Comparative Study of Structural and Electrical Study of Bismuth Doped At La and Mn Site of $La_{0.7}Sr_{0.3}mno_3$

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***Abstract*—We report the structural and electrical properties of polycrystalline bismuth (Bi) doped $La_{0.7}Sr_{0.3}MnO_3$ (x = 0, 0.1 and 0.2) at La(A) and Mn(B) site. Refinement of X-ray powder diffraction patterns show that all samples crystallize in Rhombohedral structure with *R-3C* space group. There is decrease in unit cell volume as well as metal to insulator transition temperature T_{MI} in both site Bi doping. It is found that values of resistivity are higher at B site doping compared that of A site for all concentrations. It is found that the value of T_{MI} is a 233K and 227K and resistivity at peak is 184m Ω-cm and 675mΩ-cm in La and Mn doped samples respectively for x=0.1. The competition between the Mn–O–Mn double exchange and the Bi–O–Mn super-exchange of Mn^{3+} by Bi^{3+} may explain the increase in resistivity**

***Index Terms*—Manganites, Cation vacancy, Bismuth, Polarization**

I. INTRODUCTION

In recent years, manganites with general formula $La_{1-x}A_xMnO_3$ (A= Sr, Ca Ba etc) have drawn enormous interest because of anomalous electric and magnetic properties [1-2]. In particular, $La_{1-x}Sr_xMnO_3$ is an important manganite system, as they have high transition temperatures of about 370K. The compounds, $La_{1-x}Sr_xMnO_3$, are well investigated ferromagnetic systems and the studies show that they have largest one-electron band width, and the hopping amplitude for electrons in e_g band is larger than that observed in other manganites. As far as practical applications are concerned, $La_{1-x}Sr_xMnO_3$ is good candidates for the cathode of solid oxide fuel cells. The family of Bi-based compounds has drawn immense interest as they show high charge ordering temperatures [3]. It may be mentioned that Bi doped manganites have fascinated the researchers due to its large magneto caloric effect *(MCE)* and high relative cooling power which makes these manganites possible candidates as refrigerant materials [4-5]. The study of the effects of Mn-site doping with other elements provides important clues to the mechanism of CMR behavior.

Substitution at the Mn site is expected to bring some spectacular effect because the essential degrees of freedom are closely linked to Mn ions. Cation vacancies on the manganese site should lead to a more pronounced deterioration of the electrical 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 [6-8]. 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 due to the core role of Mn ions in manganites. Also, the modification of the Mn^{+3}- O - Mn^{+4} network with Mn-site doping causes dramatic changes in the transport and magnetic properties.

II. EXPERIMENTAL

In the present work, bulk polycrystalline manganite bismuth doped $La_{0.7}Sr_{0.3}MnO_3$ (x = 0, 0.1 and 0.2) at La and Mn site were prepared using conventional solid state reaction method. After preheating La_2O_3 at 900°C for 8 hours, stoichiometric ratio of La_2O_3, $SrCO_3$, Bi_2O_3 and MnO_2 were mixed very well to obtain a homogeneous mixture. The mixture is calcinied at 900^0C for 12 hours with intermediate grinding. The calcinied mixtures were then pressed into pellets and sintered in air at 1200^0C for 24hrs. The structural information of the synthesized compounds were obtained and the observed XRD patterns are further simulated with the help of Rietveld refinement/Fullprof suite program. Electrical resistivity measurements were carried out using a four-probe technique.

III. RESULTS AND DISCUSSIONS

After analyzing the refined patterns, it is found that all the samples are single phase with rhombohedral structure with space group *R-3C*. The simulated XRD of Bi doped at La and Mn site samples are shown in figure 1a and 1b respectively. It is evident from table 1a and b that the lattice parameters 'a' and 'b' slightly decreases on contrary a increase in 'c' is observed with an increase in Bi-content at both site. The unit cell volume decreases with Bi content at La site and thus can be ascribed due to the presence of magnetic polarons which are produced due to competing behavior of larger ionic radii generated ferromagnetic-double exchange and charge ordered state [9,10]. But in doping at Mn site the decrease in unit volume with Bi is due to the electronic configuration of Bi^{3+}ions, these ions are characterized by the $6s^2$ electrons which can produce a local distortion and make hybridization with the 2p orbitals of oxygen [11].

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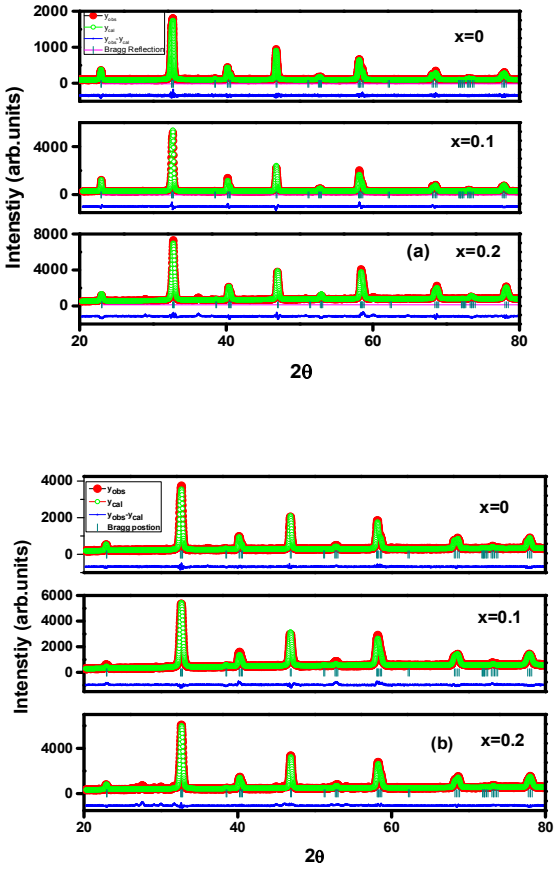

Fig.1: Rietveld defined XRD pattern of Bi doped $La_{0.3}Sr_{0.3}MnO_3$ (x = 0, 0.1 and 0.2) at (a) La and (b)Mn site

Table.1a. Structural Parameters of Bi Doped At La Site

x	0	0.1	0.2
a(Å)	*5.5042*	*5.4892*	*5.4784*
b(Å)	5.5042	5.4892	5.4784
c(Å)	13.3590	13.3342	13.3364
Volume ($Å^3$)	350.508	347.947	346.643
Structure type	Rhombohedral		
Space group	R-3C		
R_P(%)	6.03	3.26	4.37
R_{WP}	7.78	4.31	6.1
R_{Exp}	8.79	3.27	3.38
Goodness fit	0.885	1.318	1.804
$\chi 2$	0.782	1.73	3.26

Table.1b: Structural Parameters of Bi Doped At Mn Site

x	**0**	**0.1**	**0.2**
a(Å)	5.5005	5.4984	5.4941
b(Å)	5.5005	5.4984	5.4941
c(Å))	13.3548	13.3591	13.3524
Volume ($Å^3$)	349.95	349.780	349.055
Structure type	Rhombohedral		
Space group	R-3C		
R_P(%)	4.13	4.33	4.95
R_{Wp}	5.22	5.85	7.11
R_{Exp}	5.32	4.02	4.07
Goodness fit(S)	0.98	1.45	1.74
$\chi 2$	0.963	2.12	3.06

The variation of resistivity with temperature of bismuth doped $La_{0.7}Sr_{0.3}MnO_3$ (x=0, 0.1 and 0.2) at La site are shown in figure 2

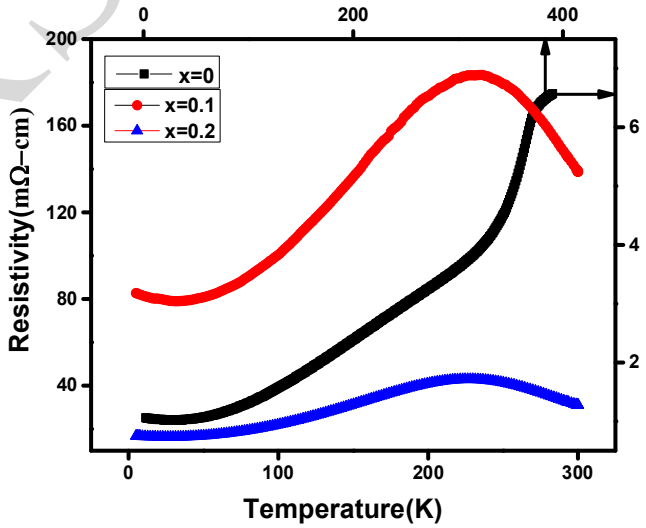

Fig.2: Resistivity Vs Temperature of Bismuth Doped $La_{0.7}Sr_{0.3}Mno3$ at La Site.

Bismuth doped at La site samples are showing metal-insulator transition temperature (T_{MI}). This itinerancy-correlated picture follows the double exchange scenario. It is found that T_{MI} decreases and the resistivity increases with increase in bismuth concentration. These observations suggest that the highly polarizable Bi^{3+} ion with $6s^2$ lone pair would cause local distortion of the perovskite lattice, which presumably reduces the mobility of carriers. Although Bi^{3+}

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and La^{3+} have very similar ionic radii in many oxides, replacement of La by Bi in this case leads to an increase of the average Mn–O–Mn distortion [12] and also the partial replacement of La by Bi narrows the Mn–O–Mn bond angle and Bi–O bond length but increases the Mn–O bond length [13]. Hence, the Bi $6s^2$ and O $2p$ orbitals hybridize. Increase in resistivity and magnetic frustration is probably due to a partial hybridization of the Bi $6s^2$ electrons with some O-$2p$ orbitals.

Similarly the variation resistivity with temperature of bismuth doped $La_{0.7}Sr_{0.3}MnO_3$ (x=0, 0.1 and 0.2) at Mn site is shown in figure 3.

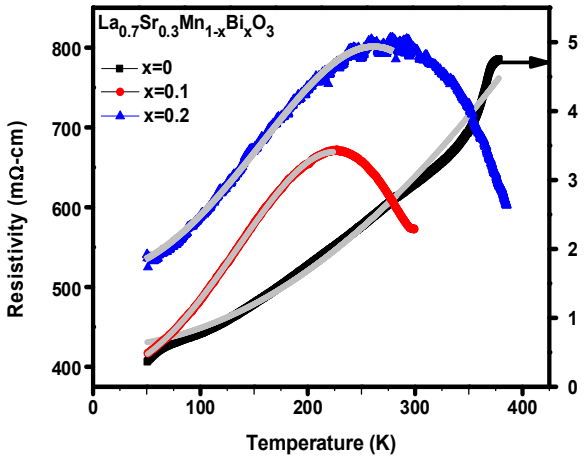

Fig.3: Resistivity Vs Temperature of Bismuth Doped $La_{0.7}$ $Sr_{0.3}$ Mno3 At Mn Site

All samples are showing metal-insulator transition temperature (T_{MI}), but the pristine sample shows T_{MI} at 377K. It is found that T_{MI} decreases and the resistivity increases with increase in bismuth concentration at Mn site. This is due to the fact that doping Mn-site directly affects the magnetic behavior and weaken the ferromagnetic interactions due to the decrease of manganese ions resulting in the reduction of double exchange mechanism. This produces an important disorder in manganese network which directly affects electrical and magnetic properties. The decrease in unit cell volume also supports the increase in resistivity and decrease in metal to insulator transition temperature with bismuth. Thus Mn site weakens double-exchange interaction is reflected in the progressive decrease in metal-insulator transition. The replacement of Mn^{3+} by Bi^{3+} destroys some ratios of Mn^{3+}–O^{2-}–Mn^{4+} bonds and the interactions between Bi–O–Mn might be antiferromagnetic super-exchange. The decrease of manganese ions resulting in the reduction of double exchange mechanism. To explain electrical resistivity in the low temperature ferromagnetic region we use a qualitative model, according to this model, the electrical resistivity in manganties arises due to the electron-electron scattering $(\rho_2 T^2)$ as well as two magnon scattering $(\rho_{4.5} T^{4.5})$ processes and is represented by equation,

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

From the fitting, it is observed that demonstrates that electron–electron scattering processes play vital part in elucidating the conduction process in both La and Mn site doping. The conduction mechanism of manganites at high temperatures, governed by thermally activated small polarons and is given by,

$$\rho = \rho_0 T \exp\left(\frac{E_\rho}{k_B T}\right) \qquad \textbf{(2)}$$

where ρ_0 is a constant, E_ρ 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. The fitted parameter polaron activation energy values increase with bismuth content due to the fact that lower the possibility of conduction electron to hop to the neighboring sites. Finally it is concluded that values of resistivity are higher at B site doping compared that of A site for all concentrations due to the core role of Mn ions in manganites. It is found that the value of T_{MI} is a 233K and 227K and resistivity at peak is 184m Ω-cm and 675mΩ-cm in La and Mn doped samples respectively for x=0.1. The weakening of double exchange mechanism reflected in higher value of resistivity in Mn doped compared to that La doped samples.

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