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Enhanced Room Temperature Magnetoresistance Property of Co and Ti Doped $La_{0.7}Sr_{0.3}MnO_3$

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Abstract: Recently, there has been a surge of interest in the study of colossal magneto resistance (CMR) manganites due to their potential applications in the field of memory storage devices, sensors etc. Among many CMR manganites, $La_{0.7}Sr_{0.3}MnO_3$ was selected as a parent material because it has metal to insulator transition near to room temperature. We have synthesized $La_{0.7}Sr_{0.3}Mn_{1-x}A_xO_3$ (where A = Ti, Co and x = 0.00, 0.06) using Auto combustion technique. The samples were characterized using X-ray Diffraction (XRD), R-T, MR (%) and Isotherm Measurements carried out at various magnetic fields. XRD results confirmed the formation of single phase of rhombohedral structure with *R-3c* space group. The Rietveld refinement was performed using FullProf software for detailed structural investigations. The variation in lattice parameters, unit cell volume, bond length (Mn-O) and bond angle (Mn-O-Mn) was observed due to effect of Co and Ti doping. The samples exhibit the characteristic CMR behavior showing metal to insulator transition near to room temperature. These properties are important for application point of view.
Keywords: manganites, electrical conductivity, colossal magnetoresistance, x-ray diffraction, effect of doping.

Introduction and Experimental:

Recently, there has been a surge of interest in the study of colossal magnetoresistance (CMR) manganites due to their potential applications in the field of memory storage devices, sensors etc. $La_{1-x}A_xMnO_3$ (where A = Ca, Sr, and Na) with perovskite structure exhibit a rich variety of crystallographic, electronic and magnetoresistive properties. Theories have been proposed to explain the mechanism of CMR in terms of double exchange (DE) and Jahn-Teller Distortion of MnO_6 octahedra[1]. In addition to this, the theory suggests that the mixed valence (Mn^{3+}/Mn^{4+}) is also a key component for understanding the CMR effect and the transition from the paramagnetic (PM) insulator–ferromagnetic (FM) metal. The magnetic Co ion doping is more interesting due to the three kinds of spin states and the spin-state transition. Ionic radius of non magnetic Ti^{4+} ion is known to be in between those of Mn^{4+} and Mn^{3+}. A fraction of Ti^{4+} ions may substitute for Mn^{3+} ions leading to oxygen non stoichiometry (cation deficiency) and ionic mismatch effect. It was found that the substitution of various ions at different sites with various atomic radius and synthesis process can use to influence the structural, electrical and magneto-resistive properties of such manganite systems[2-5].

Polycrystalline $La_{0.7}Sr_{0.3}MnO_3$ (LSMO), $La_{0.7}Sr_{0.3}Mn_{0.94}Co_{0.06}O_3$ (LSMCO) and $La_{0.7}Sr_{0.3}Mn_{0.94}Ti_{0.06}O_3$ (LSMTO) were synthesized using acetate precursor based modified sol – gel route. High purity (> 99.9 %)

chemicals of La acetate, Sr acetate, Mn acetate, Co acetate and TiO_2 were taken as starting materials in stoichiometric ratio. The starting chemicals were dissolved in de-ionized water and acetic acid. The solutions were then dehydrated at 80°C for sol state. Further heat treatment was performed at 150°C for gelation process. Gels were dried to obtain the Black powder. The Black powders were grinding and heated at 600°C for 6 hours to obtain the well calcined black powders. Finally, all the samples were palletized and sintered at 1200°C for 4 hours followed by intermediate grindings.

Results & Discussion:

The XRD patterns of LSMO, LSMCO and LSMTO and the fits obtained from Rietveld refinement are presented in Fig. 1. XRD patterns show that all the samples are single phase and have rhombohedral (in hexagonal lattice) R-3*c* space group. The obtained values from Rietveld refinement are tabulated in table 1. With the substitution of Mn ions by Co, the structure does not undergo any transformation and lattice parameters almost remain same due to the matching in the ionic radius values. There is an increase in lattice parameters with Ti doping because of the larger ionic radii of Ti^{+4} ($r_{Ti}{}^{+4}$ = 0.605 Å) ion as compared to that of Mn^{+4} ($r_{Mn}{}^{+4}$ = 0.540 Å) ion[6]. The variation in bond length and bond angle is listed in table 1. The temperature dependence of electrical resistivity of LSMO, LSMCO and LSMTO polycrystalline samples between 5 to 300 K is shown in Fig. 2. LSMO and LSMCO samples exhibit metallic behavior in the entire temperature range but from the nature of the curve, the lower value of T_{MI} is expected for Co doped sample. An increase in resistivity and a decrease in metal to insulator transition temperature (T_{MI}) are observed by doping of Ti for Mn. It is ascribed to the replacement of some Mn^{+3}-O-Mn^{+4} bonds by the Mn^{+3}-O-Ti^{+4} bonds[7]. MR% vs. H plots for all the samples at 5 K and 300 K between 0 T to 8 T are shown in Fig. 3. Higher magnitude of MR% was observed for doped samples and it may be due to the modification in conduction channel.

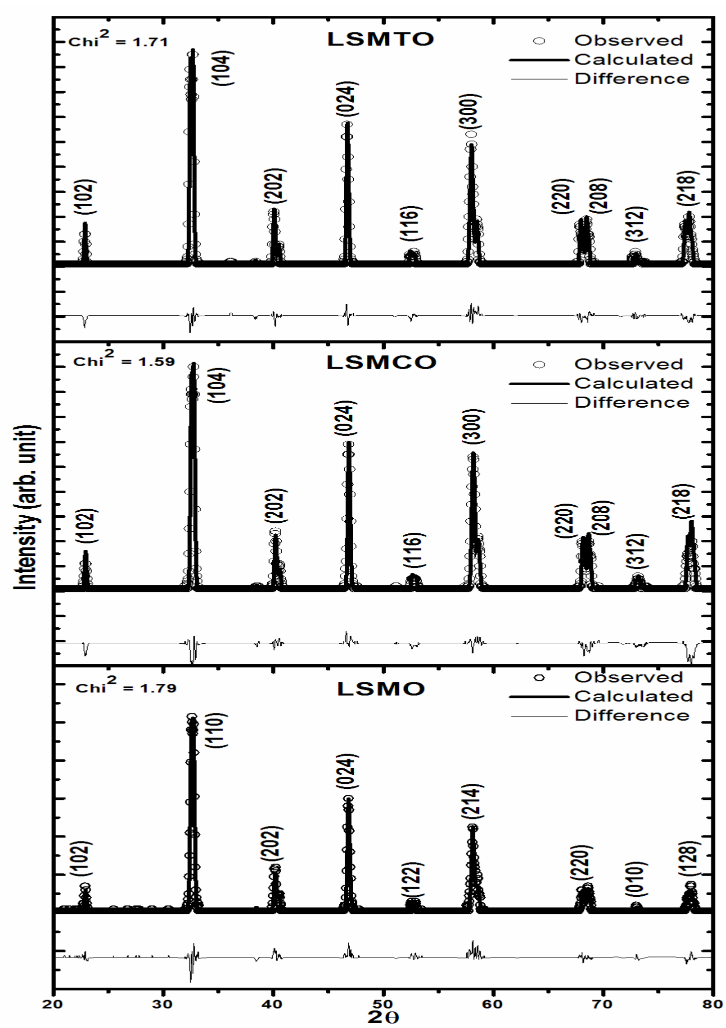

Figure 1. Rietveld fitted XRD plots of LSMO, LSMCO and LSMTO manganite.

Table 1. The values of cell parameters, space group, structure, Mn-O-Mn bond angle, average Mn-O bond length, metal-insulator transition temperature T_{MI} and maximum magnetoresistance % at 300 K.

Sample	Unit Cell Parameters (Rietveld Refinement)			Space Group	Structure	χ2	Mn-O-Mn Bond Angle	<Mn-O> Bond Length (Å)	T_{MI} (K)	MR % (300 K)
	a=b (Å)	c(Å)	V(Å^3)							
LSMO	5.50	13.35	350.16	R-3c	Rhombohedral	1.79	166.81	1.941	>300	23%
LSMCO	5.50	13.36	350.60	R-3c	Rhombohedral	1.59	166.87	1.946	300	25%
LSMTO	5.54	13.31	354.17	R-3c	Rhombohedral	1.71	167.31	1.957	240	35%

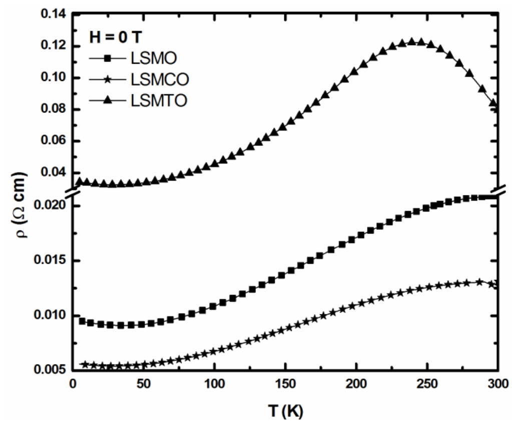

Figure 2. Temperature dependent resistivity at 0 T for LSMO, LSMCO and LSMTO samples.

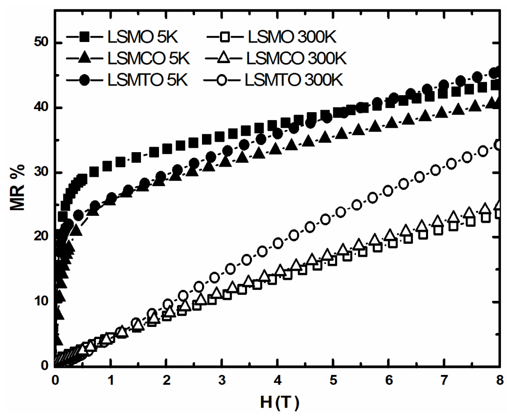

Figure 3. MR % vs. H plots for LSMO, LSMCO and LSMTO for 5 K and 300 K between 0 to 8 T.

Conclusions:

The analysis of results suggested a strong correlation between structural and magnetoresistance properties. Doping of Co and Ti at Mn-site caused variation in structural parameters, decrease of metal-insulator transition and enhanced magnetoresistance effect at room temperature. The results could be well understood by considering the different destructions on double-exchange interaction and different influences on lattice distortion caused by Co and Ti doping.

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