Journal of Alloys and Compounds 504 (2010) L39–L41

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Letter

Doped $Pr_{0.7-x}Bi_xSr_{0.3}MnO_3$ manganite: A structural, electrical and magnetic effect

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ARTICLE INFO

Article history:
Received 25 March 2010
Received in revised form 29 May 2010
Accepted 1 June 2010
Available online 11 June 2010

Keywords:
Manganites
Metal–insulator transition
Charge order

ABSTRACT

Structural, electrical and magnetic properties of $Pr_{0.7-x}Bi_xSr_{0.3}MnO_3$ ($x = 0.00, 0.15, 0.25$) compound have been studied. A decrease in unit cell volume is observed, although Bi^{3+} (1.17 Å) ion has larger ionic radii than Pr^{3+} (1.126 Å) ion and can be understood in a scenario of coexistence of charge ordered and ferromagnetic phase. “Electrical-resistivity and Magnetic” measurements show that the transition temperature (T_{MI}, T_C) increases i.e. “284.6 K, 276.5 K” to “294.04 K, ∼300 K” for $Pr_{0.70}Sr_{0.3}MnO_3$ and $Pr_{0.45}Bi_{0.25}Sr_{0.3}MnO_3$ compounds, respectively. Larger ionic size of Bi^{3+} ion encourages double-exchange (DE) interaction, which in turns result an increase in transition temperatures.

1. Introduction

$Pr_{0.7}Sr_{0.3}MnO_3/Pr_{0.6}Sr_{0.4}MnO_3$ is one of the most famous colossal magnetoresistance (CMR) manganite material having its insulator–metal transition temperature (T_{MI}) ∼284/320 K or paramagnetic–ferromagnetic transition temperature (T_C) near the room temperature, follows Holstein model/small range conduction mechanism [1–4]. In CMR materials the effects of “A” site cation mismatch and their valence fluctuation have a particular importance [5–8]. Replacing Pr^{3+} by larger La^{3+} ion or smaller Nd^{3+} ion, one can move large band metallic-ferromagnet i.e. $La_{0.7}Sr_{0.3}MnO_3$ manganite ($T_{MI} \sim 350$ K) [9] to charge ordered manganite phase [10]. Average cationic size has a direct relation between Mn–O bond and band width. So “A” site cation mismatch has very significant effect on their structural as well as electrical and magnetic properties and can be modified. Recently Garbarino and Acah reported the chemical pressure (i.e. “A” site cation mismatch)/applied pressure effect on structural and electronic parameters in $La_{0.8}Ca_{0.2-x}Sr_xMnO_3$ ceramic manganite [11]. However manganites are not homogenous rather microscopic antiferromagnetic or paramagnetic inhomogeneity may present in ferromagnetic matrix as reported earlier by many authors [12–15].

Interestingly Bi^{3+} (∼La^{3+}) has larger ionic radii than Pr^{3+} ion, it is possible to enhance remarkably the physical properties of rare earth manganite. Recently Sun et al. observed fascinating cyclic resistive state during heating and cooling cycles in Bi doped $La_{0.67}Ca_{0.33}MnO_3$ compound [16]. Although it suppresses double-exchange that is attributed due to its slightly smaller ion than La^{3+} ion, hence the transition temperature decreases. In a recent report by Boujelben et al., observed that Bi^{3+} ion doping in $Pr_{0.7}Sr_{0.3}MnO_3$ (PSMO) compound decreases the ferro–para/metal–insulator (T_C, T_{MI}) transition temperatures. On the basis of electrical resistivity and magnetization measurements claims that these results are due to smaller Bi ion as the average ionic radii of “A” site decreases [1]. Similarly Kammoun et al. reported a decrease in ferromagnetic–paramagnetic (T_C) for $Pr_{0.6}Sr_{0.4}MnO_3$ compound as Bi^{3+} ion concentration is increased and observed an increase in magnetic inhomogeneity with Bi^{+3} substitution in $Pr_{0.6}Sr_{0.4}MnO_3$ compound as bifurcation of ZFC and FC increases. For the comparison point of view, we prepared $Pr_{0.7-x}Bi_xSr_{0.3}MnO_3$ ($x = 0.00, 0.15, 0.25$) compound by solid state reaction method and studied their structural, electrical and magnetic properties.

2. Experimental

The samples in the series with nominal composition $Pr_{0.7-x}Bi_xSr_{0.3}MnO_3$ ($x = 0.00, 0.15, 0.25$) were prepared by conventional solid state reaction method. Stoichiometric ratio of Pr_6O_{11}, $SrCO_3$ and MnO_2 (all from Aldrich Chemical Ltd. with 99.9% purity) was mixed very well to obtain a homogeneous mixture and calcined at 1200 °C for 24 h with intermediate grinding. The calcined mixtures were then pressed into pellets and sintered in air at 1225 °C for 30 h. Finally the pellets of all titular composition were annealed for 12 h at 1100 °C in oxygen atmosphere for the removal of oxygen inhomogeneity. The structural information was obtained by X-ray diffraction (XRD) studies on RIGAKU machine with Cu-Kα radiation (1.54 Å) in the 2θ range of 20–80°. Electrical resistivity was measured as a function of temperature by conventional four probe method. The magnetic measurements were carried out on PPMS (physical property measurement system) from Quantum Design 14T with ACMS facility.

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doi:10.1016/j.jallcom.2010.06.011

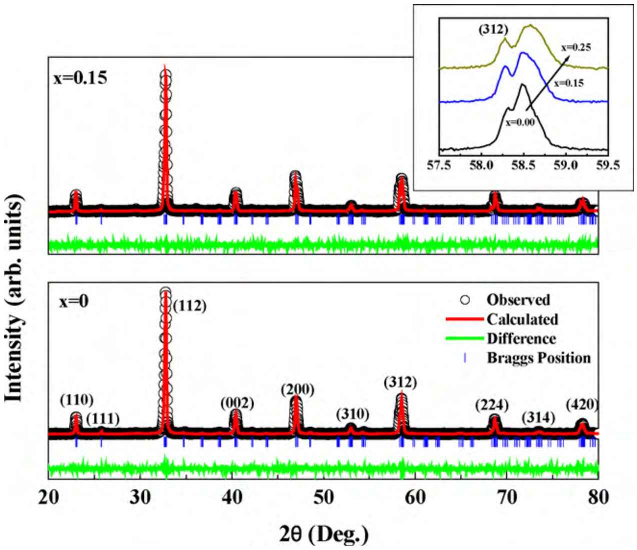

Fig. 1. Reitveld fitted pattern of $Pr_{0.7}Sr_{0.3}MnO_3$ and $Pr_{0.45}Bi_{0.15}Sr_{0.3}MnO_3$ (inset shows peak shift towards higher angle with increasing Bi^{3+} ion concentration).

3. Results and discussion

3.1. Crystal structure

For the analysis of phase formation and unit cell parameters, the observed XRD patterns are further simulated with the help of Rietveld refinement/Fullprof suite program (1.0). The simulated XRD data (Fig. 1) reveals that nominal $Pr_{0.7-x}Bi_xSr_{0.3}MnO_3$ ($x = 0.00$, 0.15 and 0.25) compounds are in single phase and crystallized in *Pbnm* space group. There is a decrease in volume similar as reported by W. Boujelben et al. [1]. Although Bi^{3+} (1.17 Å) ion has larger ionic radii than Pr^{3+} (1.126 Å) ion with coordination VIII, hence increase in volume may be ascribed due to the presence of magnetic polarons originated as a result of the competing behavior of larger ionic radii generated ferromagnetic-DE and charge order state of the end compound $BiSrMnO_3$ compound [17–19]. The calculated lattice parameters (a, b and c) and unit cell volume with fitting reliability parameter are listed in Table 1.

3.2. Resistivity measurement:

Fig. 2 shows the resistivity variation vs. temperature for all $Pr_{0.7-x}Bi_xSr_{0.3}MnO_3$ ($x = 0.00$, 0.15 and 0.25) compounds. Two important points can be concluded from the resistivity graph: first with increasing Bi doping concentration metal–insulator transition temperature (T_{MI}) increases, second with increase in Bi concentration a second peak arises near 200 K.

These results can be understood as; in perovskite manganites $AMnO_3$, the structure stability can be formulated by tolerance factor (t). For ideal perovskite structure tolerance is 1 and in this ideal combination Mn forms an octehedra (MnO_6) along with 180° angle between Mn–O–Mn. The Mn(3d)–O(2p) orbital overlap to form a band. As Bi^{3+} (1.17 Å) ions have larger ionic radii than Pr^{3+} (1.126 Å) ions that induce much effective Mn–O orbital overlapping, which causes an increase in bandwidth for e_g band. Such increase of bandwidth tends to stabilize the DE interaction that manifest in increasing of metallic and ferromagnetic transition temperature (T_{MI} and T_C). The calculated Mn–O–Mn bond angle increases i.e. 160.905(4) for the pristine compound to 168.122(4) for $x = 0.25$ doped compound. Hence T_{MI} shifts to higher temperature with increase in Bi^{3+} ions concentration as expected. Moreover Boujelben et al. reported a decrease in metal–insulator (T_{MI}) transition temperature with 10% Bi doping in $Pr_{0.7}Sr_{0.3}MnO_3$ compound [1]. In summary for the present results, as we are increasing Bi^{3+} ions, the average ionic radii increases/Mn–O hybridization increases (as Bi^{3+} (1.17 Å) ions have larger ionic radii than Pr^{3+} (1.126 Å) ions), as a result, the metal–insulator transition temperature increases as 284.46 for $x = 0.00$ to 294.04 for $x = 0.25$ Bi ion concentration.

Second the variation in resistivity and the generation of peak at 200 K can be understood in a competitive scenario of double-exchange (DE) and charge ordered phase. Larger ionic radii of Bi^{3+} ion supports DE conduction mechanism, hence resistivity decrease for $x < 0.20$ doping concentration. For $x > 0.20$, the charge ordered state of end $Bi_{1-x}Sr_xMnO_3$ (BSMO) compound starts dominating [18,19]. As a result competition between DE and charge ordered state, resistivity increases and a peak generates in low temperature regime [20]. In conclusion DE generated metallic state and charge ordered insulating state competes each other, which induce a fascinating change in resistivity behavior.

3.3. Magnetic measurement

In support of our resistivity results the ferro–para magnetic (T_C) transition temperature increases as calculated with linear extrapolation of $M(T)$ to zero magnetization method. For the pristine (PSMO) compound and Bi = 0.25 doped compound the observed T_C are 276.5 K and ~300 K, respectively. With increasing Bi concentration T_C increases and supports that Bi ion takes part in ferromagnetic–DE interaction. Also we carry out the magnetization vs. applied field (M–H) measurement at 5 K and 200 K for the series samples (For $x = 0.00$, 0.15, 0.25, shown in Fig. 2). From M–T and M–H results it can also be observed that there is a contribution of anti-ferromagnetic (AFM) interaction as ZFC and FC are quite separated that indicates inhomogeneity in long range ferromagnetic order [20]. With increase in Bi concentration, AFM contribution increases as bifurcation increases with concentration. This AFM contribution may be due to the charge order/AFM nature of $Bi_{1-x}Sr_xMnO_3$ and enhance as Bi concentration is increased [18,19].

In conclusion, it is suggested that bigger Bi^{3+} ion takes part in double-exchange mechanism due to its larger ionic radii, hence increases the electrical and magnetic transition temperatures. Side by side doping concentration also encourages AFM-charge ordered state and competes with DE interaction.

Table 1
Unit cell parameters and reliability factor (χ^2) for the refinements of $Pr_{0.7-x}Bi_xSr_{0.3}MnO_3$ ($x = 0.00$, 0.15, 0.25) phases in *Pbnm* space group.

$Pr_{0.7-x}Bi_xSr_{0.3}MnO_3$	a (Å)	b (Å)	c (Å)	Volume (Å^3)	Mn–O–Mn (°)	T_{IM} (K)	χ^2
$x = 0.00$	5.457(4)	5.483(4)	7.714(4)	230.851(4)	160.905(4)	284.46	1.39
$x = 0.15$	5.454(4)	5.487(4)	7.705(4)	230.677(4)	163.629(4)	293.29	1.65
$x = 0.25$	5.452(4)	5.490(4)	7.697(4)	230.458(4)	168.122(4)	294.04	2.09

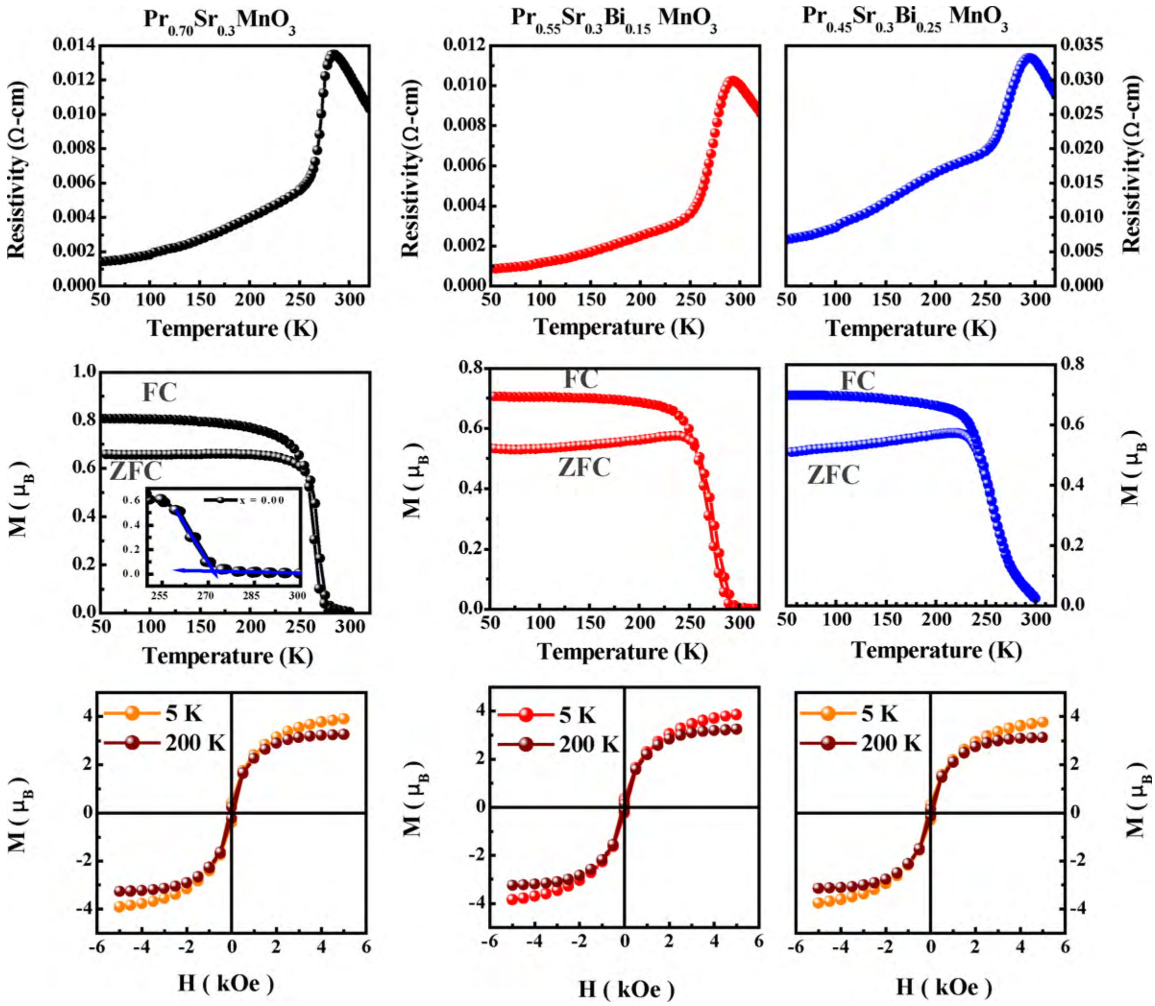

Fig. 2. Temperature (K) variation of resistivity, magnetization (*M*) vs. temperature (K) and magnetization (*M*) vs. applied field (*H*) for the $Pr_{0.7-x}Bi_xSr_{0.3}MnO_3$ ($x = 0.00, 0.15, 0.25$) compounds.

4. Conclusions

Structural, electrical and magnetic properties of $Pr_{0.7-x}Bi_xSr_{0.3}MnO_3$ ($x = 0.00, 0.15, 0.25$) compounds are studied. XRD/Reitveld refinement confirms a decrease in the lattice volume with Bi^{3+} ion doping attributed to the formation of magnetic polaron. An electrical and magnetic measurement suggests that bigger Bi^{3+} ion takes part in double-exchange mechanism, hence increases the electrical and magnetic transition temperatures.

Acknowledgements

Neeraj Kumar is thankful to Council of Scientific and Industrial Research (CSIR), India and further acknowledges the financial support from CSIR in terms of CSIR-SRF Fellowship to carry out research work at NPL and pursue for his Ph.D. thesis.

References

[1] W. Boujelben, A. Cheikh-Rouhou, M. Ellouze, J.C. Joubert, Phys. Stat. Sol. (a) 177 (2000) 503.
[2] I. Kammoun, W. Cheikhrouhou-Koubaa, W. Boujelben, A. Cheikhrouhou, J. Mater. Sci. 43 (2008) 960.
[3] J.-M. Liu, T. Yu, Q. Huang, J. Li, Z.X. Shen, C.K. Ong, J. Phys. Condens. Matter 14 (2002) L141.
[4] S. Zemni, M. Baazaoui, Ja. Dhahri, H. Vincent, M. Oumezzine, Mater. Lett. 63 (2009) 489.
[5] D.C. Krishan, P.V. enugopal Reddy, J. Alloys Compd. 479 (2009) 661.
[6] S. Othmani, M. Bejar, E. Dhahri, E.K. Hlil, J. Alloys Compd. 475 (2009) 46.
[7] G.H. Zheng, Z.X. Dai, Y.Y. Zhang, Y.P. Sun, J. Alloys Compd. 489 (2010) 348.
[8] N. Kumar, R. Tripathi, A. Dogra, V.P.S. Awana, H. Kishan, J. Alloys Compd. 492 (2009) L28–L32.
[9] O. Chmaissem, B. Dabrowski, S. Kolesnik, J. Mais, J.D. Jorgensen, S. Short, Phys. Rev. B 67 (2003) 094431.
[10] Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Tokura, Phys. Rev. B 53 (1996) R1689.
[11] G. Garbarino, C. Acha, Europhys. Lett. 88 (2009) 46003.
[12] D.D. Sarma, D. Topwal, U. Manju, S.R. Krishnakumar, M. Bertolo, S. La Rosa, G. Cautero, T.Y. Koo, P.A. Sharma, S.-W. Cheong, A. Fujimori, Phys. Rev. Lett. 93 (2004) 202.
[13] A. Moreo, S. Yunoki, E. Dagotto, Science 283 (1999) 2034.
[14] Y. Kalyana Lakshmi, P. Venugopal Reddy, J. Magn. Magn. Mater. 321 (2009) 1240.
[15] V. Yu Pomjakushin, D.V. Sheptyakov, E.V. Pomjakushina, K. Conder, A.M. Balagurov, J. Phys. Condens. Matter 22 (2010) 115601.
[16] J.R. Sun, J. Gao, L. Kang, Appl. Phys. Lett. 81 (2002) 508.
[17] R.D. Shanon, Acta Crystallogr. A 32 (1976) 751.
[18] S. Pal, A. Banerjee, P. Chatterjee, B.K. Chaudhuri, Phys. Stat. Sol. (b) 237 (2003) 513.
[19] C.N.R. Rao, B. Raveau, Colossal Magnetoresistance Charge Ordering and Related Properties of Manganese Oxide, World Scientific, Singapore, 1998.
[20] N. Kumar, H. Kishan, A. Rao, V.P.S. Awana, J. Appl. Lett. 107 (2010) 083905.