Metal-insulator phase transition and structural stability in ‘Sb’ doped CaMnO$_3$ perovskite

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Abstract: Electron doped Ca$_{1-x}$Sb$_x$MnO$_3$ ($X = 0$ to 0.4) compound when prepared by high temperature solid state reaction, exhibits orthorhombic distorted perovskite structure. A systematic, continuous doping increases the metal – insulator transition temperature to above the room temperature ($\approx$431 to 469 K); due to the mismatch of ionic radii in A site rising anti-site effect, which consequently changes the bond length. Doping induced metal – insulator transition accompanied by structural transition is reflected through the drastic changes in the parameters like cation size variance factor ($\sigma$), average ionic radius $<r>$, tolerance factor (t) and $T_{o}$, which is correlated to the bond related transport properties. Structural transition from the phase of perovskite to Brownmillerite has been found for the compositions $x = 0.3$ and 0.4, which is attributed due to the ionic radii mismatch. Doping exerts chemical pressure by modifying compression of A-O bond and relaxation of B-O bond, giving rise to strain similar to external pressure in ABO$_3$ perovskite. The dependence of electrical transport at high temperature has been studied, by employing variable range hopping and small polaron hopping model as an account for the experimental observation due to disorder induced localization.

Keywords: Phase Transition, Pervoskite, High $T_c$

1. Introduction

In manganites, optimum grain size for preferential orientations the need of the hour for low field magnetoresistance (LFMR) applications at ambience in the applied magnetic field for 100% spin polarization between the grains. Storage and retrieval of information from computer hard disk were revolutionized after the discovery of colossal magnetoresistance (CMR) based manganite read/write heads. Miniaturization, Storage increase and high magneto resistance (MR) through LFMR, kept further renewing the interest in CMR even after three decades of fundamental researches on manganite [1, 2]. However, the origin of conductivity in doping induced disordered oxide materials is not yet clear due to charge localization. The parameters like dopant atom, particle size and pressure are varied in perovskite manganites to achieve metal – insulator transition temperature ($T_{MI}$) above the room temperature. CaMnO$_3$ is an antiferromagnetic Mott-Hubbard insulator known for becoming metallic in nature at narrow doping levels itself as CaMnO$_3$ is at the edge of Metal-Insulator (M-I) transition. For electron doped CMR compounds, due to the high efficiency and minimum disorder AMnO$_3$(A=Ba,Ca,Sr) is most preferred when compared to LaMnO$_3$. In those compounds anti-ferromagnetic (AFM) to paramagnetic (PM) transition was reported by Esa Bose et al [3]. Doping induced structural changes are reported by Qingdi Zhou et al [4] in SrMnO$_3$, since MR is intrinsically connected to metal - insulator transition and charge orbital ordering. Electron doping induced cubic to tetragonal and cubic to orthorhombic phases was reported by Brendan J.Kennedy et al [5] in tetravalent Cerium (Ce$^{4+}$) doped SrMnO$_3$ due to Jahn Teller co-operative tilting of MnO$_6$ octahedra. High temperatureresistivity of Sb doped CaMnO$_3$ [6] exhibits decrease in conductivity with increase in temperature and $\ dv/dT$ became negative at around 600$^0$C indicating a transition from semiconducting to metallic. CaMnO$_3$ when doped with Sb$^{5+}$ion produces excess electrons through Mn$^{2+}$ to Mn$^{3+}$ conversion. Ping Duan et al [7] proved the existence of mixed valence states of Mn (Mn$^{2+}$ and Mn$^{3+}$) through XPS (X-ray photoemission
prepared by high temperature solid-state reaction method. All those pellets prepared were under a pressure of 3 to 5 tons. Highly pure CaCO\(_3\) (Merck, 99.9%) and MnO\(_2\) (Merck, 99.9%) were taken in the stoichiometry composition (Ca\(_{1-x}\)Sb\(_x\)MnO\(_3\)) \((0 \geq X \leq 0.4)\). The resulting powders were pelletized using hydraulic press in to small disks of 8 mm diameter and 1 mm to 2 mm thickness under a pressure of 3 to 5 tons. All those pellets prepared were sintered at 900°C continuously or 36 hours and cooled to room temperature.

All the five samples of Ca\(_{1-x}\)Sb\(_x\)MnO\(_3\) \((x = 0 \text{ to } x = 0.4)\) were prepared under exact heating conditions as described above. The samples are characterized by powder XRD (Rich-Seifert, Germany) using Cu K\(\alpha\) radiation. Electrical transport studies were carried out using Silver electrodes of 99.9% purity with Keithley electrometer (Model 617).

### 3. Results and Discussion

#### 3.1. XRD Analysis

XRD pattern of polycrystalline Ca\(_{1-x}\)Sb\(_x\)MnO\(_3\) \((X = 0 \text{ to } 0.4)\) samples belonging to orthorhombic structure are shown in Fig 1(a). In ‘Sb’ substituted samples, splitting of the X-ray peak of ‘112’ into (002) and (112) for \(x = 0.1, 0.2, 0.3 \text{ and } x = 0.4\) was observed and attributed to the increased orthorhombicity of the compound. The crystal size changes consistently with doping as 12 nm for \(x = 0.1, 21 \text{ nm for } x = 0.2, 27 \text{ nm for } x = 0.3.\) The X-ray peak (112) into (002) and (112) for \(x = 0.1, 0.2\), is found to be 66 nm, due to phase segregation and limited solubility. Smaller particle size of 12-27 nm comparable to wet chemical methods are attributed due to the sintering temperature for 36 hours at low temperature \((\text{i.e.} \ 900 \degree C)\). The smaller particle size due to low sintering temperature are attributed to the assistance of MnO\(_2\) as sintering aidlike Bi\(_2\)O\(_3\) and Li\(_2\)CO\(_3\) in synthesis of dielectrics [9,15].

![Fig 1. (a) XRD pattern of Ca\(_{1-x}\)Sb\(_x\)MnO\(_3\) \((0 \geq X \leq 0.4)\) (b) Shifting of 112 peak of Ca\(_{1-x}\)Sb\(_x\)MnO\(_3\) \((0 \geq X \leq 0.4)\).](image)

Lattice parameters of orthorhombic crystal structure as a function of Sb doping was found to be increasing from 4.8403 Å to 5.3213 Å for ‘a’, indicating that Ca\(_{25}\) being replaced by Sb\(_{25}\) along ‘a’ axis. This produces a corresponding compression in ‘b’ axis from 5.8426 Å to 5.3834 Å making the tolerance factor ‘t’ stable [Table 2]. The ‘c’ axis also found to undergo an elongation from 7.5401 Å to 7.7405 Å for doping concentration of 0.3 ≤ x ≥ 0.1. Increase in the lattice parameter for the concentration x ≤ 0.2, indicates low chemical pressure induced by doping giving rise to high transition temperature [16].

Doping induced structural disorder was found from the XRD for concentrations x = 0.3 and x = 0.4. Due to large difference in ionic radii, Mn (0.53 Å) site and Sb (0.74 Å) atom occupies Mn (0.53 Å) site instead of Ca (1.12 Å) site making A/B cation ratio deviating from perovskite structure. Doping induced charge localization and along with phase transition leading to changes in the density of states and resistivity are found from the \(T_a\) values [14].

![Diagram](image)
34° and appearance of (002) peak at 2θ = 31.5° degrees of Brownmillerite phase as shown in fig1(b). This gives rise to a non-uniform change in the lattice parameters due to chemical doping pressure and cell volume from 213.2 Å³ to 249.9 Å³. The structural distortion produced by both the phases having orthorhombic in common is a measure of average A-size cationic radius <r_A> and size variance factor (σ²).

3.2. Electrical Transport Properties

Resistivity (ρ) as a function of temperature(T) from 303 to 673 K is shown in the Fig.2. All the ρ-T curves exhibit the same behavior indicating similar structure and phase formation undergoing M-I phase transition at 303 K, 431 K, 435 K and 468 K for x = 0.1 to 0.4 respectively. For x = 0, which corresponds undoped compound does not show T_MI since it is AFM insulator. The increased T_MI for concentrations x = 0.3 and 0.4 is attributed to anti-site doping disorder, at which perovskite phase become Brownmillerite phase [17]. Low sintering temperature, presence of excess Mn⁴⁺ due to Sb doping (increase in Mn³⁺/Mn⁴⁺) ratio, nature of ‘Sb’ as both reactant and additive and structural changes due to lattice mismatch between ‘Sb’ and ‘Ca’ ionic radii are all cannot be denied as possible causes for increased T_MI.

<table>
<thead>
<tr>
<th>Crystalline size (nm)</th>
<th>15</th>
<th>12</th>
<th>21</th>
<th>27</th>
<th>66</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice parameter</td>
<td>9.34</td>
<td>171.17</td>
<td>172.23</td>
<td>61.042</td>
<td></td>
</tr>
<tr>
<td>unit cell volume</td>
<td>303K</td>
<td>1.219</td>
<td>2.228</td>
<td>0.355</td>
<td></td>
</tr>
<tr>
<td>metal insulator</td>
<td>303K</td>
<td>213.2</td>
<td>431</td>
<td>468</td>
<td></td>
</tr>
<tr>
<td>transition temperature (T)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and crystalline size of Ca₁₋ₓSbₓMnO₃ (0≥ x≤ 0.4).</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>System</th>
<th>Ionic radius &lt;r_A&gt; (Å)</th>
<th>Size variance factor σ² (Å²)</th>
<th>Tolerance factor ‘t’</th>
<th>T0 from VRH model X108</th>
<th>Small polaron hopping Activation Energy in (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaMnO₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.78</td>
<td>0.3875</td>
</tr>
<tr>
<td>Ca₀.9Sb₀.1MnO₃</td>
<td>1.136</td>
<td>0.0175</td>
<td>0.9315</td>
<td>2.44</td>
<td>0.5596</td>
</tr>
<tr>
<td>Ca₀.8Sb₀.2MnO₃</td>
<td>1.092</td>
<td>0.0310</td>
<td>0.9152</td>
<td>1.722</td>
<td>1.0441</td>
</tr>
<tr>
<td>Ca₀.7Sb₀.3MnO₃</td>
<td>1.048</td>
<td>0.0405</td>
<td>0.8989</td>
<td>1.694</td>
<td>0.8582</td>
</tr>
<tr>
<td>Ca₀.6Sb₀.4MnO₃</td>
<td>1.004</td>
<td>0.0464</td>
<td>0.8826</td>
<td>2.3868</td>
<td>1.0786</td>
</tr>
</tbody>
</table>

The room temperature resistivity of the samples decreases from 16.95 KΩcm (x = 0.0) to 0.1219 KΩcm (x=0.2) upon systematic doping, is attributed to the increase in the charge carrier concentration (Sb⁵⁺ introduces twice as many electrons per Ca²⁺ atom) enabling double exchange (DE) mechanism [7]. Every Sb⁵⁺ dopant atom makes two Mn⁴⁺ ions converted into two Mn³⁺ ions and electron hopping between ‘Mn’ ions is responsible for electrical conductivity in perovskite manganites, and it also indicates that the dopant atom ‘Sb’ exactly replaces ‘Ca’ making the double exchange possible up to x= 0.2. For increased concentrations, resistivity increases to 23.205 KΩcm and then decreases to 0.355 KΩcm respectively for x=0.3 and x = 0.4 as shown in table 1. The abrupt rise in resistance for x=0.3 is assigned to Jahn-Teller distortion indicating that no more double exchange is possible, favoring the insulating state due to localization of electrons [18,19]. The decreased resistivity of three order for x=0.4, is due to increased grain size of almost three times (27 nm to 66 nm respectively for x=0.3 to x = 0.4) and also due to the appearance of Brownmillerite phase different from the perovskite phase. The peak resistivity is also found to follow the similar trend with the exception for x=0.2. The abrupt change in size variance factor (σ²) from 0.0175 to 0.031 respectively for x=0.1 and x = 0.2 is responsible for the observed change that are tabulated in table 2.
The origin of Brownmillerite phase is attributed to limited solubility which leads to anti-site effect. Increased dopant concentration produces a chemical pressure, giving rise to a compression in the A-O band and relaxation in B-O bond making similar to external pressure which modifies the local structure of distorted orthorhombic perovskite (Pbma) to distorted orthorhombic Brownmillerite structure (Pbam)\cite{17,20}. Abrupt reduction in the peak height and broadening in the ($\rho$-T) curve for the composition $x=0.3$ and $x=0.4$ is also another form of evidence for the chemical pressure induced formation of Brownmillerite phase. Hence, the limit of increase of $T_M$ with doping is subjected to structural stability and beyond which it cannot be increased.

From the above experimental observations, we may conclude that the low sintering temperature and flux wrapping of Sb$_2$O$_3$ disfavors the formation of large grains \cite{21,22}. Therefore, the average grain size decreases (12 nm to 27 nm for $x=0$ to $x=0.3$ and 66 nm for $x=0.4$) compared to normal and the grain boundary effect increases. This prevents the charge carriers from crossing the boundary between the neighboring grains leading to charge localization. Because of the increased grain boundary effect the resistivity is largely increased over the whole range of temperature studied \cite{14}. This may be inferred from the peak broadening in XRD and consequently due to smaller particle size, grain boundary volume ratio is greater than the grains giving rise to high resistance.

High value of resistance ($\Omega$) in Semiconducting-Insulating region is attributed to lattice mismatch (Ca /Sb) and appearance of Brownmillerite phase due to anti-site doping induced structural distortion; which in turn related to distortion favours insulating state due to localization of electrons as discussed earlier\cite{18,19}. Klien et al\cite{21} reported that the lattice strain is mainly responsible for the anomalies like phase segregation and magnetic interphase disorder, which gives rise to high resistance at room temperature. Resistance dependence of temperature gives information of disordering across the grain boundaries.

### 3.3. Modeling

The experimentally observed $\rho$ - $T$ curves of Ca$_{1-x}$Sb$_x$MnO$_3$ samples are considered as the superimposition of two different transport phenomena named AFM metal-like behavior below $T_c$ and PM insulating behavior above $T_c$. The metal like nature below $T_c$ is explained with Zener’s DE mechanism with a resistivity equation of the type $\rho(T) = \rho_0 + \rho_T T^2 + \rho_p T$\cite{23} and pure magnon scattering is represented by the equation $\rho(T) = \rho_0 + \rho_p T$\cite{24,25} are fitted separately here. The corresponding $\rho_0$ values are $0.185 \times 10^6 (0.1168 \times 10^6)$ $\Omega cm$ for Ca$_{0.7}$Sb$_{0.3}$MnO$_3$, 0.270$\times 10^6 (0.166 \times 10^6)$ $\Omega cm$ for Ca$_{0.6}$Sb$_{0.4}$MnO$_3$ and 0.069$\times 10^6 (0.444 \times 10^6)$ $\Omega cm$ for both the models found to be high due to disorder induced localization.

At above $T_c$, in all the $\rho$ - $T$ curves, it is observed a deviation from the linearity when the temperature is close to 550 K, where the rising of peak resistivity starts. This deviation indicates a crossover from activated carrier to another transport mechanism. The sudden drop in resistivity over a very narrow temperature range of 431 K to 523 K and saturation over wide range of temperature 550 K to 773 K, constitutes a clear evidence of change in the transport mechanism. Hence, the semiconducting - insulating part of the $\rho$ ($T$) curve was found to exhibit two different regimes. This abrupt change in resistivity when it is close to the peak is explained by two different models in account of the actual experimental observations. It explains, to understand the transport mechanism in doping induced disordered oxide CMR materials at high temperature regime \cite{14,26,27} as a variable range hopping $\rho = \rho_0 \exp (-T_o / T)$ and a small polaron hopping $\rho = B T \exp (E / k_BT)$.\end{center}

### 3.4. Variable Range Hopping Mechanism (VRH)

Conducting behaviour in manganites is explained based on doping induced disorder which gives rise to localization of energy states close to fermi level between conduction band and valence band. At high temperatures, carriers are thermally activated to their nearest neighbour site with high mobility. But when temperature decreases, thermally activated behaviour decreases and hopping process dominates, and conduction takes place by hopping of charge carriers between the localized states distributed unevenly. Normally carrier localization at the grain boundary changes the conductivity to semiconducting or insulating and carrier delocalization leads to metal like behaviour. The hopping is characterized by the parameter $T_0$ which is related to electronic density of states $N(E_f)$ and radius of localization length($\alpha$) by $T_0 = 18/k_B N(E_f) \alpha^3$. High $T_0$ value indicates multiphonon hopping with a large increase in the localization length and increase in barrier height at the grain boundaries leads to insulating and if $T_0$ decreases, based on hopping range and energy, the material remains in the metallic state of mott’s transition\cite{8,19}. Size of the grain and width of grain boundary in the order of...
nanometers (or the localization length ‘α’ (1/α)) will correspond to 100% spin polarization by tunneling mechanism [28,29].

The resistivity data in insulator regime were fitted to the variable range hopping (VRH) proposed by Mott as shown in Fig.3 linearizing the equation \( \rho = \rho_0 \exp(T_0/T)^{1/4} \) and from the slope \( T_0 \) values are obtained. In the present work, for every one ‘Sb’ doped in CaMnO₃ makes two Mn⁴⁺ ions which is transferred to two Mn³⁺ ions due to rich in electron carrier makes the carrier density \( N(E_F) \) of the system fixed. Since VRH takes place due to excitation of charge carrier across coulomb gap \( (W/U>>1) \), Ponnambalam et al [30] reported VRH mechanism over a very large temperature range of 100 K to 900 K.

Variation of \( T_0 \), with doping concentration (8.78 X 10⁸ to 1.694 X 10⁹), decreases uniformly for \( x=0 \) to \( x=0.3 \) indicating the reduction in the disorder, which in turn changes the Mn-O-Mn bond and leads to increase in the carrier concentration which is attributed to altering of \( (t^2g-e_g) \) orbitals by giving rise to drastic change in the band width due to electron filling [31,32] except for \( x=0.4 \). And for \( x=0.4 \), \( T_0 \) further increases to 2.3868 X 10⁸ indicating Jahn-Teller distortion along with structural phase transition to Brownmillerite phase for \( x>0.3 \). The decrease of \( T_0 \) due to low sintering temperature indicates the improvement in the crystallinity and hence the quantum mechanical tunnelling between the disorder induced localized state increases reducing the resistivity.

This variations in \( T_0 \) is attributed to the variations of \( (\sigma^2) \) compared to CaMnO₃ and SrMnO₃ as shown in the Table 3. The increase in \( T_0 \) value observed for our system is correlated to the structural variations caused due to the doping induced cation size disorder \( (\sigma^2) \)[33,34]

The overall fitting of our experimental data observation indicates that at temperatures where the thermal energy is very low, the VRH model perfectly fits perfectly to the equation and at the temperature where the thermally activated process dominates the experimental data deviates from the fitted data as shown in the Fig.3. Moreover, the fitted model of VRH proves localizations of charge carriers created by doping induced disorder are mainly responsible for the electrical conduction process in manganites.

### Table 3: \( T_0 \), Cation Size VarianceFactor, Activation Energies of some reported systems along with present work.

<table>
<thead>
<tr>
<th>System</th>
<th>( T_0 ) (ev)</th>
<th>Activation energy</th>
<th>Cation size variance ( \sigma^2 )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Ca_{1-x}Sb_xMnO_3 ) ( (Sb=0,0.1,0.2,0.3,0.4) )</td>
<td>2.333x10⁸ to 1.88x10⁹</td>
<td>0.3875 to 1.0786</td>
<td>0.0175 to 0.0464</td>
<td>Present Work</td>
</tr>
<tr>
<td>( LaMnO_3 )</td>
<td>1.2x10⁸ to 1.6x10⁹</td>
<td>163 to 248.9 (meV)(VRH)</td>
<td>10 to 206(meV)(VRH)</td>
<td>Ref 29</td>
</tr>
<tr>
<td>( La(NiFe)O_3 )</td>
<td>1.37x10⁸ to 1.7x10⁷</td>
<td>6.14to 160.03(meV)(SPH)</td>
<td>92 to 116 (meV)(SPH)</td>
<td>Ref 35,36</td>
</tr>
<tr>
<td>( (NdLnSr)MnO_3 )</td>
<td>0.4243x10⁶ to 1.8x10⁶</td>
<td>6.14to 160.03(meV)(SPH)</td>
<td>92 to 116 (meV)(SPH)</td>
<td>Ref 35,36</td>
</tr>
<tr>
<td>( LaCaMnO_3 )</td>
<td>4.3x10⁷ to 1.3x10⁸</td>
<td>56.9(meV) to 65.6(meV)(SPH)</td>
<td>1.54x10⁻³ to 3.6x10⁻⁷</td>
<td>Ref 40</td>
</tr>
<tr>
<td>( LaSrMnO_3 )</td>
<td>4.3x10⁷ to 1.3x10⁸</td>
<td>56.9(meV) to 65.6(meV)(SPH)</td>
<td>1.54x10⁻³ to 3.6x10⁻⁷</td>
<td>Ref 40</td>
</tr>
<tr>
<td>( Ca_{1-x}RxMnO_3 )</td>
<td>56.9(meV) to 65.6(meV)(SPH)</td>
<td>1.54x10⁻³ to 3.6x10⁻⁷</td>
<td>Ref 40</td>
<td></td>
</tr>
<tr>
<td>( R=L a, Pr, Nd, Sm, Eu, Gd, T b, Dy, Ho, Er, Y b ) ( (x=0.1) )</td>
<td>2.5x10⁻³ to 9x10⁻⁴</td>
<td>2.5x10⁻³ to 9x10⁻⁴</td>
<td>Ref 33</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Variable range hopping of \( Ca_{1-x}Sb_xMnO_3 \) \( (0 \leq X \leq 0.4) \) \( \rho vs T \) \( \rho vs 1/T^{1/4} \)
3.5. Small Polaron Hopping Model

Zener’s double-exchange model will not be sufficient enough to explain the very large change in resistivity in the Semiconducting-Insulating phase i.e., at high temperature region, since it does not consider spin-lattice or charge-lattice interactions, i.e., Jahn–Teller (JT) interaction and polarons, which significantly contribute [14] to the conduction process in the Semiconducting-Insulating phase. Therefore, it is very essential to understand the electrical conduction in the Semiconducting-Insulating region (where T >> TMI) which is governed by polaronic effects[20,21]. The conduction mechanism in manganites at high temperatures is governed by thermally activated small polarons based on the polaronic models.

The resistivity data in Semiconducting-Insulating region were fitted to the adiabatic small polaron hopping (ASPH) equation \( \rho = B \exp\left(\frac{E_p}{k_B T}\right) \) where \( B = \left[ k_B \nu_{ph} N C (1-C) \right] \exp(2\alpha R), k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature, \( N \) is the number of ion sites per unit volume, \( R \) is the average intersite spacing obtained from the relation \( R = (1/3)^{1/3} C \). \( C \) is the fraction of sites occupied by the polaron, \( \alpha \) is the electron wave function decay constant, \( \nu_{ph} \) is the optical phonon frequency \( (\nu_{ph} = \hbar / \nu_{opt}) \) and \( E_p \) is the activation energy following Padmavathi et al[35], Sayani Bhattacharyar[36], Abdel-Khalek et al[37] and Wasi Khan et al[29] for our system as shown in Fig.4. The temperature dependent polaron hopping is verified by calculating \( \theta_D/2(\theta_D = \text{Debye’s temperature}) \), where deviation from linearity occurs in the \( \ln (\rho/T) \) vs \( 1/T \) plot and the estimated phonon frequency. Leaving the undoped compound for concentrations \( x = 0.1 \) to 0.4, \( \theta_D \) and \( \nu_{opt} \) (optical phonon frequency) are found to be varying linearly from 356 K, 459 K, 480 K, 495 K and 7.44X10^{12}, 9.53 X 10^{12}, 9.9 X 10^{12}, 10.35 X 10^{12} \) respectively and in agreement with the reported values[30, 33].

The activation energy \( E_p \) was found to be increasing continuously with the doping concentration from 0.5596 to 1.044 eV for \( x = 0.1 \) to 0.2 indicating the presence of perovskite phase and it varies from 0.8582 to 1.0786 eV for \( x = 0.3 \) and \( x = 0.4 \), which is attributed to the appearance of brownmillerite phase and increase in the localization of charge carriers[38]. The increase in the activation energy is attributed to structural phase transition associated with the inhomogeneity or disorder in the barrier height and width. As well, the insufficient crystallization of ‘Sb’ in the system due to low sintering temperature (900°C) also cannot be ruled out.

Very large variations in \( (\sigma^2) \) compared to CaMnO3 and SrMnO3 as listed in the Table 3 is attributed to the large difference in the ionic radii between Ca (Ca=1.12Å) and Sb atom (Sb=0.74Å) which is due to anti-site doping induced cation disorder[28,39] and appearance of brownmillerite phase at higher ‘Sb’ concentrations. This gives rise to large value of activation energy compared to other system as listed in Table 3. Hence, this results indicate structural parameter \( \sigma^2 \) is closely related to electrical transport properties. Existence of higher activation energy is attributed to crystal distortions which increases the potential barrier height for polaron hopping[40]. When \( \sigma^2 \) varies from 0.0175 to 0.0464 activation energy is found to be 387.5 to 1078.6 (meV)(SPH) where as Yang Wang et al [40] reported the activation energy in the range of 56.9 to 65.6 (meV) for the \( \sigma^2 \) in the range of 1.54x10^{17} to 3.6x10^{17}. In fact, this may be compared with Ca/Sb ratio to Ca/RE ionic radii ratio.

4. Conclusion

We have investigated the effect of ‘Sb’ doping on the structural and electric transport properties of CaMnO3 in orthorhombic structure. The doping of ‘Sb’ for the first time increases \( T_{MI} \) to a maximum of 468K for \( x = 0.3 \). The shifting of \( T_{MI} \) towards high temperature is attributed to the presence of Brownmillerite phase due to limited solubility of ‘Sb’ at ‘Ca’ site and increase in the lattice parameter for the concentration \( x = 0.2 \) to \( x = 0.4 \), which indicates low chemical pressure induced by doping. Increased concentration of ‘Sb’ produces doping induced structural distortion from perovskite phase to Brownmillerite phase which is confirmed from the disappearance of characteristic perovskite at high intense 112 peak, which is very well reflected in the tolerance factor(t), average ionic radii \( \langle r_i \rangle \) and size variance factor \( \sigma^2 \). Low sintering temperature
favors large change in resistance ratio, increased TMI, liquid-phase grain growth and flux wrapping of ‘Sb’ yields smaller sized crystallites. Also, increased TMI is limited only to the structural stability.

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