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### **Review on the B-site doping effects of different types of cations in ABO<sub>3</sub> type La<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub> Manganites**

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#### **ABSTRACT:**

In this communication, we discuss the B-site doping effects in ABO<sub>3</sub> type manganites on doping some different cations at the B-site of La<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub> 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<sub>p</sub>. For different doped cations the transport and magneto transport properties are changed for particular La<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub> 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<sub>p</sub> as a function of different cations on the B-site of La<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub> 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

ABO<sub>3</sub> 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 etc<sup>1-4</sup>. All properties are modified by doping effect in manganites. Dopant may be monovalent<sup>5</sup>, divalent<sup>6</sup>, trivalent<sup>7</sup>, tetravalent<sup>8</sup>, pentavalent<sup>9</sup> ions, etc. Dopant also may be either magnetic or non-magnetic ion<sup>10,11</sup>. Manganites are widely studied for doping effect at A site or B site in ABO<sub>3</sub> type manganites for modifications in their physical properties. Manganites are used in p – n junctions<sup>12</sup>, capacitors<sup>13</sup>, field effect devices<sup>14</sup>, temperature sensors<sup>15</sup>, magnetic tunnel junctions<sup>16</sup>, spin transistors<sup>17</sup>, memory devices<sup>18</sup> etc. Doping on B-site makes dramatic changes in the physical properties of manganites, several studies have been reported showing the results<sup>19-21</sup>. 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 ABO<sub>3</sub> type La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> manganites.

## 2. MATERIALS

In this review, several published articles have been discussed in detail. The doping effect on Mn-site in La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> manganite for different dopants is discussed. We also discussed the change in transport and magnetotransport properties of La<sub>0.67</sub>Ca<sub>0.33</sub>Mn<sub>1-x</sub>A<sub>x</sub>O<sub>3</sub> manganite (A= Ga<sup>+3</sup>, Sb<sup>+5</sup>, Al<sup>+3</sup> 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<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> 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

Kataria<sup>22</sup> has successfully synthesized the polycrystalline La<sub>0.67</sub>Ca<sub>0.33</sub>Mn<sub>1-x</sub>Ga<sub>x</sub>O<sub>3</sub> samples using the conventional Solid State Reaction (SSR) route and reported the change in Zener Double Exchange (ZDE) mechanism. The substitution of smaller Ga<sup>+3</sup> ion at larger Mn<sup>+3</sup> site increases the cell volume, which generates the structural disorder with increment of Ga<sup>+3</sup> content on Mn site. The transport study shows the increment in Metal to Insulator (M-I) Transition, T<sub>p</sub> shifts towards the lower temperature region while R<sub>p</sub> increases. (T<sub>p</sub>= 259 K when R<sub>p</sub>= 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  $\text{Ga}^{+3}$  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  $\text{Ga}^{+3}$  content.

Kataria et al <sup>23</sup> 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  $\text{Ga}^{+3}$  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 <sup>24</sup> 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  $\text{Al}^{+3}$  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  $\text{Al}^{+3}$  content. They observed decrement of  $\text{Mn}^{+4}$  content with increment of  $\text{Al}^{+3}$  content which affects the Zener Double Exchange phenomena. The hopping of  $e_g$  electron decreases with increasing  $\text{Al}^{+3}$  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  $\text{Al}^{+3}$  content in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$  manganites.

Kataria <sup>25</sup> 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  $\text{Sb}^{+5}$  concentration. It shows the increment in resistivity as a function of  $\text{Sb}^{+5}$  content. The Metal to Insulator transition increasing

with the substitution of  $\text{Sb}^{+5}$  content.  $R_p$  increases with the increasing  $\text{Sb}^{+5}$  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  $\text{Sb}^{+5}$  and  $\text{Mn}^{+3}$  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 <sup>26</sup> 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  $\text{Sb}^{+5}$  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  $\text{Mn}^{+3}$  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  $\text{Al}^{+3}$  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,  $\text{Sb}^{+5}$  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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