Ferromagnetism at room temperature in La–Ba–Ca–Mn–O thin films

Nguyen Hoa Hong,[a] Joe Sakai, and Syozo Imai
School of Materials Science, Japan Advanced Institute of Science and Technology, Hokuriku (JAIST), 1-1 Asahidai, Tatsunokuchi-machi, Ishikawa 923-1292, Japan

The effects of substitution of Ca by Ba in $La_{1-x}Ca_xMnO_3$ (LCMO) with $x<0.5$ were investigated systematically in order to clarify the role of the size of the *A* cations. As for the $La_{1-x}(Ba–Ca)_xMnO_3$ (LBCMO) films of ferromagnetic metallic (FMM) region ($x=0.2$; 0.3; and 0.4), by doping Ba, the ferromagnetic transition temperature (T_C) and the insulator-to-metal (IM) transition temperature (T_{IM}) were improved about 30–60 K, compared with those of LCMO thin films with the same ratio of Mn^{3+}:Mn^{4+}. Especially, $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$ thin films have an anomalously high T_C (about room temperature) and a T_{IM} of 275 K under zero field. In the ferromagnetic insulating (FMI) region ($x=0.15$; 0.1), the Ba doping enables the IM transition and remarkably heightens the T_C as well. The phase diagram shows that in the slightly doped region ($x<0.5$), Ba doping has made the FMM phase significantly expanded. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1358335]

I. INTRODUCTION

Hole doped manganites $La_{1-x}M_xMnO_3$ (M=Ba, Sr, Ca, and Pb) with perovskite structures are interesting materials which have attracted attentions of many researchers. Besides the exotic colossal magnetoresistance (CMR) effect, a lot of related phenomena have been focused on. As for magnetoresistive devices, controlling the electronic transport and magnetic properties of these materials in thin film form is very important to applications. Since the change of size of the *A* site cations (La and M) can modify the Mn–Mn distance and Mn–O–Mn angles,[1] for perovskite manganese oxides, with a fixed *x*, magnetic and transport properties can be influenced by changing the combination of *A*-site ions. Especially, Curie temperature, resistivity, and magnetoresistance effect are highly sensitive to the lattice distortion.[2,3]

In a previous work of our group,[4] Ba was chosen to dope partially for Ca in $La_{0.4}Ca_{0.6}MnO_3$ which is well known as an insulator for the whole range of temperature. The result is that the Ba doping enabled an insulator-to-metal (IM) transition even under zero field. This leads us to the question of how the Ba doping will influence a ferromagnetic metal. Therefore, in this study we partially substitute Ca by Ba in $La_{1-x}Ca_xMnO_3$ (LCMO) with $x<0.5$ in order to investigate the effects of changing size of *A*-site cations. The enhancement of the ferromagnetic metallic (FMM) phase was expected.

II. EXPERIMENT

$La_{0.9}Ba_{0.1}MnO_3$, $La_{0.85}Ba_{0.1}Ca_{0.05}MnO_3$, $La_{0.8}Ba_{0.1}Ca_{0.1}MnO_3$, $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$, and $La_{0.6}Ba_{0.1}Ca_{0.3}MnO_3$ targets (2 cm diameter and 4 mm thickness) were synthesized by mixing stoichiometric proportions of La_2O_3, $BaCO_3$, $CaCO_3$, and MnO_2 and then heating in air at 1250 °C for 5 h, at 1380 °C for 12 h, and at 1390 °C for 20 h with intermediate grindings. Film deposition on [100] $LaAlO_3$ substrates was carried out by a pulsed-laser-deposition technique by using a Lambda Physik 248 nm KrF excimer laser with 8 Hz repetition rate and 1.1 J/cm^2 energy density. The substrate temperature was 800 °C and the oxygen pressure was 300 mTorr during film deposition (92% O_2 and 8% O_3). After deposition, films were annealed at 450 °C for 30 min and then cooled to room temperature in the same atmosphere as during deposition. The typical thickness of the films is 1800 Å. X-ray diffraction analysis confirmed that all films are *c*-axis oriented. The electrical resistance has been measured in the range of 5–350 K from zero field up to 5.5 T using a conventional four-probe method and a superconducting magnet. The magnetization has been measured by a quantum design superconducting quantum interference device magnetometer.

III. RESULTS AND DISCUSSIONS

The magnetization versus temperature [$M(T)$] of $La_{1-x}Ba_{0.1}Ca_{x-0.1}MnO_3$ (LBCMO) thin films ($x=0.1$; 0.15; 0.2; 0.3, and 0.4) is shown in Fig. 1(a). The transition temperature from paramagnetism to ferromagnetism (T_C) are 220, 240, 265, 290, and 270 K, respectively. They all are pretty high compared with results of the $La_{1-x}Ca_xMnO_3$ (LCMO) bulk,[5] and also higher than the highest T_C reported so far for as-grown LCMO thin films[6] with the same ratio of Mn^{3+}:Mn^{4+}. Thus, we may assume that Ba doping caused an enhancement of about 20–70 K in T_C of this kind of material. To be able to confirm that the enhancement is not caused by some special preparation conditions for thin film form, we checked the T_C of a $La_{0.7}Ca_{0.3}MnO_3$ thin film which was prepared by exactly the same fabrication conditions as for LBCMO thin films. The $M(T)$ curve of the $La_{0.7}Ca_{0.3}MnO_3$ thin film is shown in Fig. 1(b). It can be seen that our $La_{0.7}Ca_{0.3}MnO_3$ film has the T_C of 250 K, almost the same as of $La_{0.7}Ca_{0.3}MnO_3$ bulk reported by Schiffer *et al.*,[5] while our $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$ film has a T_C of about room temperature (higher than the T_C reported for annealing $La_{0.7}Ca_{0.3}MnO_3$ film).[6,7] Therefore, Ba doping is presumed

[a]Electronic mail: hhong@jaist.ac.jp

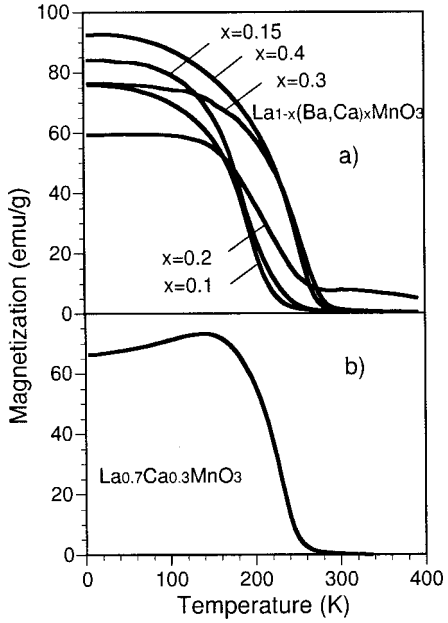

FIG. 1. Temperature dependence of magnetization at 0.2 T for (a) La_{1-x}(Ba and Ca)$_x$MnO$_3$ thin films ($x=0.1$; 0.15; 0.2; 0.3, and 0.4) and (b) a $La_{0.7}Ca_{0.3}MnO_3$ thin film.

to cause the enhancement of T_C. Our ferromagnetic resonance (FMR) data of the $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$ film[8] shows that it has a very narrow line of FMR signal and the linewidth versus temperature is rather flat. It means that the film is very magnetically homogeneous in spite of chemical doping.

Besides the remarkable enhancement in T_C, we also obtained rather high insulator-to-metal transition temperature (T_{IM}) in LBCMO thin films even under zero field (Fig. 2). As for the films of FMM region defined by Ref. 5 ($x=0.2$, 0.3, and 0.4), by doping Ba, the T_{IM}s were improved about 30–60 K, compared with those of LCMO thin films with the same x. The inset of Fig. 2(a) shows the temperature dependence of resistivity of a $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$ film at various fields. When the magnetic field was increased, the T_{IM} increased (it was 320 K at 5.5 T) and a colossal negative magnetoresistance was obtained as well. From the bulk phase diagram, $La_{0.9}Ca_{0.1}MnO_3$ and $La_{0.85}Ca_{0.15}MnO_3$ are known as insulators over the whole range of temperature. Ba doping enables the insulator-to-metal transition in both cases, and actually at rather high temperatures [see Figs. 2(b) and 2(c)]. The temperature dependence of resistivity at various fields of the sample of $x=0.15$ seems to be rather similar to those of $0.2\leqslant x\leqslant 0.4$, while in the case of $x=0.1$, we may see that the material turns to be insulating again below 150 K. The large magnitude of resistance of $La_{0.85}Ba_{0.1}Ca_{0.15}MnO_3$ sample [about one order higher than those from Fig. 2(a)] as well as the tendency of $La_{0.9}Ba_{0.1}MnO_3$ sample to become insulating again at low-temperature region seem to be consistent with the origin of LCMO with $x=0.1$ and 0.15 as insulators.

It appears that in the slightly doped region ($x<0.5$), Ba doping has made the FMM phase expanded. Figure 3 is a tentative diagram for LBCMO thin films which was summarized from all above data. The dashed line was reproduced from Ref. 5 (phase diagram of LCMO bulk). The open triangles are data reproduced from Ref. 6 (LCMO thin films). The hatched region determines the expansion of FMM phase that we obtained. From this phase diagram, we may say that the properties well beyond those of the bulk may be achiev-

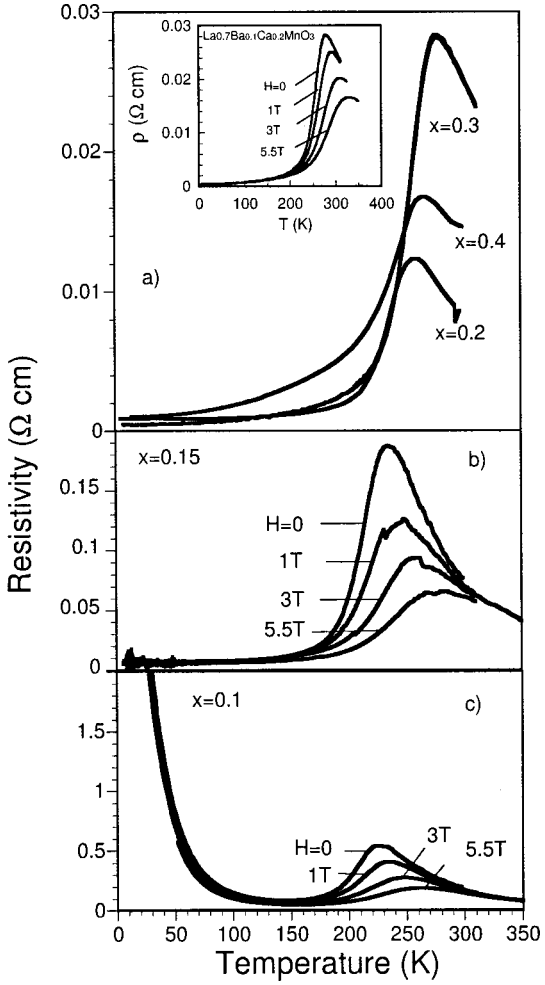

FIG. 2. Temperature dependence of resistivity at various fields for La_{1-x}(Ba and Ca)$_x$MnO$_3$ thin films ($x=0.1$; 0.15; 0.2; 0.3, and 0.4).

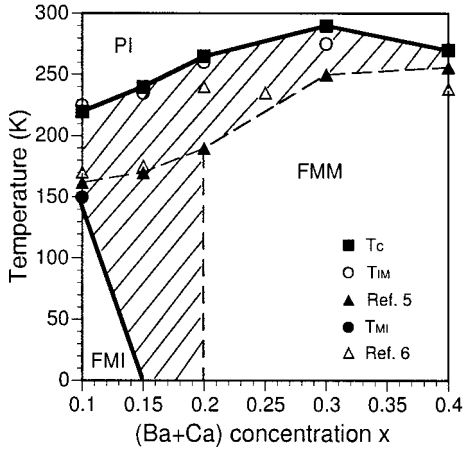

FIG. 3. Phase diagram for La_{1-x}(Ba and Ca)$_x$MnO$_3$ thin films. T_Cs are taken from the inflection point from $M(T)$ curve. Dashed line is the reproduced data from Ref. 5. The open triangles are reproduced data from Ref. 6. Solid lines are only a guide for the eyes. The hatched region indicates the expansion of FMM phase in comparison with the diagram for $La_{1-x}Ca_xMnO_3$ bulk.

able in thin films and furthermore, the Ba doping really plays a certain role in the enhancement of T_C in LCMO thin films.

Since the ionic radius of Ba is rather big, the idea of Ba doping is to induce intentionally the chemical pressure inside the lattice to cause the reduction of resistance. In general, the cations with smaller ionic radii in (RE, AE) sites of $RE_{1-x}AE_xMnO_3$ cause a big lattice distortion and as the results, it reduces the transfer interaction betweens Mn sites and a one-electron bandwidth in those manganites.[1,4,9] Ba doping relaxes the lattice distortion and enhance the metallic state (the IM transition of Ba-doped films also shifted to higher temperature). Besides, it is known that in manganites, the Curie temperature increases drastically as the average size of the *A*-site cation increases.[2] On the other hand, the strains induced by the substrates may also be assumed to suppress somewhat the charge ordering state (similar to some kind of internal pressure) to contribute to the improvement of transition temperatures. As the results, the FMM phase is significantly expanded. In summary, we should say that there are possibly two contributions for the heightening of T_{IM} and T_C in LBCMO thin films: Ba-doping and thin-film form. These assumptions need to be proved by structural studies in the future.

IV. CONCLUSION

We have obtained very high ferromagnetic transition temperature T_C and insulator-to-metal transition T_{IM} in La–(Ba–Ca)–Mn–O thin films fabricated by the PLD technique. Samples which transit to ferromagnetic metallic state at about room temperature and low field seem to be useful for application purposes. This result is expected since the expansion in volume of ferromagnetic phase or the enhancement of a metallic state is supposed to be caused by the effect of the big radius of Ba ions (T_C increases as the mean size of *A*-site cations increases). Furthermore, one thing we may say is that the properties beyond those of the bulk can be achieved in thin-film form due to the strains induced by the substrate.

ACKNOWLEDGMENT

The authors would like to thank Dr. V. V. Srinivasu for FMR measurements and helpful discussions.

[1] D. Kumar, R. K. Singh, and C. B. Lee, Phys. Rev. B **56**, 13666 (1997).
[2] F. Damay, A. Maignan, C. Martin, and B. Raveau, J. Appl. Phys. **81**, 1372 (1996).
[3] Y. Wu, Y. Suzuki, U. Rudiger, J. Yu, A. D. Kent, T. K. Nath, and C. B. Eom, Appl. Phys. Lett. **75**, 2295 (1999).
[4] N. H. Hong, J. Sakai, and S. Imai, J. Appl. Phys. **87**, 5600 (2000).
[5] P. Schiffer, A. P. Ramirer, W. Bao, and S-W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).
[6] W. Prellier, M. Rajeswari, T. Venkatesan, and R. L. Greene, Appl. Phys. Lett. **75**, 1446 (1999).
[7] R. Shreekala *et al.*, Appl. Phys. Lett. **74**, 1886 (1999).
[8] N. H. Hong, V. V. Srinivasu, T. Endo, and S. Imai (unpublished data).
[9] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, Phys. Rev. B **51**, 14103 (1994).