JOURNAL OF MATERIALS SCIENCE 35 (2000) 5939–5943

Magnetic and magneto-resistive properties of Bi-doped (LaCa)MnO_3

DUKSIL KIM, JAEKYONG CHO
Department of Materials Engineering, RIIT, Gyeongsang Natioanl University, 900 Gazwa, Chinju, Gyeongnam 660-701, South Korea
E-mail: jkcho@nongae.gsnu.ac.kr

Bi-doped lanthanum manganites with chemical compositions of $Bi_xLa_{0.67-x}Ca_{0.33}MnO_3$ ($x = 0$, 0.04, 0.1, 0.2) have been prepared by the standard ceramic process. The crystallinity and microstructures of the samples have been investigated by x-ray diffractometry and optical microscopy, respectively. The magnetic and magneto-resistive properties of the samples have been measured by vibrating sample magnetometery and van der Pauw method, respectively, at the temperatures ranging 100 K–300 K with applied magnetic field of 0.4–0.5 T. Good crystallinity and high Curie temperature (275 K) have been obtained for the Bi-doped samples with small dosage ($x = 0.04, 0.1$) even they were sintered at 1200°C, which is about 200°C lower than normal sintering temperature of undoped sample. The Bi-doped samples with the small dosage showed lower relative electrical resistivity and higher magneto-resistive ratio compared to the undoped sample in the most temperatures measured. The Bi-doped samples also exhibited large magneto-resistive ratio (maximum of 15% for $x = 0.1$) at room temperature even under a weak magnetic field of 0.4 T.

1. Introduction

Recent discovery of lanthanum manganites showing clossal magneto-resistance give rise to intense theoretical and applied studies on magneto-resistance [1].

Lathanum manganese oxides with chemical formular of $La_{1-x}B_xMnO_3$ (B = Ca, Sr, Ba, Pb) and crystal structure of proveskite type exhibit unique ferromagnetism and metallic conductivity. The host material, $LaMnO_3$, is an antiferromagnetic semiconductor having only Mn^{3+} ions. Upon substituting part of La^{3+} by 2+ cations such as Ca, Sr, Ba and Pb, Mn^{4+} is generated, which conduct double exchange interaction with Mn^{3+} resulting in the ferromagnetism and metallic conductivity [2].

Thin films of lanthanum manganites epitaxialy grown on single crystal substrates show the greatest magneto-resistance ratio ($((\rho_0 - \rho_H/\rho_0) \times 100$, where ρ_H and ρ_0 denote the resistivity with and without magnetic field, respectively) of 10^6% to date [3]. The clossal magneto-resistance of lathanum manganites have been qualititively explained by the electron hopping between Mn^{3+} and Mn^{4+} ions which occurred more easily under a magnetic field. That is, the transition temperature from ferromagnetism (metal) to paramagnetism (insulator) is increased by applying a magnetic field so that the resistance near the transition temperature is reduced through the transition from high resistive state to low resistive state by applying a magnetic field.

However, not all the epitaxial thin films of lanthanum manganite show the clossal magneto-resistance. The magneto-resistance greater than 1000% have been obtained only for the films with Ca as 2+ ions, $La_{1-x}Ca_xMnO_3$, and the Ca content of $x = 0.3$–0.5 having cubic peroveskite structure or ferromagnetism and metallic conductivity. When 2+ ion was Sr or Ba the clossal magneto-resistance have not been shown [1].

In addition, even for the epitaxial films with Ca^{2+} ions, the clossal magneto-resistance have only been observed at low temperatures under a strong magnetic field (about 6T). The reason why the films showed the clossal magneto-resistance only at low temperatures is because the maximum Curie temperature of bulk $La_{1-x}Ca_xMnO_3$ is 275 K when $x = 0.3$, which is under room temperature, and for thin films the Curie temperature is lower in many case than bulk samples because the chemical composition is not stoichiometric and the crystallinity is not as good as bulk samples [4].

The magneto-resistance ratio of bulk samples are much smaller compared to the epitaxial films; the maximum ratio reported is 85% at 275 K and only 10% at room temperature or 300 K even under a strong magnetic field of 4T [5]. And this ratio have been only obtained for the sample heat treated with complex temperature schedule including maximum temperature of 1400 °C [5].

In the application point of view a material is desirable which shows large magneto-resistance ratio under a weak magnetic field and low resistivity at room temperature.

In this work, we prepared Bi-doped lanthanum manganite samples and investigated how the Bi-doping

improve the magnetic and magneto-resistive properties of lanthanum managnites.

2. Experiments

Lanthanum manganite discs with chemical compositions of $Bi_xLa_{0.67-x}Ca_{0.33}MnO_3$ ($x = 0$, 0.04, 0.1, 0.2) have been prepared by the standard ceramic process. The law materials of Bi_2O_3, La_2O_3, $CaCO_3$, MnO_2 powders have been used. The disc samples were prepared by weighing, mixing and pressing the powders and sintered in an electrical furnace at temperatures of 900, 1000, 1100, 1200, 1300°C for 5, 10, 15 hours in the air.

The crystallinity and microstructure of the samples have been investigated by x-ray diffractometry (Cu-K_α) and optical microscopy, respectively. The magnetic and magneto-resistive properties of the samples have been measured by vibrating sample magnetometery and van der Pauw method, respectively, at the temperatures ranging 100 K–300 K with applied magnetic field of 0.4–0.5 T.

3. Results and discussion

Fig. 1 shows the x-ray diagrams of the samples sintered at 1200 °C for 10 hours. As shown in the figure only the diffraction lines of cubic peroveskite are obtained for all samples. The diffraction lines shift to lower angle as Bi content (x) is increased up to $x = 0.1$. While not shown similar trend has been obtained for the samples sintered at 1300°C. The lattice constants calculated from Fig. 1 is shown in Fig. 2. The lattice constant of undoped sample is 3.875 Å, which agrees well with the literature value of 3.87 Å [6]. The lattice constant is almost linearly decreased as Bi content is increased up to $x = 0.1$ and does not change much above $x = 0.1$. The reduction of lattice constant in the Bi-doped samples may be because the Bi ions replace La ions and the ionic radius of Bi^{3+} is smaller than that of La^{3+}. It is considered that the Bi ions in the sample with $x = 0.2$ only partially replace La ions and the excess Bi ions remain at grain boundaries etc.

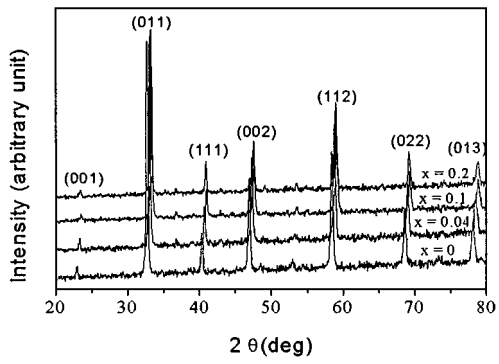

Figure 1 X-ray diffraction diagrams of $Bi_xLa_{0.67-x}Sr_{0.33}MnO_3$ sintered at 1200°C for 10 hours.

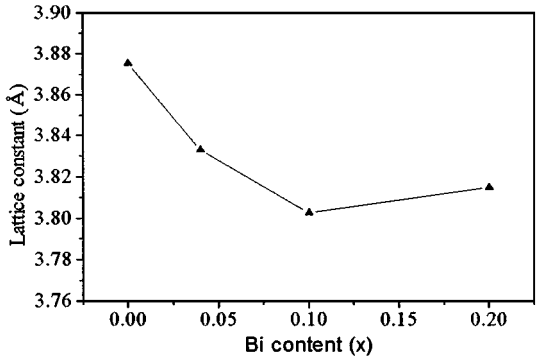

Figure 2 Lattice constant variation as a function of Bi content (x).

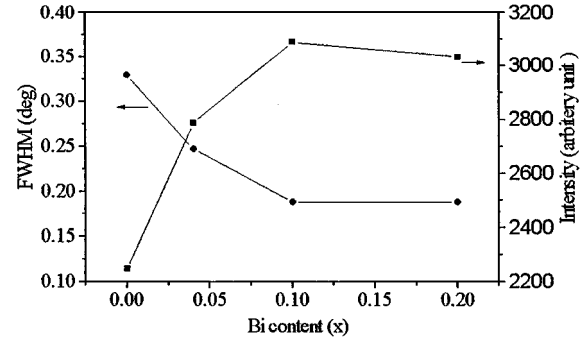

Figure 3 Dependence of full width at half maximum (FWHM) and diffraction intensity on Bi content (x).

Fig. 3 shows how the intensity and full width at half maximum (FWHM) of (112) lines of the samples vary as a function of Bi content, which is calculated from Fig. 1. As shown in the figure the intensity and FWHM are increased and decreased, respectively, as Bi content is increased up to $x = 0.1$. This indicates that Bi_2O_3 powders play a roll of a sintering promotor due to its low melting temperature resulting in improvement of crysatllinity of the samples.

Fig. 4 shows the optical micrographs of the surfaces of the samples sintered at 1200°C for 10 hours. The size of the crystal grains is increased as Bi content is increased. This also indicates that Bi plays a roll of a sintering promotor.

Fig. 5 shows the temperature dependence of the saturation magnetization as a function of Bi content for the samples sintered at 1200°C for 10 hours. As shown the saturation magnetization and Curie temperature of the undoped sample are lower than reported in literatures but increased with Bi content showing maximum at $x = 0.04$, then decreased slightly at $x = 0.1$ (note that still greater than undoped sample) and then rapidly decreased at $x = 0.2$. The undoped sample seem to be not fully sintered because it is sintered at 1200°C which is about 200°C lower than usual sintering temperature [5]. The saturation magnetization and Curie temperature of the sample with $x = 0.04$ agree well with those reported in literature for the undoped sample carefully prepared at 1400 °C [5]. This may be because Bi promotes sintering resulting in good crystallinity even at 1200°C. According to the literature [7] Bi decreases the Curie temperature in the system of $Bi_xLa_{0.7}Sr_{0.3-x}MnO_3$. The similar effect may be expected in the present system of $Bi_xLa_{0.67-x}Ca_{0.33}MnO_3$. For the sample with $x = 0.04$ it seems the sintering promotion effect is dominant compared to the reduction effect of Curie temperature

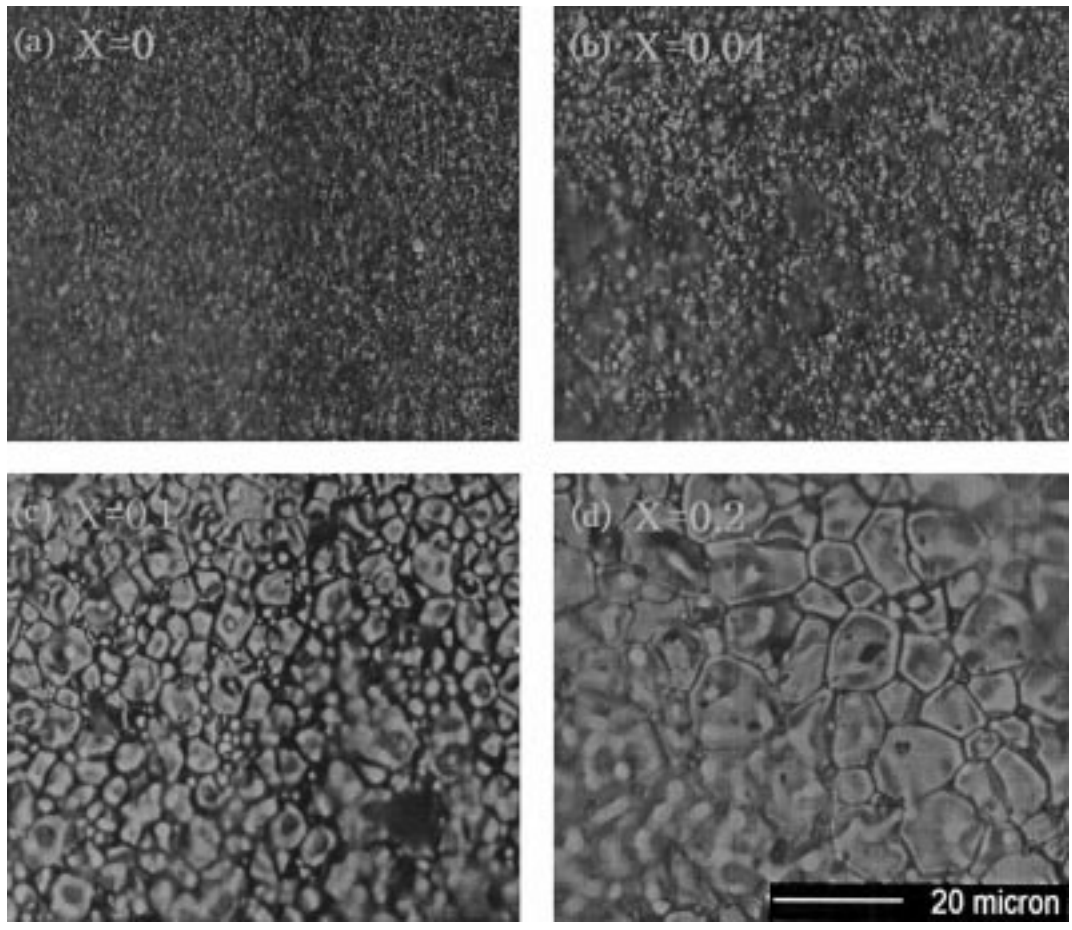

Figure 4 Microstructure variation as a function of Bi content (x). The samples were sintered at 1200°C for 10 hours.

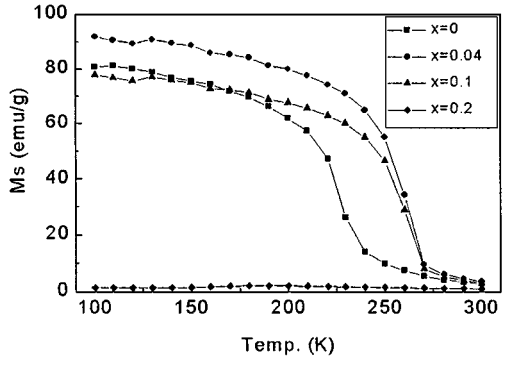

Figure 5 Variation of saturation magnetization dependence on temperature as a function of Bi content (x). The samples were sintered at 1200°C for 10 hours.

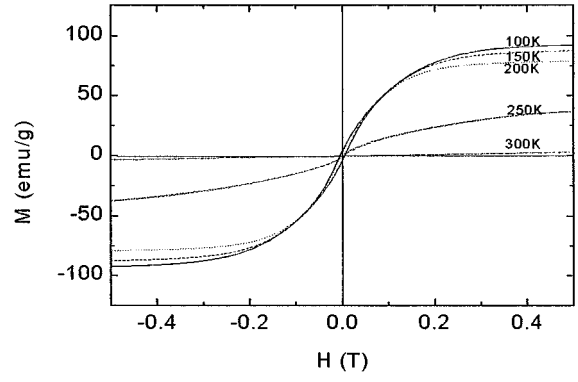

Figure 6 Magnetic hysteresis loops of the sample with $x = 0.04$ at several temperatures. The sample was sintered at 1200°C for 10 hours.

by Bi doping, which results in the increase of Curie temperature and saturation magnetization. For the sample with $x = 0.1$ the above two effects seem to be comparable. For the sample with $x = 0.2$, however, the letter effect appears to be much dominant and the above mentioned excess Bi may be segregated as nonmagnetic phase resulting in further reduction of saturation magnetization.

Fig. 6 shows the hysteresis loops of the sample with $x = 0.04$ traced at some temperatures. As shown the sample is magnetically soft with small coercivity.

Fig. 7 shows the temperature dependence of electrical resistivity as a function of Bi content for the samples sintered at 1200°C for 10 hours. The closed and open marks denote the values obtained with and without a magnetic field, respectively. The magnetic field applied was 0.4 T, which is smaller by about a factor of ten compared to the value reported in most literatures [5]. While the undoped sample shows a maximum near 170°C, the sample with $x = 0.04$ shows a maximum at 260°C, and the sample with $x = 0.1$ shows only slightly curved graph having a small maximum near 240°C. This may be correspond to the Curie temperature variation with Bi content mentioned above. It is worth nothing that the resistivity of the Bi-doped samples are lower than that of the undoped sample at low temperatures.

Fig. 8 shows the temperature dependence of electrical resistivity as a function of Bi content for the samples

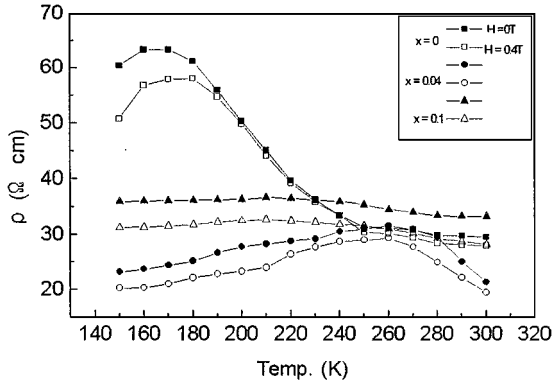

Figure 7 Vatiation of relative resistivity (ρ) dependence on temperature with and without magnetic field (0.4 T) as a function of Bi content (x). The samples were sintered at 1200°C for 10 hours.

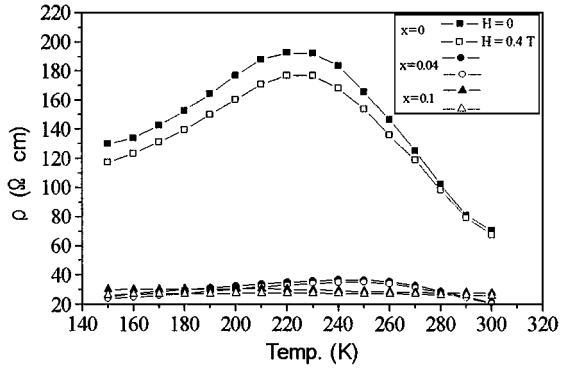

Figure 8 Vatiation of relative resistivity (ρ) dependence on temperature with and without magnetic field (0.4 T) as a function of Bi content (x). The samples were sintered at 1300°C for 10 hours.

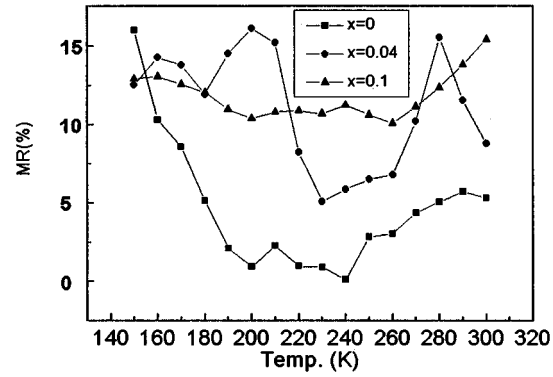

Figure 9 Vatiation of magneto-resistance ratio (MR) dependence on temperature as a function of Bi content (x). The samples were sintered at 1200°C for 10 hours.

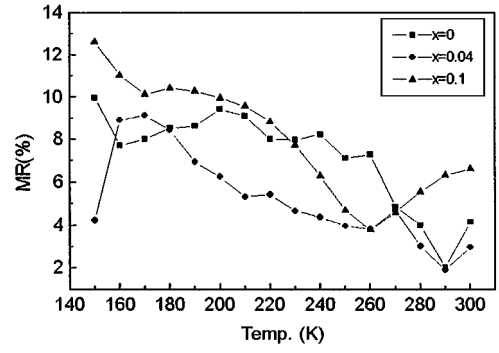

Figure 10 Vatiation of magneto-resistance ratio (MR) dependence on temperature as a function of Bi content (x). The samples were sintered at 1300°C for 10 hours.

sintered at 1300°C for 10 hours. The undoped sample shows a maximum near 230°C which is higher than that (170°C) obtained for the sample sintered at 1200°C. The higher maximum may be attributed to the increase in Curie temperature due to the better sintering at higher temperature. The resistivity of the undoped smaple sintered at 1300°C is higher than that of the sample at 1200°C. The samples with Bi content of 0.04 and 0.1, however, show maxima at slightly lower temperatures compared to the samples sintered at 1200°C. This may be attributed to the evaporation of Bi due to the heat treatment at higher temperature. Therefore the proper sintering temperature for the Bi-doped samples may be near 1200°C.

Figs 9 and 10 show magneto-resistance ratio (MR) of the samples sintered at 1200°C and 1300°C for 10 hours, respectively. The MR is defined as $\mathrm{MR}(\%) = [\{\rho(0\mathrm{T}) - \rho(0.4\mathrm{T})\}/\rho(0\mathrm{T})] \times 100$, where $\rho(0\mathrm{T})$ is the resistivity obtained without a magnetic field and $\rho(0.4\mathrm{T})$ is the resistivity measured under a magnetic field of 0.4 T. As shown in Fig. 9 for the samples sintered at 1200°C, the Bi-doped samples show greater MR at most temperature than the undoped sample. In addition the samples with Bi content of 0.04 and 0.1 show large MR of 8% and 15%, respectively, at room temperature (300 K) even under a weak magnetic field of 0.4 T. For the samples sintered at 1300°C (Fig. 10) the MR of the undoped sample is greater at most temperature than that of the sample sintered at 1200°C but the MR of the Bi-doped is smaller than that of the sample sintered at 1200°C showing small values at room temperature.

4. Conclusion

Bi-doped lanthanum manganites with chemical compositions of $\mathrm{Bi}_x\mathrm{La}_{0.67-x}\mathrm{Ca}_{0.33}\mathrm{MnO}_3$ ($x = 0$, 0.04, 0.1, 0.2) have been prepared by the standard ceramic process. The crystallinity, microstructure, magnetic and magneto-resistive properties have been investigated. Good crystallinity and high Curie temperature (275 K) have been obtained for the Bi-doped samples with small dosage ($x = 0.04$, 0.1) even they were sintered at 1200°C, which is about 200°C lower than normal sintering temperature of undoped sample. The Bi-doped samples with the small dosage showed lower relative electrical resistivity and higher magneto-resistive ratio compared to the undoped sample in the most temperatures measured. The Bi-doped samples also exhibited large magneto-resistive ratio (maximum of 15% for $x = 0.1$) at room temperature even under a weak magnetic field of 0.4 T.

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Received 13 August 1999
and accepted 1 May 2000