Physics Letters A 379 (2015) 175–178

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Anomalous thermopower in bismuth doped La–Li–Mn–O manganite

Kalyana Lakshmi Yanapu [a,b], Gunadhor Singh Okram [c], Venugopal Reddy Paduru [a,*]

[a] Department of Physics, University College of Science, Osmania University, Hyderabad, Telangana, India
[b] Department of Physics, Nizam College, Osmania University, Basheerbagh, Hyderabad, Telangana, India
[c] UGC–DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore, MP, India

ARTICLE INFO

Article history:
Received 14 August 2014
Received in revised form 24 October 2014
Accepted 30 October 2014
Available online 5 November 2014
Communicated by R. Wu

Keywords:
Ceramics
Electrical properties
Magnetic materials
Wet chemical
Thermoelectric effects
Antiferromagnetic

ABSTRACT

Two polycrystalline samples, $La_{5/6}Li_{1/6}MnO_3$ and $La_{2/3}Bi_{1/6}Li_{1/6}MnO_3$ having the same Mn^{3+}/Mn^{4+} ratio were synthesized by the wet chemical method. After characterizing the samples by X-ray powder diffraction studies, dc magnetization, electrical resistivity and thermopower measurements were also carried out. It has been found that bismuth doped sample exhibits huge thermopower of 0.9 V/K in the low temperature region. The observed anomalous behavior is explained on the basis of the coexistence of antiferromagnetic phase in ferromagnetic matrix. The huge thermopower exhibited by these samples might find applications in thermoelectric devices.

1. Introduction

In recent years perovskite type manganites have attracted considerable attention because of their importance both for fundamental research in solid state physics and for practical application in magnetoelectronics. The properties of these materials [1–4] such as magnetoresistance, metal-insulator transition, charge, magnetic ordering, etc., have generated an impulse in the research. Depending on the doping level, external magnetic field, applied pressure, temperature, etc., these systems present different phases of conduction and complicated magnetic phase transitions [1–4]. Recent investigations have demonstrated that variations at A-site play an important role in the magnetic and transport properties of these manganites for a given carrier doping [5,6]. Substitution of divalent or other trivalent rare earth ions at A-site results in varying the average cationic radii ($\langle r_A \rangle$). These size variations introduce changes in bond angles and bond lengths significantly affecting their magnetism and conductivity. Along with divalent doped ones, the monovalent doped manganites such as Li, Na, K, Rb etc., have also attracted the scientific community due to their potential applications in the field of spintronics [7–10]. This is due to the fact that the substitution of alkali metal ions, whose valence is $+1$, affects the ratio of Mn^{3+} and Mn^{4+} ions, which in turn influences various physical properties [7–10] and gives rise to different interplay amongst charge, spin and lattice degree of freedom. In particular the $La_{1-x}Li_xMnO_3$ system has attracted additional attention due to superior magneto-transport properties [7,8]. Moreover, when Li is incorporated into the lattice for La ions, A-site disorder is induced giving rise to interesting electrical and magnetic properties. Therefore, lithium substituted lanthanum manganites have been taken up for in the present investigation.

Over the past few years, extensive work has been carried out on the partial substitution of A-site by trivalent or divalent ions [11–13] and the corresponding electrical properties were discussed based on structural effects. Apart from rare earth ion doping, substitution of a non-magnetic ion such as bismuth (Bi) at A-site shows strong effects on electrical and magnetic properties of manganites because it is stable with an oxidation state 3+ and an average ionic radius consistent with the geometrical rule of the tolerance factor [14–16]. Moreover, compared with rare earth ions, Bi^{3+} ion has a lone pair with strong $6s^2$ character. The polarized $6s^2$ lone pair causes lattice distortion in the crystal and is responsible for the complexity in the observed magnetic and electrical properties [14–16]. In view of this a systematic investigation of Bi doping at A-site has been undertaken.

Among the transport properties, thermopower has attracted considerable attention due to its sensitiveness to the charge carriers and their interaction with spins. The thermopower (S) of the manganite system shows interesting behavior. A survey of literature reveals that these materials exhibit a large Seebeck

---

[*] Corresponding author. Tel.: +91 40 27682242; fax: +91 40 27009002.
E-mail addresses: kalyaniyanapu@gmail.com (Y. Kalyana Lakshmi), paduruvenugopalreddy@gmail.com (P. Venugopal Reddy).

http://dx.doi.org/10.1016/j.physleta.2014.10.040

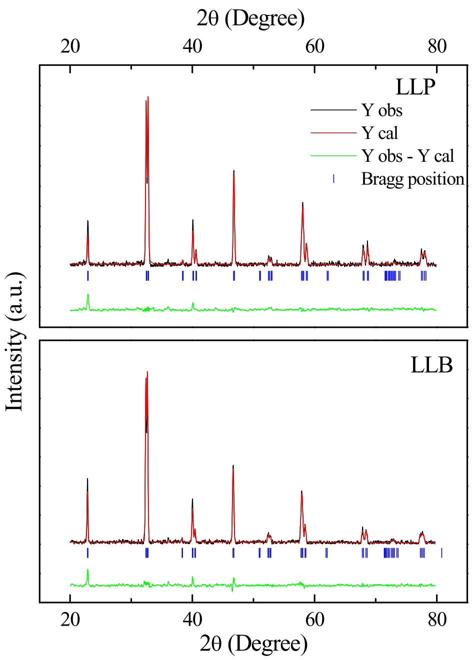

Fig. 1. Room temperature powder X-ray diffraction patterns for $La_{5/6}Li_{1/6}MnO_3$ and $La_{2/3}Bi_{1/6}Li_{1/6}MnO_3$ from 20° to 80°, together with standard peak positions (blue vertical lines) and fit (solid line) of the model to the intensities. The green solid line at the bottom is the difference spectrum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

coefficient and are attractive for the potential applications in the fields of energy conversion, thermal sensors and thermoelectric cooling for electronic devices [17–19]. Taking these factors into account, in the present work two samples with compositional formula, $La_{5/6}Li_{1/6}MnO_3$ and $La_{2/3}Bi_{1/6}Li_{1/6}MnO_3$ were prepared using a wet chemical method. By maintaining a constant ratio of Mn^{3+}/Mn^{4+}, a systematic investigation of influence of Bi^{3+} on magnetic and thermopower properties was undertaken and the results of such an investigation are presented here.

2. Experimental details

$La_{5/6}Li_{1/6}MnO_3$ and $La_{2/3}Bi_{1/6}Li_{1/6}MnO_3$ samples were synthesized by a wet chemical method using La_2O_3, $LiCO_3$, $Bi(NO_3)_3 \cdot 5H_2O$, manganous acetate and nitric acid. More details of the sample preparation are given elsewhere [19]. The phase purity, homogeneity and cell dimensions were determined by powder X-ray diffraction (XRD) at room temperature. Structural refinement was carried out using standard Rietveld refinement technique. The cations in the samples were estimated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, JY 2000) while the valence state of Mn was obtained by iodometric redox titration method. Magnetization measurements were performed on a vibrating sample magnetometer (Quantum Design). The transport and magneto-transport measurements were carried out using four probe method (14 T/2.0 K PPMS, QD-USA) in the magnetic fields of 10, 50 and 100 kOe over a temperature range 10–300 K. Finally, thermopower $S(T)$ measurements were carried out on an automated precision measurement system [20] in the temperature range of 10–300 K. A circular pellet of 9 mm diameter and thickness of 3 mm was used for thermopower measurements. $La_{5/6}Li_{1/6}MnO_3$ and $La_{2/3}Bi_{1/6}Li_{1/6}MnO_3$ samples are hereafter referred as LLP and LLB respectively.

3. Results and discussion

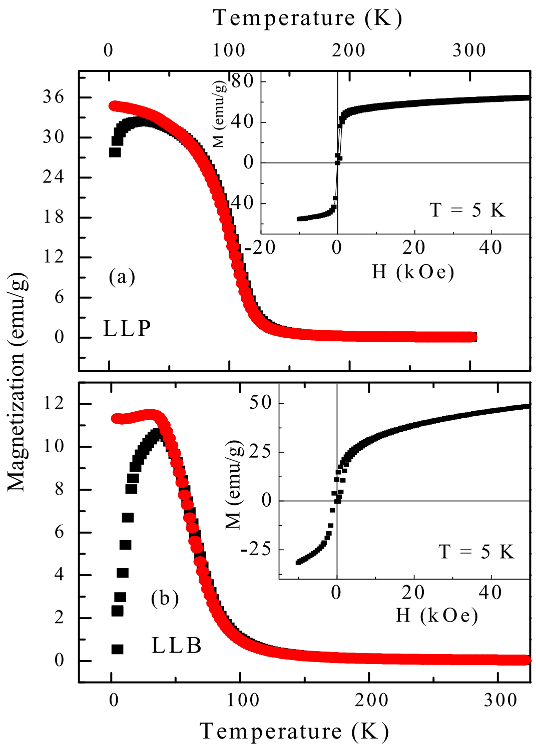

Fig. 2. (a, b) Temperature dependence of dc magnetization of the $La_{5/6}Li_{1/6}MnO_3$ and $La_{2/3}Bi_{1/6}Li_{1/6}MnO_3$ samples in ZFC (black squares) and FC (red circles) configurations. Inset shows the magnetization (M) vs. applied magnetic field strength (H) plots of the samples recorded at $T = 5$ K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The room temperature XRD patterns and the Rietveld refined patterns of LLP and LLB samples (Fig. 1) indicate that they are single phase with no detectable secondary phase and have rhombohedral symmetry with R-3c space group. The lattice parameters of LLP, $a = b = 5.513$ Å, $c = 13.324$ Å are relatively smaller than those of LLB, $a = b = 5.522$ Å, $c = 13.375$ Å. The values of Mn^{4+}/Mn^{3+} ratio and oxygen content determined by iodometric titrations are close to their nominal compositions without any oxygen deficiency.

The temperature dependence of zero field cooled (ZFC) and field cooled (FC) magnetization data, $M(T)$ of LLP and LLB samples in an applied magnetic field of 500 Oe is shown in Fig. 2. As the temperature is decreased from 300 to 10 K, the samples undergo a ferromagnetic (FM) to paramagnetic (PM) phase transition (T_C). The values of T_C estimated from the minimum of the dM_{ZFC}/dT against T plot are found to be 105 and 61 K for LLP and LLB samples respectively. It is interesting to note from these results that because of Bi doping the T_C value decreases by 44 K. The reduction in T_C with bismuth substitution may be explained based on the role of $6s^2$ lone pair electrons of Bi ions. In bismuth doped manganites, O:2p electrons are simultaneously shared by Mn:t_{2g} orbitals and $6s^2$ lone pair of Bi^{3+} [21,22]. Due to the competition between these electrons double exchange interaction between Mn^{3+}–Mn^{4+} becomes weak thereby reducing T_C towards low temperature side [22]. It can be seen from Fig. 2 that the bifurcation between ZFC and FC curves of LLB sample is found to be larger than that of LLP suggesting the absence of long range magnetic order and is attributed to the coexistence of antiferromagnetic (AFM) and ferromagnetic domains rather than distinct long range FM or AFM ordering [23]. To investigate the low temperature magnetic phase, isothermal magnetization $M(H)$ measurements were carried out at 5 K (inset of Fig. 2 (a, b)). One may observe that both the samples exhibit a small coercive field (H_C) at low temperature indicating soft ferromagnetic behavior. It can also be seen from the figure that the magnetization of LLB sample increases linearly with increasing field and it does not saturate even at $H = 50$ kOe,