International Journal of Physics and Applications.
ISSN 0974-3103 Volume 7, Number 1 (2015), pp. 71-78
© International Research Publication House
http://www.irphouse.com

Effect of Smaller Ga Substitution on Temperature Sensitivity of $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ Manganites

B.R. Kataria*

Department of Physics, Saurashtra University, Rajkot – 360 005, India

Abstract

In this communication, I report the results of the studies on transport properties and temperature sensitivity behavior of 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) ceramic manganites grown using conventional solid state reaction route. Structural investigations have been carried out using X-ray diffraction (XRD) measurement which reveals the single phasic nature of all the samples understudy. Variation in resistance and metal to insulator transition temperature has been discussed in the light of structural disorder and magnetic lattice distortion. Large temperature sensitivity (TCR) ~ 2585.50%/K has been achieved for 10% Ga substituted LCMGO sample.

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

1. Introduction

Researchers are attracted towards the studies on colossal magnetoresistive mixed valent manganites mainly due to the substitutional effects and tunability of their transport and magnetism under applied electric and magnetic fields [1, 2]. Various interactions among spin, charge, orbital and lattice degrees of freedom in manganites can be understood on the basis of field dependent modifications in their transport behavior. Observation of large magnetoresistance (MR), i.e. colossal magnetoresistance (CMR), metal to insulator transition temperature (T_P) and ferromagnetic to paramagnetic transition temperature (T_C) exhibited by mixed valent manganites make them prominent candidates for better spintronic based applications. Further, manganites can be useful for temperature sensors [3], magnetic field sensors

[4], p – n junctions [5], capacitors [6], field effect devices [7], magnetic tunnel junctions [8], spin transistors [9], etc.

Many reports are available on the studies on substitutional effect on the transport, magnetotransport and magnetic properties of mixed valent manganites [10 – 15]. All the physical properties of doped manganites can be tuned by doping of monovalent [11, 14], divalent [12, 15], trivalent [10, 13], tetravalent [16] or pentavalent [17] ions at either A-site [11, 12, 14, 15] or B-site [10, 13, 16, 17] in ABO_3 type of mixed valent manganites. B-site substituting ion can be either nonmagnetic [10, 13] or magnetic [18 – 20] in nature resulting in the modifications in the transport properties of manganites depending upon the ionic radius, magnetic nature of the compound and possible magnetic interactions between the Mn ion/s and dopants.

Also, few reports exist on the temperature sensitivity [3, 4, 21 – 25] and field sensitivity [3, 4, 21 – 25] of mixed valent manganites. Temperature sensitivity can be calculated using the expression: temperature coefficient of resistance (TCR) (%/K) = $(1 / R) \times (dR / dT) \times 100$ (T is the temperature) while field sensitivity can be calculated by: field coefficient of resistance (FCR) (%/Oe or %/T) = $(1 / R) \times (dR / dH) \times 100$ (H is the applied magnetic field). Vachhani et al [21] have studied substrate dependent TCR for manganite based multilayers grown on $SrTiO_3$ (STO) and $NdGaO_3$ (NGO) single crystalline substrates. Markna et al [22] have reported ~ –60%/K negative TCR and ~ +15%/K positive TCR for $La_{0.5}Pr_{0.2}Ba_{0.3}MnO_3$ manganite films and modifications in these values due to swift heavy ion (SHI) irradiation. Similarly, Parmar et al [23] have reported ~ 5%/K TCR and its dependence on the ion dose for chemically grown $La_{0.7}Ba_{0.3}MnO_3$ manganite films. Markna et al [24, 25] have also observed ~ 1.7%/K TCR in $La_{0.5}Pr_{0.2}Sr_{0.3}MnO_3$ / $SrTiO_3$ film which becomes almost double in $La_{0.5}Pr_{0.2}Sr_{0.3}MnO_3$ / Al_2O_3 / $La_{0.5}Pr_{0.2}Sr_{0.3}MnO_3$ / $SrTiO_3$ thin film heterostructure. SHI irradiation induced modifications in TCR for $La_{0.7}Pb_{0.3}MnO_3$ manganite films grown using chemical solution deposition (CSD) method have been reported [3]. Thickness dependence of TCR in ZnO/$La_{0.5}Pr_{0.2}Sr_{0.3}MnO_3$ / Nb–$SrTiO_3$ heterostructures has been studied and found large TCR ~ 18%/K well above 300K which makes this heterostructure a potential candidate for better spintronic based future applications [4].

By keeping in mind all the above aspects of manganite compounds and their possible application as a temperature sensor, in this communication, I report the results the studies on resistance behavior and temperature 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) ceramic manganites grown using conventional solid state reaction route.

2. Experimental Details

The bulk polycrystalline 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) ceramic manganites have been synthesized using conventional solid state reaction method by stoichiometric mixing of the respective metal oxides and carbonates subjected to successive calcinations. The calcined powder was palletized and sintered at various temperatures between 1050°C to 1150°C for 48hrs to 72hrs with intermediate grindings. Hereafter, the samples will be known by the following symbols: MG00, MG02, MG04, MG06, MG08 and MG10 for x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10, respectively. X-ray diffraction (XRD) measurements were carried out to confirm the single phasic nature of the sample. D.C. four probe resistance studies were performed in the temperature range 5 – 300K to understand the transport behavior of the samples understudy.

3. Results and Discussion

Figure 1 shows the Rietveld refinement of typical XRD pattern of $La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO_3$ (x = 0.00; MG00) sample. It is obvious that the difference between experimental and calculated data is practically linear which signifies the quality of the refinements. It can be seen from the Rietveld refined XRD pattern that MG00 sample (and hence all the samples, not shown here) are single phasic in nature without any detectable impurities within the measurement range and crystallizes in orthorhombic unit cell structure having *Pnma* space group (no. 62). It is found that the cell parameters are: a = 5.4110Å, b = 7.6366Å and c = 5.4477Å while unit cell volume is found to be ~ 225.1079Å^3. Cell volume gets enhanced upon the substitution of Ga^{3+} at Mn^{3+} site which may be due to the substitution of smaller ion Ga^{3+} (0.62Å) at larger ion Mn^{3+} (0.645Å) site. This in turn results into the enhancement in structural disorder with increase in Ga – content.

Variation in resistance (in logarithmic scale) with temperature (range: 5 – 300K) is shown in figure 2 for all the LCMGO ceramic manganites understudy. It is clearly seen that all the samples show metal to insulator transition at temperature T_P where resistance vs. temperature plots show peak behavior. At T_P, resistance shows peak in resistance (R_P) above (below) which resistance decreases with increase (decrease) in temperature. Also, R_P increases with increase in Ga content while T_P shifts towards lower temperature. This can be understood as:

(i) Substitution of smaller sized Ga^{3+} ion at larger Mn^{3+} ionic site introduces structural disorder resulting in the reduction in hopping of charge carriers (i.e. e_g electrons of Mn^{3+} ion) thereby suppressing the conduction and enhancing the resistance (R_P) [10].

(ii) Substitution of nonmagnetic Ga^{3+} ion at magnetic Mn^{3+} ionic site introduces magnetic lattice distortion resulting in the variation in Mn – O – Mn bond angles and Mn – O bond lengths thereby reduces the transfer integral of Mn^{3+} itinerant e_g electrons and deteriorates the transport (enhances R_P) with increase in Ga content in LCMGO system [10].

(iii) As result of enhancement in magnetic lattice distortion, zener double exchange (ZDE) mechanism gets weakened resulting in the reduction in T_P with increase in Ga content in presently studied LCMGO samples [10, 26].

It is important to observe in figure 2 that with increase in Ga content, the sharpness of the resistance peak gets increased. This behavior can be expected for the better temperature sensitivity in higher Ga substituted LCMGO samples. In order to explore the application potential of the presently studied LCMGO system, the temperature sensitivity has been calculated: temperature coefficient of resistance (TCR) (%K^{-1}) =

[(1/R) × (dR/dT) × 100] at 300K. Figure 3 shows the variation in TCR with temperature for LCMGO samples studied. It can be seen that all the samples exhibiting high temperature sensitivity at 300K. A sharp maxima peak has been observed in TCR plots for all the samples which increases with increase in Ga^{3+} ion density which can be correlated with the sharpness of metal to insulator transition peak (T_P) (figure 2). For example, MG00 shows TCR ~ 1.5%/K which increases and becomes ~ 2585.50%/K, which is 1724 times larger in MG10.

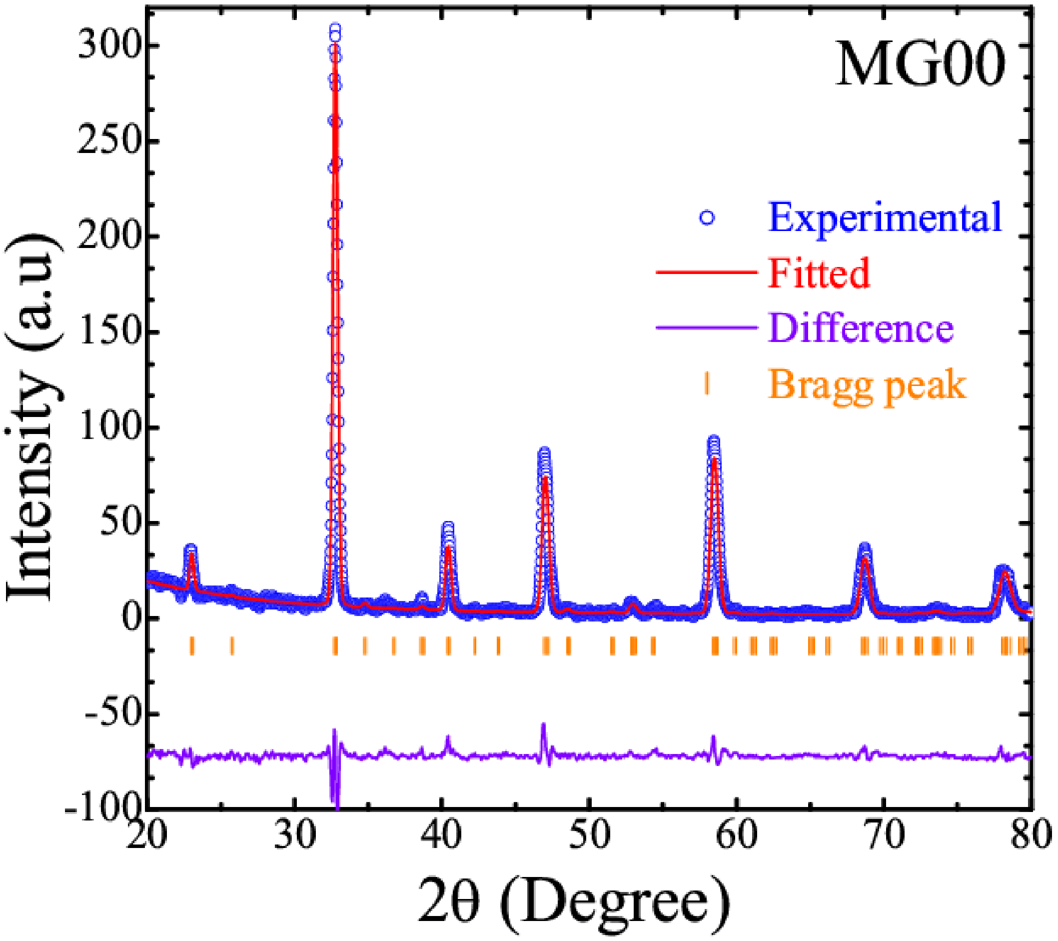

Figure 1: Rietveld refined typical XRD pattern of $La_{0.7}Ca_{0.3}MnO_3$ (MG00) ceramic manganite

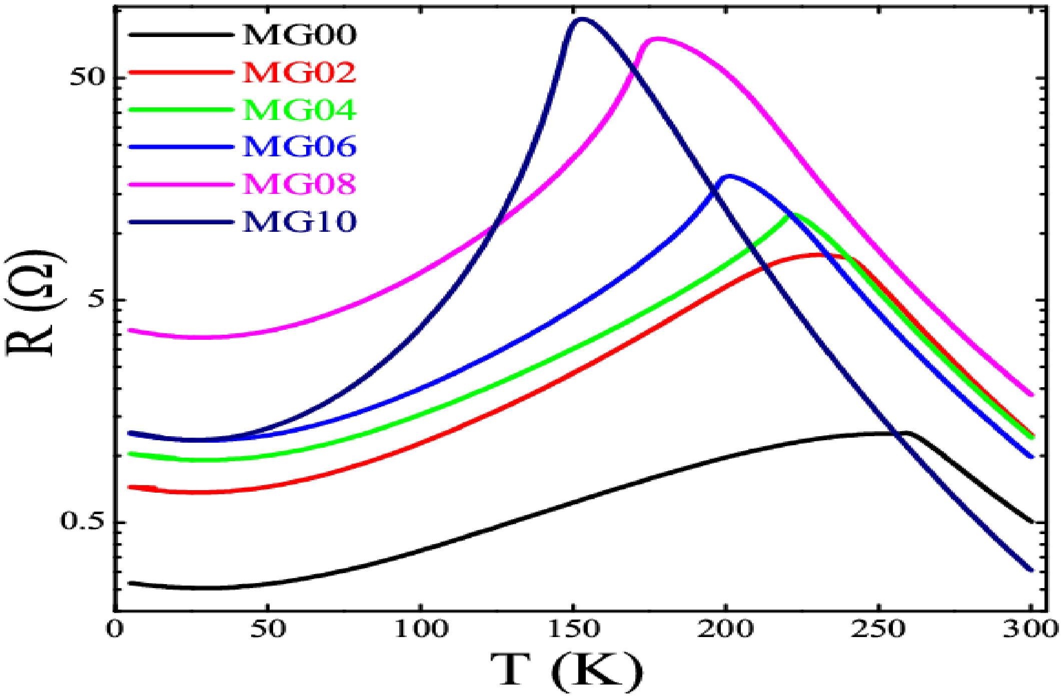

Figure 2: Variation in resistance with temperature for $La_{0.7}Ca_{0.3}Mn_{1-x}Ga_xO_3$ (LCMGO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) ceramic manganites

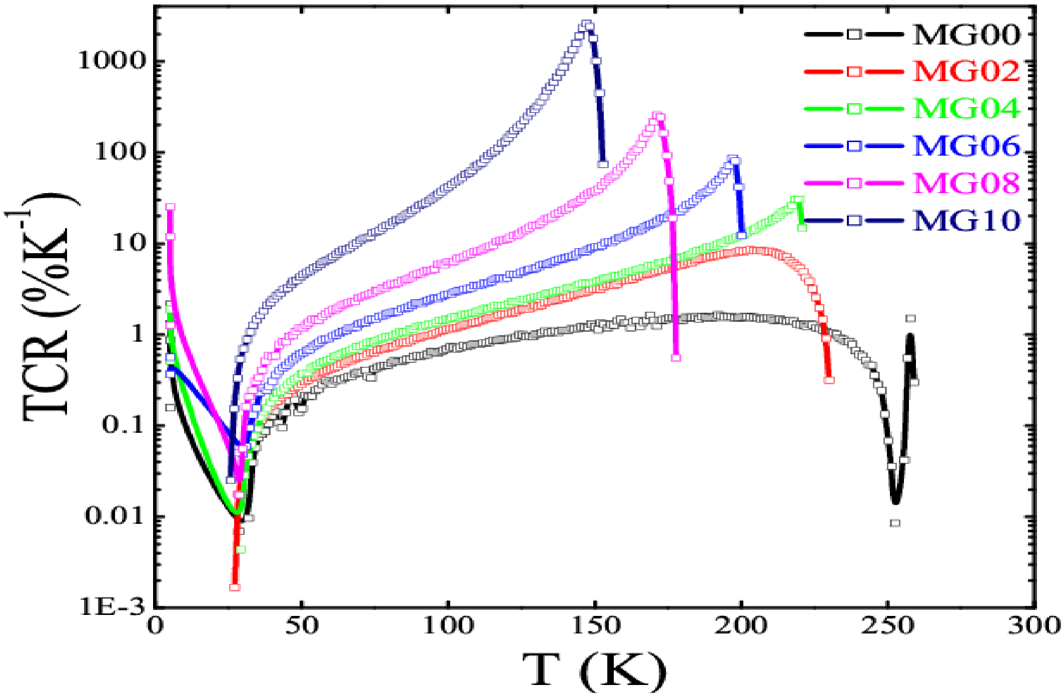

Figure 3: Variation in temperature sensitivity (TCR) with temperature for $La_{0.7}Ca_{0.3}Mn_{1-x}Ga_xO_3$ (LCMGO; x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10) ceramic manganites

4. Conclusion

In conclusion, I have successfully synthesized high purity ceramic samples of 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 using conventional solid state reaction method. X-ray diffraction (XRD) measurements, performed on all LCMGO samples understudy, reveal the single phasic nature of the samples and confirming the orthorhombic unit cell structure with *Pnma* space group (no. 62). It has been observed that with increase in Ga content, unit cell parameters and cell volume get increased. Transport studies, carried out by performing temperature dependent resistance measurements, show an increase in resistance and decrease in metal to insulator transition temperature with increase in Ga content which has been discussed on the basis of smaller nonmagnetic Ga ion substitution induced enhancement in structural disorder and Mn magnetic lattice distortion. Ga content induced modifications in the temperature sensitivity (TCR) show that MG00 (x = 0.00) exhibits TCR ~ 1.5%/K which increases and becomes ~ 2585.50%/K, which is 1724 times larger in MG10 (x = 0.10). These samples are important not only from the view point of fundamental physics but also from the view point of spintronic based practical applications.

Acknowledgement

Author is thankful to Dr. V. Ganesan and Dr. R. Rawat, UGC – DAE Consortium for Scientific Research, Indore for providing experimental facilities for carrying out this work. Also, BRK is thankful to Department of Physics, Saurashtra University, Rajkot for providing some initial experimental facilities.

References

[1] Helmolt, R. von, Wecker, J., Holzapfel, B., Schultz, L., and Samwer, K., 1993, “Giant Negative Magnetoresistance in Perovskite Like $La_{2/3}Ba_{1/3}MnO_x$ Ferromagnetic Films”, Phys. Rev. Lett. 71(14), pp. 2331-2333

[2] Jin, S., Tiefel, T.H., Cormack, M. Mc, Fastnacht, R.A., Ramesh, R., and Chen, L.H., 1994, “Thousandfold Change in Resistivity in Magnetoresistive La–Ca–Mn–O Films”, Science 264(5157), pp. 413-415

[3] Kataria, Bharat, Solanki, P.S., Khachar, Uma, Vagadia, Megha, Ravalia, Ashish, Keshvani, M.J., Trivedi, Priyanka, Venkateshwarlu, D., Ganesan, V., Asokan, K., Shah, N.A., and Kuberkar, D.G., 2013, “Role of Strain and Microstructure in Chemical Solution Deposited $La_{0.7}Pb_{0.3}MnO_3$ Manganite Films: Thickness Dependent Swift Heavy Ions Irradiation Studies”, Rad. Phys. Chem. 85(1), pp. 173-178

[4] Khachar, Uma, Solanki, P.S., Choudhary, R.J., Phase, D.M., and Kuberkar, D.G., 2013, “Positive MR and Large Temperature–Field Sensitivity in Manganite Based Heterostructures”, J. Mater. Sci. Technol. 29(10), pp. 989-994

[5] Khachar, Uma, Solanki, P.S., Choudhary, R.J., Phase, D.M., Ganesan, V., and Kuberkar, D.G., 2012, "Current–Voltage Characteristics of PLD Grown Manganite Based ZnO/$La_{0.5}Pr_{0.2}Sr_{0.3}MnO_3$/$SrNb_{0.002}Ti_{0.998}O_3$ Thin Film Heterostructure", Solid State Commun. 152(1), pp. 34-37

[6] Dhruv, Davit, Joshi, Zalak, Kansara, Sanjay, Keshvani, M.J., Pandya, D.D., Asokan, K., Solanki, P.S., Kuberkar, D.G., and Shah, N.A., 2015, "Investigations on Device Characteristics of Chemically Grown Nanostructured $Y_{0.95}Ca_{0.05}MnO_3$/Si Junctions", Adv. Sci. Lett. (In Press)

[7] Solanki, P.S., Khachar, Uma, Vagadia, Megha, Ravalia, Ashish, Katba, Savan, and Kuberkar, D.G., 2015, "Electroresistance and Field Effect Studies on Manganite Based Heterostructure", J. Appl. Phys. 117(14), pp. 145306:1-6

[8] Jo, M.H., Blamire, M.G., Ozkaya, D., and Petford – Long, A.K., 2003, "Spin- and Charge- Modulated Trilayer Magnetic Junctions: $La_{0.7}Ca_{0.3}MnO_3$/ $La_{0.45}Ca_{0.55}MnO_3$/ $La_{0.7}Ca_{0.3}MnO_3$", J. Phys.: Condens. Matter 15(30), pp. 5243-5251

[9] Gajek, M., Bibes, M., Varela, M., Fontcuberta, J., Herranz, G., Fusil, S., Bouzehouane, K., Barthelemy, A., and Fert, A., 2006, "$La_{2/3}Sr_{1/3}MnO_3$–$La_{0.1}Bi_{0.9}MnO_3$ Heterostructures for Spin Filtering", J. Appl. Phys. 99(8), pp. 08E504: 1-3

[10] Rathod, J.S., Khachar, Uma, Doshi, R.R., Solanki, P.S., and Kuberkar, D.G., 2012, "Structural, Transport and Magnetotransport in Nonmagnetic Al^{3+} Doped Mixed Valent $La_{0.7}Ca_{0.3}Mn_{1-x}Al_xO_3$ Manganites", Int. J. Mod. Phys. B 26(24), pp. 1250136: 1-11

[11] Kansara, Sanjay, Pandya, D.D., Nimavat, Bhumika, Thaker, C.M., Solanki, P.S., Rayaprol, S., Gonal, M.R., Shah, N.A., and Kuberkar, D.G., 2013, "Structure – Property Correlations in Mono–valent Na^+ Doped $La_{1-x}Na_xMnO_3$ Manganites", Adv. Mater. Res. 665(1), pp. 1-7

[12] Ravalia, Ashish, Vagadia, Megha, Trivedi, Priyanka, Keshvani, M.J., Khachar, Uma, Savalia, B.T., Solanki, P.S., Asokan, K., and Kuberkar, D.G., 2013, "Swift Heavy Ion Irradiation Studies on the Transport in $La_{0.8-x}Pr_{0.2}Sr_xMnO_3$ Manganite Films", Adv. Mater. Res. 665(1), pp. 63-69

[13] Krichene, A., Solanki, P.S., Rayaprol, S., Ganesan, V., Boujelben, W., and D.G. Kuberkar, 2015, "B–site Bismuth Doping Effect on Structural, Magnetic and Magnetotransport Properties of $La_{0.5}Ca_{0.5}Mn_{1-x}Bi_xO_3$", Ceram. Int. 41(2), pp. 2637-2647

[14] Kansara, S.B., Dhruv, Davit, Kataria, Bharat, Thaker, C.M., Rayaprol, S., Prajapat, C.L., Singh, M.R., Solanki, P.S., Kuberkar, D.G., and Shah, N.A., 2015, "Structural, Transport and Magnetic Properties of Monovalent Doped $La_{1-x}Na_xMnO_3$ Manganites", Ceram. Int. 41(5), pp. 7162-7173

[15] Solanki, P.S., Doshi, R.R., Ravalia, Ashish, Keshvani, M.J., Pandya, Swati, Ganesan, V., Shah, N.A., and Kuberkar, D.G., 2015, "Transport Studies on $La_{0.8-x}Pr_{0.2}Sr_xMnO_3$ Manganite Films", Physica B 465(1), pp. 71-80

[16] Liu, X., Xu, X., and Zhang, Y., 2000, "Effect of Ti Dopant on the Carrier Density Collapse in Colossal Magnetoresistance Material $La_{0.7}Ca_{0.3}Mn_{1-y}Ti_yO_3$", Phys. Rev. B 62(22), pp. 15112-15119

[17] Ang, R., Sun, Y.P., Ma, Y.Q., Zhao, B.C., Zhu, X.B., and Song, W.H., 2006, “Diamagnetism, Transport and Magnetothermoelectric Power, and Magnetothermal Conductivity in Electron – Doped $CaMn_{1-x}V_xO_3$ Manganites”, J. Appl. Phys. 100(6), pp. 063902: 1-11

[18] Sun, Y., Tong, W., Xu, X., and Zhang, Y., 2001, “Tuning Colossal Magnetoresistance Response by Cr Substitution in $La_{0.67}Sr_{0.33}MnO_3$”, Appl. Phys. Lett. 78(5), pp. 643-645

[19] Leung, L.K., and Morrish, A.H., 1977, “Nuclear – Magnetic – Resonance Study of the Magnetically Ordered Manganite $La_{1-x}Pb_xMn_{1-y}Fe_yO_3$”, Phys. Rev. B 15(5), pp. 2485-2492

[20] Young, S.L., Chen, Y.C., Chen, H.Z., Horng, L., and Hsueh, J.F., 2002, “Effect of the Substitutions of Ni^{3+}, Co^{3+}, and Fe^{3+} for Mn^{3+} on the Ferromagnetic States of the $La_{0.7}Pb_{0.3}MnO_3$ Manganite”, J. Appl. Phys. 91(10), pp. 8915-8917

[21] Vachhani, P.S., Solanki, P.S., Doshi, R.R., Shah, N.A., Rayaprol, S., and Kuberkar, D.G., 2011, “Substrate Dependent Transport and Magnetotransport in Manganite Multilayer”, Physica B 406(11), pp. 2270-2272

[22] Markna, J.H., Parmar, R.N., Kuberkar, D.G., Kumar, Ravi, Rana, D.S., and Malik, S.K., 2006, “Thickness Dependent Swift Heavy Ion Irradiation Effects on Electronic Transport of $(La_{0.5}Pr_{0.2})Ba_{0.3}MnO_3$ Thin Films”, Appl. Phys. Lett. 88(15), pp. 152503: 1-3

[23] Parmar, R.N., Markna, J.H., Kuberkar, D.G., Kumar, Ravi, Rana, D.S., Bagve, Vivas C., and Malik, S.K., 2006, “Swift-Heavy-Ion-Irradiation-Induced Enhancement in Electrical Conductivity of Chemical Solution Deposited $La_{0.7}Ba_{0.3}MnO_3$ Thin Films”, Appl. Phys. Lett. 89(20), pp. 202506: 1-3

[24] Markna, J.H., Vachhani, P.S., Parmar, R.N., Kuberkar, D.G., Misra, P., Singh, B.N., Kukreja, L.M., Rana, D.S., and Malik, S.K., 2007, “Enhancement of Electronic Transport and Magnetoresistance of Al_2O_3–Impregnated $(La_{0.5}Pr_{0.2})Sr_{0.3}MnO_3$ Thin Films”, Europhys. Lett. 79(1), pp. 17005: 1-5

[25] Markna, J.H., Vachhani, P.S., Kuberkar, D.G., Shah, N.A., Misra, P., Singh, B.N., Kukreja, L.M., and Rana, D.S., 2009, “Nano-Engineering by Implanting Al_2O_3 Nano Particle as Sandwiched Scattering Centers in Between the $La_{0.5}Pr_{0.2}Sr_{0.3}MnO_3$ Thin Films Layers”, J. Nanosci. Nanotechnol. 9(12), pp. 5687-5691

[26] Solanki, P.S., Doshi, R.R., Thaker, C.M., Pandya, Swati, Ganesan, V., and Kuberkar, D.G., 2009, “Transport and Magnetotransport Studies on Sol-Gel Grown Nanostructured $La_{0.7}Pb_{0.3}MnO_3$ Manganites”, J. Nanosci. Nanotechnol. 9(12), pp. 5681-5686