Study of Conduction Behavior in Co-doped $Nd_{0.67}Sr_{0.33}Mn_{0.90}Co_{0.10}O_3$ Manganite

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Abstract. We have studied the structural and conduction mechanism of $Nd_{0.67}Sr_{0.33}Mn_{0.90}Co_{0.10}O_3$ manganite prepared through conventional solid state reaction route. The synthesized sample is single phase in nature and crystallizes in orthorhombic perovskite structure with Pbnm space group which is confirmed with the study of X-ray diffraction data through Rietveld refinement. The resistivity versus temperature measurement for sample $Nd_{0.67}Sr_{0.33}Mn_{0.90}Co_{0.10}O_3$ was performed in the range 0-300K and at 0T field. The conduction mechanism of the sample is analyzed and explained by different theoretical models, for temperatures below and above T_P.

INTRODUCTION

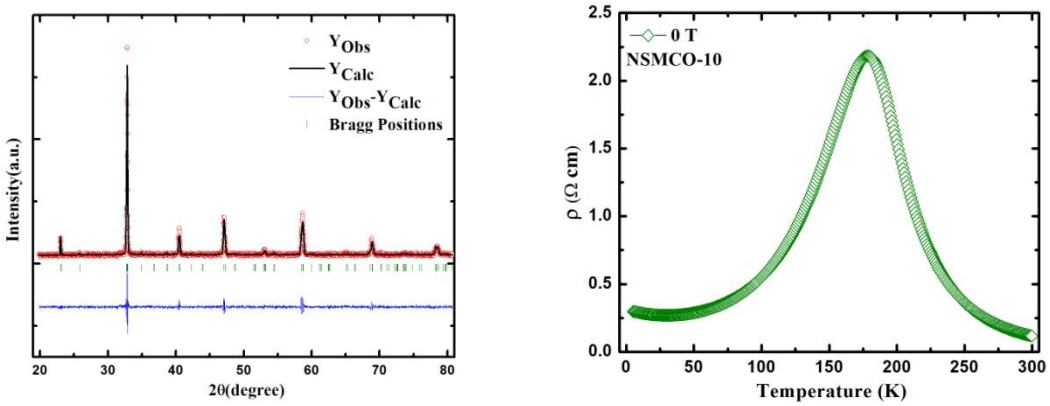
In recent years technological advancement in the field of magnetic storage, spintronics and bolometers is achieved through doping of interesting and potential elements in the ABO_3 type perovskite compounds [1, 2]. The mixed oxide manganites with parent compound $Nd_{0.67}Sr_{0.33}MnO_3$ are most promising candidate for tunable device based properties [2]. The doping of a Transition Metal ion at Mn-site introduces a number of effects such as weakening of ZDE mechanism, change in charge carrier concentration and lattice distortion. The ionic mismatch at Mn-site due to the difference in ionic radii distorts the lattice on substitution which results in the change of Mn-O-Mn bond angle and Mn-O bond length [3, 4]. The doping of Co^{3+} ion at Mn-site is interesting because Mn ions are responsible for the electrical properties of the system and interaction of Co^{3+} ion (0.545 Å) with Mn^{3+} ion (0.645 Å), having a large ionic-mismatch results in the increase of resistivity and shifting of M-I transition temperature (T_P) to a lower temperature[5, 6]. The doping of Co ion helps in understanding the change in conduction behavior of $Nd_{0.67}Sr_{0.33}MnO_3$ compound through study of Resistivity-Temperature graph by various theoretical models [8].

EXPERIMENT

The polycrystalline $Nd_{0.67}Sr_{0.33}Mn_{0.90}Co_{0.10}O_3$ sample is synthesized using the conventional solid-state reaction route. The stoichiometric oxide powders of each elements are thoroughly mixed and calcinated at 800-1000 ˚C for 12 hours with intermediate grinding. The calcined powder were reground, pressed into pellets and sintered at 1250 ˚C for 24 hours in air. The samples were characterized structurally by X-ray diffraction (XRD) technique using a Bruker D8 Advance X-ray diffractiometer with CuK_α radiation at room temperature. Rietveld refinement of the diffraction data was carried out using the FULLPROF suite. The resistivity versus temperature measurement is performed using the standard four probe technique in the temperature range of 5-300 K without magnetic field.

RESULTS AND DISCUSSION

In Fig. 1 (a), we depict the XRD pattern and analysis of the data using Rietveld refinement for $Nd_{0.67}Sr_{0.33}Mn_{0.90}Co_{0.10}O_3$ compound at room temperature. The sample exhibits orthorhombic type symmetry with *Pbnm* space group and it is clear from the Fig. 1(a) that calculated diffraction patterns are in good agreement with the measured diffraction patterns. The details obtained from Rietveld refinement are the lattice parameters a=5.4662 Å, b=5.4419 Å, c=7.6863 Å and cell volume=228.64 $Å^3$ with the χ^2 value finalized at 1.45. The stability of the perovskite compound is determined by the Goldschmidt tolerance factor $t = (r_A + r_O)/\sqrt{2}\,(r_B + r_O)$[7]. The value of the tolerance factor for the sample is found to be less than t <0.96, which confirms that the sample is in orthorhombic structure.



(a) (b)

FIGURE 1. (a) XRD with Rietveld Refinement, (b) Resistivity as a function of Temperature at 0 T.

The resistivity (ρ) versus temperature (T) measurement of the sample is performed in the range 0-300K at 0T field and illustrated in Fig. 1 (b). The compound shows the transition from metal to insulator at 178 K (T_P). The degree of ionic mismatch at Mn-site increases as ionic radius of Co^{3+} (0.545 Å) is smaller as compared to Mn^{3+} (0.645 Å). The increase in the degree of ionic mismatch results in greater distortion of MnO_6 octahedra which increases the magnitude of resistivity. The resistivity behavior is analyzed and confirmed by the temperature coefficient of resistivity ($\delta\rho/\delta T<0$ shows the semiconducting/insulator behavior and $\delta\rho/\delta T>0$ shows the metallic behavior) above the transition temperature ($T>T_P$) and below the transition temperature ($T<T_P$).

In order to understand the conduction behavior, the resistivity data is analyzed in temperature region that is paramagnetic-insulating region ($T>T_P$). The resistivity data in the paramagnetic region is analyzed using Mott's Variable range hoping (VRH) Model ($T_P<T<\theta_D/2$) and Small Polaron Hopping (SPH) Model ($T>\theta_D/2$) which helps us to understand the electrical transport mechanism, the semiconducting paramagnetic region between T_P and $\theta_D/2$ is analyzed using VRH Model given by

$$\rho = \rho_0 \exp\left(\frac{-T_0}{T}\right)^{1/4} \quad (1)$$

With Density of States calculated using

$$K_B T_0 = \frac{24}{\pi N(E_F)\xi^3} \quad (2)$$

Where ρ_0 is the residual resistivity, T_0 is the characteristic temperature, near the Fermi level the density of states is calculated through N (E_F), K_B is the Boltzmann constant and ξ is the localization length. The hopping energy W_h (T) and the probable hopping distance can be written at a given temperature T as

$$W_h(T) = \frac{1}{4} K_B T^{3/4} (T_0)^{1/4} \quad (3)$$

$$R_h(T) = \frac{3}{8} \xi (T_0/T)^{1/4} \quad (4)$$

The linear behavior and fitted data of the resistivity region with solid line is plotted between Log (ρ) versus $(1/T)^{-1/4}$ as shown in Fig. 2. We have estimated the values of $N(E_F)$, $W_h(T)$ and $R_h(T)$ with the help of T_0 obtained from the fitting of above equations on semiconducting resistivity region. The given temperature 'T' is considered near room temperature for all the above calculations.

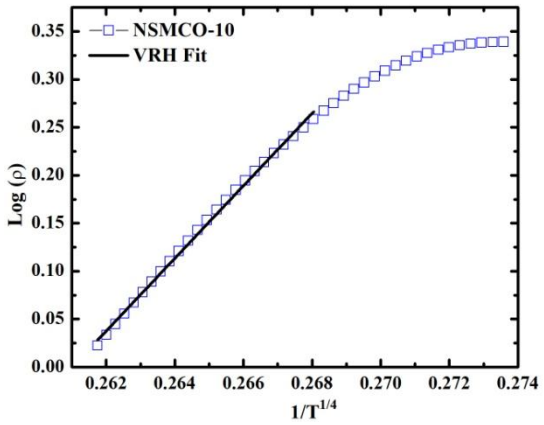


FIGURE 2. Fitted data of Resistivity using VRH model

TABLE 1. Fitted curve and calculated values of the resistivity data using VRH model above T_P for $Nd_{0.67}Sr_{0.33}Mn_{0.90}Co_{0.10}O_3$ sample.

Sample Code	T_0(x 10^6 K)	$N(E_F)$ x 10^{19}(eV^{-1}cm^{-3})	R_h (Å)	W_h (mev)
NSMCO-10	2.0551	9.504	26.223	58.79

The electrical resistivity behavior in paramagnetic-insulating region that is temperature greater than $\theta_D/2$ ($T>T_P$) was analyzed using various theoretical models. In the semiconducting/insulator region the resistivity follows the nearest neighbor small polaron hopping (SPH) model and the activation energy (E_a) is calculated using equation.

$$\rho(T) = \rho_0 T \exp(E_a / k_B T) \quad (5)$$

where ρ_0 is the resistivity coefficient, E_a is the activation energy and k_B is the Boltzmann constant. The electrical resistivity in semiconducting/insulator region is fitted with Small polaron hoping model shown in Fig. 3. The activation energy (E_a) from SPH model above T_P for $Nd_{0.67}Sr_{0.33}Mn_{0.90}Co_{0.10}O_3$ sample is 69.673 mev.

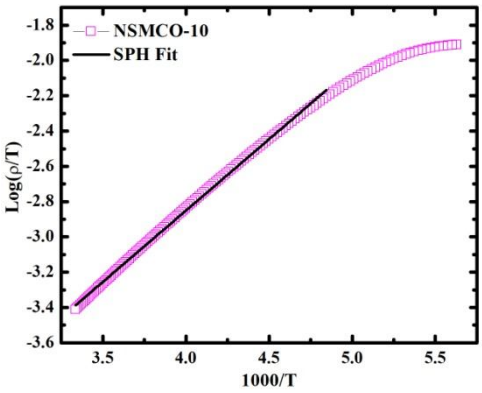


FIGURE 3. Variation of resistivity fitted with SPH model

CONCLUSION

We have successfully synthesized the $Nd_{0.67}Sr_{0.33}Mn_{0.90}Co_{0.10}O_3$ sample using the solid state reaction technique. The structural symmetry and phase purity is confirmed through Rietvield refinement of the XRD data. The metal to insulator transition is significantly decreased with Co doping at Mn-site and increase in resistivity is observed. The resistivity data in the paramagnetic semiconducting region is analyzed with VRH model with Density of states, hopping energy and probable hopping distance is tabulated in the results. The resistivity in semiconducting/insulator regime is also analyzed and fit is obtained for SPH model through which activation energy (E_a) is calculated for the sample.

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