinsic grain ferromagnetism that means a weakening of the double exchange interaction between Mn^{3+} and Mn^{4+} ions and consequently decreases the Curie temperature [27].

Resistivity of a material provides information of electronic scattering dynamics of the material at various temperature regions. It is a physical property that is intimately related to the band structure and energy bands of the conduction electrons. The electrical transport properties of the LCMO and LCMCO were investigated as a function of temperature. Fig. 3(a) shows the zero-field resistivity vs temperature curves for the LCMO and LCMCO materials. Both materials exhibit a ferromagnetic-metallic (FM) to paramagnetic-insulator (PI) transitions at the temperature T_P. At low temperature the magnetic moment is large and the resistivity is characterized by strong ferromagnetic coupling between the magnetic ions which prevents formation of magnetic polarons and any significant spin disorder. Consequently, the scattering potential is weak yielding a low resistance state and metallic conduction. It is noted that the transition temperature T_P values are larger than the T_C. The values of T_P and T_C are listed in Table 1. In the inset of Fig. 3(a), the 1 T field resistivity vs temperature curves for the LCMO and LCMCO materials are presented.

The variation of resistance with temperature change accompanying with an insulator-metal transition is known as TCR which is defined as TCR (%)=1/ρ (dρ/dT) x 100, gives high sensitivity of the bolometric device. In this study, the TCR as a function of temperature of LCMO and LCMCO is shown in Fig. 3(b). As can be seen the temperature dependence of the TCR is similar to the ρ (T) dependence exhibiting a FM to PI transition at a critical temperature (T_m). The TCR values are summarized in Table 1. The maximum values of TCR are 10.5% K^{-1} at T_m=246 K and 5.5% K^{-1} at T_m=194.5 K for LCMO and LCMCO respectively. These values especially LCMO (10.5% K^{-1}) value is comparable to and even larger than those reported in different manganites [18,28,29] and could be the potential candidate for the bolometric application.

To recognize conduction mechanism nature above and below T_P, resistivity data were analysed with well-established models and experimental equations in each region. Resistivity data in the metallic region below T_P ($T < T_P$), for LCMO and LCMCO can be fitted by the following equations.

$$\rho = \rho_0 + \rho_2 T^2 \quad (1)$$

$$\rho = \rho_0 + \rho_{2.5} T^{2.5} \quad (2)$$

$$\rho = \rho_0 + \rho_2 T^2 + \rho_{4.5} T^{4.5} \quad (3)$$

where ρ_0 represents the residual resistivity, $\rho_2 T^2$ represents the

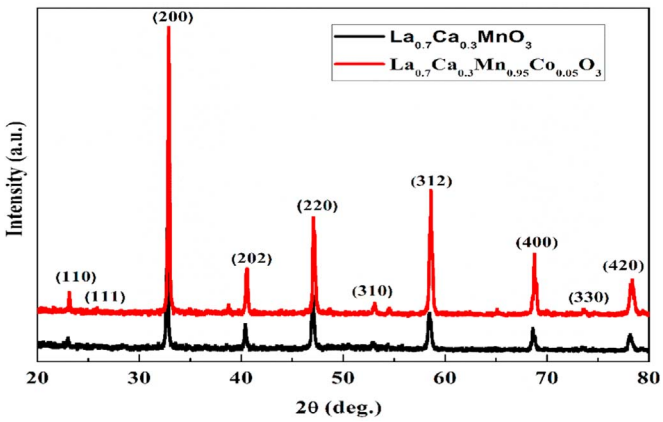

Fig. 1. XRD patterns of $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Ca_{0.3}Mn_{0.95}Co_{0.05}O_3$ samples.