Resistivity Studies on Mn Site Substituted LCMSO Manganites

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ABSTRACT

Effect of Mn-site disorder in La$_{0.67}$Ca$_{0.33}$Mn$_{1-x}$Sb$_x$O$_3$ (LCMSO) created by the substitution of Sb$^{5+}$ 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 Sb$^{5+}$ content has been discussed in detail in the context of modifications in the structural and magnetic lattices and structural disorder.

1. INTRODUCTION

Most of the attention to date has been concentrated 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$_x$MnO$_3$, which shows 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 $0.2 < x < 0.5$, which 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$_{0.65}$Ca$_{0.35}$Mn$_1$...
s, SbO₃ system, in modifying the structural lattice distortion due to smaller ion (Sb⁵⁺; 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 Mn⁴⁺ ion density) and magnetic Mn lattice modifications (through a magnetic interaction between the Sb and Mn ions).

2. RESEARCH METHOD

Polycrystalline samples of La₀.₆₇Ca₀.₃₃Mn₁₋ₓSbₓO₃ (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 La₂O₃, CaCO₃, MnO₂ and Sb₂O₅ 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 1 shows the flow diagram containing various heating, grinding and pelletizing steps involved in the conventional solid state reaction route used for synthesizing La₀.₆₇Ca₀.₃₃Mn₁₋ₓSbₓO₃ manganites. X-ray diffraction pattern was recorded on Philips diffractometer (PW 3040/60, X'pert PRO) using CuKα radiation at RT. Structural analysis was carried out 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.

Figure 1. Flow diagram containing various heating, grinding and pelletizing steps involved in the conventional solid state reaction route and used for synthesizing La₀.₆₇Ca₀.₃₃Mn₁₋ₓSbₓO₃ manganites

3. RESULTS AND ANALYSIS

In order to understand the structure, structural phases present and phase purity of LCMSO system, XRD studies on all the Sb-doped La₀.₆₇Ca₀.₃₃Mn₁₋ₓSbₓO₃ (LCMSO) (x = 0.00, 0.02, 0.04, 0.06, 0.08 and 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 20 degree and converted into doublet which can be attributed to the substitution of smaller Sb⁵⁺ (0.6Å) at larger Mn⁴⁺ (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

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3.1. Four Probe Resistivity Measurements

In order to understand the substitutional effect of Sb$^{5+}$ ion at Mn-site on the transport in La$_{0.67}$Ca$_{0.33}$Mn$_{1-x}$Sb$_x$O$_3$ (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 3(a). All the samples exhibit metal (dρ > 0) to insulator (dρ < 0) transition temperature (T$_P$). Substitutional effect of Sb$^{5+}$ doped at Mn site clearly indicates the increase in peak resistivity (ρ$_P$) and reduction in T$_P$ with increasing Sb$^{5+}$ content (x). Values of ρ$_P$ and T$_P$ for all the LCMSO samples studied are tabulated in Table 1.

![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](image)

| 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:

1. Ionic size, valence state, coordination number and structure of Sb$^{5+}$ and Mn$^{3+}$ 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.

2. 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.

3. Magnetic interactions between the magnetic Mn$^{3+}$ and diamagnetic Sb$^{5+}$ come into the picture.

4. 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.

5. 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.

6. 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 3(a). 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].

4. CONCLUSION

In this chapter, structural and phase transition measurements have been performed on LSCO and Mn site substituted LSCO manganites in order to understand the substitutional effect of diamagnetic Sb$^{5+}$ on the properties. All the LCMSO samples are found to be single phasic, show the strong dependence of peak resistivity ($\rho_p$) and metal to insulator transition temperature ($T_p$) on Sb 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 in detail on 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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