

Magnetotransport Properties of Manganite Ceramics with non-stoichiometric composition $(\text{La}_{0.6}\text{Sr}_{0.4})_{1-x}\text{MnO}_3$ ($0 \leq x \leq 0.10$)

Minoru Takemoto, Toshihiro Onodera, and Hiroyuki Ikawa

Faculty of Engineering, Department of Applied Chemistry, Kanagawa Institute of Technology,
1030 Shimo-Ogino Atsugi-shi, Kanagawa 243-0292, JAPAN
Fax: 81-46-242-8760, e-mail: takemoto@chem.kanagawa-it.ac.jp

It has been pointed out that the magnetoresistive properties of the polycrystalline manganites with certain chemical compositions differ from those of single crystals of manganites with the same composition. We, therefore, prepared manganite ceramics with nominal compositions of $(\text{La}_{0.6}\text{Sr}_{0.4})_{1-x}\text{MnO}_3$ ($0 \leq x \leq 0.10$) based on the prospect that the microstructures of the ceramics are modified by the ion-deficient nominal compositions. Perovskite-type phase and Mn_3O_4 were formed and the amount of the latter increased with increase in x . Deviations of chemical compositions of the perovskite-phases formed for all samples were within 2 % from the nominal composition x dependence of lattice constants. Grains grew remarkably for the samples with $0.02 \leq x \leq 0.06$. These samples show higher resistivities than the remaining samples and also show stepwise increases in negative magnetoresistances when reducing temperature in the vicinity of 360 K, while the remaining samples show maximal negative magnetoresistances in the vicinity of 360 K. We present two plausible reasons for the properties of the samples with $0.02 \leq x \leq 0.06$ based on grain boundaries.

Key words: Magnetoresistance, Non-stoichiometry, Grain boundary, Manganite, Perovskite-type structure

1. INTRODUCTION

Since it was reported that the electric resistivity is sensitive to magnetic field, especially lower field at lower temperature in ceramics of perovskite-type manganites [1], the relationship between microstructure and magnetoresistive properties has been studied extensively for various the perovskite-type manganite ceramics [2 - 6].

The authors sintered for various time manganite ceramics with chemical composition of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ and found that the ceramic samples were also more sensitive to magnetic field when they were sintered for shorter time, *i.e.*, they have smaller grain [7, 8]. The microstructures of ceramics are modified by additives. The authors also sintered the above manganite ceramics with SiO_2 as additive. Grains grow with increase in the amount of SiO_2 and increase in magnetoresistance around room temperature is achieved [9, 10].

It is well known that grains grow remarkably when perovskite-type oxides of which chemical compositions are *A*-site ion deficient are sintered. Thus, the authors prepared the title manganite ceramic of which nominal chemical compositions are *A*-site ions deficient. They also investigated the microstructures of the ceramics and the electric and magnetoresistive properties in the present study.

2. EXPERIMENTALS

The samples were prepared by solid state reaction. The starting materials, La_2O_3 (99.9 %), SrCO_3 (99.9%) and Mn_3O_4 (99.9%) were weighed with molar ratio of $(\text{La}_{0.6}\text{Sr}_{0.4}) : \text{Mn} = 1 - x : 1$ ($0 \leq x \leq 0.10$). Ignition losses of the materials were determined previously. Mixtures of the materials were calcined twice at 900 °C in air for 12 h with an intermediate grinding. The calcined powders were pressed into pellets by cold isostatic pressing under pressure of 1 GPa. The pellets were sintered at 1500 °C

in O_2 for 2 h and subsequently, annealed at 700 °C in O_2 for 12 h.

Crystalline phases were identified by means of X-ray diffractometer (RINT2500VHF, Rigaku). The lattice constants were calculated by a least square method from diffraction angles which were corrected by the angles of Si as an internal standard. Microstructures of the ceramic samples were observed by SEM.

The temperature dependence of electric resistivity was measured by dc four-probe method from 300 K to 500 K under magnetic field of 0 and 15 kOe. Magnetoresistance in this study is defined as the reduction rate of the electric resistivity when magnetic field is applied.

3. RESULTS AND DISCUSSIONS

From X-ray diffraction profiles, rhombohedrally distorted perovskite phases were formed in all samples. Small amount of La_2O_3 exists in the sample with $x = 0.0$ and Mn_3O_4 exists in the samples except $x = 0.0$ sample. Therefore, the proper chemical composition deviates from the nominal chemical composition and the stoichiometric chemical composition is achieved between x of 0.0 and 0.02. The amount of Mn_3O_4 increases with increase in x . Figure 1 shows the lattice constants, which are transformed to those of hexagonal cells. The lattice constants of the sample with $x = 0.0$ are $a = 0.54876(2)$ nm and $c = 1.33519(6)$ nm, and decrease with increase in x from 0.0 to 0.02. They, however, are nearly constant with further increase in x . There are several reports about *A*-site ion deficient perovskite-type manganites, such as $\text{La}_{0.97}\text{Mn}_{0.99}\text{O}_3$ (Ref. [11], the deficiency is 2 %), $\text{La}_{0.93}\text{Mn}_{0.95}\text{O}_3$ ([11], 2 %), $\text{La}_{0.91}\text{Mn}_{0.95}\text{O}_3$ ([12], 4 %), $\text{La}_{0.88}\text{MnO}_3$ ([13], 12 %), $\text{La}_{0.7}\text{MnO}_{3-d}$ ([14], 30 %) and $\text{Pr}_{0.7-x}\text{Sr}_{0.3}\text{MnO}_3$ ($0 \leq x \leq 0.23$) ([15], 0 % ~ 23 %). The nominal composition x dependence of the lattice constants for our system

indicates that the samples with $x \geq 0.02$ are the *A*-site ion deficient perovskite-type manganites and the amount of the deficiency is less than 2 % and is not changed with increase in x . In other words, the samples with $0.02 \leq x \leq 0.10$ have the same chemical composition.

Figures 2 show the SEM photographs of the samples. Dark phases are dispersed at grain boundaries in the samples except the sample with $x = 0.0$ and the number of the phase increases with increase in x . Only Manganese is detected in the phases by energy dispersive X-ray spectra so that the phase is Mn_3O_4 , comparing with XRD profiles. The average grain size is 3 μm for the sample with $x = 0.0$ and grains grow remarkably (14 μm) with increase in x from 0.0 to 0.02. With further increase in x , the grain size reduces gradually, 12 μm for $x = 0.04$, 11 μm for $x = 0.06$, 6 μm for $x = 0.08$ and 4 μm for $x = 0.10$. Generally, the grains grow remarkably when sintering perovskite-type oxide with chemical composition of *A*-site ion deficiency. Thus, the grain growth of the sample with $x = 0.02$ is due to the deficiency, while the reduction of grain size with further increase in x may be due to the prevention of grain growth by the impurity phase Mn_3O_4 .

Figure 3 shows the temperature dependence of electric resistivity measured under no magnetic field. The sample with $x = 0.0$ has the lowest resistivity among all samples. The resistivity increases with increase in x to 0.06 and tends to decrease remarkably with further increase in x . The sample having larger grain seems to have larger resistivity. The temperature dependence of the resistivity is positive from 300 K to 360 K and negative from 360 K to 500 K for the $x = 0.0$ sample. On the other hand, the samples with $0.02 \leq x \leq 0.10$ have negative temperature dependences whole temperature range.

Figure 4 shows the temperature dependence of magnetoresistance measured under magnetic field of 15 kOe. All samples have the same magnetoresistances of

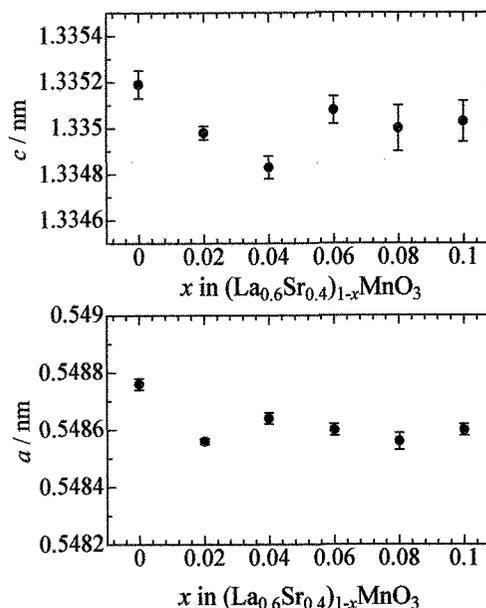


Figure 1 Nominal chemical composition x dependence of lattice constants for $(\text{La}_{0.6}\text{Sr}_{0.4})_{1-x}\text{MnO}_3$.

–5.0 % at 300 K, but different temperature dependences. Negative magnetoresistance is maximal in the vicinity of 360 K for the sample with $x = 0.0$. For the samples with $0.02 \leq x \leq 0.06$, however, the negative magnetoresistances increase stepwise in the vicinity 360 K when reducing temperature. Further, they show maximal values again in the vicinity of 360 K for the samples with $x = 0.08$ and 0.10. The samples having smaller grains seems to show a peak and those having

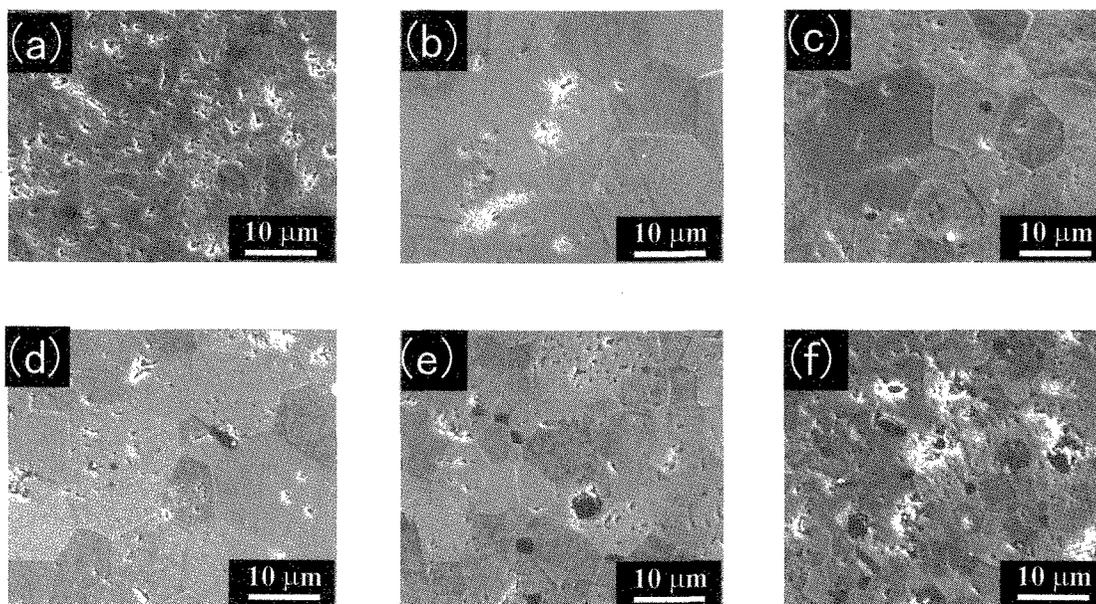


Figure 2 SEM micrographs of surfaces of the samples (a) $x = 0.0$, (b) $x = 0.02$, (c) $x = 0.04$, (d) $x = 0.06$, (e) $x = 0.08$ and (f) $x = 0.10$. The surfaces were thermally etched.

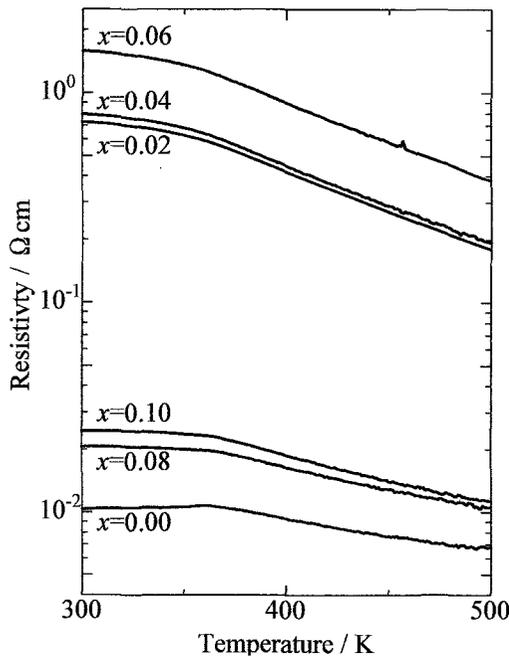


Figure 3 Temperature dependence of electric resistivity measured under zero magnetic fields.

larger grains seems to show a step in the magnetoresistance – temperature curves, referring Figs. 2.

Remarkable increases in negative magnetoresistance are found generally around ferromagnetic Curie temperature T_C for single crystalline manganite samples. Moreover, the T_C depends on the average valence of manganese ions, which is controlled by the amount of cationic substitution, like $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [16]. The very similar temperatures at which the remarkable increase in magnetoresistance are found for the sample with $x = 0.0, 0.08$ and 0.10 indicate that the three samples have very similar chemical composition. The samples with $x = 0.02, 0.04$ and 0.06 also show abnormal stepwise changes in magnetoresistance-temperature curves at the similar temperature so that they have also very similar chemical composition with the former three samples. The conclusion is consistent with that derived from the nominal chemical composition dependence of lattice constants.

The electric and magnetoresistive properties of the samples with $x = 0.02, 0.04$ and 0.06 , however, are different from those of the remaining samples, *i.e.* the higher resistivities and the stepwise increase in the negative magnetoresistances. Many physical properties depend on the average valence of manganese ions, *i.e.* chemical composition for perovskite-type manganites, as mentioned briefly above. The chemical compositions of all samples in the present study are supposed to agree each other within 2%. Therefore, we cannot conclude that the difference in the electric and magnetoresistive properties are due to the difference in chemical composition.

We have two plausible reasons for the difference of the properties. First, electric insulating films exist, such as Mn_3O_4 at grain boundaries for the samples in which

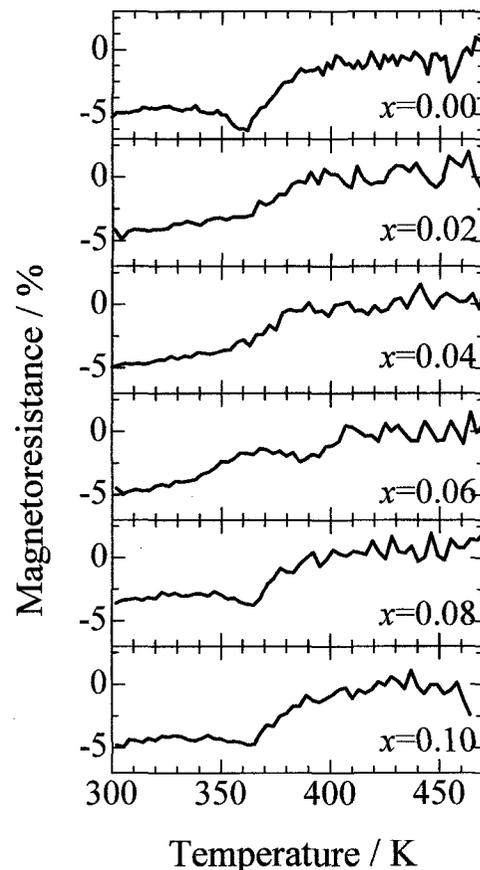


Figure 4 Temperature dependence of magnetoresistance measured under magnetic field of 15 kOe for the samples (a) $x = 0.0$, (b) $x = 0.02$, (c) $x = 0.04$, (d) $x = 0.06$, (e) $x = 0.08$ and (f) $x = 0.10$.

grains grow abnormally. They cause the higher electric resistivities. Furthermore, form ferromagnetic metal – insulator – ferromagnetic metal junctions. It has been predicted that tunneling magnetoresistance (TMR) appears through the junction [17]. Ceramic manganite samples sintered at various temperatures have different microstructure and show magnetoresistive properties, which are explained by the TMR [1, 4]. Therefore, we can conclude that the sample having larger grains shows higher resistivity and abnormal temperature dependence of magnetoresistance.

Second, the lattices in the vicinity of grain boundaries are strained for the samples in which grains grow abnormally. Many results have been reported for the manganite films deposited on various bicrystals to investigate the relationship between grain boundary and magnetoresistive properties. Negative magnetoresistance through artificial grain boundary increases stepwise around T_C when reducing temperature in the reports, as our samples with $x = 0.02, 0.04$ and 0.06 . Layers in the vicinity of grain boundaries are supposed to have lower T_C and lower magnetization than the grain due to structural disorder [18]. The difference in magnetization form potential barrier, as pointed out by Furukawa [19] and tunneling of carrier through the barrier is analyzed to causes magnetoresistance at grain boundary [18]. The layers in the vicinity of grain

boundaries distort structurally more in the ceramic sample having larger grain. Thus, we also conclude that the sample having larger grains show higher resistivity and abnormal temperature dependence of magnetoresistance.

4. SUMMARY

We prepared the perovskite-type manganite ceramic samples with *A*-site ion deficient nominal composition, $(La_{0.6}Sr_{0.4})_{1-x}MnO_3$ ($0.0 \leq x \leq 0.10$). The proper chemical compositions of perovskite phase formed are supposed to agree within 2 % for all samples. The samples with $x = 0.02, 0.04$ and 0.06 have larger grains than the remaining samples. They also show higher resistivity and abnormal temperature dependence of magnetoresistance. Two plausible reasons relating grain boundaries are proposed for the properties.

ACKNOWLEDGMENT

This work was partially supported by the Grant-in-Aid for Scientific Research of Japan ("KAKENHI", No. 13750632) and also partially supported by the High-Tech Research Center Project of Ministry of Education, Culture, Sport, Science and Technology of Japan (No. 343).

REFERENCES

- [1] H.Y.Hwang, S-W.Cheong, N.P.Ong, and B.Batlogg, *Phys. Rev. Lett.*, **77**, 10, 2041-4 (1996).
- [2] R.Mahesh, R.Mahendiran, A.K.Raychaudhuri, and C.N.R. Rao, *Appl. Phys. Lett.*, **68**, 16, 2291-3 (1996).
- [3] K.H.Kim, J.Y.Gu, H.S.Choi, D.J.Eom, J.H.Jung, and T.W.Noh, *Phys. Rev. B***55**, 7, 4023-6 (1997).
- [4] N.Zhang, S.Zhang, W.P.Ding, W.Zhong, and Y.W.Du, *Solid State Commun.*, **107**, 8, 417-22 (1998).
- [5] X.L.Wang, S.X.Dou, H.K.Liu, M.Ionescu, and B.Zeimet, *Appl. Phys. Lett.*, **73**, 3, 396-8 (1998).
- [6] Y.-H.Huang, C.-H.Yan, Z.-M.Wang, C.-S.Liao, and G.-X.Xu, *Solid State Commun.*, **118**, 541-6 (2001).
- [7] M.Takemoto, Y.Umeshita, S.Yamashita, and H.Ikawa, *Trans. Mater. Res. Soc. Jpn.*, **25**, 1, 245-8 (2000).
- [8] M.Takemoto, Y.Umeshita, S.Yamashita, and H.Ikawa, *Key Eng. Mater.*, 181-182, 235-8 (2000).
- [9] M.Takemoto, K.Yamagiwa, Y.Umeshita, and H.Ikawa, *Trans. Mater. Res. Soc. Jpn.*, **26**, 1, 15-8 (2001).
- [10] M.Takemoto, K.Yamagiwa, Y.Umeshita, and H.Ikawa, *Key Eng. Mater.* **216**, 145-8 (2002).
- [11] M.Itoh, T.Shimura, T.Hayashi, and Y.Inaguma, *Solid State Commun.*, **97**, 3, 179-82 (1996).
- [12] V.Markovich, E.Rozenberg, G.Gorodetsky, B.Revzin, J.Pelleg, and I.Felner, *Phys. Rev. B***62**, 21, 14186-90 (2000).
- [13] R.Suryanarayanan, V.Gasumyants, and N.Ageev, *Phys. Rev. B***59**, 14, 9019-22 (1999).
- [14] S.V.Pietambaram, D.Kumar, R.K.Singh, and C.B.Lee, *Appl. Phys. Lett.*, **78**, 2, 243-5 (2001).
- [15] W.Boujelben, A.Cheikh-Rouhou, and J.C.Joubert, *J. Solid State Chem.*, **156**, 68-74 (2001).
- [16] A.Urushibara, Y.Morimoto, T.Arima, A.Asamitsu, G.Kido, and Y.Tokura, *Phys. Rev.*, **51**, 20 14103-9 (1995).
- [17] M.Julliere, *Phys. Lett.* **54A**, 3, 225-6 (1975).
- [18] R.Gross, L.Alf, B.Büchner, B.H.Freitag, C.Höfener, J.Klein, Y.Lu, W.Mader, J.B.Philipp M.S.R.Rao, P.Reutler, S.Ritter, S.Thienhaus, S.Uhlenbruck, and B.Wiedenhorst, *J. Mag. Mag. Mater.*, **211**, 150-9 (2000).
- [19] N.Furukawa, *J. Phys. Soc. Jpn.*, **66**, 2523 (1997).

(Received December 20, 2002; Accepted January 31, 2003)