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Effect of Nonmagnetic Ga Substitution on Magnetic Field Sensitivity of $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ Manganites

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Abstract

In this communication, I report the results of the studies on structural and transport behavior of polycrystalline nonmagnetic Ga substituted $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ (LCMGO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) manganites synthesized by conventional solid state reaction route. Structural investigations, done by carrying out X-ray diffraction (XRD) measurements and by performing Rietveld analysis on raw data of XRD results, suggest the single phasic nature of all the samples. Applied magnetic field dependent resistivity measurements show an existence of negative magnetoresistance (MR) and a strong effect of Ga content on the resistivity of the samples. Field sensitivity (FCR) results suggest the increase (decrease) in FCR with increase in applied magnetic field (Ga content) which has been correlated with the role of structural disorder. Observation of fluctuations in FCR has been attributed to the Ga substitution induced structural disorder in the LCMGO manganite system.

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

1. Introduction

Mixed valent manganites exhibit various potential and highly correlated properties such as insulator to metal transition at temperature T_P, paramagnetic to ferromagnetic transition at temperature T_C, large magnetoresistance (MR) at low temperature, colossal magnetoresistance (CMR) effect at high temperature ~ T_P / T_C, charge ordering (CO) state, orbital ordering (OO) state, spin ordering (SO) states, etc which depends upon various crystallographic orders and structural disorders [1, 2]. Various groups have studied the manganites for their structural properties [3], magnetic structure [4], transport properties [5], transport mechanisms [6], magnetism [7], magnetotransport behavior [8], etc in the form of polycrystalline bulk [9], thin films [10], nanostructures [11], nanostructured thin films [12], devices [13], heterostructures [14], multilayers [15], etc. Manganites have been studied well for various practical applications such as p-n junctions [16], capacitors [17], field effect devices [18], field sensors [19], temperature sensors [20], magnetic tunnel junctions [21], switching devices [22], spin transistors [23], etc.

Tuning of transport and magnetic properties of mixed valent ceramic manganites is possible by substituting monovalent [24], divalent [25], trivalent [26], tetravalent [27], and / or pentavalent [28] ions at either A-site (La-site) and / or B-site (Mn-site) in manganites. Modifications in the transport, magnetotransport and magnetic properties of mixed valent manganites depend upon the nature of the ions doped at Mn-site in manganites, i.e. either nonmagnetic in nature [9, 26] or magnetic in nature [29 – 31]. In other words, ionic radius of dopants, magnetic nature of dopants, and possible magnetic interactions between the dopant/s and Mn ion/s govern the transport and magnetic properties of Mn-site doped mixed valent manganites.

Few reports are available on the magnetic field sensitivity [15, 19, 20, 32 – 35] and temperature sensitivity [15, 19, 20, 32 – 35] of mixed oxide manganites. Magnetic field sensitivity can be calculated using the expression: field coefficient of resistance (FCR) (%/Oe or %/T) = (1 / R) × (dR / dH) × 100 (H is the applied magnetic field) while temperature sensitivity can be calculated by: temperature coefficient of resistance (TCR) (%/K) = (1 / R) × (dR / dT) × 100 (T is the temperature). Vachhani et al [15] have discussed the role of substrate used and effect of interfacial strain on the field sensitivity (FCR) for manganite based multilayered structures grown on two different single crystalline substrates. They observed negative 35% FCR at zero applied field for manganite multilayer grown on single crystalline STO substrate. Khachar et al [19] have observed fluctuating FCR (maximum FCR ~ 40%/T) across ZnO – manganite and manganite SNTO interface of manganite based heterostructure which has been attributed to disordered interfaces. Film thickness dependent FCR has been reported for $La_{0.7}Pb_{0.3}MnO_3$ manganite films grown by low cost chemical solution deposition (CSD) method and improvement in FCR (~ 400% increase in FCR values) is obtained due to swift heavy ion (SHI) irradiation effect [20]. Similar SHI induced improvement in FCR has been reported by various authors in last decade for manganite based thin films and heterostructures [32 – 35].

By keeping in mind all the above aspects of manganites and their possible practical applications as field sensor, in this communication, I report the results of the studies on applied magnetic field dependent resistance behavior and field sensitivity of nonmagnetic Ga substituted $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ (LCMGO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) manganites synthesized by conventional solid state reaction route.

2. Experimental Details

Polycrystalline manganite samples of $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ (LCMGO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) ceramics have been successfully synthesized using conventional solid state reaction route. La_2O_3, $CaCO_3$, MnO_2 and Ga_2O_3 were taken as starting materials. All the starting materials were mixed together in appropriate stoichiometric ratio followed by thorough grinding for 3 hours and calcination at 950^{o}C for 24 hours. Calcined powder was then ground and palletized under high pressure followed by sintering at various temperatures between 1050^{o}C to 1150^{o}C for 248 hours to 72 hours with intermediate grindings. Hereafter, the samples will be known by the following symbols: G0%, G2%, G4%, G6%, G8% and G10% for x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10, respectively. To understand the structural properties of LCMGO samples, X-ray diffraction (XRD) measurements were performed and Rietveld refinement was carried out to confirm the single phasic nature of the samples. D.C. four probe resistance was measured as a function of applied magnetic field (range: 0 – 8T) at different temperatures in the range: 5 – 300K.

3. Results and Discussion

Figure 1 shows typical Rietveld refined XRD patterns of (a) $La_{0.67}Ca_{0.33}MnO_3$ (G0%) and (b) $La_{0.67}Ca_{0.33}Mn_{0.9}Ga_{0.1}O_3$ (G10%) ceramic manganites. It is seen that all the LCMGO samples possess single phasic nature without any detectable impurities within the measurement range. Clear matching between the experimental and calculated data and almost straight difference line for both the samples (G2% and G10%) reveal high structural quality of the samples. All the samples crystallize in orthorhombic unit cell having *Pnma* space group (no. 62). It is found that the cell parameters increase form a = 5.4732Å (G2%) to 5.5201Å (G10%), b = 7.6367Å (G2%) to 7.7064Å (G10%) and c = 5.4567Å (G2%) to 5.6577Å (G10%) resulting in the enhancement in unit cell volume from V = 225.1079Å^3 to 240.6791Å^3 with increase in Ga content. This can be ascribed to the substitution of smaller Ga^{3+} (0.62Å) ion at larger ionic site of Mn^{3+} (0.645Å) resulting in the enhancement in structural disorder with increase in Ga content.

Figure 2 shows the variation in resistivity with applied magnetic field (range: 0 – 8T) recorded at different temperatures, 5, 100, 200 and 300K. For all the samples understudy, at all the temperatures, resistivity gets suppressed upon increase in applied magnetic field indicating an existence of negative magnetoresistance [MR: MR (%) = $\{(\rho_H - \rho_0) / \rho_0\} \times 100$] in the presently studied system. Reduction in resistivity with increase in applied magnetic field can be attributed to the field induced reduction in scattering of the charge carriers at the grain boundaries and suppression in magnetic disorder at Mn – O – Mn bond angles and Mn – O bond lengths. Almost at all the temperatures, resistivity increases with increase in Ga content which can be understood as: with increase in Ga content, structural disorder increases due to size mismatch between Ga and Mn ions resulting in the increase in resistivity and substitution of nonmagnetic Ga at magnetic Mn site consequences in the deterioration of magnetic lattice of manganites understudy. This in turn results in the suppression in transfer integral of e_g electrons and hence enhancement in resistivity with increase in Ga content.

Figure 3 shows the variation in field sensitivity (FCR) with applied magnetic field for all the LCMGO samples studied. It can be seen that with increase in field, FCR increases while with increase in nonmagnetic Ga^{3+} content, FCR decreases which can be correlated with the enhanced magnetic disorder due to the nonmagnetic Ga^{3+} ion substitution at magnetic Mn^{3+} site. All the samples exhibit negative field sensitivity at all the field values. Maximum field sensitivity is found to be ~ – 4.5%/T for G2% sample which decreases up to ~ – 2.0%/T for G10% manganite sample. Also, it is observed that all the samples exhibit slight fluctuations in the field sensitivity with applied magnetic field which can also be seen by Khachar et al [19] in manganite based p-n junctions wherein they have attributed the fluctuations to the disordered junction interface. For the present case of LCMGO manganites, it can be suggested that smaller ion Ga3+ substitution induces large structural disorder in the system which in turn results in the fluctuating nature of FCR with applied magnetic field. This can be confirmed by the observation of large fluctuations in higher Ga substituted LCMGO manganites as compared to lower Ga content based samples, since larger the Ga content, higher the structural disorder.

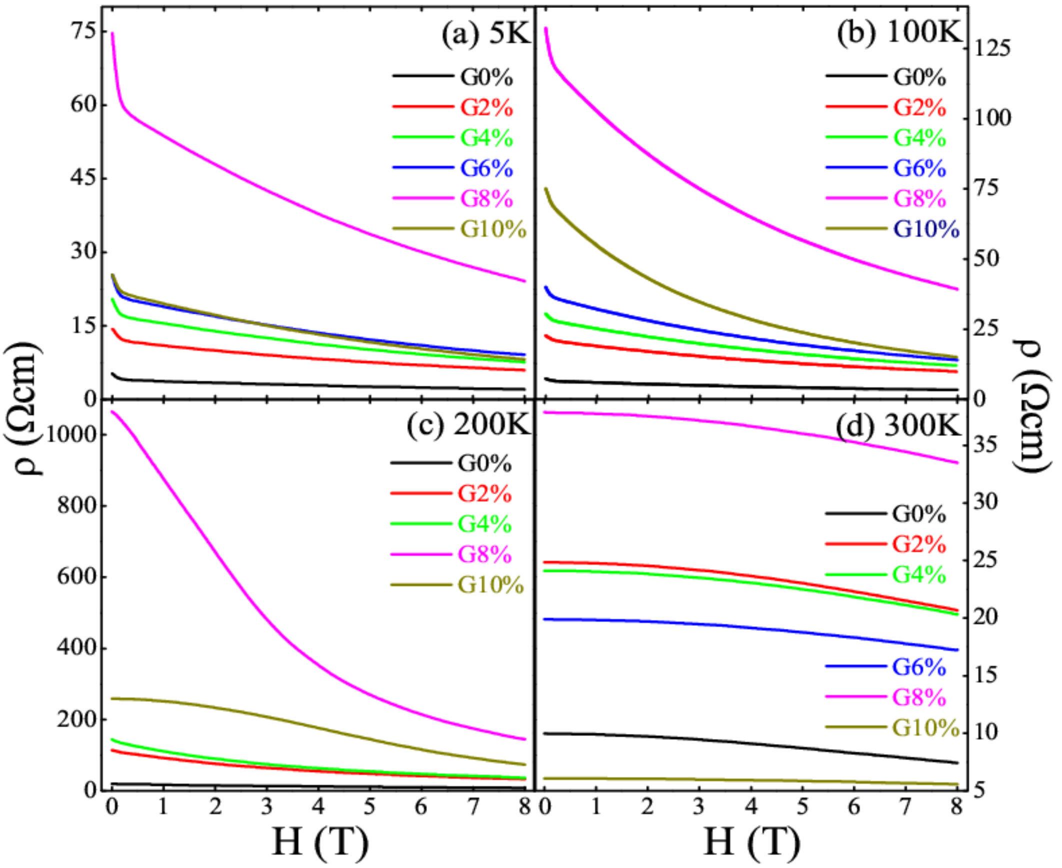

Figure 1: Rietveld refined typical XRD patterns of $La_{0.67}Ca_{0.33}MnO_3$ (G0%) and $La_{0.67}Ca_{0.33}Mn_{0.9}Ga_{0.1}O_3$ (G10%) ceramic manganites

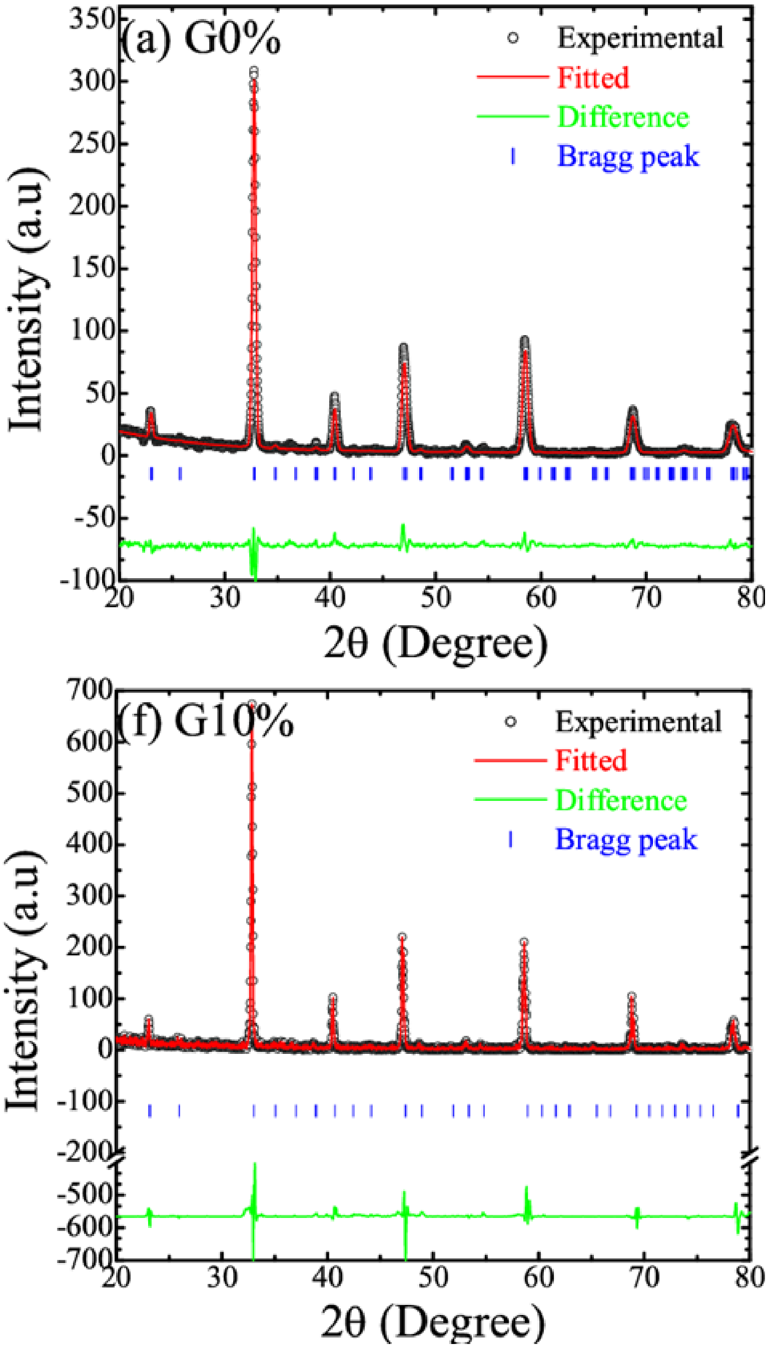

Figure 2: Variation in resistivity with applied magnetic field at (a) 5K, (b) 100K, (c) 200K and (d) 300K for $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ (LCMGO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) ceramic manganites

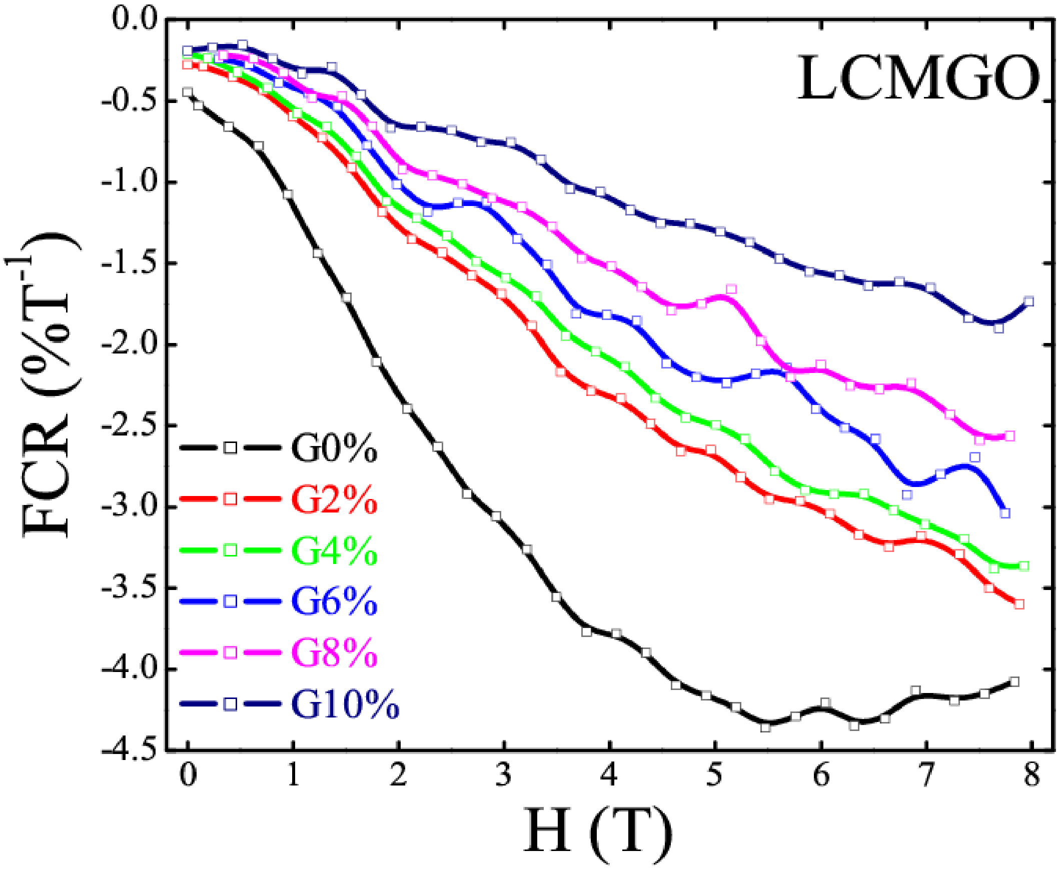

Figure 3: Variation in field sensitivity (FCR) with applied magnetic field for $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ (LCMGO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) ceramic manganites

4. Conclusion

In conclusion, I report the results of the studies on structural and transport studies on nonmagnetic smaller Ga ion substituted $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ (LCMGO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) manganites successfully synthesized by conventional solid state reaction route. X-ray diffraction (XRD) results show a single phasic nature of all the samples without any detectable impurities within the measurement range studied. Rietveld analysis performed on all the XRD patterns reveal the high quality structure of the samples having *Pnma* space group (no. 62) crystallize in orthorhombic unit cell structure. Increase in lattice parameters and cell volume with increase in Ga content has been correlated with the increase in size mismatch and hence structural disorder. Decrease (increase) in resistivity with applied magnetic field (Ga content) has been ascribed to the field induced suppression in scattering of the charge carriers at the grain boundaries and nonmagnetic ion substitution induced enhancement in magnetic disorder at magnetic lattice in LCMGO manganite system. Suppression and fluctuations in FCR with increase in Ga content has been discussed in the context of Ga substitution induced increase in magnetic disorder.

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