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Effects of Ba doping on physical properties of La–Ca–Mn–O thin films

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Abstract

Transport and magnetic properties of La–Ba–Ca–Mn–O thin films fabricated by the pulsed laser deposition technique had been investigated systematically to see the effects of substitution of the small atom Ca by Ba which is much bigger. The induced insulator-to-metal (IM) transition was obtained not only in compositions near 0.5 and 0.18 which are boundaries between metallic and insulating phases but also in the heavily doped region. In the region of $x > 0.5$, the Ba doping causes an anomalous response of the system to the magnetic field and a positive magnetoresistance was observed. Besides, our results concerning the vicinity of 0.5 imply the existence of phase separation. As for $x < 0.5$, the doping enhances remarkably the paramagnetism–ferromagnetism transition and the IM transition temperatures.

1. Introduction

Recently, hole doped manganites $La_{1-x}M_xMnO_3$ (M = Ba, Sr, Ca, Pb) have been attracting the attention of many researchers. Besides the colossal magnetoresistance (CMR) effect, many related phenomena have been investigated. As for magnetoresistive devices, controlling the electronic transport and magnetic properties of these materials in thin film form is very important to applications [1, 2]. Since the magnetoresistance (MR) behaviour in manganites relates strongly to the exchange interaction between two magnetic cations separated by an anion, for perovskite manganites with a fixed x, transport properties including CMR phenomena can be strongly affected by changing the combination of A-site ions (RE, AE) [3, 4]. Based on those factors, we have chosen Ba as a dopant for La–Ca–Mn–O (LCMO) to investigate the doping effects on LCMO thin films in order to work out the intrinsic properties of that kind of material. The LCMO system was chosen because not so much work on it has been done so far (in contrast, La–Sr–Mn–O has been investigated professionally by many recognized groups),

and on the other hand, the phase diagram of LCMO bulk has been already established, which may be taken as a basic suggestion.

In this study, we partially substituted Ca by Ba in $La_{1-x}Ca_xMnO_3$ (LCMO) for the whole range of x in order to investigate the effects of changing size of A site cations. The induced insulator-to-metal (IM) transition in some insulating compositions and the enhancement of the ferromagnetic metallic (FMM) phase in ferromagnetic compositions were obtained as expected, while phase separation (PS) near the critical point of $x = 0.5$ was evidenced by accident.

2. Experiment

$La_{1-x}(Ba, Ca)_xMnO_3$ (where $0.1 \leqslant x \leqslant 0.9$ and Ba concentration is 0.1 in most cases) targets (2 cm diameter, 4 mm thickness) were synthesized by a conventional solid state reaction method [5]. Film deposition on [100] $LaAlO_3$ substrates was carried out by a pulsed-laser-deposition (PLD) technique. The preparation conditions were described elsewhere [5, 6]. 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 9 T using a conventional four-probe method and a superconducting magnet. Contacts were prepared by putting In and Ag paste onto terminals which were created by Pt–Pr sputtering. In the cases where the resistance of samples was extremely small or large, some micro-fabrications were used for creating paths. The magnetization has been measured by a Quantum Design superconducting quantum interference device magnetometer. The temperature range for the measurements extends from 5 to 400 K and the magnetic field was applied from 0.2 up to 5.5 T.

3. Ferromagnetism at high temperature in the low doping region

3.1. The enhancement of the paramagnetism–ferromagnetism transition temperature

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 figure 1. The transition temperatures from paramagnetism (PR) to ferromagnetism (FM) T_Cs are pretty high (the highest is 290 K for $x = 0.3$), compared with the results of the $La_{1-x}Ca_xMnO_3$ (LCMO) bulk [7], and also higher than the highest T_C reported so far for as-grown LCMO thin films [8] with the same ratio of Mn^{3+}:Mn^{4+}. Thus, we may assume that Ba doping enhances T_C by about 20–70 K in this kind of material. To confirm that the enhancement is not caused by some special preparation conditions for thin films, we checked the T_C of a $La_{0.7}Ca_{0.3}MnO_3$ thin film and a $La_{0.7}Ba_{0.3}MnO_3$ thin film which were prepared by exactly the same fabrication conditions as of LBCMO thin films. The $M(T)$ curve of the $La_{0.7}Ca_{0.3}MnO_3$ thin film is shown in figure 2(a). Even though the magnetization decreases a bit at low temperature due to the thin film effect (in comparison with bulk, the curve is rather flat in the low temperature region [7], but in the thin film form it may turn down a bit and can be influenced by fabrication conditions [8]); we can say 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, while our $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$ film has a T_C of about room temperature (higher than that of the annealed films [8, 9]). Therefore, Ba doping is presumed to cause the enhancement of T_C. This is also confirmed by the magnetization data of $La_{0.7}Ba_{0.3}MnO_3$ thin films (figure 2(b)). In this case, a very high T_C of 320 K was achieved. By calculating the mean size of A site cations, we found that $\langle r_A \rangle$ values of LCMO, LBCMO, LBMO are 1.357, 1.384 and 1.438 Å, respectively. As a result, their T_Cs are 260, 290 and 320 K. It is obvious that T_C increases drastically as the average size of the A site cation increases.

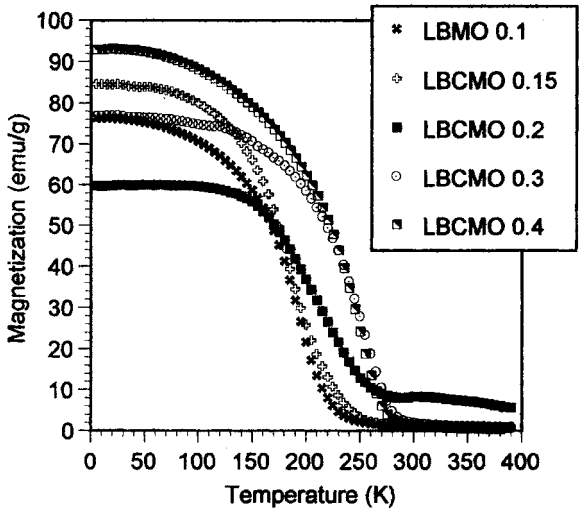

Figure 1. The temperature dependence of magnetization at 0.2 T for $La_{1-x}(Ba, Ca)_xMnO_3$ thin films ($x = 0.1$, 0.15, 0.2, 0.3 and 0.4).

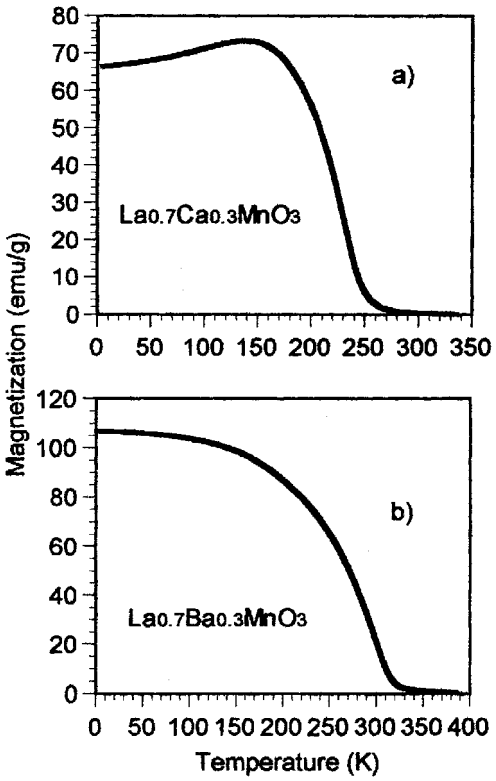

Figure 2. The temperature dependence of magnetization at 0.2 T for (a) a $La_{0.7}Ca_{0.3}MnO_3$ thin film and (b) a $La_{0.7}Ba_{0.3}MnO_3$ thin film.

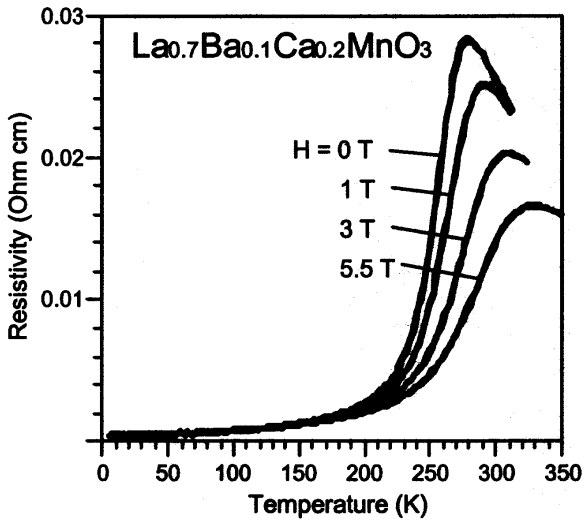

Figure 3. The temperature dependence of resistivity at various fields for a $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$ thin film.

3.2. Insulator-to-metal transition

Besides the remarkable enhancement in T_C, we also obtained rather high IM transition temperature T_{IM} in LBCMO thin films. As for the films of FMM region defined by [7] ($x = 0.2, 0.3, 0.4$), by doping with Ba, the T_{IM}s were improved by about 30–60 K, compared with those of LCMO thin films with the same x. As an example, the temperature dependence of resistivity of a $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$ film at various fields is shown in figure 3. When the magnetic field was increased, the T_{IM} increased (it was 320 K at 5.5 T) and a colossal negative MR was obtained as well.

Not only does the Ba doping enhance T_{IM} in the LBCMO with $x = 0.2$, 0.3 and 0.4, but it also causes an IM transition in insulating compositions. In 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 IM transition in both cases, and actually at rather high temperatures (see figure 4). The temperature dependence of resistivity at various fields of the sample of $x = 0.15$ seems to be rather similar to those of $0.2 \leqslant x \leqslant 0.4$ [6], while in the case of $x = 0.1$ we may see that the material turns out to be insulating again below 150 K. The large magnitude of resistance of the $La_{0.85}Ba_{0.1}Ca_{0.05}MnO_3$ sample (about one order higher than those from figure 3) as well as the tendency of the $La_{0.9}Ba_{0.1}MnO_3$ sample to become insulating again in the low temperature region seem to be consistent with the origin of LCMO with $x = 0.1$ and 0.15 as insulators.

The fact that Ba doping causes the IM transition at rather high temperatures, and the metallic state dominates over a wide region of temperatures, was unexpected. As for LCMO thin films, Prellier *et al* [8] also obtained the IM transition with the composition of $x = 0.1$ but the film had to be postannealed for about 10 h under flowing oxygen. It is known that the oxygen annealing can remarkably improve the conductivity of manganites. Our films are as-grown films, but we also obtain the metallic phase as in the case of annealing, so it is sure that Ba doping has some advantage. Urushibara *et al* [10] also reported on an FMM phase observed in LSMO with $x = 0.15$ and 0.1 (in a very narrow region) and a ferromagnetic insulating (FI) phase which was more dominantly observed at low temperatures in those two.

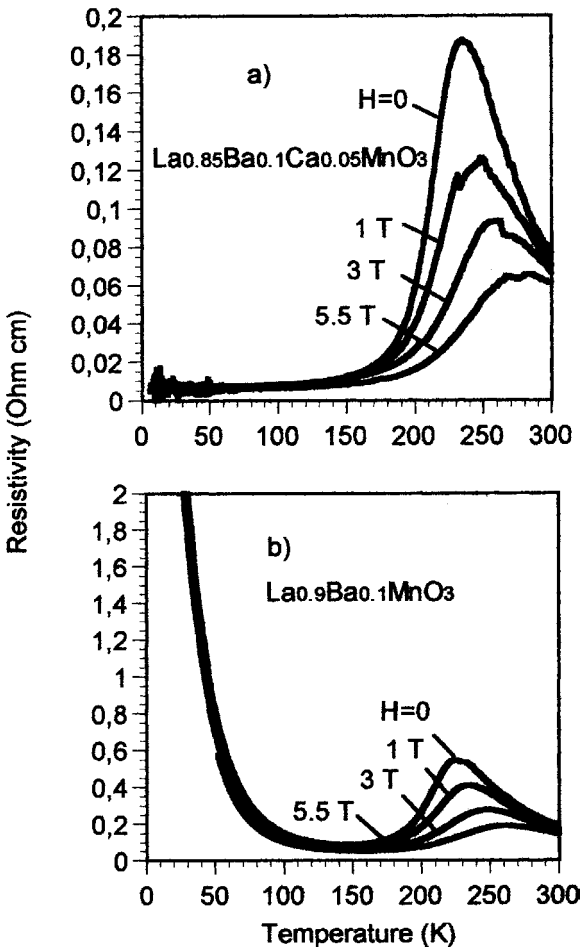

Figure 4. The temperature dependence of resistivity at various fields for (a) a $La_{0.85}Ba_{0.1}Ca_{0.05}MnO_3$ thin film and (b) a $La_{0.9}Ba_{0.1}MnO_3$ thin film.

Okuda *et al* [11] compared LCMO and LSMO single crystals, and found out that in the LCMO case, for both $x = 0.15$ and 0.1, the material is insulating, while LSMO with $x = 0.15$ can show a metallic behaviour in a narrow region of temperatures. Along with our case, this evidence proves the size effect. Ba doping really can enable IM transition. Moreover, the state of $La_{0.9}Ba_{0.1}MnO_3$ below 150 K is further evidence of the FI phase which has not been well explained by double-exchange (DE) theory. One reasonable explanation for this state is the model of big FM domains which are isolated (as a whole they contribute to FM, which is why the magnitude of magnetization is big, but they could not be conductive due to that isolation).

3.3. Conclusion

It appears that in the slightly doped region ($x < 0.5$), Ba doping has made the FMM phase expand. We may say that properties well beyond those of the bulk may be achieved in thin films and, furthermore, 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

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 a result, it reduces the transfer interaction between Mn sites and a one-electron bandwidth in those manganites [4, 10]. Ba doping relaxes the lattice distortion and enhances the metallic state (the IM transition of Ba-doped films also shifts 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 [3]. On the other hand, the strains induced by the substrates may also be assumed to suppress somewhat the charge ordering (CO) state (similar to some kind of internal pressure) to contribute to the improvement of transition temperatures. As a result, 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.

4. Phase separation in the heavily doped region

4.1. Phase separation in compositions around $x = 0.5$

The variation of electrical resistance of a $La_{0.45}Ba_{0.05}Ca_{0.5}MnO_3$ film as a function of temperature in zero and applied fields is shown in figure 5. Under zero field, the resistance of the film increases as the temperature decreases. At about 42 K (denoted as insulator–metal transition temperature T_{IM}), it drops abruptly to a very low value (about one order) and then immediately rises up again (CO state). When the magnetic field is increased, the $\rho(T)$ curve shifts towards the low temperature side or in other words T_{IM} decreases as magnetic field increases (33 K at 6 T) while the height of the jump does not change much. Accompanying the jump, in the low temperature part of the $\rho(T)$ curve, there is a kink which is rather noticeable. One interesting point is that the temperature at which the kink appears T_{kink} also depends obviously on the magnetic field (see figure 6). On the other hand, a difference between $\rho(T)$ measured on warming and cooling has been observed (see the inset).

According to the literature so far, $La_{0.45}Ca_{0.55}MnO_3$ is an insulator over the whole range of temperature [7, 12, 13]. At low temperature, ferromagnetic (FM) and charge-ordering antiferromagnetic (COAF) states coexist. In fact, charge-transport in LCMO ($x \approx 0.5$) is amenable to the CO of Mn^{3+} and Mn^{4+} [13]. Furthermore, in general, the cations with smaller ionic radii in (RE, A) sites of $RE_{1-x}A_xMnO_3$ cause a big distortion-dependent reduction of one-electron bandwidth in these manganites causing a CO state, and simultaneously stabilize the AF spin structure [4, 10].

A big jump observed in the $\rho(T)$ curve shows a clear tendency of changing from an insulating to metallic state but that state remains in just a very narrow region of temperature after the resistive transition. The effect of Ba doping is to reduce the lattice distortion and, above all, to induce the chemical pressure inside the lattice to cause the drastic drop in resistance. It can be understood in terms of the changing Mn–O bond which increases the transfer interaction between the neighbouring Mn sites. However, the tendency that T_{IM} shifts to a lower temperature when the magnetic field is increased is really an anomalous behaviour compared to the way a conventional LCMO material responds to magnetic fields. The positive MR observed in our films, as well as $T_{IM}(H)$ (figure 6), is out of the frame of the DE mechanism.

The appearance of the kink in the low temperature part of the $\rho(T)$ curve which is the starting point of the insulating state enables us to think about the possibility that an AF phase occurs in competition with the FM phase (according to DE theory, an insulating state must be in PR or AF phases and the metallic state used to be in a FM phase). On the other hand, that supposition is enforced by the fact that T_{kink} shifts to a lower temperature when a higher

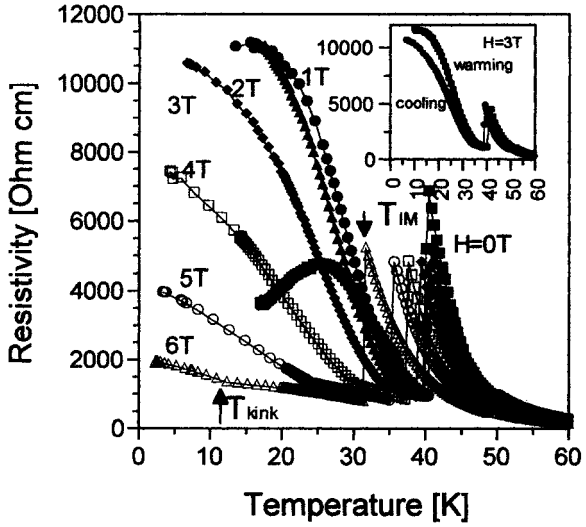

Figure 5. The temperature dependence of resistivity at various fields for a $La_{0.45}Ba_{0.05}Ca_{0.5}MnO_3$ film.

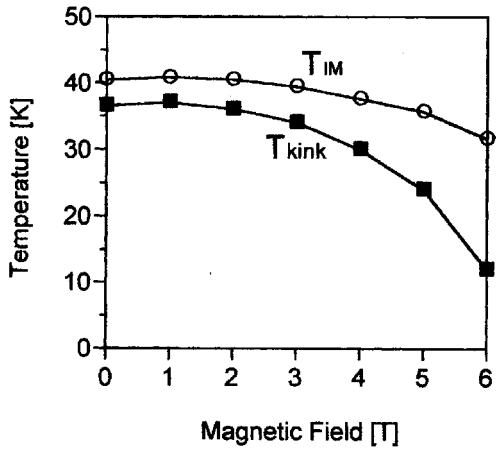

Figure 6. The magnetic field dependence of the IM transition temperature (T_{IM}) and kink temperature (T_{kink}) for $La_{0.45}Ba_{0.05}Ca_{0.5}MnO_3$ films.

field is applied. The magnetic field dependence in this kind of material can be understood by knowing that, as for AF materials, T_{Neel} is suppressed when the applied field is increased. The temperature dependence of the magnetization curve is fairly monotonic and the magnitude is pretty small and it shows a slight tendency of becoming AF at low temperature (below T_{IM}) (figure 7). There may exist an antiferromagetic metallic (AFM) phase which is responsible for the metallic state at low temperature in this material.

Transport behaviours of $La_{0.45}Ba_{0.05}Ca_{0.5}MnO_3$ thin films that we discussed above are somewhat related to the PS phenomenon in compositions which are near to the critical point $x = 0.5$ [12]. Charge inhomogeneities involve large clusters or, in other words, there are two phases with different densities and they compete with each other.

A very similar picture for magnetic and transport properties with the feature of IM transition at low temperature as well as the PS in $La_{0.4}Ba_{0.1}Ca_{0.5}MnO_3$ thin films was discussed

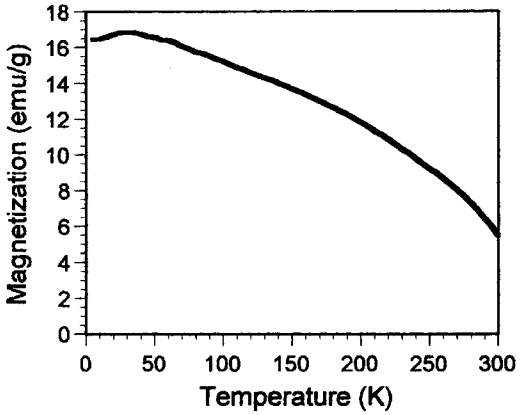

Figure 7. The temperature dependence of magnetization at 3 T for the $La_{0.45}Ba_{0.05}Ca_{0.5}MnO_3$ film.

in a previous work [5]. Based on the fact that the material turns out to be metallic at about 37 K while the magnetization data did not show a big change from the PR to FM phase, and no bulk effect of the FM phase as well (the $M(T)$ curve is very monotonic, and the magnitude of magnetization is very small as well, several emu g^{-1}), in that report, it was assumed that there might be a coexistence of two phases, the canted antiferromagnetic insulating (CAFI) state and ferromagnetic metallic (FM) domains (where FM domains are very small and connected to each other by FM filaments), or CAFI and A-type AFM (FM in the ab-plane but AF along the c-axis) states at low temperature. But due to the fact that in $La_{0.4}Ba_{0.1}Ca_{0.5}MnO_3$ thin films, positive MR was observed, and later in this paper it will be shown that above $x = 0.65$, the AF state will be dominant, the assumption of coexisting CAFI and A-type AFM states (PS) seems to be more convincing.

IM transition is also observed at the composition of $x = 0.65$. The temperature dependence of resistivity is shown in figure 8(a). Under zero field, the sample has very low resistivity at room temperature (about 0.015 Ω cm) and as the temperature decreases it shows semiconductor-like behaviour but then turns metallic at about 80 K with a very sharp jump in the $\rho(T)$ curve (the sharp jump is probably the signal of the breaking of the CO state). The resistance versus temperature measured by the two-probe method four months after the first measurement is shown in figure 8(b). It appears that the sample still shows an IM transition, although it shifts to a lower temperature. This may be related to the aging effect of manganites (the material may become less conductive after a certain duration of time). The $M(T)$ feature of $La_{0.35}Ba_{0.1}Ca_{0.55}MnO_3$ thin films is very much the same as the one of $La_{0.45}Ba_{0.05}Ca_{0.5}MnO_3$ in figure 7 in which the magnetization versus temperature is very monotonic, has a rather small magnitude, no bulk effect of FM phase and a very slight tendency to turn AF at low temperature. Therefore we may say that at the composition of $x = 0.65$ the magnetic picture is similar to that of 0.55 and 0.6 that we discussed above. It is assumed that there are small FM domains which are contributed over an AFM sea and they are connected to each other by FM filaments, and these FM domains are responsible for the metallic state. But the possibility of an A-type AFM phase at low temperature is not ruled out.

4.2. Magnetoresistance behaviour of $La_{0.2}Ba_{0.1}Ca_{0.7}MnO_3$ thin films

According to the phase diagram of Schiffer *et al* [7], $La_{0.2}Ca_{0.8}MnO_3$ is an insulator over the whole range of temperatures. It is very surprising that Ba doping causes a very sharp IM

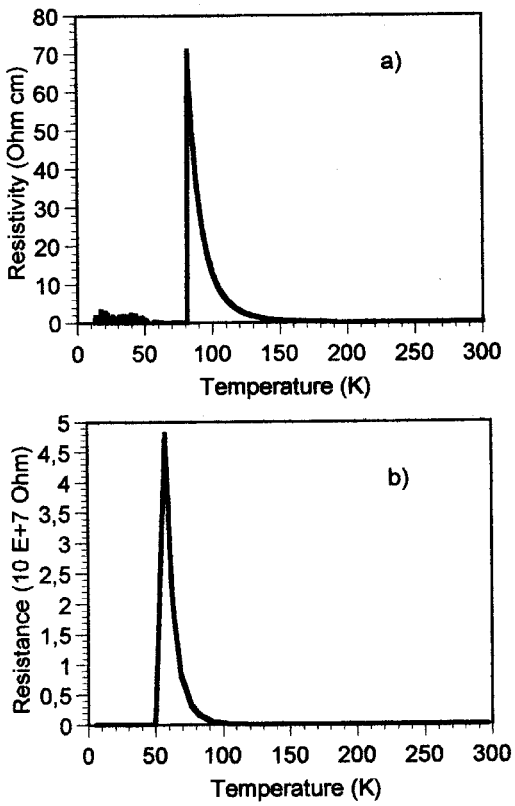

Figure 8. The temperature dependence of (a) resistivity under zero field by the four-probe method and (b) resistance under zero field by the two-probe method (measured four months after the measurement whose data are shown in (a)) for a $La_{0.35}Ba_{0.1}Ca_{0.55}MnO_3$ thin film.

transition at about 75 K even under zero field (see figure 9(a)). However, its MR behaviour which has been shown in figure 9(b) is very anomalous. At $H = 1$ T, T_{IM} shifts to a lower temperature (at about 32 K), and finally the material turns insulating at very low temperature (below 25 K). When the magnetic field increases above 1 T, the $\rho(T)$ curves remain the same as the case of $H = 1$ T. Somehow we may say that, above some critical value of magnetic field, $La_{0.2}Ba_{0.1}Ca_{0.7}MnO_3$ thin films are rather insensitive to the change of the magnetic field (usually a complete antiferromagnetic state has nothing to do with the magnetic field). The question arising here is why, under an application of the magnetic field, the material becomes less metallic or, in other words, it has a positive MR below T_{IM}. This cannot be explained by DE theory.

One more thing that should be mentioned here is that the material has a history effect. After applying a magnetic field of 5.5 T, the $\rho(T)$ curve under zero field measured on warming shows exactly the same behaviour as under 5.5 T. It is completely different from the cooling curve of $H = 0$ which was measured at the beginning.

The magnetization as a function of temperature and magnetic field, $[M(T)]$ and $[M(H)]$, can be seen from figure 10. The $M(T)$ curve shows that the magnitude of magnetization of the sample is rather small, and it just shows a very slight tendency of turning to an AF phase at low temperatures. There is no transition from PR to FM along with an IM transition at 70 K. However, from the $M(H)$ curve measured at 40 K (figure 10(b)), the assumption of the AF state

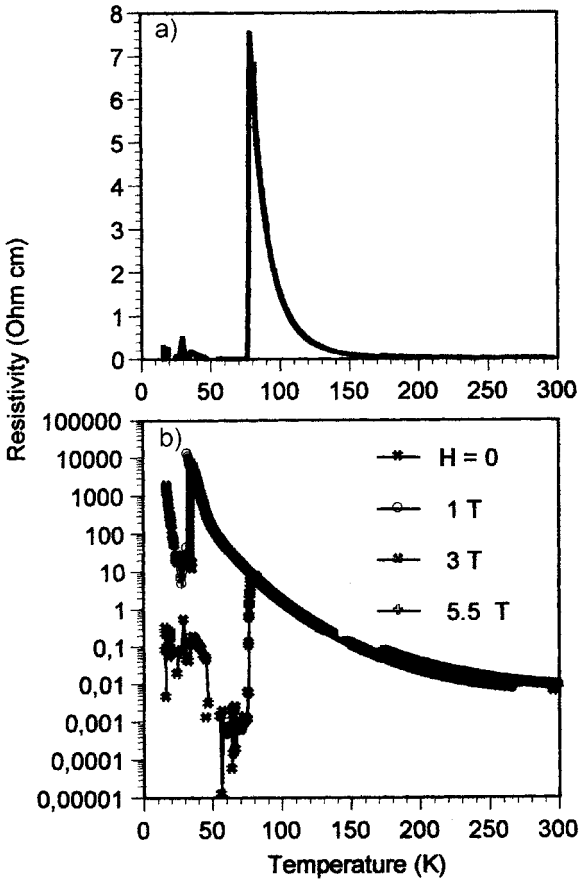

Figure 9. The temperature dependence of resistivity (a) under zero field and (b) under applied fields for a $La_{0.2}Ba_{0.1}Ca_{0.7}MnO_3$ thin film.

at low temperatures seems to be confirmed. It appears that $La_{0.2}Ba_{0.1}Ca_{0.7}MnO_3$ is an example of an AF metal. If AF is responsible for the metallic state, the anomalous field dependence mentioned above seems to be well explained. When the magnetic field increases, the AF phase is diminished, so that the material becomes more insulating. The antiferromagnetic metallic (AFM) phase in manganites has been reported by several groups recently [14–16] and in most cases, AFM is A-type. There is another possibility in that there might be some kind of structure like ferromagnetic filaments and those are distributed over the antiferromagnetic sea. However, since the samples are not single crystals, it is difficult to be so confirmative about their anisotropic behaviours. It may be discussed in the future.

4.3. Other compositions

$La_{0.3}Ba_{0.1}Ca_{0.6}MnO_3$, $La_{0.25}Ba_{0.1}Ca_{0.65}MnO_3$ and $La_{0.1}Ba_{0.1}Ca_{0.8}MnO_3$ thin films all have very similar transport and magnetic behaviours: having semiconductor-like temperature dependence in the whole range of temperatures, no IM transition and no influence of magnetic field on electrical properties (as the magnetic field increases, there is almost no change in resistance of the sample or we may say that the samples have no MR effect). The temperature dependence of the resistivity of a $La_{0.1}Ba_{0.1}Ca_{0.8}MnO_3$ thin film is shown in figure 11 as a

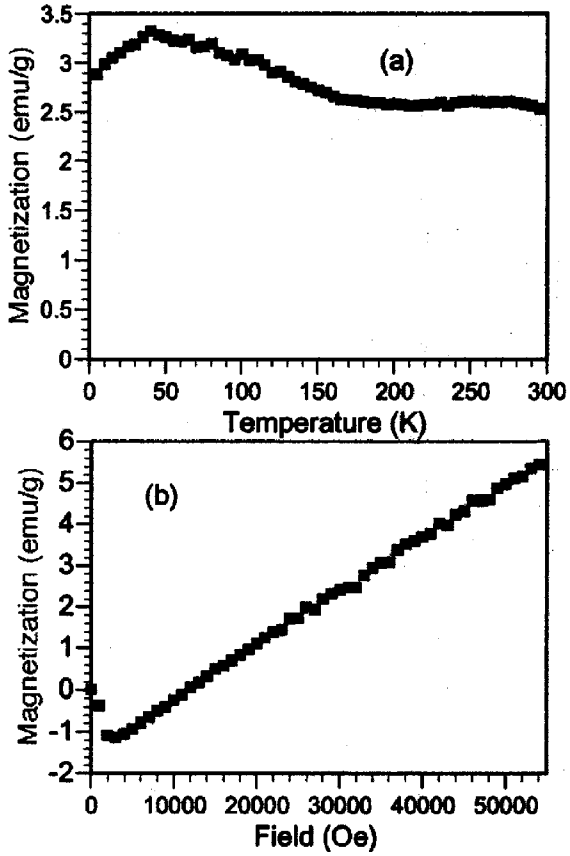

Figure 10. The magnetization of the $La_{0.2}Ba_{0.1}Ca_{0.7}MnO_3$ thin film (a) versus temperature at 3 T and (b) versus magnetic field at 40 K.

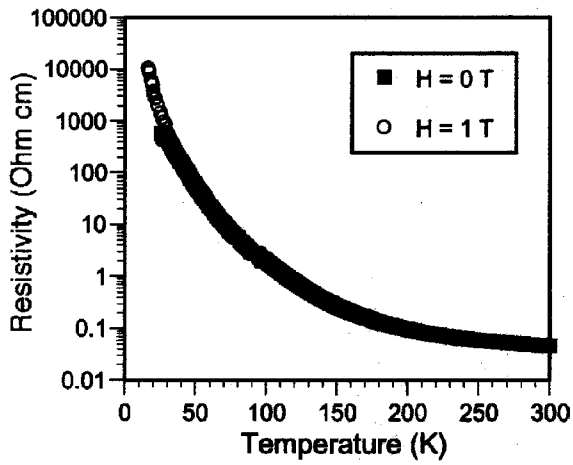

Figure 11. The temperature dependence of resistivity at various fields for a $La_{0.1}Ba_{0.1}Ca_{0.8}MnO_3$ film.

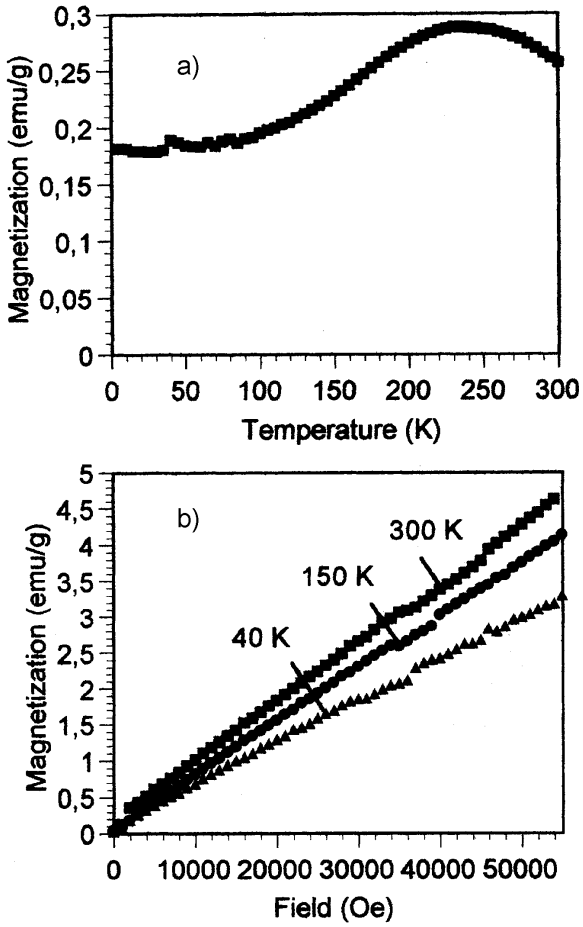

Figure 12. The magnetization of the $La_{0.1}Ba_{0.1}Ca_{0.8}MnO_3$ thin film (a) versus temperature at 3 T and (b) versus magnetic field at various temperatures.

typical example of compositions in this heavily doped region. The material has very low resistivity at room temperature (about 0.015 Ω cm), but when the temperature decreases it shows semiconductor-like temperature dependence. It is in accord with its magnetic property of being PR and then AF below T_{Neel} (seen from $M(T)$ data in figure 12(a)). Of course T_{Neel}s are a bit different for those three cases of $x = 0.7$, 0.75 and 0.9 (260, 270 and 240 K respectively). The AF phase is confirmed by $[M(H)]$ data at various temperatures (figure 12(b)).

4.4. Conclusion

Basically we may say that the diagram for compositions around 0.5 is very complicated. In the region between $x = 0.55$ and 0.65, at low temperature, there are presumably two possibilities: one is the coexistence of a CAFI phase and A-type AFM phase and another is the coexistence of a CAFI background and small FM domains (those FM domains connected to each other by FM filaments, that is why the material can be conductive).

In the heavily doped region, except $La_{0.2}Ba_{0.1}Ca_{0.7}MnO_3$ which shows IM transition (and it may be A-type AFM) and has positive MR (the sample becomes less metallic as a higher field is applied), all other compositions appear to be antiferromagnetic insulators. Since they

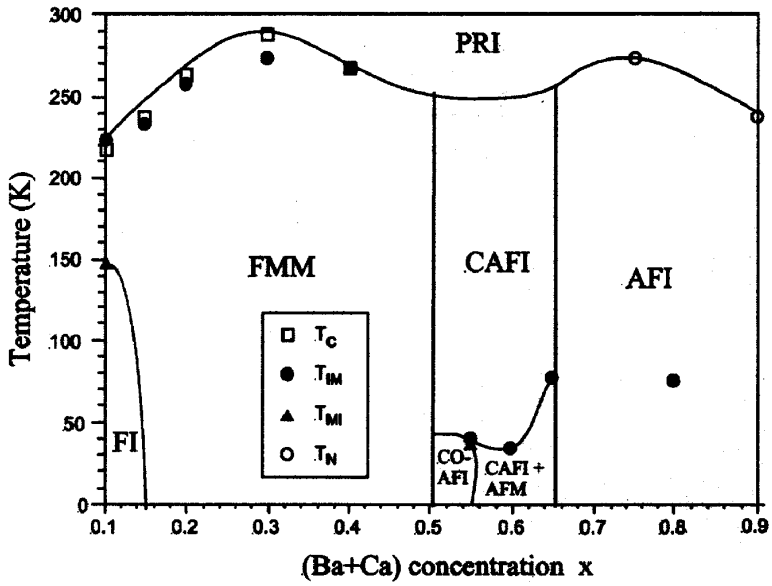

Figure 13. A tentative diagram for La–Ba–Ca–Mn–O thin films. (Actually in the region between $x = 0.55$ and 0.65, at low temperature, there are presumably two possibilities: one is the coexistence of CAFI phase and A-type AFM phase and another is the coexistence of CAFI background and small FM domains (those FM domains connected to each other by FM filaments, that is why the material can be conductive). But since there is a positive MR in this region, and also when x goes above 0.65, AFI phase dominates widely, then the first possibility is more likely.)

are completely AF, the magnetic fields have no influence on them, or in other words, they are very insensitive to the field. On the other hand, there is no trace of PS in this region.

By seeing the behaviours of compositions with $x > 0.65$, we may find that the AFI phase widely dominates in the heavily doped region. Along with the positive MR observed in the region of x in between 0.55 and 0.65, the assumption of the coexistence of CAFI and AFM states at low temperature in this critical interval seems to be more convincing.

5. Phase diagram for La–Ba–Ca–Mn–O thin films

A tentative diagram for $La_{1-x}(Ba, Ca)_xMnO_3$ (where Ba concentration in all cases is kept as 0.1 but 0.05 for the case of $x = 0.55$) is plotted in figure 13.

In the slightly doped region ($x < 0.5$), below T_C, the FMM phase dominates over most values of x, except the composition of $x = 0.1$ which shows insulating behaviour below 150 K. The FMM phase is remarkably expanded.

Ba doping induces IM transition in the case of $x = 0.8$, but it does not change much the transport and magnetic properties of other compositions (those materials are AF below 270–240 K as in the case of LCMO).

The biggest change appears in the region around 0.5. The phase diagram is very complicated because, around 0.5, there is a CO-AFI state, while above 0.55 the coexistence of two phases (CAFI and A-type AFM or CAFI and small FM domains) prevails.

6. Summary

Ba doping causes remarkable effects on transport and magnetic properties of LCMO thin films. We have obtained the IM transition in several compositions. This effect is expected

since the decrease in resistance is supposed to be caused by the effect of the big radius of Ba ions. The induced IM transition appears not only in compositions near 0.5 and 0.18 which are boundaries between metallic and insulating phases, but also in the heavily doped region ($x = 0.8$), which is well known as insulating over the whole range of temperature. What needs to be emphasized here is that the Ba doping causes an anomalous response of the system to the magnetic field ($x > 0.5$). When the magnetic field increases, T_{IM} shifts to a lower temperature and a positive MR was observed. These cannot be explained by DE theory. Besides, the results of compositions near 0.5 imply the existence of PS. As for the region of $x < 0.5$, Ba doping well enhances the FMM phase. In some cases, the materials have T_C and T_{IM} about room temperature which might be useful for applications.

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References

[1] Wu Y, Suzuki Y, Rudiger U, Yu J, Kent A D, Nath T K and Eom C B 1999 *Appl. Phys. Lett.* **75** 2295
[2] Prellier W, Lecoeur Ph and Mercey B 2001 *J. Phys.: Condens. Matter* **13** R915
[3] Damay F, Maignan A, Martin C and Raveau B 1996 *J. Appl. Phys.* **81** 1372
[4] Kumar D, Singh R K and Lee C B 1997 *Phys. Rev.* B **56** 13666
[5] Hong N H, Sakai J and Imai S 2000 *J. Appl. Phys.* **87** 5600
[6] Hong N H, Sakai J and Imai S 2001 *J. Appl. Phys.* **89** 6976
[7] Schiffer P, Ramirer A P, Bao W and Cheong S W 1995 *Phys. Rev. Lett.* **75** 3396
[8] Prellier W, Rajeswari M, Venkatesan T and Greene R L 1999 *Appl. Phys. Lett.* **75** 1446
[9] Shreekala R, Rajeswari M, Srivastava R C, Ghosh K, Goyal A, Srinivasu V V, Lofland S E, Bhagat S M, Downes M, Sharma R P, Ogale S B, Green R L, Ramesh R, Venkatesan T, Rao R A and Eom C B 1999 *Appl. Phys. Lett.* **74** 1886
[10] Urushibara A, Moritomo Y, Arima T, Asamitsu A, Kido G and Tokura Y 1995 *Phys. Rev.* B **51** 14103
[11] Okuda T, Tomioka Y, Asamitsu A and Tokura Y 2000 *Phys. Rev.* B **61** 8009
[12] Moreo A, Yunoki S and Dagotto E 1999 *Science* **283** 2034
[13] Lawler J F, Lunney J G and Coey J M D 1994 *Appl. Phys. Lett.* **65** 3017
[14] Yoshihara H, Kawano H, Fernandez-Baca J A, Kuwahara H and Tokura Y 1998 *Phys. Rev.* B **58** R571
[15] Akimoto T, Maruyama Y, Moritomo Y, Nakamura A, Hirota K, Ohoyama K and Ohashi M 1998 *Phys. Rev.* B **57** R5594
[16] Moritomo Y, Akimoto T, Nakamura A, Ohoyama K and Ohashi M 1998 *Phys. Rev.* B **58** 5544