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Ru-doped $La_{0.7}(Ba–Ca)_{0.3}MnO_3$ thin films: indirect evidence of phase separation

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Abstract

Magnetic and transport properties of thin films of $La_{0.7}Ba_xCa_{0.3-x}Mn_{1-y}Ru_yO_3$ (where $x = 0.1$, 0.2, 0.3 and $y = 0$, 0.1) fabricated using the pulsed laser deposition technique have been investigated. While La–Ba–Ca–Mn–O samples with no doping on B-sites show very strong ferromagnetism with a rather high T_C, Ru-doped samples have a much lower T_C. This reduction of ferromagnetism is consistent with the results obtained from transport measurements: under zero field, $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin films shows an insulator-to-metal transition at 75 K, the transition temperature shifts to lower temperatures under applied magnetic fields, and a positive magnetoresistance (MR) was observed. It is likely that Ru doping creates some antiferromagnetic insulating matrix which separates a basically ferromagnetic background into isolated ferromagnetic domains so that, even though the phase is ferromagnetic, it is not conductive. A ferromagnetic-insulating state appears in the composition of $x = 0.3$ hole-doped concentration, which is very unexpected, and the positive MR is also very anomalous.

1. Introduction

Thin films of manganese oxides $Re_{1-x}A_xMnO_3$ (where Re is a rare earth and A is an alkali earth element) have attracted many researchers over the last decade, since these materials appear to be rather good candidates for potential applications in industry due to them exhibiting a large change in electrical resistance when an external magnetic field is applied [1–3]. Along with work that has been searching for the colossal magnetoresistance (CMR) effect under very low fields, the search for materials that have an insulator-to-metal (IM) transition along with a paramagnetism-to-ferromagnetism transition above room temperature has received intensive focus. In order to achieve this goal, many groups have also tried various types of dopants on the A-site (Re, A) and the B-site (Mn) [4–7].

According to the results reported so far, $Re_{1-x}A_xMnO_3$ compounds with Ba, Sr and Pb substituted partially on the A-site have rather a high T_C, while doping on the Mn site usually reduces T_C [8]. Some reports on La–Ba–Ca–Mn–O thin films with a Ba concentration of 0.1 showed that the Ba doping has a remarkable advantage in the enhancement of T_C [9]. On the other hand, some groups tried to dope Ru on the B-site in several manganese oxide compounds and obtained some opposite effects: Ru doping increases remarkably both the ferromagnetism (heightening T_C) and the metallicity in manganites with a hole-doped concentration x of around 0.5 [7, 10, 11] but it decreases T_C by 30 K in $La_{0.7}Sr_{0.3}MnO_3$ thin films [8, 12]. Since Ru appears to be an interesting dopant which may bring about some drastic changes in the physical properties of manganites, in this work, Ru was chosen to substitute partially for Mn in $La_{0.7}Ba_xCa_{0.3-x}MnO_3$ with $x = 0.1$, 0.2 and 0.3. $La_{0.7}(Ba–Ca)_{0.3}MnO_3$ was taken as a parent composition, since it is well established as a ferromagnetic metal over a wide range of temperatures with a rather high T_C. Some big changes in magnetic and transport properties are expected.

2. Experiment

$La_{0.7}Ba_xCa_{0.3-x}Mn_{1-y}Ru_yO_3$ targets (with $x = 0.1, 0.2, 0.3$ and $y = 0, 0.1$) were prepared by either a conventional solid-state reaction method or a sol–gel method, which has been described elsewhere [9, 15]. Film deposition on [100] $LaAlO_3$ substrates was carried out using the pulsed laser deposition technique (for fabrication conditions, see [9, 16]). The typical thickness of the films was 200 nm. X-ray diffraction (XRD) confirmed that all our ceramic targets are single phase and crystallized, and all films are highly epitaxial and c-axis oriented (from figure 1, one can see that only the (100) and (200) peaks that align to the orientation of the substrate appear, and that those peaks of the films are very sharp). On the other hand, we can also see from the XRD pattern that the peaks in the spectrum of a Ru-doped film are shifted compared to those of a non-Ru-doped film (indicating that, even though Ru doping does not change the type of structure, it shortens the c-axis length by about 0.5% and it is remarkable enough for such a low doping). One can say that Ru really gets 'into' the structure. This is in accord with our energy dispersive x-ray (EDX) data: even though, as for thin films, it is very difficult to determine the contents precisely, the Ru content is determined to be about 0.056 in the case of $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ films for example, so it is evident that Ru is incorporated into our films. The electrical resistance has been measured upon cooling from 350 K down to He temperature under magnetic fields from zero up to 6 T using a conventional four-probe method and a superconducting magnet. The magnetization of the films has been measured using a quantum design superconducting quantum interference device magnetometer (SQUID).

3. Results and discussions

Magnetization under 0.2 T as a function of temperature for $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$, $La_{0.7}Ba_{0.2}Ca_{0.1}MnO_3$ and $La_{0.7}Ba_{0.3}MnO_3$ thin films is shown in figure 2. As we can see, when the concentration of Ba increases, T_C increases. This is in accord with the argument of many previous reports that says that, when the average size of the A-site ion increases, T_C increases [4, 9]. In all cases T_C is rather high—around room temperature—which is much higher than that of $La_{0.7}Ca_{0.3}MnO_3$ bulk (at 250 K) [13] and $La_{0.7}Ca_{0.3}MnO_3$ thin films [14] reported so far. Along with the heightening of T_C, the Ba doping also enhances insulator-to-metal transition temperature (T_{IM}) remarkably. So, as a result, one must say that doping with Ba made the ferromagnetic metallic phase of La–Ca–Mn–O expand greatly.

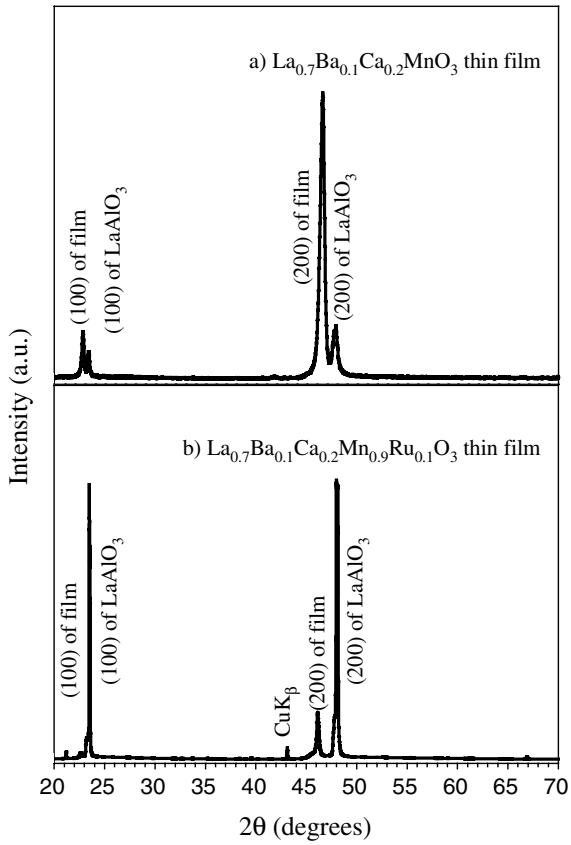

Figure 1. An XRD pattern for (a) a $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$ thin film and (b) a $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin film.

The temperature dependence of magnetization at 0.2 T for Ru-doped films is shown in figure 3. Due to Ru doping, T_C has been reduced greatly. In $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin films T_C is about 190 K (about 100 K lower than that of $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$ thin films prepared by exactly the same growth conditions) and in $La_{0.7}Ba_{0.2}Ca_{0.1}Mn_{0.9}Ru_{0.1}O_3$ thin films T_C is 240 K (70 K lower than that of $La_{0.7}Ba_{0.2}Ca_{0.1}MnO_3$ thin films, compared with the data from figure 2). Since Ru doping heightens T_C in many compounds [7, 10, 11] and the decrease in T_C of about 30 K by doping was reported as a very 'unusual' effect [8, 12], it is then very surprising that in Ru-doped La–Ba–Ca–Mn–O thin films, the Ru doping lowers T_C drastically or, in other words, it reduces the ferromagnetism remarkably.

Resistance measurements for thin films of $La_{0.7}Ba_xCa_{0.3-x}MnO_3$ with $x = 0.1$, 0.2 and 0.3 show that those films have a rather high T_{IM}—almost the same as T_C (only a few degrees lower)—and exhibit a typical magnetoresistance (MR) picture, with the resistance depressed when a magnetic field is applied (the CMR effect). The temperature dependence of resistivity at various fields for $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$, $La_{0.7}Ba_{0.2}Ca_{0.1}MnO_3$ and $La_{0.7}Ba_{0.3}MnO_3$ film is shown in figure 4. Under zero field, the values of T_{IM} are 275, 305 and 320 K, respectively. When a higher field is applied, T_{IM} shifts to a higher temperature and the resistance is depressed greatly (a negative MR is observed). It is known that, when the mean size of A-site cations increases, T_C (and T_{IM}, as a result) increases, but the MR ratio decreases. Therefore, figure 4

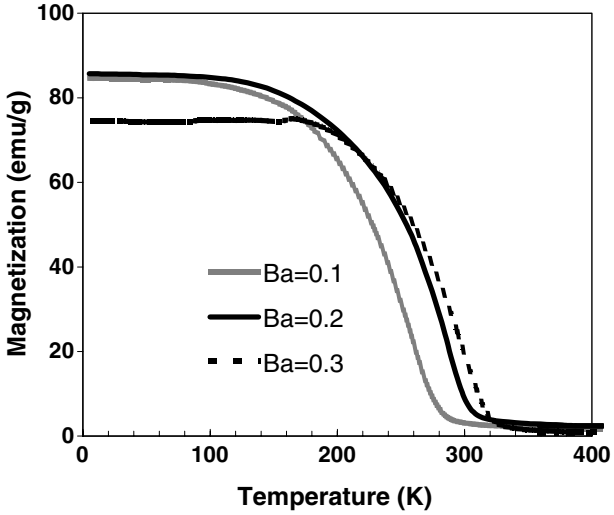

Figure 2. The temperature dependence of magnetization at 0.2 T for $La_{0.7}Ba_xCa_{0.3-x}MnO_3$ thin films ($x = 0.1, 0.2, 0.3$).

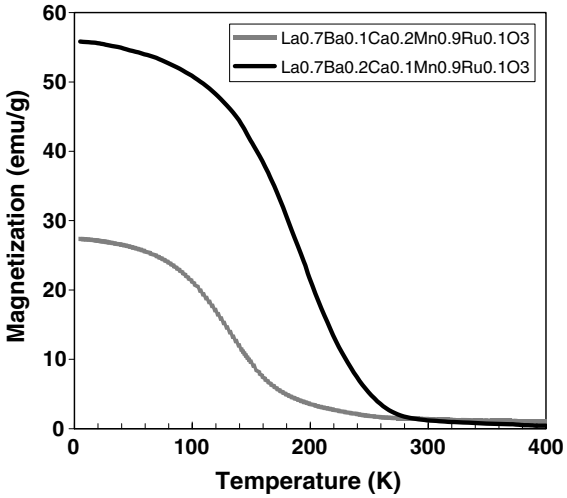

Figure 3. Temperature dependence of magnetization at 0.2 T for $La_{0.7}Ba_xCa_{0.3-x}Mn_{0.9}Ru_{0.1}O_3$ thin films ($x = 0.1$ and 0.2).

just reflects this conventional behaviour: when the Ba concentration is increased, T_{IM} increases (in accord with the increase of T_C as x increases, which can be seen from figure 2(a)).

The MR picture of $La_{0.7}Ba_{0.2}Ca_{0.1}Mn_{0.9}Ru_{0.1}O_3$ films (figure 5(a)) is not very different from that of $La_{0.7}Ba_{0.2}Ca_{0.1}MnO_3$ films (figure 4(b)). Ru-doped $La_{0.7}Ba_{0.2}Ca_{0.1}MnO_3$ films have a T_{IM} that is 13 K lower than T_C (T_{IM} under zero field is 227 K while T_C is about 240 K, as seen from figure 2). Also, T_{IM} shifts to the higher-temperature region when the magnetic field is increased and, as a result, a negative MR is obtained.

It is very surprising that Ru doping causes completely different effects on $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$ films. Figure 5(b) shows the resistivity of a $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$

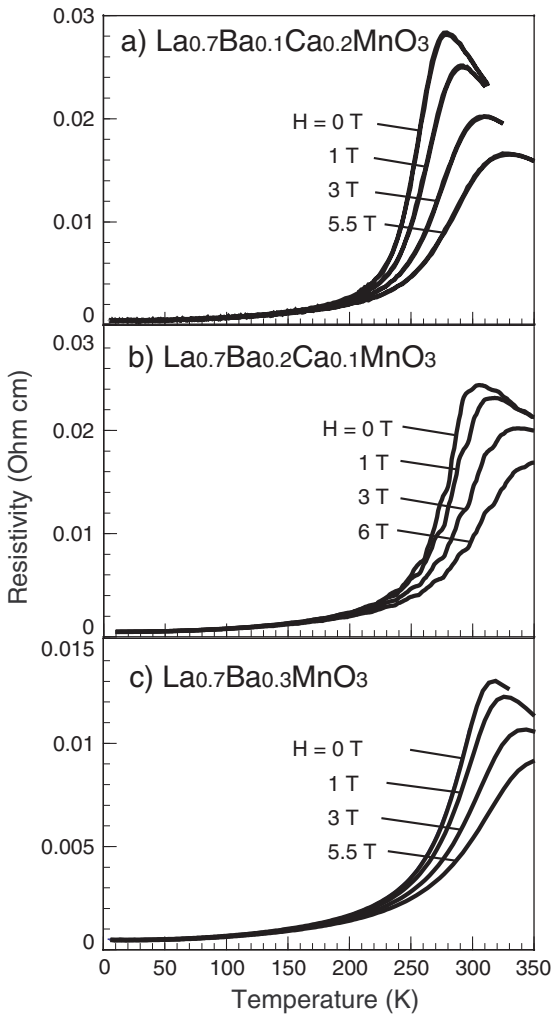

Figure 4. The temperature dependence of resistivity at various fields for $La_{0.7}Ba_xCa_{0.3-x}MnO_3$ thin films ($x = 0.1, 0.2, 0.3$).

film measured at various fields upon cooling. Under $H = 0$, the material is insulating in the high-temperature region, but it turns to showing metallic behaviour at about 75 K. When the magnetic field increases, T_{IM} shifts to the lower-temperature region ($H = 1$ T, $T_{IM} = 65$ K; $H = 3$ T, $T_{IM} = 57$ K) and, along with this anomalous response to the magnetic field and somewhat below T_{IM}, a positive MR is clearly observed. Another point that should be noticed here is that the resistivity of the $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ film is several orders of magnitude larger than that of the $La_{0.7}Ba_{0.2}Ca_{0.1}Mn_{0.9}Ru_{0.1}O_3$ film (from the comparison between figures 5(a) and (b)). This is in accord with the fact that the T_{IM} of the $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ film is much lower than that of the $La_{0.7}Ba_{0.2}Ca_{0.1}Mn_{0.9}Ru_{0.1}O_3$ film or, in other words, the $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ sample is much less metallic.

From the data of figures 3 and 5(b), it appears that $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ is in a ferromagnetic-insulating (FI) phase between 75 and 190 K. Actually, so far the FI phase has not been explained satisfactorily by the double exchange (DE) theory. However, it does exist

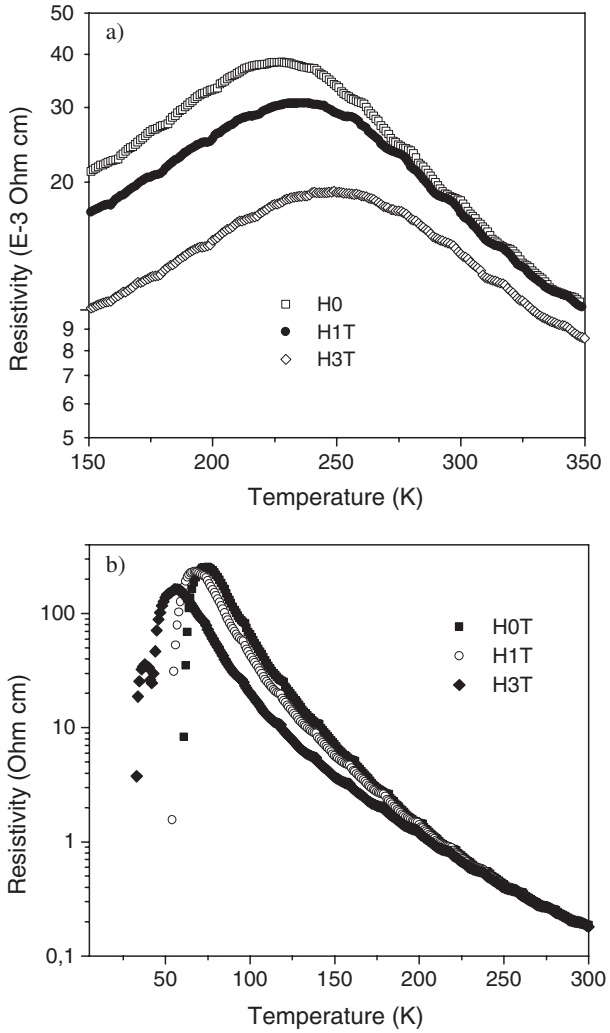

Figure 5. The temperature dependence of resistivity at various fields for (a) a $La_{0.7}Ba_{0.2}Ca_{0.1}Mn_{0.9}Ru_{0.1}O_3$ thin film and (b) a $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin film.

in manganites, basically in very low-doped compositions. One reasonable explanation for this state is a model of large FM (ferromagnetic) domains which are isolated (as a whole, they contribute to ferromagnetism, which is why T_C is still 190 K and the magnitude of magnetization is not very small, but the material cannot be conductive because of the isolation). Basically, since manganites with a hole-doped concentration of 0.3 are known to be strongly ferromagnetic metals over a wide range of temperatures with a rather high T_C, the FI phase appearing in $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ is very unexpected. It is assumed that Ru doping creates some kind of antiferromagnetic insulating (AFI) matrix which separates the ferromagnetic metallic (FMM) background into isolated domains (which are still large in volume), but then, on the whole, they are not conductive, therefore both ferromagnetism and metallicity decrease. As an aid to the imagination, a schematic diagram is shown in figure 6. On the other hand, the magnitude of magnetization of $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ films (see figure 3) is much

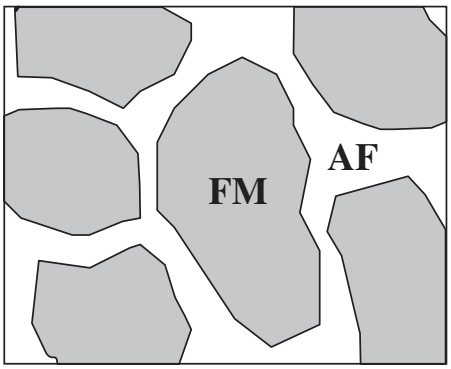

Figure 6. A schematic diagram of the phase separation, which is assumed to be responsible for the ferromagnetic insulating phase between 75 and 190 K of $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin films. The grey parts indicate FM domains (separated by a kind of AF matrix).

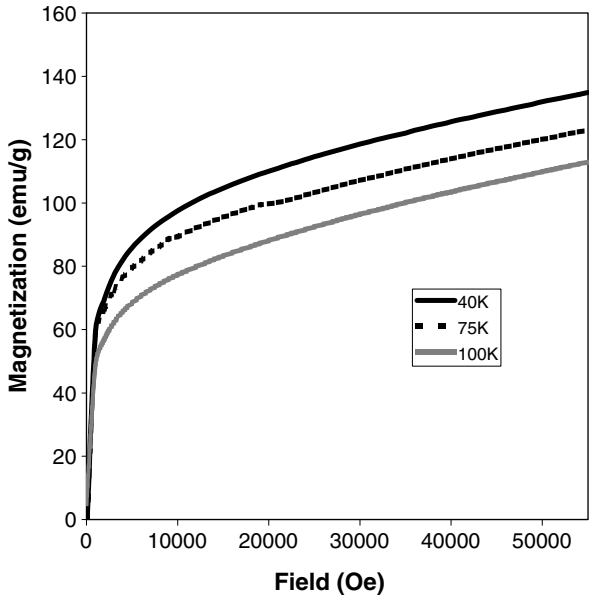

Figure 7. The field dependence of magnetization at 40, 75 and 100 K for the $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin film.

smaller than that of other manganite films with $x = 0.3$ (about a third—see a typical example in figure 2), so the assumption about the coexistence of FM and antiferromagnetic (AF) phases seems to be reasonable. This assumption is enforced by the $M(H)$ curves taken at various temperatures (figure 7): the magnetization does not reach saturation right after the steep rise at low field but a down slope exists for a wide range of fields, and also no remanent magnetic moment is observed. It appears that the sample is not strongly ferromagnetic and there must be some partial contribution to the magnetization from the AF phase. From the shape of those curves, one may say that the AF phase mentioned above seems to be canted AF (CAF). The feature of the FI state is seen not only in Ru-doped films but also in Ru-doped bulk. The resistivity and magnetization versus temperature of $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ bulk (which,

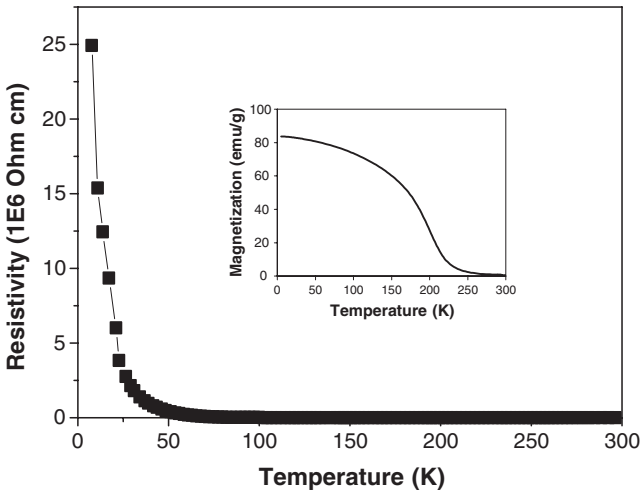

Figure 8. Temperature dependence of resistivity under zero field of a $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ bulk sample (a piece cut from the target). The inset shows the magnetization versus temperature at 0.2 T.

by using a small piece cut from the target from which the films were fabricated, should be the most meaningful data to compare) are shown in figure 8. The T_C (determined from the inflection of the $M(T)$ curve undertaken at 0.2 T) is about 220 K (a bit higher than that of the corresponding film), but the sample shows completely insulating behaviour over the whole range of temperatures, with no transition to the metallic state. It is usual that in the bulk, due to the grain boundary effects, the metallicity is often much weaker than that in the films (for example, in the case of $La_{0.7}Ba_{0.1}Ca_{0.2}MnO_3$, the T_{IM} of a piece of the target is 100 K, while it is 275 K for the corresponding films [17]). Figure 8 shows clearly that the FI phase is well observed in $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ bulk, therefore one can say that the FI phase observed in Ru-doped La–Ba–Ca–Mn–O films is due to Ru doping, but not due to any special quality of the films. On the other hand, this unusual effect occurs in only one special composition (x and $y = 0.1$) but no anomaly was observed in the other case (such as $x = 0.2$ and $y = 0.1$). Thus some assumptions about the cause of the unexpected FI phase, such as strain effects due to the substrate etc, are ruled out.

Besides the unexpected FI phase, the observation of T_{IM} far below T_C is another anomaly. Many papers have reported that T_{IM} and T_C are almost the same (see reference [18]). This is in accord with DE theory, which claims that a material used to be FM if it is in a metallic state. Lofland *et al* [18] reported that, in $La_{0.8}Sr_{0.2}MnO_3$ single crystal, T_{IM} is about 318 K while T_C is 302 K, and it was assumed that it was very important that this difference was taken into account while completing the theory of CMR materials. Krisnan and Ju [12] ascribed the difference of about 35 K between T_C and T_{IM} to the effect of grain boundaries or the loss of oxygen, based on the fact that they noticed that the target was not well sintered (T_{IM} became almost the same as T_C when they re-sintered the target). In other La–Ba–Ca–Mn–O thin films we usually obtained a T_{IM} of a few degrees lower than T_C [9], therefore the difference of 115 K between these two transition temperatures observed in $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ films is really worth noting. However, the effect of the grain boundaries or oxygen loss does not seem to be the reason for them being far apart, because our target was very well sintered.

The fact that the FI phase appears over a very wide range of temperatures for the composition $x = 0.3$ is less anomalous than the MR behaviour in these materials. The positive

MR had already been observed in $La_{0.4}Ba_{0.1}Ca_{0.5}MnO_3$ thin films and other compositions with x near 0.5 [16], and those features are somehow similar to what has been observed in Ru-doped films with $x = 0.3$. In manganites, the application of a magnetic field usually enhances T_{IM} and the resistance is significantly suppressed (the CMR phenomena). The tendency of the magnetic field dependence of T_{IM} and the positive MR observed in compositions with x near 0.5 as well as in $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin films cannot be explained by the DE mechanism. In [16] it was assumed that it is due to the phase separation for compositions with x around the critical region of 0.5, and the FM domains in those compositions were assumed to be rather small. Since the magnitude of magnetization of the $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin films is about one order larger than that of $La_{0.4}Ba_{0.1}Ca_{0.5}MnO_3$ thin films and the material is clearly in the FM phase, the FM domains that exist in $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin films are definitely not small. However, the mechanisms which govern the MR behaviour of $La_{1-x}(Ba–Ca)_xMnO_3$ thin films (with x near 0.5) and $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ are probably the same.

The positive MR was also reported in [19–21], but in [19, 20] it was observed at the charge-ordering phase transition (at the PR–FM transition the MR is negative, as expected from DE theory). Our case is more similar to the case of [20] concerning the positive MR at low temperature between 50 and 4.2 K for a $La_{0.7}Pb_{0.3}MnO_3$ single crystal. However, in this report, Chen *et al* ascribed the positive MR to the quantum interference effects at low temperatures only, below 30 K (it is assumed that, at low temperatures, Coulomb interaction and disorder might play important roles), since at high temperature they obtained a normal negative MR with T_{IM} shifted to a higher temperature when a higher magnetic field is applied. Therefore, the nature of the positive MR in our case could not be the same.

Based on the positive MR feature of $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$, one may say that there is a possibility that, at low temperatures, there are some antiferromagnetic metallic (AFM) domains that coexist with isolated FM domains and the AFI matrix. If the AF is responsible for the metallic state, the anomalous field dependence seems to be well explained. When the magnetic field increases, the AF phase is diminished so that the material becomes more insulating. The AFM phase in manganites has recently been reported by several groups, in most cases for the critical region near $x = 0.5$, and AFM is A-type, i.e. FM on the *ab* plane and AF along the *c*-axis [22–24]. This assumption needs to be clarified in the near future with supportive data from STM/MFM measurements performed on those films.

So far, in manganites, the reduction of T_C caused by Ru doping has been found only in thin-film form, but in our case it is also found in both films and bulks (a similar feature was observed in $La_{0.75}Sr_{0.25}Mn_{1-y}Ru_yO_3$ and $La_{0.8}Sr_{0.2}Mn_{1-y}Ru_yO_3$ bulks, where $y = 0.05$, 0.1, 0.15 and 0.2 [25]). Therefore, we can say that the Ru doping may improve the ferromagnetism and metallicity in the 'charge-ordering' compounds [7, 10, 11] but the mechanism is completely different for the low-doped region. In a ferromagnetic metallic composition, it is likely that Ru doping reduces the ferromagnetism and metallicity as well. On the other hand, since the responses of the resistance to the magnetic field are completely different for $La_{0.7}Ba_{0.2}Ca_{0.1}Mn_{0.9}Ru_{0.1}O_3$ thin films and $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin films, the balance of chemical pressures inside the lattice (on A-sites and B-sites) should be taken into account [26]. In the case of $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin films, there must be strong competition between the two phases.

4. Conclusion

In summary, while doping with Ba partially on A-sites in $La_{0.7}Ca_{0.3}MnO_3$ thin films enhances T_C, doping with Ru on B-sites (Mn) reduces T_C drastically. In the special case of $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin films, besides the reduction of T_C of 100 K, Ru doping

also causes other anomalous effects: since the IM transition appears at much lower temperature ($T_{IM} = 75$ K, 115 K lower than T_C), it is obvious that there is a ferromagnetic insulating (FI) phase over a wide range of temperatures. On the other hand, when the magnetic field increases, T_{IM} shifts to the lower-temperature region and a positive MR is observed. This phenomenon cannot be explained by DE theory. It is assumed that, in $La_{0.7}Ba_{0.1}Ca_{0.2}Mn_{0.9}Ru_{0.1}O_3$ thin films, Ru doping creates some antiferromagnetic matrix in the form of separating a ferromagnetic (FM) background into isolated FM domains. Moreover, in the low-temperature region, there might be an antiferromagnetic metallic phase which coexists and is responsible for the observed metallic state.

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