Physica B 498 (2016) 82–91

Contents lists available at ScienceDirect

Physica B

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

Magnetic inhomogeneity and Griffiths phase in Bi substituted $La_{0.65-x}Bi_xCa_{0.35}MnO_3$ manganites

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ARTICLE INFO

Article history:
Received 3 November 2015
Received in revised form
10 May 2016
Accepted 28 June 2016
Available online 29 June 2016

Keywords:
Manganites
Griffiths phase
Thermoelectric power

ABSTRACT

In the present communication, we report the effect of Bi substitution on structural, magneto-transport, magnetic and thermal properties of $La_{0.65-x}Bi_xCa_{0.35}MnO_3$ ($0 \le x \le 0.2$) compounds. Rietveld refined XRD patterns confirm that all the samples are single phase and crystallize in rhombohedral symmetry with *R*-3*C* space group. It was observed from electrical and magnetic studies that with increasing Bi content both the metal-insulator transition temperature (T_{MI}) and ferromagnetic–paramagnetic (FM–PM) transition temperature (T_C) shift towards lower temperatures. Deviation of the temperature dependence of inverse susceptibility curves from the Curie–Weiss law suggests the existence of Griffiths-like phase. The electrical resistivity data were analyzed by utilizing various theoretical models. It is revealed that the electron–electron scattering is dominating in the metallic region, while the insulating region is well-described by the polaron hopping model. Analysis of thermoelectric power data further reveals that the small polaron hopping (SPH) mechanism is operative in the high-temperature insulating regime. The entropy change associated with the FM–PM transition is found to decrease with increasing *x*, which is presumably due to the increase in magnetic inhomogeneity with increasing Bi content.

1. Introduction

Perovskite manganites with general formula $R_{1-x}A_xMnO_3$ (*R* is trivalent rare earth and *A* is divalent alkaline earth) have been extensively investigated due to the unusual electrical and magnetic properties they exhibit [1–4]. In addition to their peculiar physical properties, the existence of inhomogeneity and preformation of ferromagnetic clusters in the paramagnetic region, known as Griffiths phase (GP), have attracted considerable interest [5–8]. The Griffiths phase in manganites arises at a characteristic temperature T_G in which the Curie–Weiss law is inapplicable in the temperature range $T_C < T < T_G$. The system exhibits neither pure paramagnetic phase nor the long-range FM order in this range of temperature. Usually A-site substitution is one the main factors for the existence of GP in manganites [5,9–12]. However, there are other factors, viz. Jahn–Teller distortion [9,13] and grain size effect [14] which could also lead to the appearance of Griffiths phase in manganites. Salmon et al. proposed that the colossal magnetoresistance property of manganites is a Griffiths singularity [5]. On the other hand, Pramanik et al. argued that the quenched disorder is prerequisite for the formation of GP [6]. Recently, Dayal et al. observed an evolution of Griffiths phase around T_C while Ti was substituted at Mn site in the $La_{0.4}Bi_{0.6}MnO_3$ system. The presence of GP is attributed to the increase in magnetic inhomogeneity with Ti substitution [7]. The size of the ferromagnetic clusters in the Griffiths phase region can be diverged by application of an external magnetic field which results in the sharp increase in the magnetization [15]. Jiang et al. [15] have reported an extreme sensitivity of GP to the applied magnetic field in single crystal $La_{0.73}Ba_{0.27}MnO_3$. They have reported that the depression of χ^{-1} vs *T* curves below the GP is completely quenched on application of only 150 Oe of static magnetic field. Such sensitivity can be used for applications in magnetic sensors. Nevertheless, there are systems which exhibit colossal magnetoresistance (CMR) effect without the presence of GP [13,16]. Therefore, the physical mechanisms of the GP need to be further investigated.

Recently, the effect of Bi^{+3} substitution on a variety of properties in $La_{1-x}Ca_xMnO_3$ (LaCaMnO) system has been studied [17–21]. It is well-known that $BiMnO_3$ exhibits multiferroic nature where phases like ferroelectric, ferromagnetic and ferroelastic are coexisting in this material. It is also important to mention that Bi-substituted compounds exhibit a high charge ordering temperature (T_{CO} ~475 K) [22]. Gencer et al. and Atalay et al. have

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http://dx.doi.org/10.1016/j.physb.2016.06.031
0921-4526/

proposed that substituting Bi in LaCaMnO system introduces excellent magnetocaloric properties with a high relative cooling power [17,18]. However, there are relatively few reports in exploring the existence of Griffiths phase in the Bi-substituted LaCaMnO systems. In this regard, we have performed a throughout investigation on the structural, magnetic, magneto-transport and thermoelectric properties of Bi-substituted $La_{0.65-x}Bi_xCa_{0.35}MnO_3$ ($0 \le x \le 0.2$) system. We have also made an effort to account for the enhancement of the Griffiths-like phase in the paramagnetic region with increase in Bi concentration.

2. Experimental

The compounds $La_{0.65-x}Bi_xCa_{0.35}MnO_3$ ($0 \le x \le 0.2$) [LaBiCaMnO] were prepared using solid state reaction method. Stoichiometric proportions of high purity (99.9% pure, Sigma-Aldrich) La_2O_3, Bi_2O_3, Ca_2CO_3 and MnO_2 precursors were mixed homogeneously in an agate mortar for about 6 h to obtain a homogenous mixture. The mixture was calcined at 900 °C with two intermediate grindings to exhaust carbonates present in the mixture. The calcined mixtures were taken in the form of rectangular shaped pellets and were sintered at 1000 °C for 24 h. Finally, the samples were furnace cooled to room temperature. X-ray diffraction (XRD) studies were done using Bruker D8 Advance X-ray diffractometer. The surface morphology of the samples was examined using scanning electron microscopy (SEM) using Oxford EVO MA18.

The temperature-dependent electrical resistivity and magnetoresistance measurements were performed using the standard four probe technique with a superconducting magnetic system (Oxford Spectromag) in the temperature range 5–300 K. Magnetic measurements were carried out using quantum design magnetic property measurement system (MPMS). Thermoelectric power and thermal conductivity measurements were carried out in a closed cycle refrigerator using a heat-pulse technique. Specific heat measurements were performed in temperature range 90–300 K using a high resolution ac calorimeter. The details of the thermal measurements techniques have been described elsewhere [23].

3. Results and discussion

3.1. Structure and surface morphology

We have performed the X-ray diffraction studies to confirm the purity of the samples and determine the lattice parameters. Recorded XRD patterns were further analyzed by employing the Rietveld refinement technique using Fullprof program. The Rietveld refined XRD pattern for all the samples is depicted in Fig. 1 and the structural parameters along with Mn–O–Mn bond angle and bond lengths for all the samples are summarized in Table 1. There is a slight decrease in lattice parameters a and c with increase in Bi-content. In addition to this the cell volume also decreases with Bi-content. This trend in cell parameters can be attributed 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. The results indicate that the Mn–O–Mn bond angle decreases and Mn–O bond length increase with substituting smaller Bi ion. This may be due to successive substitution of Bi at the slightly larger La, resulting in reduced values A-site atomic radius. The Rietveld refinement parameters such as R_p, R_{wp} and R_{exp} are also presented in Table 1 and the estimated values for presently investigated samples suggest that the fittings are good. It is found from the Rietveld analysis that all the samples in the present work are single phase and crystallize in rhombohedral structure with R-3C space group.

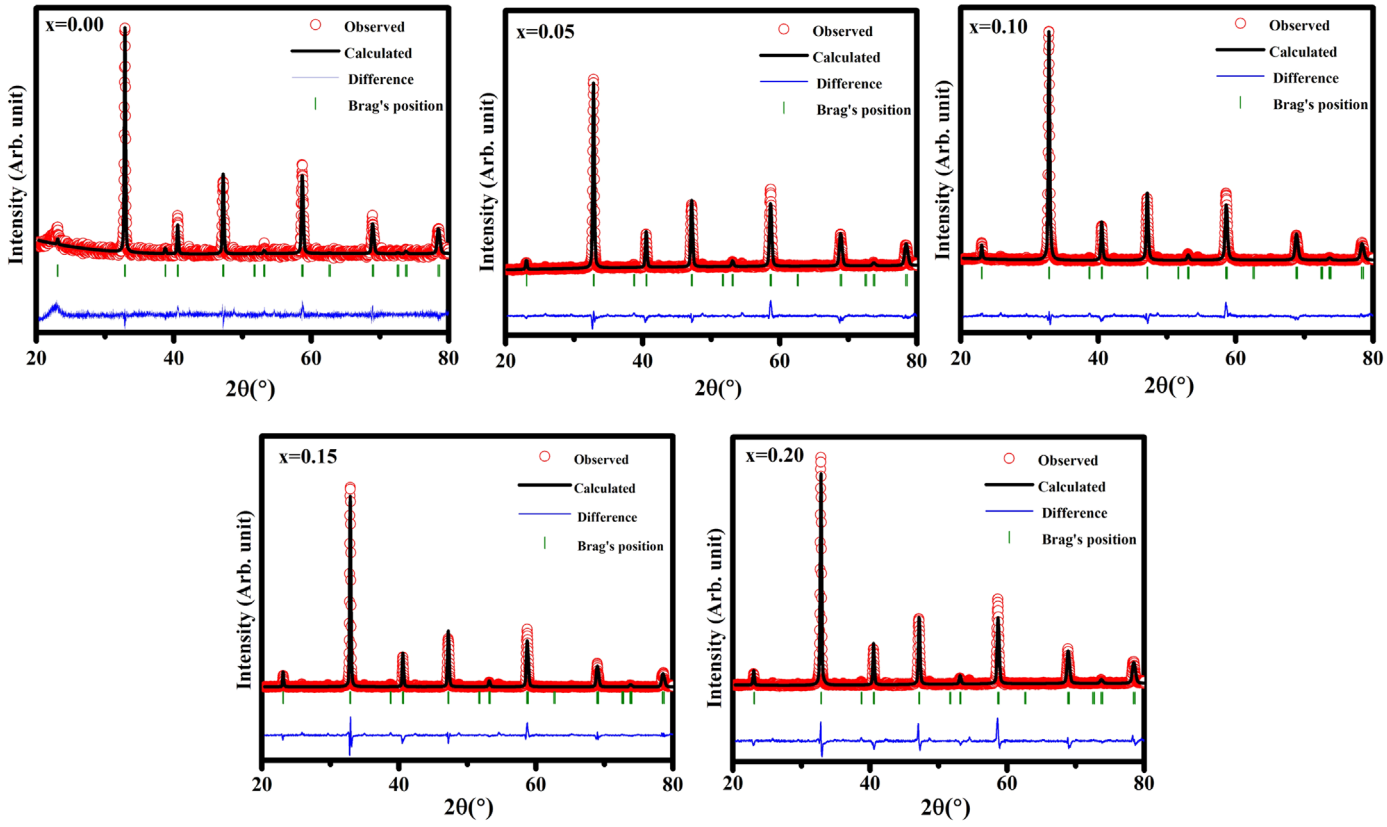

Fig. 1. Rietveld refinement for the $La_{0.65-x}Bi_xCa_{0.35}MnO_3$ samples.