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Review on the B-site doping effects of different types of cations in ABO₃ type La_{1-x}Ca_xMnO₃ Manganites

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ABSTRACT:

In this communication, we discuss the B-site doping effects in ABO₃ type manganites on doping some different cations at the B-site of La_{1-x}Ca_xMnO₃ manganites, the transport and magneto transport properties are changed and material also shows the change in Metal to Insulator (M-I) transition at the T_p. For different doped cations the transport and magneto transport properties are changed for particular La_{1-x}Ca_xMnO₃ manganites. In this communication various reported works on the Mn site doping is used to compare the structural modifications, transport and magneto transport properties of the doped perovskite structures. The shifting of T_p as a function of different cations on the B-site of La_{1-x}Ca_xMnO₃ manganites is been discussed. The structural modifications, for that the reported XRD data for different cations are used. For this comparative study, the MR%, XRD results, Resistivity measurements, with and without fields from the previously reported works have been considered.

KEY WORDS: -Resistivity, Transport, Magneto-transport, B-site Doping effects, Spin Scattering

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1. INTRODUCTION

ABO₃ type perovskite structured manganites are famous for their different properties like Colossal Magnetoresistance, Metal to Insulator transition, Paramagnetic to ferromagnetic transition, Zener Double Exchange (ZDE), Jahn-Teller (JT) Distortion, Orbital Ordering (OO), Charge Ordering (CO), Spin Ordering(SO), Size Variance etc¹⁻⁴. All properties are modified by doping effect in manganites. Dopant may be monovalent⁵, divalent⁶, trivalent⁷, tetravalent⁸, pentavalent⁹ ions, etc. Dopant also may be either magnetic or non-magnetic ion^{10,11}. Manganites are widely studied for doping effect at A site or B site in ABO₃ type manganites for modifications in their physical properties. Manganites are used in p – n junctions¹², capacitors¹³, field effect devices¹⁴, temperature sensors¹⁵, magnetic tunnel junctions¹⁶, spin transistors¹⁷, memory devices¹⁸ etc. Doping on B-site makes dramatic changes in the physical properties of manganites, several studies have been reported showing the results¹⁹⁻²¹. In this communication, we report the overview and important features of few reported work, as a review on the Mn-site doping effect of different types of cation in ABO₃ type La_{0.67}Ca_{0.33}MnO₃ manganites.

2. MATERIALS

In this review, several published articles have been discussed in detail. The doping effect on Mn-site in La_{0.67}Ca_{0.33}MnO₃ manganite for different dopants is discussed. We also discussed the change in transport and magnetotransport properties of La_{0.67}Ca_{0.33}Mn_{1-x}A_xO₃ manganite (A= Ga⁺³, Sb⁺⁵, Al⁺³ and x= 0.02, 0.04, 0.06, 0.08 & 0.1). All samples were synthesized in air by Solid State Reaction (SSR) route with sintering temperature ~1150°C for ~72 hours. The substitution of non-magnetic cation at Mn site of La_{0.67}Ca_{0.33}MnO₃ manganite can change the resistivity as a function of temperature. The increment of resistivity shows the decrement in Zener Double Exchange (ZDE) phenomena.

3. REVIEW

Kataria²² has successfully synthesized the polycrystalline La_{0.67}Ca_{0.33}Mn_{1-x}Ga_xO₃ samples using the conventional Solid State Reaction (SSR) route and reported the change in Zener Double Exchange (ZDE) mechanism. The substitution of smaller Ga⁺³ ion at larger Mn⁺³ site increases the cell volume, which generates the structural disorder with increment of Ga⁺³ content on Mn site. The transport study shows the increment in Metal to Insulator (M-I) Transition, T_p shifts towards the lower temperature region while R_p increases. (T_p= 259 K when R_p= 25.42 Ωcm for doping level x= 0.0,

$T_p=158$ K when $R_p= 1843 \Omega\text{cm}$ for doping level $x= 0.1$). The doping of non-magnetic Ga^{+3} change the Mn-O-Mn bond angle and Mn-O bond lengths, thereby, the hopping of e_g electrons is reduced, the reduction of hopping of e_g electron decreases the ZDE mechanism. The decrement of ZDE shows increment in resistivity with increasing Ga^{+3} content.

Kataria et al ²³ have reported the magnetotransport characteristics of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Ga}_x\text{O}_3$ manganites. They studied the change in MR at various temperatures (5, 100, 200 & 300 K) in the different applied magnetic fields (0-8 T). They reported the negative MR, calculated using the relation $\text{MR} (\%) = \{(\rho_H - \rho_0) / \rho_0\} \times 100$. The negative MR indicates the decrement in resistivity for all samples. The low field MR ($\sim 0.25\text{T}$) gives the sharp rise in MR due to the granular structure of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Ga}_x\text{O}_3$ manganites. This shows the spin scattering at the grain boundaries. For high field MR ($\sim 8\text{T}$), %MR decreases with increasing applied field at different temperatures. It shows the strong effect of non-magnetic Ga^{+3} at Mn-site. At high temperatures $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Ga}_x\text{O}_3$ shows the large %MR due to the field induced reduction in Mn-O-Mn bond angles and decrement in scattering of spin at the grain boundaries.

J. Rathod et al ²⁴ have reported transport and magnetotransport studies on $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ manganites. They observed that substitution of non-magnetic Al^{+3} creates the structural disorder in crystalline orthorhombic structure of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ manganites. The resistivity measurement shows the shifting of T_p towards the lower temperature ($T_p=276$ becomes $T_p=147$), R_p also increases with increasing Al^{+3} content. They observed decrement of Mn^{+4} content with increment of Al^{+3} content which affects the Zener Double Exchange phenomena. The hopping of e_g electron decreases with increasing Al^{+3} doping. The magnetoresistance (%MR) measurements show the increment in negative MR with increasing field. At low applied field MR increases with increasing Al content, for high applied field the MR increases as a function of magnetic field at different temperatures. It induces the scattering of electrons at grain boundaries which affects the conductivity of the samples. Study of large MR is attributed to the structural disorder at the grain boundaries and field induced suppression in scattering of electron, which enhanced MR at lower temperatures with increasing in Al^{+3} content in $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ manganites.

Kataria ²⁵ also reported “Temperature Sensitivity of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Sb}_x\text{O}_3$ manganites: Role of Smaller Sb Substitution”. He reported the transport measurement of Sb-doped $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ manganite. The cell volume increases with the increase in smaller Sb^{+5} concentration. It shows the increment in resistivity as a function of Sb^{+5} content. The Metal to Insulator transition increasing

with the substitution of Sb^{+5} content. R_p increases with the increasing Sb^{+5} content, then T_p shifts towards the lower temperature ($R_p=0.019 \Omega\text{cm}$ at $T_p= 259 \text{ K}$ for $x= 0.0$ and $R_p=377.130 \Omega\text{cm}$ at $T_p= 77 \text{ K}$ for $x= 0.1$).The large ionic size difference between Sb^{+5} and Mn^{+3} introduces a structural disorder, which modifies the Mn-O-Mn bond angles and Mn-O bond lengths. The decrement in Mn-O-Mn angle and increment in Mn-O bond length. The change in such properties degrade the Zener Double Exchange Mechanism while rise the resistivity.

Kataria ²⁶ has reported the magnetotransport analysis on the of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Sb}_x\text{O}_3$ manganites. The low field MR attributed spin dependent scattering processes through the grain boundaries at low temperature. For high field MR, field induced the spin polarization or reorientation of the spins of e_g electrons at the grain boundaries. All over Low field MR decreases, while high field MR increases with the increasing Sb^{+5} content in $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Sb}_x\text{O}_3$ manganites, increment of negative MR introduced at different temperature. The field induced reduction in structural disorder at Mn-O-Mn bond angle and the scattering of electrons suppressed at the grain boundaries.

4. CONCLUSION

In Conclusion, Doping on B –site of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ manganites modifies the transport and magnetotransport properties. The size variance in Mn^{+3} and doped ($\text{B}^{+3}/\text{B}^{+5}$) induce cell volume change affects the Mn-O-Mn bond angles and Mn-O bond lengths as a result Zener Double Exchange Mechanism decreases. The cell volume also affects the electrical properties, M-I transition is also affected by the ionic radius of dopant element. M-I transition is less affected by Al^{+3} doping compare to that doping of $\text{Ga}^{+3}/\text{Sb}^{+5}$. For low applied magnetic field MR is decreased, for higher values of applied magnetic field, Sb^{+5} substitution induced drastic decrement in MR values at higher temperatures compared to $\text{Ga}^{+3}/\text{Al}^{+3}$ substitution, this may attributed to the scattering of e_g electrons at grain boundaries.

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6. REFERENCES

- [1] C.N.R Rao, R. Mahesh, A.K. Raychaudhari and R. Mahendiran, J. Phys. Chem. Solid, 1998; 59:487.
- [2] P. G. De Gennes, Phys. Rev., 1960; 118:141 .

- [3] J. A. Alonso, M. J. Martinex-Lope, and M. T. Casais M. T. Fernandez-Diaz American Chemical Society, 2000; 5: 39.
- [4] J. Garcia and G. Sibias, *J. Phys. Condens matter*, 2004;16: R145.
- [5] S.B Kansara, Dhruv, Davit, Kataria, Bharat, Thaker et al, “Structural, Transport and Magnetic Properties of Monovalent Doped $\text{La}_{1-x}\text{NaxMnO}_3$ Manganites”, *Ceram. Int.*, 2015;41(5): 7162-7173.
- [6] Solanki, P.S., Doshi, R.R., Ravalia, Ashish, et al, “Transport Studies on $\text{La}_{0.8-x}\text{Pr}_{0.2}\text{SrxMnO}_3$ Manganite Films”, *Physica B*, 2015; 465(1): 71-80.
- [7] M. Sahana, K. Dörr, U. K. Röbler, and K.-H. Müller, *Physical Review B*, 2002; 66: 064414.
- [8] Liu, X., Xu, X., and Zhang, Y., “Effect of Ti Dopant on the Carrier Density Collapse in Colossal Magnetoresistance Material $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-y}\text{Ti}_y\text{O}_3$ ”, *Phys. Rev.*, 2000; B 62(22): 15112-15119.
- [9] Ang, R., Sun, Y.P., Ma, Y.Q., Zhao, B.C., Zhu, X.B., and Song, W.H., “Diamagnetism, Transport and Magnetothermoelectric Power, and Magnetothermal Conductivity in Electron – Doped $\text{CaMn}_{1-x}\text{V}_x\text{O}_3$ Manganites”, *J. Appl. Phys.* 2006, 100(6), 063902: 1-11.
- [10] Krichene A., Solanki P.S., Rayaprol, S., et al, “B–site Bismuth Doping Effect on Structural, Magnetic and Magnetotransport Properties of $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$ ”, *Ceram. Int.*, 2015; 41(2): 2637-2647.
- [11] Young S.L., Chen Y.C., Chen H. Z., et al., “Effect of the Substitutions of Ni^{3+} , Co^{3+} , and Fe^{3+} for Mn^{3+} on the Ferromagnetic States of the $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ Manganite”, *J. Appl. Phys.* 2002; 91(10): 8915-8917.
- [12] Uma Khachar, P.S. Solanki, R.J. Choudhary et al, *Solid State Commun.*, 2012; 152: 34–37.
- [13] Davit Dhruv, Zalak Joshi, Sanjay Kansara, et al, *Mater. Res. Express*, 2016; 3: 036402: 1–9.
- [14] P.S. Solanki, Uma Khachar, Megha Vagadia, et al, *J. Appl. Phys.*, 2015; 117: 145306: 1–6.
- [15] Bharat Kataria, P.S. Solanki, Uma Khachar, et al, *Rad. Phys. Chem.*, 2015; 85: 173–178.
- [16] M.H. Jo, M.G. Blamire, D. Ozkaya and A.K. Petford–Long, *J. Phys.: Condens. Matter*, 2003; 15: 5243–5251.
- [17] M. Gajek, M. Bibes, M. Varela, J. Fontcuberta, G. Herranz, S. Fusil, K. Bouzehouane, A. Barthelemy and A. Fert, *J. Appl. Phys.*, 2006; 99: 08E504: 1–3.
- [18] D.Q. Liu, H.F. Cheng, G. Wang, X. Zhu, Z.Z. Shao, N.N. Wang and C.Y. Zhang, *IEEE Electron Device Lett.*, 2013; 34: 1506–1508.

- [19] Kalpataru Pradhan, Journal of Applied Physics, 2016; 119: 033901.
 - [20] B. Raveau,¹ Y. M. Zhao,² C. Martin, M. Hervieu, and A. Maignan, J. Solid State Chem., 2000; 149: 203-207.
 - [21] S. Hebert, V. Hardy, A. Maignan, et al, J. Solid State Chem., 2000; 165: 6-11.
 - [22] Bharat Katria , “Effect of Smaller Ga Substitution on Temperature Sensitivity of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Ga}_x\text{O}_3$ Manganites, International Jour. of Phy. And Appli., 2015; 7: 71-78.
 - [23] Bharat Kataria, Kunal Rathod, jayshukh Markna, International Jour. of Latest Research in Science and Technology, 2015; 4: 46-49.
 - [24] Jalshikhaba Rathod, Uma Khachar, R. R. Doshi, et al, “ Structural, Transport and Magneotransport in non-magnetic Al^{+3} doped mixed valant $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ manganite, Physica B, 2012; 26: 1250124-1250136.
 - [25] Bharat Katria, “Temperature Sensitivity of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Sb}_x\text{O}_3$ manganites: Role of Smaller Sb Substitution”, International Jour. of Materials Phy., 2015; 6: 21-28.
 - [26] Bharat Kataria, Ph.D Thesis, Department of Physics, Saurashtra University, Rajkot, 2012; Chapter-IV: 24-26
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