Electrical transport and low-field magnetoresistance in the series of mixed polycrystals (1-*m*)$La_{2/3}Ca_{1/3}MnO_3$ + *m*$La_{2/3}Sr_{1/3}MnO_3$

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Electrical transport and low-field magnetoresistance in the series of mixed polycrystals $(1 - m)La_{2/3}Ca_{1/3}MnO_3 + mLa_{2/3}Sr_{1/3}MnO_3$

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Abstract

The perovskites of $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) and $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) were synthesized by the sol–gel method. The two perovskites were mixed into polycrystalline materials, $(1 - m)$LCMO + mLSMO, where m is the relative weight ratio of LSMO. The compound with $m \sim 0.3$–0.5 has the lowest semiconductor–metal transition temperature T_p and the largest low-T resistivity. Moving away from this ratio, T_p increases while the low-T resistivity decreases with increasing or decreasing m. Measurements of the magnetoresistance (MR) show that the mixed polycrystals exhibit a sizable MR effect in low magnetic fields which increases upon cooling and reaches its largest value for $T \to 0$ K. It is also interesting to observe the almost T-independent MR effect over a wide temperature window below 300 K for the mixed materials with smaller m.

1. Introduction

The discovery of colossal magnetoresistance (CMR) in $La_{1-x}B_xMnO_3$ (B = Ca, Sr, Ba) ABO_3-type perovskites has renewed interest in achieving a theoretical understanding of the fundamental physics and in its potential applications [1]. For most CMR materials, a semiconductor–metal (S–M) transition characterized by a peak in the zero-field ρ-versus-T curve at the temperature T_p is usually accompanied by a simultaneous paramagnetic-to-ferromagnetic transition at the Curie temperature T_c [2]. Therefore, the metallic conduction below T_p is naturally thought to be due to the alignment of Mn spins. This has been well understood within the framework of the double-exchange mechanism [3]. Because the alignment of Mn spins around the magnetic transition is highly sensitive to the applied magnetic fields, the application of the fields causes a substantial reduction in resistance near T_c and hence also the CMR. This effect is commonly thought to be related to the intrinsic properties of the system and usually achieved by applying high fields (typically a few teslas).

Besides the CMR, growing attention is also being paid to another kind of magnetoresistance [4–12], namely the so-called low-field magnetoresistance (LFMR). The LFMR

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is thought to be extrinsic in nature and its origin lies in the existence of grain boundaries. Many methods are used for synthesizing fine grains in order to increase the boundary effect and hence to improve the LFMR, for example the sol–gel method [6], the mechanical alloying method [8] and mechanochemical processing [11]. From a practical viewpoint, both the larger MR effect at low fields and the temperature-independent MR behaviour over a wide temperature window around room temperature are of importance. However, as recently demonstrated for LSMO [10], the LFMR has a saturation value of about 30% if only altering the size of the grains is considered. The LFMR, on the other hand, is shown to increase with decreasing temperature and reach its largest value as $T \rightarrow 0$ K, as observed in polycrystalline thin films and bulk materials [5, 13, 14].

Although the grain boundaries are thought to play an essential role in improving the LFMR, attention is generally focused on grain boundaries between grains of the same kind. For mixed polycrystals consisting of two different manganites, besides the grain boundaries between grains of the same kind, additional boundaries between grains of different kinds would be introduced into the system. This introduction of additional boundaries is likely to further improve the LFMR. In order to realize a wider temperature window over which the MR keeps constant, on the other hand, a possible route is to mix two kinds of manganite using their different transition temperatures. On the basis of these considerations, in the present work we report the preparation of various mixed polycrystals consisting of LCMO and LSMO, and the investigation of their transport properties at low magnetic fields.

2. Experiment

The LCMO and LSMO powders, with nominal compositions of $La_{2/3}Ca_{1/3}MnO_3$ and $La_{2/3}Sr_{1/3}MnO_3$, respectively, were prepared by a sol–gel method similar to that described in reference [6]. This method has the advantage of using low-temperature synthesis, which results not only in smaller grains but also produces high-purity and homogeneous powders. The thus-prepared powders were ground, pelletized and then sintered in air at ∼1100 °C for 12 h for LCMO and at ∼1150 °C for 12 h for LSMO. The resulting samples were reground in order to powder them. The thus-prepared LCMO and LSMO powders were taken as the starting materials for preparing the mixed polycrystals in a weight ratio m, where

$$m = \frac{M_{\mathrm{Sr}}}{M_{\mathrm{Ca}} + M_{\mathrm{Sr}}}$$

(M_{Sr} and M_{Ca} are the weights of the LSMO and LCMO powders, respectively). The mixture was ground and mixed thoroughly, then pelletized and finally annealed at 1050 °C for two hours in air. The structure was examined by powder x-ray diffraction with a 12 KW D/max-RB diffractometer at room temperature with Cu Kα radiation. The temperature- and magnetic-field-dependent resistivity was measured with the standard dc four-probe method.

3. Results and discussion

The structural characterization of the powder samples was carried out by means of x-ray diffraction. The x-ray patterns obtained for four samples with $m = 0$, 0.25, 0.67 and 1 are shown in figure 1. The results indicate that the two end numbers of the mixed materials ($m = 0$ and 1) crystallize in a single phase, showing the characteristic peaks of the perovskite as previously reported [6]. Because the two end materials have the same crystalline structure and close lattice parameters, almost the same diffraction pattern should be expected when they are mixed. As shown in figure 1 for the samples with $m = 0.25$ and 0.67, no detectable difference

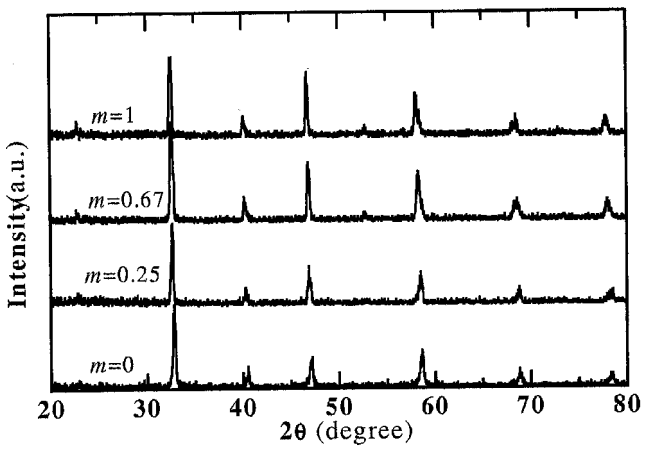

Figure 1. Powder x-ray diffraction patterns for the mixed polycrystals of $(1-m)La_{2/3}Ca_{1/3}MnO_3 + mLa_{2/3}Sr_{1/3}MnO_3$.

in diffraction pattern is indeed observed except for a slight decrease in each corresponding diffraction angle upon increasing m. This fact, however, does not imply that mixed materials have a single-phase perovskite crystalline structure.

Measurements of the resistivity for the two end materials show conduction behaviours similar to those previously reported for them [2, 15]. The LCMO (figure 2(a)) shows activated semiconducting behaviour at high temperatures and a transition to metallic behaviour at low temperatures. The transition is characterized by a resistance maximum at the temperature $T_p \sim 260$ K. The application of a low magnetic field causes sizable MR effects. Defining the magnetoresistance effect by $\mathrm{MR}(\%) = [(\rho(0,T) - \rho(H,T))/\rho(0,T)] \times 100\%$, we obtain the MR as a function of temperature which is also plotted in the figure. Two kinds of MR effect can be readily distinguished in the figure. The first one appears around the transition which corresponds to the so-called CMR commonly observed in LCMO. The second one is due to the grain boundaries and basically shows an increase with decreasing temperature over the whole temperature range studied. The temperature dependences of the resistivity measured in zero field and in an applied magnetic field are shown in figure 2(b) for LSMO. As commonly reported in the literature, this compound exhibits metallic conduction over the whole temperature range below room temperature. The application of the field also causes a sizable MR effect that increases with decreasing temperature and the largest MR effect appears as the temperature decreases towards 0 K.

We also measured the resistivity as a function of temperature for the mixed polycrystals. Shown in figure 3(a) is the temperature dependence of the normalized resistivity measured in zero field for mixed polycrystals with $0.1 \leqslant m \leqslant 0.9$. It can be seen that each mixed polycrystal shows a semiconductor-like conduction behaviour at high temperatures and undergoes a transition to metal-like conduction behaviour at low temperatures. The transition temperature T_p determined from the maximum in the $\rho/\rho(300\ \mathrm{K})$–$T$ curve is plotted in figure 3(b) as a function of m. It can be seen that T_p decreases with increasing m, reaches a minimum when $m \sim 0.3$–0.5 and then increases upon further increasing m. It is also noted that for all of the mixed polycrystals studied, T_p is always lower than that for the pure LSMO and that for the pure LCMO and the transition occurs smoothly over a wide temperature range.

The effects observed in the mixed polycrystals cannot be simply considered to be a result of replacing Ca^{2+} with Sr^{2+} as reported [8, 12] for $La_{0.7}(Ca_{1-x}Sr_x)_{0.3}MnO_3$. For the latter,

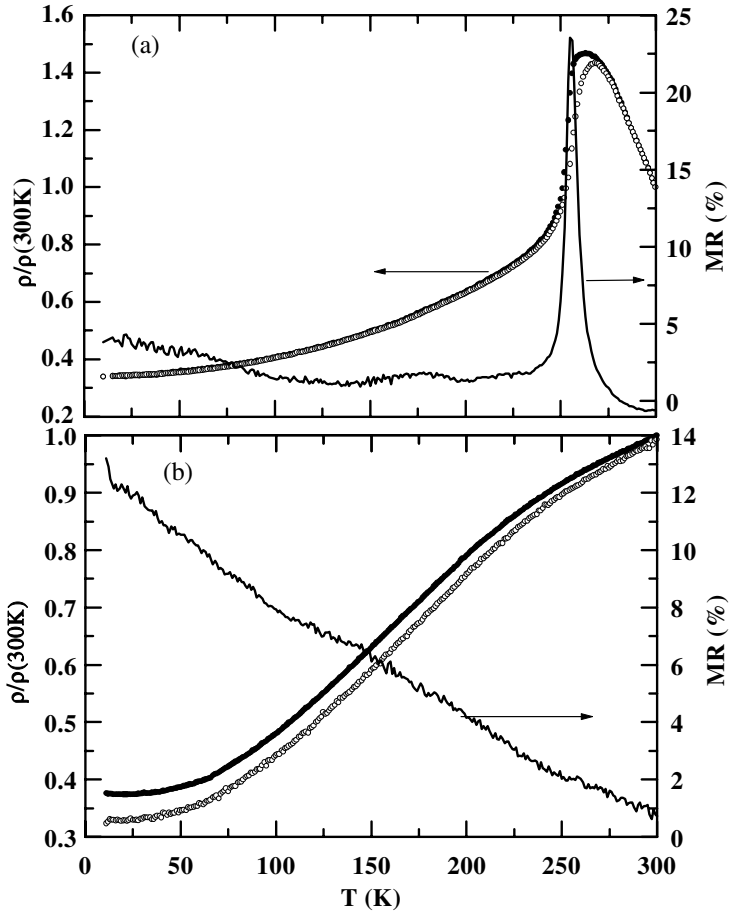

Figure 2. Temperature dependences of the normalized resistivity measured in zero field and in an applied field (∼2000 Oe) for both pure manganites: $La_{2/3}Ca_{1/3}MnO_3$ (a); $La_{2/3}Sr_{1/3}MnO_3$ (b). The corresponding magnetoresistances are also indicated.

replacing Ca^{2+} with larger Sr^{2+} increases the A-site cation size, leading to broadening of the one-electron e_g band and, consequently, T_p increases with increasing Sr content. Clearly, this is not the case for the present mixed polycrystals. The variation in T_p shown in figure 3(b) can be explained by the effect of the boundaries between LSMO and LCMO grains. The boundary effect in nanocrystalline $La_{0.67}Ca_{0.33}MnO_3$ has been widely studied [6]; it leads to a decrease in T_p with decreasing grain size. Because the same preparation routine was used to produce the present mixed materials, the grains would be expected to have the same size. Therefore, the effect of grain size on T_p can be neglected; the main effects arise from boundaries between LCMO and LSMO grains. This may result in amorphous surface layers that hinder the charge carriers from passing across boundaries between LCMO and LSMO grains. The effect arising from boundaries between LCMO and LSMO grains would be expected to be the most pronounced, as their volume ratio (being approximately equal to the weight ratio) is 1:1. This may be why T_p reaches its minimum near $m \sim 0.3$–0.5. Moving away from this ratio, the contribution arising from boundaries between LCMO and LSMO grains decreases with increasing or decreasing m, resulting in the increase in T_p, as indicated in figure 3(b).

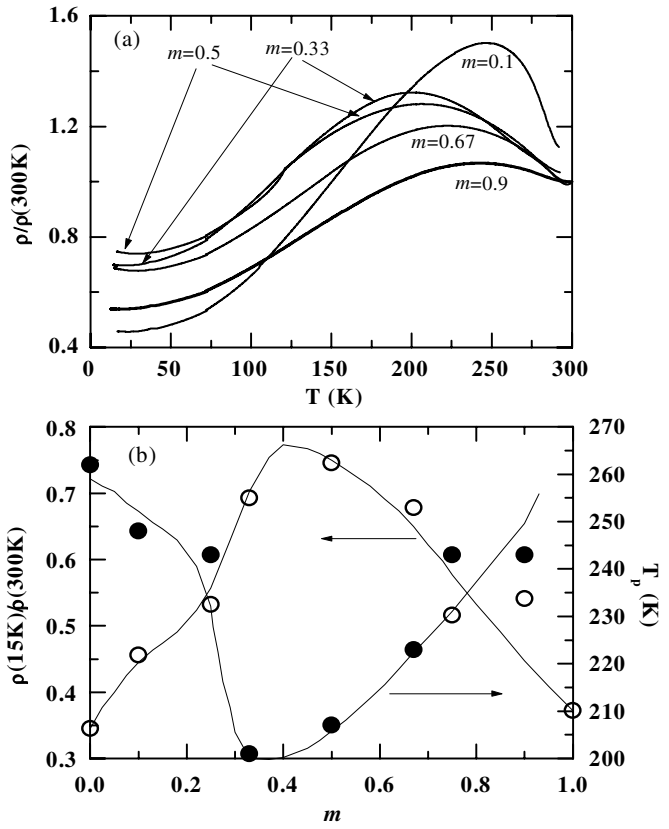

Figure 3. (a) Zero-field $\rho/\rho(300\ \mathrm{K})$–$T$ curves for the mixed polycrystalline samples with $0.1 \leqslant m \leqslant 0.9$. (b) T_p (solid circles) and $\rho(15\ \mathrm{K})/\rho(300\ \mathrm{K})$ (open circles) as functions of m. Solid lines are present merely to guide the eye.

To provide insight into the role of grain boundaries, the normalized resistivity at $T = 15$ K, $\rho(15\ \mathrm{K})/\rho(300\ \mathrm{K})$, as a function of m is also plotted in figure 3(b). For the two end materials (LCMO and LSMO), almost the same values of $\rho(15\ \mathrm{K})/\rho(300\ \mathrm{K})$ are obtained. Once they are mixed, the boundaries between LCMO and LSMO grains form, leading to an increase in the low-T resistivity. By an argument similar to that given above, the most obvious effect of boundaries between LCMO and LSMO grains should correspond to the case of $m \sim 0.3$–0.5, resulting in a maximum near this ratio. Moving away from this ratio, the boundary effect decreases with increasing or decreasing m and hence the low-T resistivity decreases as indicated in figure 3(b).

The magnetoresistance was measured for fields up to ∼9000 Oe at various constant temperatures. Shown in figure 4 is the field response of the resistivity at temperatures ranging between 15 K and 295 K for the mixed polycrystalline sample with $m = 0.1$, where the magnetoresistance is again given by $\mathrm{MR}\ (\%) = [(\rho(0,T) - \rho(H,T))/\rho(0,T)] \times 100\%$. A similar response is observed in the other mixed materials. The results shown in the figure clearly indicate a large response in magnetic fields well below ∼1000 Oe and a weak field dependence for the high-field range. This phenomenon is similar to what has been observed in granular ferromagnets [16]. Therefore, we note that the observed low-field magnetoresistance can be attributed to the spin-polarized transport across grain boundaries, since the magnetoresistance

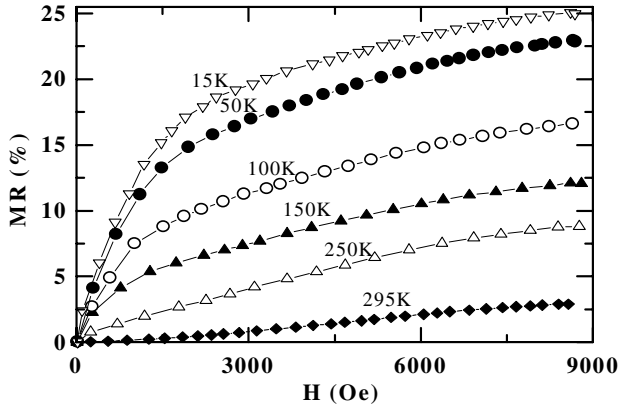

Figure 4. The field dependence of the magnetoresistance at various constant temperatures for the mixed sample with $m = 0.1$.

associated with the grain-boundary tunnelling is expected to be at its most pronounced at low fields where the magnetic domains associated with the grains progressively align with the field.

The measurement of the resistivity as a function of temperature in low applied magnetic fields was performed for all of the mixed polycrystalline materials studied. The MR effect versus temperature is illustrated in figure 5 for the three mixed samples for a field of $H = 8800$ Oe. It can be observed that although each mixed sample exhibits a S–M transition at T_p, there is no feature in the MR–T curve around this temperature. Two striking features of the MR effect can be found in figure 5. One is that the temperature-dependent MR behaviours at low temperatures are almost the same for all the mixed materials studied: the MR increases upon cooling and reaches its largest value ($\sim$30%) as $T \to 0$ K. The other is that the MR at high temperatures clearly shows different behaviours for different mixed materials. For the mixed material with $m = 0.1$, the MR takes values as high as $\sim$10% and remains almost unchanged over a wide temperature window between $\sim$150 K and $\sim$280 K. On increasing m to $\sim$0.33, the platform-type MR behaviour is still clearly observed, but the value becomes

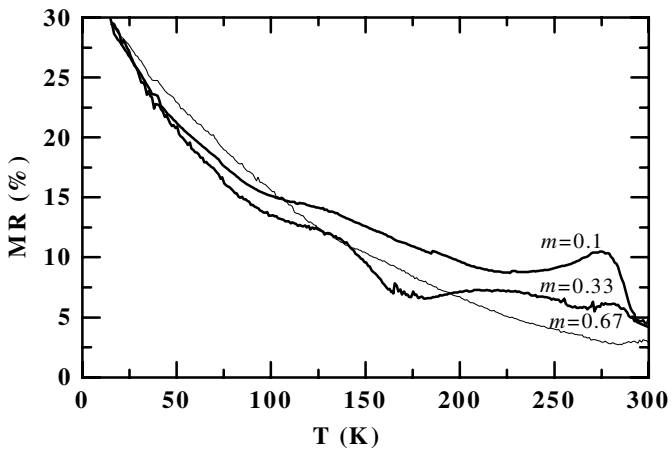

Figure 5. The temperature dependence of the magnetoresistance for the three mixed samples, with $m = 0.1, 0.33$ and 0.67, where MR is defined by MR (%) $= [(\rho(T) - \rho(T, H))/\rho(T, H)] \times 100\%$.

smaller. On further increasing m, the platform-type MR behaviour disappears. For the mixed polycrystalline sample with $m \geqslant 0.67$, as indicated in the figure, the MR increases monotonically with decreasing temperature over the whole temperature range studied.

We explain the platform-type behaviour of the MR observed in mixed polycrystals of lower m as a competition between two kinds of MR effect. As seen in figure 2(a), the first kind of MR effect shows an increase on cooling towards T_p, reaches its maximum near T_p and then decreases on further cooling, whereas the second kind of MR effect shows a monotonic increase with decreasing temperature. With increasing m, the first kind of MR effect is reduced, while the second one is enhanced. They compete to yield a platform-type magnetoresistance behaviour around T_p, as observed in mixed polycrystals with lower m. Upon increasing m to a higher value, e.g., $m \geqslant 0.67$, the first kind of MR effect disappears and only the second one is operative. For this case, as seen in figure 5 for the sample with $m = 0.67$, the MR effect shows a monotonic increase with decreasing temperature over the whole temperature range studied.

4. Conclusions

In summary, $La_{2/3}Ca_{1/3}MnO_3$ and $La_{2/3}Sr_{1/3}MnO_3$ perovskites have been successfully mixed. Besides the boundaries between grains of the same kind which have been widely studied, boundaries between grains of different kinds have been introduced into the compounds. We show that the mixed polycrystalline materials exhibit electrical transport and low-field magnetoresistance behaviours different from those previously observed in $La_{0.7}(Ca_{1-x}Sr_x)_{0.3}MnO_3$. It is interesting to see the platform-type MR behaviour over a wide temperature window slightly below room temperature for a low-field range. This finding is encouraging as regards the potential application of mixed-valence manganites.

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