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RESISTIVITY STUDIES ON MN SITE SUBSTITUTED $La_{0.67}Ca_{0.33}(Mn_{1-x}Sb_x)O_3$ MANGANITES

Physics

KEYWORDS : Transition temperature, CMR, Low temperature Resistance

Dr. Bharat R. Kataria Department of Physics, Government Science College, Jhalod – 389170, Gujarat, India

Mr. Chirag R. Savaliya Department of Nanotechnology V.V.P. Engineering College, Rajkot – 360 005, Gujarat,

Dr. Jaysukh H. Markna Department of Nanotechnology V.V.P. Engineering College, Rajkot – 360 005, Gujarat, India

ABSTRACT

Effect of Mn-site disorder in La0.67Ca0.33Mn1-xSbxO3 (LCMSO) created by the substitution of Sb5+ at Mn-site is studied through X-ray diffraction (XRD) and temperature dependent resistivity measurements to identify the role of size mismatch at Mn-site and their resistivity property correlations. XRD patterns collected at room temperature for all the LCMSO samples reveal single phasic nature without any detectable impurities within the measurement range studied. XRD data shows that all the samples possess orthorhombic structure without any structural phase transition. Variation in resistivity with Sb5+ content has been discussed in detail in the context of modifications in the structural and magnetic lattices and structural disorded.

INTRODUCTION

Most of the attention to date has been focused on doping the parent compound of $LaMnO_3$ with divalent alkaline earths (e.g., Ca, Ba, Sr), such as the prototype materials of $La_{1-x}Ca_xMnO_3$, which exhibit a very rich phase diagram [1]. At low Ca doping ($x < 0.2$), these are ferromagnetic (FM) insulators, whereas at higher Ca doping ($x > 0.5$), they become antiferromagnetic (AF) insulators. In the intermediate doping range of $0.2 < x < 0.5$, one observes both FM and metallic behavior, which leads to CMR near the onset of FM ordering [2, 3]. Interestingly, in the AF

insulating phase ($x \approx 0.5$), CMR with a large magnitude has also been observed [4].

Since the essential degrees of freedom (such as spin, charge, orbital and lattice) are closely linked to the Mn ions, substitutional study at the Mn site is expected to bring about a dramatic effects. A large number of studies have reported the effect of Mn site substitution on the physical properties of different manganite systems. Generally, it has been found that possible substitutions by various ions such as 3d transition metals [5 – 10], Al [11 – 13], In [14], Ga [15], Sn [16] and Ge [17] results in the lowering of transition temperatures [i.e. metal to insulator (T_p) and FM to paramagnetic (PM) (T_C)], but to different extents, and eventually lead to insulating states exhibiting cluster/spin glass properties. The reduction in the T_p / T_C has been broadly attributed to the weakening of the DE interaction strength. No systematic attempts have been made to define the various factors affecting the transition temperatures. It can be understood that, there are at least two major contributions, (i) local structural effects and (ii) local magnetic coupling effects, influencing the transition temperatures of the CMR manganites. Local structural effects play a dominant role, both, in affecting the phase transition temperatures and in the ground state properties of CMR manganites.

Keeping in mind the above mentioned aspects of Mn-site substitutional effects in manganites, in this chapter, an attempt has been made to understand the effect of $3d^{10}$ Sb^{5+}, doping at Mn-site in $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ system, in modifying the structural lattice distortion due to smaller ion (Sb^{5+}: 0.6Å) substitution at large ionic Mn-site, variation in Mn valance states due to substitution of higher valance (5+ of Sb at Mn-site results into the reduction in Mn^{4+} ion density) and magnetic Mn lattice modifications (through a magnetic interaction between the Sb and Mn ions.

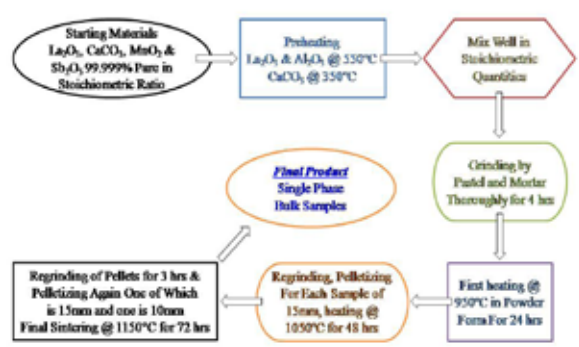
EXPERIMENTAL

Polycrystalline samples of $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ (LCMSO) with x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10 (hereafter referred as S0, S2, S4, S6, S8 and S10, respectively) were synthesized using conventional solid state reaction (SSR) route. The dried starting powders of La_2O_3, $CaCO_3$, MnO_2 and Sb_2O_5 were mixed in stoichiometric proportions and calcined at 950°C for 24 hrs. Samples were then pressed into pellets and sintered at 1050°C for 48 hrs followed by a sintering at 1150°C for 72 hrs. Figure 4.4 shows the flow diagram containing various heating, grinding and pelletizing steps involved in the conventional solid state reaction route used for synthesizing $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ manganites. X-ray diffraction (XRD) patterns were recorded on Philips diffractometer (PW 3040/60, X'pert PRO) using CuKα radiation at RT. Structural analysis was carried out using Rietveld refinement using the standard FULLPROF code [18]. Electrical resistivity and magnetoresistance measurements (temperature range: 5 - 300K and field range: 0 - 8T) were performed using the standard four probe dc method.

RESULT AND DISCUSSION

In order to understand the structure, structural phases present and phase purity of LCMSO system, XRD studies on all the Sb-doped $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ (LCMSO) (x = 0.00, 0.02, 0.04, 0.06, 0.08 and

Figure 1 Flow diagram containing various heating, grinding and pelletizing steps involved in the conventional solid state reaction route and used for synthesizing $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ manganites



0.10) samples were carried out at RT. Figure 2(A) depicts the XRD raw data of all the LCMSO samples showing single phasic nature without any detectable impurities and any structural phase transition. Figure 2(B) shows an enlarged view of most intense *(121)* XRD peak of LCMSO system depicting the shifting of *(121)* peak towards lower 2θ degree and converted into doublet which can be attributed to the substitution of smaller Sb^{5+} (0.6Å) at larger Mn^{3+} (0.645Å) site and hence enhancement in lattice parameters and unit cell volume.

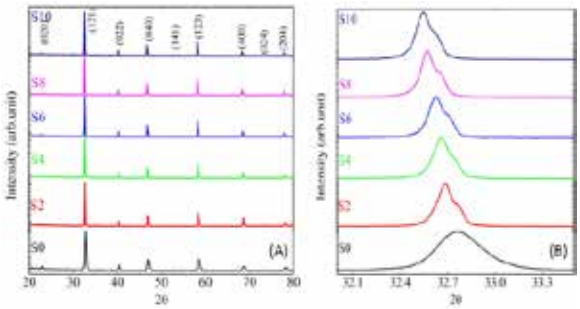


Figure 2. (A) XRD patterns of LCMSO samples. (B) Enlarge view of (121) XRD peak of LCMSO samples

Four Probe Resistivity Measurements

In order to understand the substitutional effect of Sb+5 ion at Mn-site on the transport in La0.67Ca0.33Mn1-xSbxO3 (LCMSO) manganites, temperature dependent resistance manganites have been carried out in the temperature range 5 – 300K under zero applied field.Plots of temperature dependence of resistivity under zero applied field for all the LCMSO samples are shown in figure 4.4. All the samples exhibit metal ($d\rho > 0$) to insulator ($d\rho < 0$) transition temperature (TP). Substitutional effect of Sb5+ doped at Mn site clearly indicates the increase in peak resistivity (ρP) and reduction in TP with increasing Sb5+ content (x). Values of ρP and TP for all the LCMSO samples studied are tabulated in

Figure 3. (A) Temperature dependence of resistivity (in logarithmic scale) under zero applied filed for LCMSO Samples. (B)Variation in T_p and ρ_p (in logarithmic scale) with Sb^{5+} content (x) for LCMSO Samples.

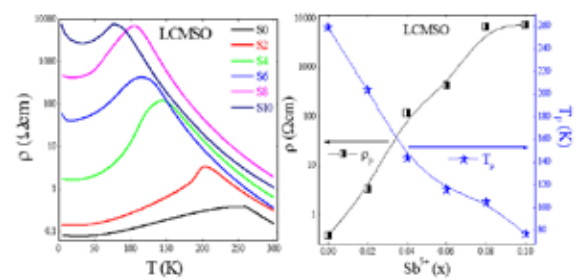


Table 1. Values of resistivity at peak (ρ_p) and transition temperature (T_p) for $La_{0.67}Ca_{0.33}Mn_{1x}Sb_xO_3$ samples

Sample Code & Content (x)	Peak Resistivity (ρ_p) (Ωcm)	Transition Temperature T_p (K)
S0 (0.00)	0.381	259
S2 (0.02)	3.325	204
S4 (0.04)	118.344	144
S6 (0.06)	426.579	116
S8 (0.08)	6960.562	105
S10 (0.10)	7542.592	77

Increase in resistivity and reduction in T_p in LCMSO system can be understood as follow:

- Ionic size, valence state, coordination number and structure of Sb^{5+} and $Mn^{3+/4+}$ ions lead us to believe that, in the desired six-fold coordination, Sb^{5+} ions (0.60Å) would replace Mn^{4+} (0.53Å) rather than Mn^{3+} (0.645Å) ionic site due to lesser valence difference between Sb^{5+}/Mn^{4+} pair than Sb^{5+}/Mn^{3+} pair.
- Substitution of smaller Sb^{5+} ions at Mn^{4+} site introduces a structural disorder at B-site in ABO_3 perovskite structure due to a large ionic size difference between them.
- Magnetic interactions between the magnetic Mn^{3+} and diamagnetic Sb^{5+} come into the picture.
- Structural disorder result in the modifications of Mn-O-Mn bond angles and Mn-O bond lengths which resulting in the deterioration in e_g electron transfer from Mn^{3+} to Mn^{4+} via O^{2-} and hence reduces the transfer integral of itinerant electrons. This in turn enhances the resistivity and suppresses T_p with increasing x.
- With increasing Sb^{5+} content (x) in LCMSO system, Mn^{4+} ionic density decreases by a factor of 2x and Mn^{3+} increases by a factor of x. The deficient Mn^{4+} magnetic site suppresses the possibility of zener double exchange (ZDE) mechanism while on the other hand increased Mn^{3+} ionic density enhances overall Jahn-Teller effect which weakens the transport in the manganites and reduces T_p with increasing Sb^{5+} content.
- Favorable indirect FM interactions between Mn^{3+} and Mn^{4+} ions through ZDE mechanism can be controlled by reduced Mn^{4+} ionic density and possible magnetically destructive Mn^{3+} - O^{2-} - Sb^{5+} interactions suppress the ferromagnetism of manganites due to diamagnetic nature of Sb^{5+} ($3d^{10}$) ions.
- All the LCMSO samples studied exhibit a low temperature anomaly in resistivity vs. temperature plots, as shown in figures 4.4. With increasing temperature, resistivity decreases in metallic region (at low temperature) below their respective T_p, which can be understood using various possible mechanisms responsible for low temperature transport in manganites. These includes, grain boundary, kondo effect, phase separation, electron – electron scattering (EES), etc [19 – 23].

CONCLUSION

In this chapter, structural and phsse transition measurements have been performed on $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ manganites in order to understand the substitutional effect diamagnetic Sb^{+5} on the properties. All the LCMSO samples are found to be single phasic, show the strong dependence of peak resistivity (α_p) and metal to insulator transition temperature (T_p) on Sb^{5+} content (x). This has been discussed in detail on the basis of smaller ionic substitution at larger ionic site, high valance Sb ionic substitutional effect on the generation of Jahn-Teller Mn^{3+} ions and reduction in non-Jahn-Teller ions – Mn^{4+} resulting into the suppuration of ZDE mechanism and transfer integral and finally on the basis of magnetic interactions between the magnetic Mn and diamagnetic Sb ($3d^{10}$) ions. Due to the presence of diamagnetic Sb^{5+} ions in the magnetic lattice of the LCMSO samples, transport channels are blocked and hence at low temperature, sharp rise in resistivity has been observed which has been understood on the basis of coulomb blocked model. Blocking energy, energy required to move the charge carriers form one Mn to next nearest Mn-site, increases with increasing x. LCMSO sample which is a useful for possible spintronic applications.

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