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Effect of Cr Substitution in Structure, Magneto-transport and Energy Band gap Properties of ($La_{0.67}Sr_{0.33}$) MnO_3

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Abstract

The study of perovskite manganites $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ ($0 \leq x \geq 0.10$) has been carried out. The structure and magneto-transport properties of $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ manganites are strongly dependent on the substitution level x. Polycrystalline samples of $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ ($0 \leq x \geq 0.10$) were prepared by solid state reaction method. The little difference between the ionic radii of Cr^{3+} and Mn^{3+} causes no change in the structure, the structure remains rhombohedral. The temperature dependence of the resistivity is measured from 5 – 400 K without and with magnetic field up to 5 T. The value of metal-insulator (M-I) transition temperature (T_P) decreases when resistivity increases for all the samples while doping level x increases. The value of magnetoresistance (MR %) increases with increases Cr doping level for all samples. We have calculated energy band gap (E_g) for all samples and it is revealed that as per doping level increases E_g increases which is comparable with experimental data. So, the structure and magneto-transport behavior affected by Cr substitution.

Keywords: Colossal magnetoresistance, metal-insulator transition.

PACS: 75.47.Gk; 71.30.+h;

INTRODUCTION

The physical properties of the hole doped manganites is one of the most studied topics in the last one and half decade due to the observation of ‘‘colossal’’ magnetoresistance (CMR) [1]. The basic magnetic and structural properties of $R_{1-x}A_xMnO_3$ (R: rare earth, A: Ca, Ba, Sr) were widely studied in the past. Both end members – $LaMnO_3$ and $AMnO_3$ – of $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Pb, Ba, etc) are antiferromagnetic insulators, but, doped compounds ($0.2<x<0.4$) exhibit metal-insulator transition in concomitant with the ferromagnetic-paramagnetic transition. The extraordinary electronic and magnetic properties of colossal magnetoresistance (CMR) materials $R_{1-x}A_xMn_{1-y}B_yO_3$ (where R is a trivalent rare earth and A is a divalent alkali earth, B is transition metal) have attracted considerable attention during the past decade. In these perovskite compounds, interplay between magnetism, charge ordering, and electronic transport have been studied in detail [2]. In manganites Mn ions play a crucial role in shaping the magnetic properties. Effects of Mn site substitution with different elements such as Fe, Ni, Co etc. on the T_C and other physical properties have been reported by some workers [3]. We report here a thorough study on the effects of the replacement of Mn by Cr in the colossal magnetoresistive $La_{0.67}Sr_{0.33}MnO_3$. Replacing trivalent Cr ion with Mn ion provides us a system to understand weakened double-exchange (DE) interaction (Mn^{3+}- O- Cr^{3+}) and the effect of co-doping of electrons on the system with a network of Mn^{3+}- O- Cr^{3+} and Mn^{4+}- O- Cr^{4+}. In this paper, we report the results of structural and transport properties and also energy band gap calculation on $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ ($0 \leq x \geq 0.10$) compounds. This made it possible to determine change in the electrical transport near the metal- insulator transition in this compound.

EXPERIMENTAL

Polycrystalline samples of $La_{0.67}Sr_{0.33}MnO_3$ (LSMO), $La_{0.67}Sr_{0.33}Mn_{0.95}Cr_{0.05}O_3$ (LSMCO-5) and $La_{0.67}Sr_{0.33}Mn_{0.90}Cr_{0.10}O_3$ (LSMCO-10) were synthesized by the solid state reaction method. Stoichiometric mixture of respective oxide powders was ground and reacted at 1100 ºC for 24 h in air. The samples were reground, pressed into pellets, heated again and sintered at 1300 ºC for 24 h. The structure and phase purity of samples were confirmed by Powder X-ray diffraction using Cu K_α radiation at room temperature. The temperature dependence of the resistivity was measured from 5 – 400 K without and with applied magnetic field up to 5 T. The magnetic field dependence magnetoresistance carried out at various temperatures.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ with x=0, 0.05 and 0.10. The XRD analysis indicates that all samples are single phase with perovskite rhombohedral structure and lattice cell parameters and unit cell volume are tabulated in Table 1. No impurity phase is observed in the XRD patterns, which suggest that the doped Cr substitute mainly for Mn. The similarity between the crystal structures of pure and Cr-doped samples imply that the doped Cr^{3+} ion does not change the crystalline structure of pure LSMO, which may mainly result from the similar ionic size of Mn^{3+} and Cr^{3+} and the structure remains rhombohedral.

Table 1. Lattice Parameters and Unit Cell Volume for $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ samples.

Sample Code	Lattice Parameters (*Å*)			Unit Cell Volume $(Å)^3$
	a (Å)	*b (Å)*	*c (Å)*	
LSMO	5.4797	5.4797	13.4040	402.483
LSMCO-5	5.4767	5.4767	13.3749	401.169
LSMCO-10	5.4741	5.4741	13.3600	400.342

Figure 2 demonstrates the temperature dependence of resistivity under 0 T, 1 T, 3 T and 5 T magnetic fields. When Mn is partly substituted by Cr, the system displays a complicated and interesting transport behavior. With increasing Cr content, the M–I transition near T_P shifts to lower temperature; meanwhile an additional bump grows up subsequent to it. The coexistence of two bumps of CMR results in CMR remains in a broad temperature range from the lowest (T_2) to above room temperature (T_1). The double-peaked feature of ρ-T curve has been also observed in high doping level ($y \geq 0.07$) $La_{0.67}A_{0.33}Mn_{1-y}B_yO_3$ [4]. In the absence of a magnetic field LSMCO shows T_{min} in the vicinity of 60 K. Assorted possible causes for the low-temperature resistivity minimum in the LSMCO sample are considered. These include the grain boundary, phase-separation, and electron-electron localization [5]. To confirm these reasons, work is under process by using theoretical model. The values of metal-insulator (M-I) transition temperature and resistivity are tabulated in Table 2.

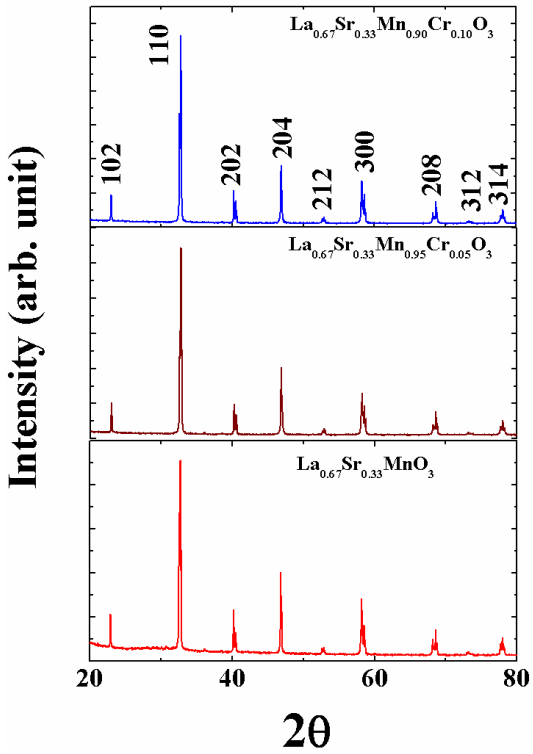

Figure 1. X-ray diffraction patterns for $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ with x=0, 0.05 and 0.10 samples.

Table 2. Metal-Insulator Transition Temperature and Resistivity for $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ samples.

Sample Code	M-I Transition (T_P) K	Resistivity (ρ) Ω*cm
LSMO	373	0.0356
LSMCO-5	351 (T_1)	0.0450
	289 (T_2)	0.0419
LSMCO-10	327 (T_1)	0.0548
	257 (T_2)	0.0506

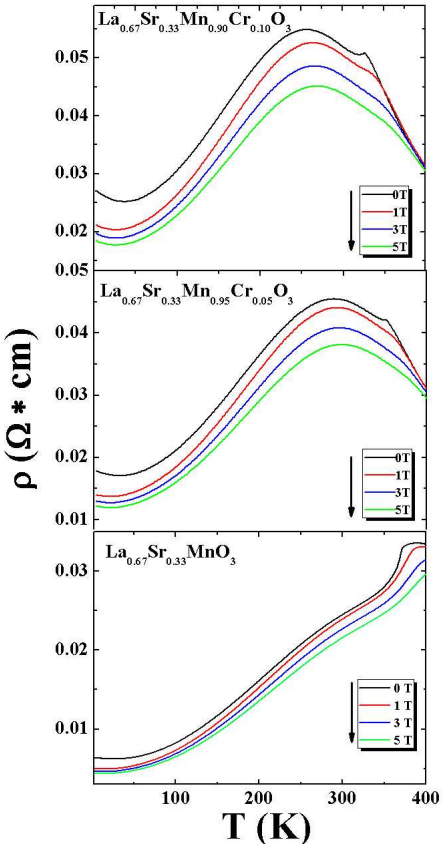

Figure 2. Temperature dependence of resistivity of $La_{0.67}Sr_{0.33}$ $Mn_{1-x}Cr_xO_3$ samples in with and without magnetic fields.

Therefore, it should be ascribed to the crucial role of Cr. It suggests that Cr element substitution on Mn site can be a potent way in tuning CMR response. This suggests that it originates from the same mechanism based on the DE between Mn ions as in undoped $La_{0.67}Sr_{0.33}MnO_3$. As we mentioned that, there is a possibility of DE through Mn^{3+}–O–Cr^{3+} due to the identical electronic configuration between Cr^{3+} and Mn^{4+}. The present results of CMR behavior in $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ could be supporting evidence to this view. We have calculated energy band gap (E_g) of for all samples and it is revealed that as per doping level increases E_g increases which is comparable with experimental data as well as due to the interruption of well known phenomena of exchange between Mn^{3+} and Mn^{4+}while as the magnetic field increases E_g decreases for each samples which is theoretically provide evidenced of CMR [6] and E_g values for each samples tabulated in Table 3. One can see that Cr substitution is inefficiency in lowering T_P, which imply that there might exist FM interaction between Mn^{3+} and Cr^{3+}. Considering those electrical properties, we assume that a FM interaction between Cr^{3+} and Mn^{3+} is similar to the traditional Mn^{3+}-O-Mn^{4+} DE process. Because of the different effect of the crystal field over Mn^{4+} and Cr^{3+}, this cause an energetic difference between e_g orbital levels of Mn^{3+} and Cr^{3+}, which becomes strong enough to result in that electronic exchange between them that is not equivalent to that between Mn^{3+} and Mn^{4+}.

Table 3. Energy Bandgap of $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ samples in with and without magnetic field.

Sample Code	Energy Band gap (E_g) eV		
	0 T	1T	5 T
LSMO	0.0102	0.0037	-
LSMCO-5	0.1732 (T_1) 0.0282 (T_2)	0.0471	0.0414
LSMCO-10	0.1807 (T_1) 0.0297 (T_2)	0.0480	0.0472

Hence, the DE interaction between Mn^{3+} and Cr^{3+} is similar to the DE interaction between Mn^{3+} and Mn^{4+} but the former is weaker than the latter.

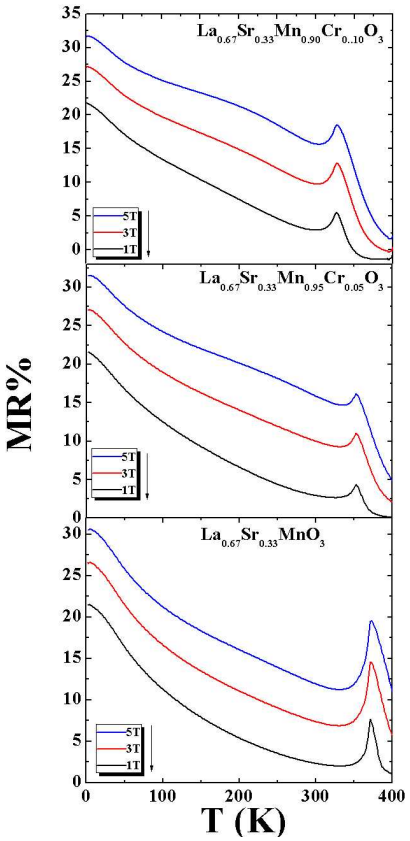

Figure 3. Temperature vs. MR % for $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ samples at various magnetic fields.

The samples show a significant change in resistance with the applied magnetic field. In other words, they bear varying amount of MR. We show in Fig. 3, the variation of MR value with applied magnetic field at different temperatures, which are tabulated in Table 4. It is clear from Fig. 3 that the prominent MR at very low temperature, the low-field (< 1 T) MR for Cr doped samples of about 32 % may be attributed to the intergranular spin polarized tunneling (SPT) of carriers [7]. Thus, it is noted that, at low temperatures, the grain boundary has a significant contribution to the electrical resistivity of the bulk sample. This is usually observed in polycrystalline

samples and may result from the grain boundary effect. MR value increases gradually with magnetic field for all samples.

Table 4. Temperature dependent MR % at 1, 3 and 5 T magnetic fields for $La_{0.67}Sr_{0.33}Mn_{1-x}Cr_xO_3$ samples.

Sample Code	Magnetoresistance (MR %)					
	1 T		3 T		5 T	
	MR %	T (K)	MR %	T (K)	MR %	T (K)
LSMO	8	371	10	372	17	372
LSMCO-5	9	354	12	353	18	354
LSMCO-10	11	327	13	327	20	327

CONCLUSION

In conclusion, Cr substitution at Mn site weakened double-exchange interaction is reflected in the progressive decrease in metal-insulator transition (T_P) and transport and magneto transport properties in manganite as well as energy band gap calculation is theoretically provide evidenced of CMR. The FM interaction between Cr^{3+} and Mn^{3+} is similar to the traditional Mn^{3+}-O-Mn^{4+} DE process.

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