SYNTHESIS, CHARACTERISATION AND RESISTIVITY STUDY OF BI DOPED AT MN SITE OF $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ MANGANITES

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Abstract: We report structural and electrical studies of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$ ($x=0, 0.1$ and 0.2) manganites. In manganites Mn ions play a crucial role in shaping the physical properties. Possible reasons for the observed structural, changes of resistivity behavior with Bi doping are discussed. Replacing trivalent Bi ion with Mn ion provides us a system to understand weakened double-exchange (DE) interaction ($\text{Mn}^{3+}\text{-O-Mn}^{4+}$). X-ray powder diffraction showed that all synthesized samples are single phase and crystallize in the orthorhombic symmetry with $Pnma$ space group. The unit cell volume decreases with increasing Bi content. The value of metal-insulator (M-I) transition temperature (T_{MI}) decreases and resistivity increases as doping level x increases. The drop in resistivity at T_{MI} results from the reduced contribution of magnetic scattering. Ferromagnetic metallic resistivity is observed well below the metal-insulator transition temperature. Above the metal insulator transition temperature the electrical conductivity is dominated by small polaron hopping (SPH) model.

Keywords: Manganites, Electrical resistivity, Space group, Small polaron hopping model, Metal-insulator transition, Double exchange interaction

Introduction:

PrSrMnO_3 system was chosen because this system has one of the largest bandwidths ($t=0.9232$) in manganites. This is an important criterion for the present study because we wish to study the effect of Mn-site doping on the ferromagnetic metallic state. The motion of the e_g electron can be strongly influenced by average ionic radius of the A site which exhibits a closed relationship between the bending of the Mn-O-Mn bond angle and narrowing of the electronic bandwidth.[1]

The family of Bi- based manganites became of recent interest because of the physics that lies behind the unusually high charge ordering (CO) temperature ($T_{\text{CO}} \sim 475\text{K}$) [2]. It has been proposed that the anomalously high T_{CO} is related to the $6s^2$ lone pair towards a surrounding anion (O^{2-}) can produce a local distortion or even hybridization between Bi- $6s$ -orbitals and O^{2-} -orbitals [3]. The metallic region has been explained on the basis of electron-electron and electron-magnon scattering processes[4].

Substitution at the Mn site is expected to bring some spectacular effect because the essential degrees of freedom are closely linked to Mn ions. The substitutions lead to a reduction of T_{C} and magnetization, an increase of resistivity, and an enhancement

of the magneto resistance (MR).. It is clear that the actual distribution of the cation vacancies between the A and B sites must strongly affect the physical properties of manganites (ABO_3) due to the core role of Mn ions in manganites. For example, cation vacancies on the manganese site should lead to a more pronounced deterioration of both the electrical and magnetic properties compared to vacancies on the lanthanum site, due to the blocking of the magnetic interaction paths and their influence on the Mn-O conduction band.

Experimental studies:

Preparation of series $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$ ($x=0, 0.1$ and 0.2) using solid state reaction method:

In the present work, stoichiometric ratio of Pr_6O_{11} , SrCO_3 , Bi_2O_3 and MnO_2 (all from Aldrich chemical Ltd with 99.9% purity) were mixed very well to obtain a homogeneous mixture. The mixture is calcined at 1200°C for 24 hours with intermediate grinding. The calcined mixtures were then pressed into pellets) and sintered in air at 1300°C for 36hrs.

XRD Measurement:

In the present work, the structural information of the synthesized samples $\text{Pr}_{0.6-x}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$ ($x=0, 0.1$ and 0.2) obtained by X-ray diffraction (XRD) studies on Bruker D8 Advance X-ray diffractometer. The XRD

data were analyzed using Rietveld refinement technique to confirm the phase formation as well as to obtain the structural parameters lattice parameters, space group, crystal system.

Resistivity Measurement:

Conventional four probe method is used to measure resistivity of the samples under present investigation using closed cycle refrigerator.

Results and Discussions:

XRD study: X-ray diffraction analysis using Rietveld refinement method indicates that all synthesized samples $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$ ($x=0, 0.1$ and 0.2) are single phase, orthorhombic structure with Pnma space group without any detectable impurity. X-ray diffraction pattern for all our samples is shown in figure 1. Unit cell volume and the lattice parameters along with R factors, goodness fit are given in table 1. By Bi doping no apparent structural changes can be identified. While the a , b and c parameter decreases with bismuth. The unit cell volume decreases for $x=0.1$ and increases for $x=0.2$ compared with 0.1 . With checking the intense peak of X-ray powder diffraction patterns for the (Fig.2), we can notice that for $x=0.2$ of bismuth induces a shift to low θ values which indicates an increase of unit cell volume. Similarly shifting to high θ values for $x=0.1$ compared to pristine sample indicates decrease in unit cell volume.

Table-1. Summary of structural parameters of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$

x	0	0.1	0.2
a(Å)	5.4806	5.4771	5.4769
b(Å)	7.6684	7.6632	7.6663
c(Å)	5.4376	5.4321	5.4350
Volume(Å ³)	228.534	228.002	228.208
Structure type	Orthorhombic		
Space group	Pnma	Pnma	Pnma
R _p (%)	2.84	3.63	3.04
R _{wp}	3.59	4.98	4.13
R _{exp}	3.41	3.44	3.52
Goodness fit(S)	1.05	2.77	1.17
χ^2	1.11	2.19	1.37

Fig.-1. Rietveld fitted XRD pattern of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$ ($x=0, 0.1$ and 0.2) compound

Fig.2. Intense peak of X-ray powder diffraction patterns for the samples $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$ ($x=0, 0.1$ and 0.2)

Electrical study:

Figure 3 shows the resistivity evolution as a function of temperature in zero magnetic applied field.

With decreasing temperature, sample exhibit a transition from a semiconducting to metallic state (values are given in table 2). The maximum value of the resistivity is and the transition temperature T_{MI} is 233K for pristine sample. The drop in $\rho(T)$ at T_{MI} results from the reduced contribution of magnetic scattering.

Fig.-3. Resistivity versus Temperature of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$ ($x=0, 0.1$ and 0.2)

It is found that metal-insulator transition temperature decreases with bismuth content due to the fact that as the bismuth ions enters into the samples as Bi^{3+} and takes place of the Mn^{3+} cations, it vanishes the double exchange between Mn^{3+} and Mn^{4+} ions. The replacement of Mn^{3+} by Bi^{3+} destroys some ratios of $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ bonds and the interactions between $\text{Bi}-\text{O}-\text{Mn}$ might be antiferromagnetic super-exchange. The competition between the $\text{Mn}-\text{O}-\text{Mn}$ double exchange and the $\text{Bi}-\text{O}-\text{Mn}$ super-exchange may explain the weakening of the ferromagnetism samples. For concentration $x=0.2$ resistivity remains thermally activated; similar type of behavior is also observed in bismuth doped at rare earth site of $\text{Pr}_{0.6-x}\text{Bi}_x\text{Sr}_{0.4}\text{MnO}_3$ ($x=0.2$) shown in figure 4.

Here resistivity increases when bismuth doped at Mn site compared to that at Pr site because the Bi doping at Mn site induces a weakening of the ferromagnetism. But resistivity values decreases with bismuth this is ascribed to the difference between ionic radii of Mn^{3+} and Bi^{3+} ions. In fact, substituting Mn^{3+} ($r=0.645\text{\AA}$) by Bi^{3+} ($r=1.03\text{\AA}$) with anionic radius larger than that of manganese ion. Larger ionic radii of Bi^{3+} ion supports DE conduction mechanism.

Fig.-4. Resistivity versus Temperature of bismuth doped at Pr and Mn site of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$

To find the conduction mechanism, conductivity data below the metallic phase, resistivity data of the samples follow the relation,

$$\rho = \rho_0 + \rho_2 T^2 + \rho_{4.5} T^{4.5} \quad (1)$$

where ρ_0 is the residual resistivity arising from the temperature independent processes such as domain wall, grain boundary, vacancies, $\rho_2 T^2$ attributed to electron-electron scattering and $\rho_{4.5} T^{4.5}$ indicates two magnon scattering process in FM phase. The low temperature fitting curve is shown in figure 5. The parameters obtained from best fitting of the low-temperature metallic part of the resistivity are shown in table 2.

Fig.-5. Low temperature resistivity fit of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$ ($x=0$ and 0.1)

This indicates that with increasing Bi concentration and with increase of resistivity, electron-electron scattering

contribution to the resistivity data becomes predominant.

Conduction mechanism above metal-insulator transition temperature (T_{MI}) has been studied to support the presence of magnetic polaron form=0, 0.1 and 0.2. Figure 6 shows the fitted data for Holstein's model (small range hopping conduction),

$$\rho = \rho_0 T \exp\left(\frac{E_p}{k_B T}\right) \quad (2)$$

Table.2. Low and High temperature Resistivity fitting data and T_{MI} values of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$

Concentration	T_{MI} (K)	ρ_0 ($\Omega\text{-cm}$)	ρ_2 ($\Omega\text{-cm/K}^2$)	$\rho_{4.5}$ ($\Omega\text{-cm/K}^{4.5}$)	Activation energy meV
0	233	0.213074	1.05E-05	-6.2E-12	53.48
0.1	213	4.246E-02	9.848E-07	-7.581E-13	23.2
0.2	19				5.28

Where ρ_0 is a constant, E_p is the polaron hopping energy, and k_B is the Boltzmann constant. The

activation energy of the samples estimated from the slope of $\ln(\rho/T)$ - $1/T$ curve for $x=0, 0.1$ and

0.2. Above the transition temperature the conduction mechanism is accounted for thermally activated polaron hopping. The calculated values of polaron hopping energy (E_p) listed in table 2. The decrease in activation energy (E_p) can be understood in terms of larger ionic radii and Bi^{3+} - $6s^2$ orbital further supports DE conduction mechanism.

Fig.-6. High temperature resistivity fit of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$ ($x=0, 0.1, 0.2$)

Conclusions:

Synthesis, structural and electrical properties of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Bi}_x\text{O}_3$ ($x=0, 0.1, 0.2$) are studied. The unit cell volume decreases with increasing Bi content. The value of metal-insulator (M-I) transition temperature (T_{MI}) decreases and resistivity increases as doping level x increases.

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