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Magnetic Field Sensitivity of $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ Manganites: Role of Nonmagnetic Sb Substitution

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Abstract

In this communication, I report the results of the studies on structural, transport and field sensitivity of nonmagnetic Sb substituted $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ (LCMSO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) manganites grown by conventional solid state reaction route. X-ray diffraction (XRD) measurements reveal the single phasic nature of the samples while Rietveld analysis performed on all the XRD raw data suggests the orthorhombic unit cell structure with *Pnma* space group (no. 62) for all the samples understudy. Resistivity is found to decrease with increase in applied magnetic field indicating an existence of negative magnetoresistance (MR) effect. Field and Sb content dependent variation in field sensitivity (FCR) has been discussed in this communication.

Keywords: Solid State Reaction, Manganites, Nonmagnetic, X-ray Diffraction, Magnetic Field Sensitivity, Structural Disorder, Magnetic Lattice Distortion

1. Introduction

Synthesis and characterization of colossal magnetoresistance (CMR) manganites has been a subject of intense research due to their unique structural, transport, magnetotransport and magnetic properties. Studies on CMR manganites are interesting because of their intrinsic interrelated structural and physical properties, i.e. structure – property correlations, exhibited by them [1 – 3] and their possible technological applications in p-n junctions [4], capacitors [5], temperature sensors [6], magnetic field sensors [7], field effect devices [8], magnetic tunnel junctions [9], spin transistors [10], switching devices [11], etc. Apart from these practical potential for spintronic based applications of mixed valent manganites, various fundamental properties are exhibited by perovskite manganites such as metal to insulator transition at temperature T_P, ferromagnetic transition temperature at T_C, magnetoresistance (MR), CMR effect, temperature and field dependent intrinsic and extrinsic MR, charge ordering (CO), orbital ordering (OO), spin ordering (SO), etc.

Control over various physical properties of mixed valent manganites such as phase transitions, charge ordering, orbital ordering, T_P, T_C, MR, resistivity, magnetization, etc can be possible through substitution of monovalent [12], divalent [13], trivalent [14], tetravalent [15], pentavalent [16] or hexavalent [17], ions at either A site or B site in mixed valent ABO_3 type perovskite manganites. Physical properties, especially magnetotransport and magnetism, of mixed valent manganites have been modified by substitution of either magnetic ions [18 – 20] or nonmagnetic ions [14, 21] depending upon magnetic interactions between dopant ions and Mn ions in manganites. Modifications in physical properties of Mn site substituted mixed valent manganites have been discussed in the context of substitution induced structural disorder and magnetic lattice distortion.

Manganites are known to exhibit field sensitivity [6, 7, 22 – 26] and temperature sensitivity [6, 7, 22 – 26] in the form of thin films, multilayers and heterostructures. Magnetic field sensitivity can be calculated using the expression: field coefficient of resistance (FCR) (%/Oe or %/T) = $(1 / R) \times (dR / dH) \times 100$ (H is the applied magnetic field) while temperature sensitivity can be calculated by: temperature coefficient of resistance (TCR) (%/K) = $(1 / R) \times (dR / dT) \times 100$ (T is the temperature). Swift heavy ion (SHI) irradiation induced improvement in field sensitivity exhibited by chemically grown $La_{0.7}Pb_{0.3}MnO_3$ manganite has been reported [6]. Large FCR ~ + 20%/T and – 50%/T has been obtained for manganite based heterostructure [7]. FCR ~ 35%/T at zero applied field at room temperature (RT) has been reported by Vachhani et al [22]. Markna et al [23] have reported SHI irradiation induced improvement in FCR in manganite based thin films. Parmar et al [24] have reported an increase in FCR by 200% due to irradiation on $La_{0.7}Ba_{0.3}MnO_3$ thin films. Maximum FCR ~ – 12%/T is obtained for $La_{0.5}Pr_{0.2}Sr_{0.3}MnO_3$ thin film at 250K which gets increased up to – 20%/T at 220K in $La_{0.5}Pr_{0.2}Sr_{0.3}MnO_3$ / Al_2O_3 (1nm) / $La_{0.5}Pr_{0.2}Sr_{0.3}MnO_3$ heterostructure [25]. Temperature dependent FCR studies have been carried out by Markna et al [26] for nanostructured Al_2O_3 based manganite heterostructure.

By keeping in mind all the above mentioned various aspects of potential for practical applications of mixed valent manganites and fundamental physics exhibited by them, in this communication; I report the results of the studies on mixed valent $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ (LCMSO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) manganites grown by conventional solid state reaction route for their magnetic field sensitivity. Variation in resistivity and magnetic field sensitivity have been discussion in the context of structural disorder and magnetic lattice distortion in the presently studied LCMSO system generated due to substitution of smaller nonmagnetic Sb at larger magnetic Mn site in LCMSO manganite system.

2. Experimental Details

Polycrystalline bulk samples of $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ (LCMSO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) manganites were synthesized by conventional solid state reaction route at high temperatures. Stoichiometric mixture of 99.99% pure La_2O_3, $CaCO_3$, MnO_2 and Sb_2O_5 was thoroughly ground in an agate mortar and then by fired at 950°C for 24 hours followed by several cycles of grinding, pelletizing and heating (calcination and sintering) for 48 hours and 72 hours at 1050°C and 1150°C, respectively. Hereafter, the samples will be referred as S0%, S2%, S4%, S6%, S8% and S10% for x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10, respectively. X-ray powder diffraction (XRD) at room temperature was used to verify phase purity and homogeneity. Rietveld analysis was done on XRD raw data using FULLPROF computer program to understand the structural aspects of the system. Resistivity measurements have been carried out by performing applied magnetic field dependent resistance measurements at different temperatures in the field range: 0 – 8T and temperature range: 5 – 300K.

3. Results and Discussion

Figure 1 shows the typical Rietveld fitted XRD patterns of $La_{0.67}Ca_{0.33}MnO_3$ (S0%) and $La_{0.67}Ca_{0.33}Mn_{0.9}Sb_{0.1}O_3$ (S10%) ceramic manganites suggesting single phasic nature of all the samples understudy without any detectable impurities within the measurement range studied. Also, the analysis of the XRD raw data using Rietveld program: FULLPROF code, indicate that all the LCMSO samples possess orthorhombic unit cell structure having *Pnma* space group (no. 62). For Rietveld refinements, the line shape of the diffraction peaks was generated by a modified Lorentzian function. Matching between the experimental data and calculated data indicates better crystalline nature of the samples. The values of Rietveld refined lattice parameters are: a = 5.4718Å, b = 7.7064Å and c = 5.4686Å resulting in cell volume V = 230.5993Å^3 for S0% sample which get enhanced for S10% and become a = 5.4941Å, b = 7.7716Å and c = 5.4915Å resulting in cell volume V = 234.4758Å^3. Observed enhancement in cell volume upon substitution of Sb ion at Mn site may be ascribed to the smaller size of Sb^{5+} (0.60Å) substituted at larger size of Mn^{3+} (0.645Å) in LCMSO manganite system.

Figure 2 shows the variation in resistivity with applied magnetic field (range: 0 – 8T) at different temperatures (5, 75, 200 and 300K) for presently studied LCMSO samples. It can be seen that with increase in applied magnetic field, resistivity decreases which can be attributed to the field induced suppression in the scattering of charge carriers at grain boundaries and reduction in Mn – O – Mn bond angles. Reduction in resistivity with increase in applied magnetic field suggests an existence of negative magnetoresistance [MR: MR (%) = $\{(\rho_H - \rho_0) / \rho_0\} \times 100$] effect in the presently studied LCMSO system. Also, it can be seen that with increase in Sb content up to 6%, resistivity increases while for higher doping level, it varies non-monotonically with Sb content. This can be understood as: (i) with increase in smaller Sb content, due to size mismatch between the Sb and Mn ions, structural disorder increases resulting in the deteriorated Mn – O – Mn bond angles and Mn – O bond lengths which further suppressing the transfer integral of e_g electrons between Mn ions through oxygen intermediate ion and hence enhances resistivity. (ii) Also, with increase in nonmagnetic Sb content, magnetic distortion gets enhanced which in turn results into the disorder in Mn lattice and hence reduces the hopping of e_g electrons across the Mn magnetic lattice and hence enhances the resistivity with Sb content.

Variation in field sensitivity (FCR) with applied magnetic field for all the LCMSO samples understudy is shown in figure 3 for the applied magnetic range: 0 – 8T at room temperature (RT). Variation in FCR with field reveals that negative FCR increases with field while FCR continuously decreases with Sb content from S0% to S6%, while irregular variation in FCR value has been observed for higher substitution levels. Specifically, S8% sample shows fluctuating nature of FCR with field which may be due to high structural disorder in the sample. Maximum FCR ~ 4.0%T^{-1} which is a potential of LCMSO for practical applications.

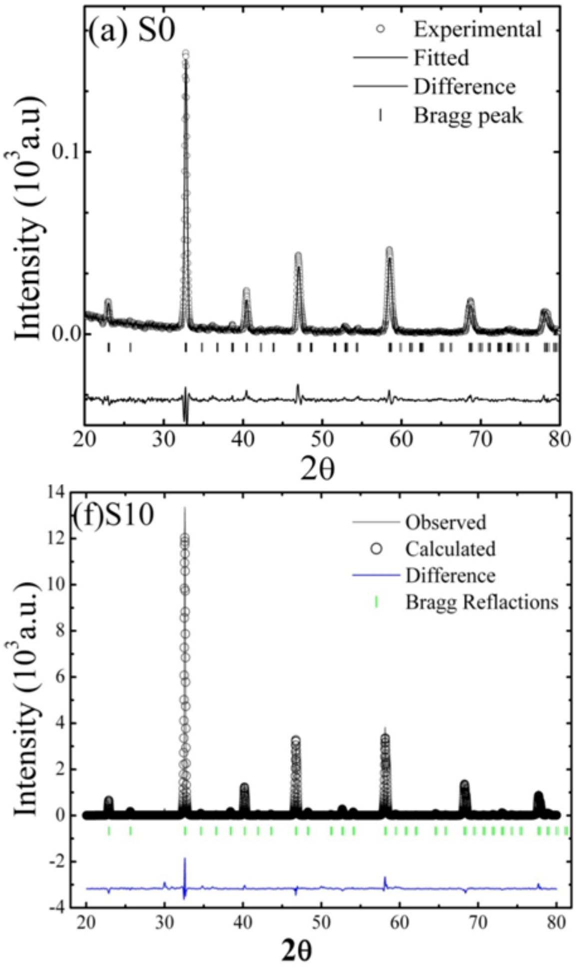

Figure 1: Rietveld refined typical XRD patterns of $La_{0.67}Ca_{0.33}MnO_3$ (S0%) and $La_{0.67}Ca_{0.33}Mn_{0.9}Sb_{0.1}O_3$ (S10%) ceramic manganites

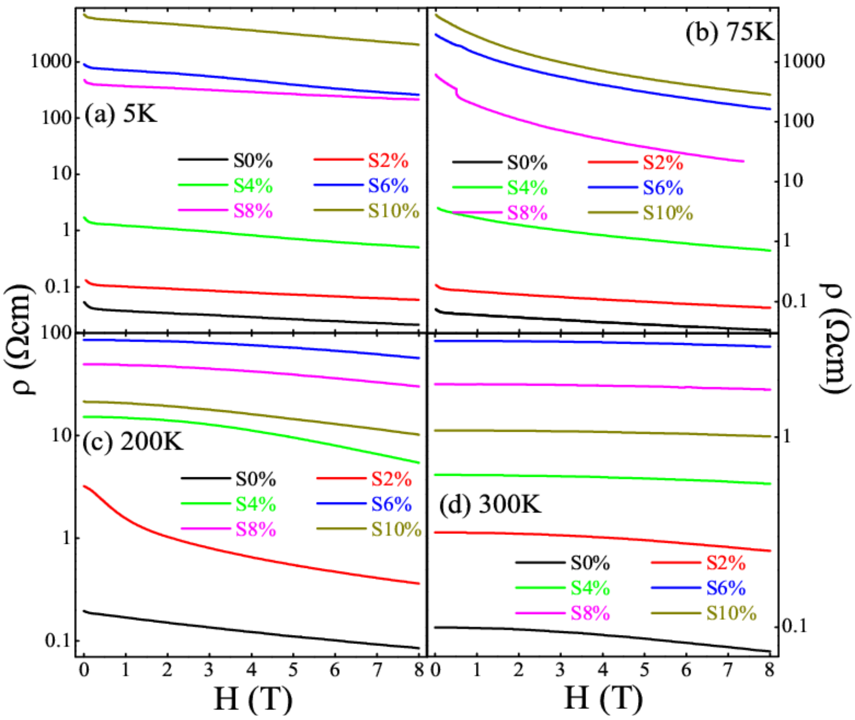

Figure 2: **Variation in resistivity with applied magnetic field at (a) 5K, (b) 75K, (c) 200K and (d) 300K for $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ (LCMSO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) ceramic manganites**

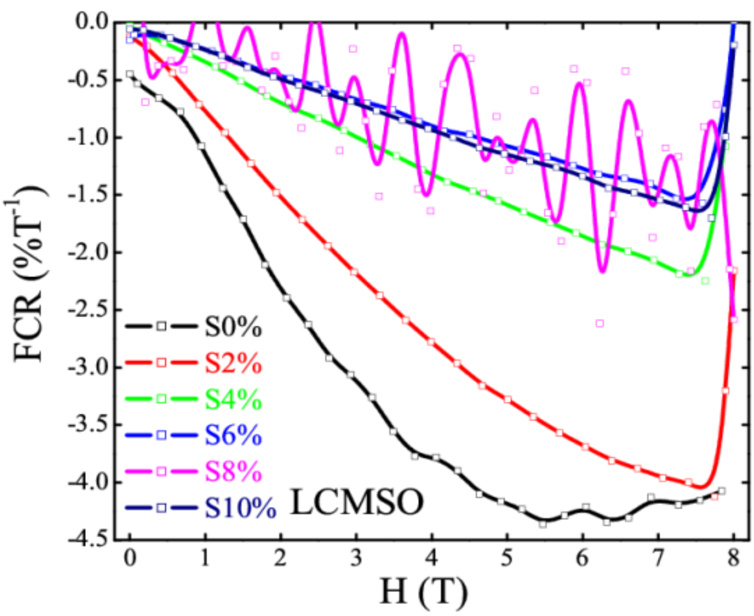

Figure 3: **Variation in field sensitivity (FCR) with applied magnetic field for $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ (LCMSO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) ceramic manganites**

4. Conclusion

In conclusion, high purity crystalline manganite samples of $La_{0.67}Ca_{0.33}Mn_{1-x}Sb_xO_3$ (LCMSO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) have been grown by conventional solid state reaction route. Structural studies using X-ray diffraction (XRD) and Rietveld analysis suggest that all the samples are single phasic in nature without any detectable impurities within the measurement range studied. All the samples possess orthorhombic unit cell structure having *Pnma* space group (no. 62) and it is found that cell parameters and unit cell volume increase with increase in Sb substitution level at Mn site. Field induced suppression in resistivity has been discussed in detail in the context of field induced modifications in the charge carrier scattering phenomenon, change in Mn – O – Mn bond angle, structural disorder and magnetic lattice distortion. Dependence of field sensitivity on applied magnetic field and Sb content for the presently studied LCSMO ceramic manganites has been discussed and fluctuations in the field sensitivity has been correlated with the presence of high structural disorder in the samples.

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