Electrical Transport and Low-Field Magnetoresistance in $La_{2/3}Ca_{1/3}MnO_3$/YSZ Composites *

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Electrical transport and low-field magnetoresistance (MR) are reported for $(1-x)$LCMO/xYSZ composites ($0 < x < 80\%$) (LCMO is $La_{2/3}Ca_{1/3}MnO_3$ and YSZ is yttria-stabilized zirconia). Different transport and MR behaviours are observed for $x < 2\%$ and $x > 2\%$. In particular, the composite with $x \leq 1\%$ shows a wide temperature window with a large constant MR below the transition. Based on microscopy analysis, a possible interpretation is presented for different observations for $x < 2\%$ and $x > 2\%$ with emphasis on the boundary effect arising from insulating YSZ layers.

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Manganites such as $La_{1-x}Ca_xMnO_3$ have been the subject of renewed interest, due to the colossal magnetoresistance (CMR/MR) exhibited near the Curie temperature T_C.[1,2] CMR, however, is found on a magnetic field scale of several tesla for a narrow temperature range near the Curie temperature (T_C), which is not very appealing for applications. Much effort has been made to understand the physical properties of manganites, which has led to the discovery of another type of MR, namely, the intergrain MR (IGMR) in polycrystalline manganites.[3−7] IGMR can be observed at low fields, but it increases on cooling and the larger value is obtained only at $T \ll T_C$. Several groups[8−11] have tried to merge the high degree of spin polarization presented in manganites with the advantages of a heterogeneous granular structure. The results indicate that the mixture of a metallic ferromagnetic perovskite with an insulator is followed by an MR enhancement. The purpose of this Letter is to investigate transport and MR properties of composites designed with half metallic $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) and insulating yttria-stabilized zirconia (YSZ).

A sol–gel method was used to prepare LCMO nanometric powders. The prepared powders were sintered at 1300°C for 10 h to obtain larger LCMO grains with an average size of $\sim 20\mu$m. The larger LCMO grains were mixed with finer ($\sim 2\mu$m) grains of YSZ according to the ratio of $(1-x)$LCMO/xYSZ with x ranging from 0% to 80%. The resulting homogeneous $(1-x)$LCMO/xYSZ powder was pelletized and sintered at 1350°C for 10 h. The structural characterization was carried out through x-ray diffraction (XRD) at room temperature. The parent compound ($x = 0$) is shown to crystallize in a single phase, showing characteristic peaks of the perovskite. Compared to the parent compound, XRD peaks of LCMO do not shift in the composite. XRD peaks corresponding to YSZ are observable in the composites, and their intensity increases with x. This is an indication that no reaction between LCMO and YSZ occurs, without which it is impossible to draw conclusions about the composite properties.

The electronic transport behaviour is studied by measuring the resistivity as a function of temperature. The parent compound shows a behaviour similar to that recently reported,[12] in which the metal–insulator (MI) transition occurs at $T_{MI} \sim 260$ K. Upon the application of low magnetic fields (e.g. $H \sim 2000$ Oe), both the effects, i.e. CMR characterized by a peak in MR versus T near T_{MI} and IGMR showing a monotonic increase on cooling, are presented at the same time.

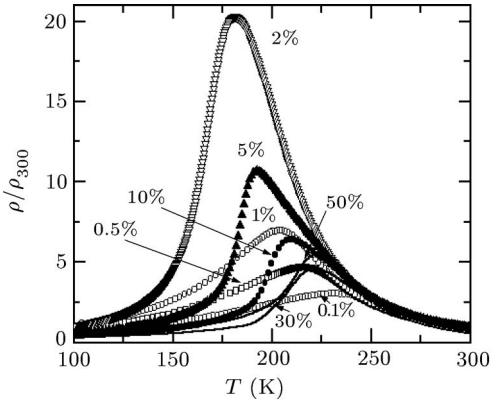


Fig. 1. Temperature dependence of normalized resistivity in zero field for the $(1-x)$LCMO/xYSZ composites with x in the range of 0.1–50%.

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Figure 1 shows the resistivity normalized by the room-temperature value as a function of temperature measured for zero field in the $(1-x)$LCMO/xYSZ composites with $x = 0.1\%$, 0.5%, 1%, 2%, 5%, 10%, 30% and 50%. It can be found that each composite undergoes a transition from high-T insulating behaviour of $\partial\rho/\partial T < 0$ to low-T metallic behaviour of $\partial\rho/\partial T > 0$. As a common feature, the transition is characterized by a maximum ($\rho_{\max}$) in the $\rho/\rho_{300} - T$ curve at $T_{\rm MI}$. However, one could note a special value x_d by which transport behaviour for $x < x_d$ is obviously distinguished from that for $x > x_d$. Empirically, this value is found to be ~2%. For $x < x_d$, increasing x moves the transition towards the low-temperature regime and causes a large increase of $\rho_{\max}$. In contrast, the transition is moved towards the high-temperature regime and the $\rho_{\max}$ value is obviously decreased as x is increased for $x > x_d$. We also note that resistivity dependences on temperature are almost the same for composites with high x values as indicated in Fig. 1 for the composites with $x = 30\%$ and 50%. In Fig. 2 we plot ρ_{100}/ρ_{300} and $T_{\rm MI}$ versus x. Two distinguishable regions can obviously be found in this plot. For $x < x_d$, $T_{\rm MI}$ largely decreases while ρ_{100}/ρ_{300} sharply increases with x. For $x > x_d$, increasing x causes a sharp increase of $T_{\rm MI}$ and a large decrease of ρ_{100}/ρ_{300}. With the further increase of x above 10%, both $T_{\rm MI}$ and ρ_{100}/ρ_{300} tend to become constant. The resistivity versus temperature dependence for $x \geq 80\%$ is also measured (not displayed in Fig. 1), which shows the insulating behaviour below room temperature.

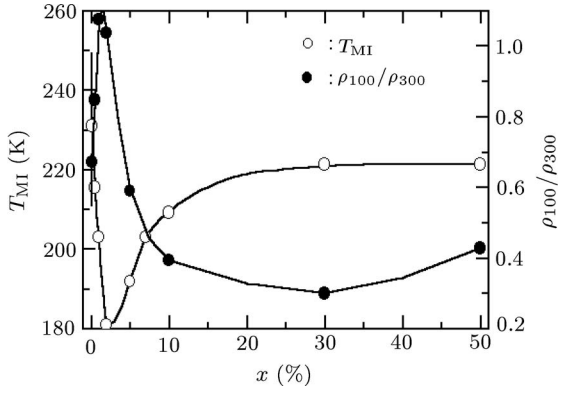


Fig. 2. MI transition temperature (open circles) and low-temperature resistivity (closed circles) versus YSZ percentages. The lines are drawn to guide the eyes.

The results presented here are different from those recently reported on the other manganite/insulator composites such as $(1-x)La_{2/3}Sr_{1/3}MnO_3/xCeO_2$ [13] and $(1-x)La_{2/3}Ca_{1/3}MnO_3/xAl_2O_3$ [10]. Experiments[13] on $(1-x)La_{2/3}Sr_{1/3}MnO_3/xCeO_2$ have indicated that the composite is insulating for $x > 80\%$ and the similarity of the resistivity versus temperature dependence is found for $x < 80\%$, which is a behaviour similar to the present observation. However, anomalous transport observation in the present composite with smaller x is not presented in $(1-x)La_{2/3}Sr_{1/3}MnO_3/xCeO_2$. The $(1-x)La_{2/3}Ca_{1/3}MnO_3/xAl_2O_3$ composite, on the other hand, shows the behaviour to be different either from that in $(1-x)La_{2/3}Sr_{1/3}MnO_3/xCeO_2$ or from that in the present composite. In fact, as recently reported[10] on $(1-x)La_{2/3}Ca_{1/3}MnO_3/xAl_2O_3$, the MI transition largely moves towards the low-temperature regime with increasing x, and the composites become insulating in the whole temperature range studied as x exceeds ~ 10%.

For a two-phase system dealing with the random distribution of insulating and conducting particles, the transport phenomena are usually understood within the framework of percolation theory.[14] According to this theory, as the conductor fraction exceeds a percolation threshold p_c (~ 10–30% for three dimensions corresponding to a critical value of insulator fraction x_c between 90% and 70%), the conductor regions are connected in a percolative manner. In this case, the transport properties in the two-phase system show a behaviour similar to that observed in the absence of the insulating phase. From our experiments, the x_c value of the present composite is estimated to be ~80%, which is in agreement with the percolation theory. This is the reason why the composite with $x < 80\%$ shows a similarity of the resistivity versus temperature. However, one should note that anomalous transport behaviour observed for x around 2% is not expected by the percolation mechanism. On the other hand, this anomaly is not observed in other manganite/insulator composites. This suggests that other effects should be taken into account, which will be discussed later based on scanning electronic microscopy (SEM) experiments.

MR as a function of temperature behaves in an interesting manner. Here the MR effect is defined as

$$MR_0(\%) = \frac{\rho(T,0) - \rho(T,H)}{\rho(T,0)} \times 100\%,$$

where $\rho(T,0)$ and $\rho(T,H)$ are the resistivity values in zero and applied fields, respectively. As a common feature of the present composite showing metallic conduction behaviour at low temperatures, a sizable IGMR effect is presented at temperatures well below $T_{\rm MI}$ due to the existence of grain boundaries. As indicated in Fig. 3 for $x = 0.1\%$, 1% and 5% in a field of $H = 3800$ Oe, IGMR increases with cooling, which is generally observed in granular ferromagnets.[15] The largest IGMR is observed in the composite with $x \sim 1\%$, and the IGMR clearly becomes smaller when varying x from 1%. At temperatures near $T_{\rm MI}$, MR for $x > x_d$ is clearly different from that for $x < x_d$. For

$x > x_d$, as seen in the composite with $x = 5\%$, besides the IGMR, the composite shows the CMR behaviour characterized by a peak near $T_{\rm MI}$ in the $MR_0 - T$ curve which is similar to that observed in the polycrystalline LCMO sample. For $x < x_d$, as displayed in Fig. 3 for the composites with $x = 0.1\%$ and 1%, the MR shows a sharp increase with cooling from $T_{\rm MI}$ and remains almost unchanged (with a value as high as $\sim 10\%$) over a wide temperature window. This finding is encouraging as regards the potential application of manganese perovskites.

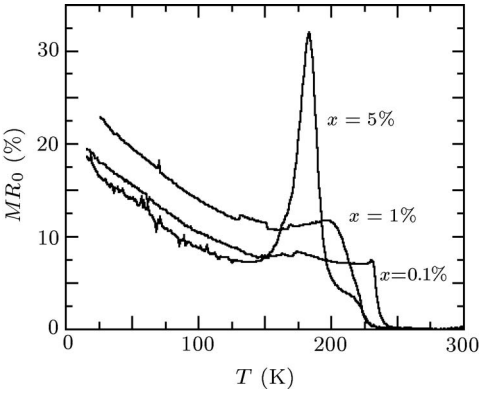


Fig. 3. Temperature dependence of MR for the three typical composites with $x = 0.1\%$, 1% and 5%, where $MR_0(\%) = \frac{\rho(T,0)-\rho(T,H)}{\rho(T,0)} \times 100\%$.

The CMR presented in the composite with higher x can be understood if one notes the fact mentioned above. For x high enough but not exceeding x_c, the LCMO regions are connected in a percolative manner. This means that the transport behaviour in the composite with higher x is actually dominated by LCMO. This is the reason why the composite with higher x shows CMR near the transition similar to that in pure LCMO. For the composite with $x < x_d$, another effect mentioned below causes a decrease of CMR and an increase of IGMR. These compete to yield a platform-type MR behaviour below $T_{\rm MI}$, as observed in both composites with $x = 0.1\%$ and 1%.

Now we turn to the central issue of this Letter. That is, what is responsible for the anomalous observation of transport behaviour in the composite with smaller x? To understand this, we have examined the distribution of insulating YSZ particles within the conducting LCMO matrix by means of SEM. Figure 4 shows the SEM photographs obtained in three typical composites with $x = 1\%$ (a), 2% (b) and 10% (c). For small x, as seen in the $x = 1\%$ composite, the composite as a two-phase system has a structure in which LCMO grains are condensed into larger clusters and each cluster is completely surrounded by a YSZ insulating layer. This is essentially different from the conventional granular metals embedded in an insulator in which both insulating and metallic particles are randomly distributed over the sample. With increasing x towards x_d, as displayed in Fig. 4(b) for $x = 2\%$, the structural feature is basically similar to that observed in the $x = 1\%$ sample. However, the average size of LCMO clusters decreases and the number of LCMO clusters increases. With the further increase of x, the LCMO clusters are no longer surrounded by the YSZ insulating layer. As indicated in Fig. 4(c) for the $x = 10\%$ composite in which LCMO and YSZ are contrasted, LCMO clusters are connected so that LCMO paths are formed.

Knowing the distribution features for the two phases, we can explain why the composites show different transport and MR behaviour for the ranges of $x < x_d$ and $x > x_d$. It is been well known that the boundary effect can play an essential role in determining transport properties of manganites. In the case of $x < x_d$, the main boundary effect arises from the insulating YSZ layer that hinders the charge carriers from passing between neighbouring LCMO clusters. Therefore, the composite with $x < x_d$ has lower $T_{\rm MI}$ and

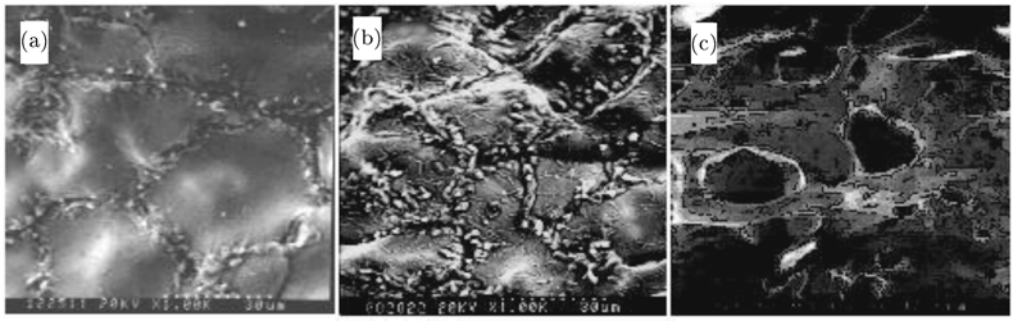


Fig. 4. SEM photographs obtained in three typical composites with $x = 1\%$ (a), 2% (b) and 10% (c). In (a) and (b), the boundaries arising from YSZ can be clearly seen. In (c), both the LCMO and YSZ phases are distinguished by a different contrast, where the bright regions indicate YSZ grains.

higher low-T resistivity compared to the pure LCMO. The existence of the YSZ insulating layer, on the other hand, decreases the CMR but increases the IGMR. As a result, a constant MR is observed near the transition. With increasing x towards x_d, the boundary effect arising from YSZ increases. Therefore, increasing x causes a decrease of $T_{\rm MI}$ and an increase of low-T resistivity as shown in Fig. 2 in the range of $x < x_d$. For the case of $x > x_d$, as indicated in Fig. 4(c) for the $x = 10\%$ composite, LCMO paths are formed within the sample. This is the reason why the composites with higher x show transport and MR behaviour similar to that observed in pure LCMO polycrystalline samples.

In summary, we have investigated the transport and low-field MR in LCMO/YSZ composites. It is interesting to observe the constant MR effect with a value as high as 10% at a low magnetic field over a wide temperature window below the MI transition for the composites with lower YSZ. This result opens new opportunities to improve the performance of CMR devices.

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