Transport properties and magnetoresistance in $La_{0.8}Te_{0.2}MnO_3/ZrO_2$ composites*

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The transport properties and magnetoresistance of electron-doped manganate / insulator composites $(La_{0.8}Te_{0.2}MnO_3)_{1-x}/(ZrO_2)_x$ (x = 0, 0.3, and 0.5) are investigated. It is found that the metal-insulator transition temperature of this system shifts to a lower value as the ZrO_2 content increases. The introduction of ZrO_2 enhances both the domain scattering and electron relative scattering in the metal transport region. In the adiabatic small polaron hopping transport region, the thermal activation energy seems invariable regardless of the ZrO_2 content. The application of a magnetic field promotes the charge transportation capabilities of the composites, and the magnetoresistance is enhanced with an increase of the ZrO_2 content. This could be attributed to the more remarkable modification effect of magnetic field on ordering degree in the composites than in pure $La_{0.8}Te_{0.2}MnO_3$.

Keywords: manganate, composite, transport property, magnetoresistance

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1. Introduction

The doped manganese oxides $R_{1-x}A_xMnO_3$ (R = trivalent rare earth elements, and A=Ca, Sr, Ba, Sb etc.) have been widely investigated for more than 10 years for their colossal magnetoresistance effect and other interesting properties.[1–7] In these manganese oxides, the Mn element exists as mixed valences of Mn^{3+} or Mn^{4+} (when A exists as A^{+2} or A^{+1}), and Mn^{2+} or Mn^{3+} (when A exists as A^{+4} or A^{+5}), which belong to the hole-doped and the electron-doped types, respectively. However, there are several disadvantages, such as the low sensitivity of the resistance variation to magnetic fields, and instability with change of temperature, limiting their practical applications. An effective way for improving the properties is to add insulators, such as Al_2O_3,[8] ZrO_2,[9] and ZnO[10] into manganates and form manganate/insulator composites. Up to now, almost all the reports are focused on hole-doped manganate (p-manganate)/insulator composites, and the main effect of insulators in the systems is the enhancement of low-field magnetoresistance due to the spin-dependent tunneling or scattering at the grain boundaries. However, the transport properties and magnetoresistance of electron-doped manganate (n-manganate)/insulator composites are not well known thus far. In this paper, the n-manganate/insulator composites $(La_{0.8}Te_{0.2}MnO_3)_{1-x}/(ZrO_2)_x$ (x = 0, 0.3 and 0.5) are prepared with different ZrO_2 contents, and the effect of the ZrO_2 insulator on the transport properties and magnetoresistance in n-manganate is studied.

2. Materials and methods

$La_{0.8}Te_{0.2}MnO_3$ (LTMO) powder was prepared from analytically pure oxides La_2O_3, TeO_2, and $Mn(NO_3)_2$ by the sol–gel method with the additives citric acid and polyglycol. Then, the LTMO powder was mixed with analytically pure ZrO_2 powder at fixed mole ratios to form $(LTMO)_{1-x}/(ZrO_2)_x$ (x = 0, 0.3, and 0.5) powders. Each mixture was compressed into a rectangular block with dimensions of 10 mm×15 mm×2 mm, and was sintered at 800 °C for 12 h in air. After preparation, the bulk samples were placed in a variable temperature LAKESHORE electrical measurement system. The resistances of the samples R were determined by the standard four-probe method. A magnetic field was supplied by a DC electromagnet with a maximum intensity of 1.0 T. Data points were not recorded until the system reached an equilibrium state.

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3. Results and discussion

3.1. Phase structure

X-ray diffraction (XRD) is performed in order to check the phase constitutions of the three bulk samples at different ZrO_2 contents, and the corresponding XRD patterns are illustrated in Fig. 1. Pure LTMO is composed of a single phase and exhibits a monoclinic structure (Fig. 1(a)). By contrast, the other two kinds of composites are both made up of pure LTMO and ZrO_2 phases (Figs. 1(b) and 1(c)). This indicates that no chemical reactions take place in the mixtures of LTMO and ZrO_2.

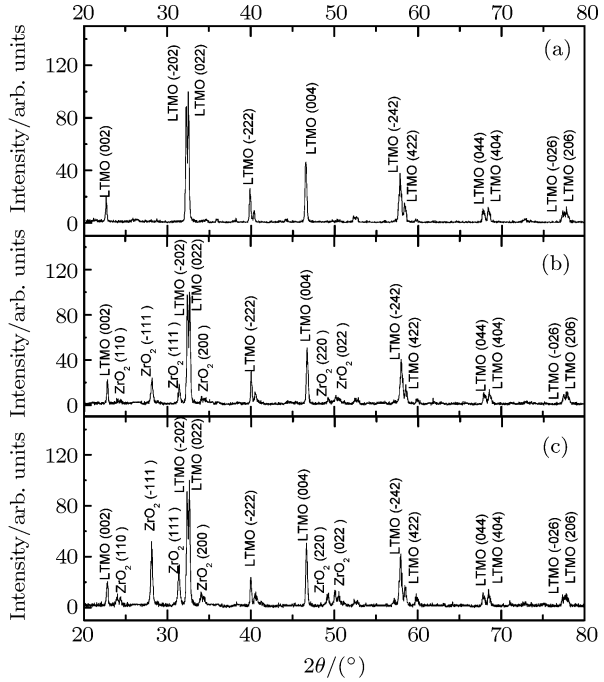


Fig. 1. XRD patterns of different samples: (a) pure LTMO, (b) $(LTMO)_{0.7}/(ZrO_2)_{0.3}$, (c) $(LTMO)_{0.5}/(ZrO_2)_{0.5}$.

3.2. Transport properties

The resistances of the three bulk samples in the temperature range of 100–310 K are plotted in Fig. 2. Metal-insulator transition (MIT) characteristics of the samples are studied. For pure LTMO, its resistance reaches the maximum value at the critical MIT temperature (T_{MI}). When $T < T_{MI}$, $dR/dT > 0$, LTMO exhibits metallic conductivity; when $T > T_{MI}$, $dR/dT < 0$, it shows an insulator property. This is a typical MIT profile in pure LTMO. The samples of $x = 0.3$ and 0.5 also display MIT in the temperature range. However, the values of T_{MI} show a decreasing trend with the increase of ZrO_2 content, from 214 K at $x = 0$ to 209 K at $x = 0.3$, and finally to 202 K at $x = 0.5$. The changes of T_{MI} in these samples are different from those of common composites based on p-manganate, such as the $La_{2/3}Ca_{1/3}MnO/Cr_2O_3$ system.[11] As the doping ratio of Cr_2O_3 increases from 0 to 10%, the T_{MI} of $La_{2/3}Ca_{1/3}MnO_3/Cr_2O_3$ exhibits a sharp drop from 255 K to 90 K, the variation of which is much greater than the $LTMO/ZrO_2$ system. Furthermore, $La_{2/3}Ca_{1/3}MnO_3/Cr_2O_3$ shows a complete insulator property when the doping ratio of Cr_2O_3 reaches 15%. Similarly, in $La_{2/3}Ca_{1/3}MnO_3/Sb_2O_5$,[12] there are also huge changes of T_{MI}. Clearly, compared with $La_{2/3}Ca_{1/3}MnO_3/Cr_2O_3$ and $La_{2/3}Ca_{1/3}MnO_3/Sb_2O_5$ systems, $LTMO/ZrO_2$ exhibits rather good transporting stability. This might originate from the different intrinsic transportation characteristics between the n- and p-mangantes. In the n-mangantes (such as $LTMO/ZrO_2$), the transportation is based on Mn^{2+}–O^{2-}–Mn^{3+} whereas the p-type one (such as $La_{2/3}Ca_{1/3}MnO_3/Cr_2O_3$ and $La_{2/3}Ca_{1/3}MnO_3/Sb_2O_5$) is based on Mn^{4+}–O^{2-}–Mn^{3+}. The relative small variation of T_{MI} in this work indicates that the long-range jumping in the electron-doped system by means of Mn^{2+}–O^{2-}–Mn^{3+} is more difficult to break than those of Mn^{4+}–O^{2-}–Mn^{3+} in the hole-doped systems. This explains the good transporting stability of the LTMO/ZrO system.

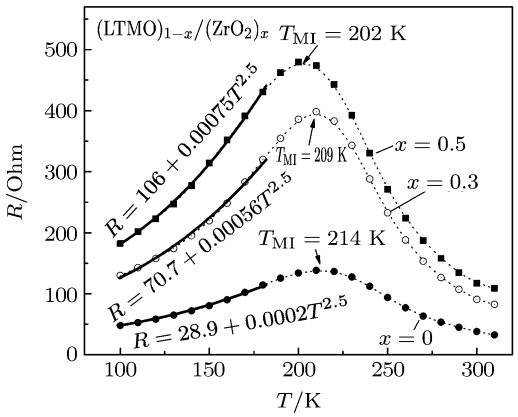


Fig. 2. The resistances of $(LTMO)_{1-x}/(ZrO_2)_x$ ($x = 0$, 0.3, and 0.5) composites in the temperature range from 100 to 310 K. The solid lines are the fitting curves with $R = R_0 + R_1T^{2.5}$.

On the other hand, at a fixed temperature, the resistance increases monotonically with ZrO_2 content x. This suggests that the capacity of charge transportation becomes weaker due to the introduction of ZrO_2. Numerical analyses are carried out in order to determine the microscopic transport mechanism of the LTMO/ ZrO_2 systems. According to the Schiffer model,[3] the resistance of materials showing metallic

conductivity is expressed as

$$R = R_0 + R_1 T^{2.5}, \tag{1}$$

where R_0 stands for the resistance from domain scattering and other temperature-independent scattering, and the term $R_1 T^{2.5}$ represents the combination of electron–electron, electron–phonon and electron–magnon scattering. In the metallic conductivity region, the fitted relationships between the resistance and temperature for the three samples are as follows:

$$x = 0: \quad R = 28.9 + 2.0 \times 10^{-3} \cdot T^{2.5}, \tag{2}$$

$$x = 0.3: \quad R = 70.7 + 5.6 \times 10^{-3} \cdot T^{2.5}, \tag{3}$$

$$x = 0.5: \quad R = 106 + 7.5 \times 10^{-3} \cdot T^{2.5}. \tag{4}$$

It is apparent that all of the relationships agree well with the Schiffer model. However, both the parameters R_0 and R_1 rise as ZrO_2 content increases. This demonstrates that the introduction of ZrO_2 enhances both the domain scattering and electron relative scattering inside the LTMO systems.

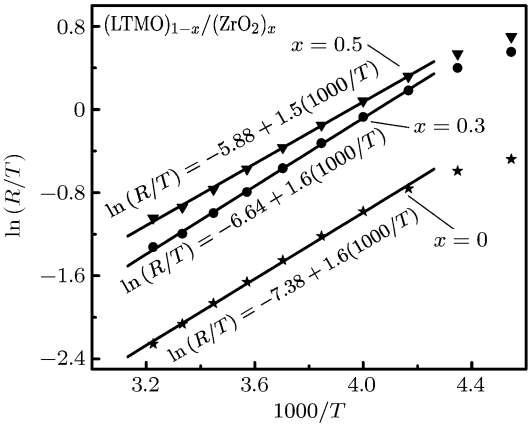


Fig. 3. The linear fittings based on $\ln(R/T) \sim 1000/T$ for the samples of $(LTMO)_{1-x}/(ZrO_2)_x$ ($x = 0$, 0.3 and 0.5).

There are several kinds of classic models describing the resistance variation of insulators, such as the variable-range-hopping (VRH) model,[13] the semiconductor thermal activation model,[14] and the small polarons hopping (SPH) model[15,16] As shown in Fig. 3, linear regressions of the experimental data show that the resistance is related to temperature in the insulator region by

$$x = 0: \quad \ln(R/T) = -7.38 + 1.6(1000/T), \tag{5}$$

$$x = 0.3: \quad \ln(R/T) = -6.64 + 1.6(1000/T), \tag{6}$$

$$x = 0.5: \quad \ln(R/T) = -5.88 + 1.5(1000/T). \tag{7}$$

The three well-fitted curves indicate that the relationships between R and T of the $LTMO/ZrO_2$ systems in the insulator region are in good agreement with the adiabatic SPH model,[15] which can be written as

$$\ln(R/T) = C + (E_g/k_B) \cdot (1/T), \tag{8}$$

where C is a constant, E_g is the thermal activation energy, and k_B is Boltzmann's constant. Moreover, the three lines in Fig. 3 with very similar slopes suggest that the addition of ZrO_2 does not change the thermal activation energy (E_g) of the LTMO systems.

3.3. Magnetoresistance

As illustrated in Fig. 4(a), the resistances R_H of $(LTMO)_{1-x}/(ZrO_2)_x$ ($x = 0$, 0.3 and 0.5) bulk samples are measured when a magnetic field of 0.9 T intensity is applied. In comparison with those under null field conditions, the application of a magnetic field results in the decrease of resistances for all of the composites. This is due to the fact that the external magnetic field enhances the degree of magnetic ordering in $LTMO/ZrO_2$ systems and promotes the compatibility of the electron spin orientation. These are responsible for the advancement of charge transportation capability. To evaluate the variation degree in resistance, magnetoresistance (MR) is defined as follows:

$$r_{MR} = \frac{R - R_H}{R} \times 100\%, \tag{9}$$

where R is the null-field resistance, and R_H denotes the resistance in a magnetic field. Figure 4(b) shows the MR of the samples in the temperature range from 100 to 310 K. As temperature rises, all the MR values initially go up slightly to the peak values and then decline sharply to very low levels. For pure LTMO system, MR has a peak value of 10.3%. For $x = 0.3$ and 0.5, the maximum MRs ($r_{MR,max}$) of the composites reach up to 11.2% and 12.7%, respectively. This indicates that the introduction of the insulator into n-mangante is an effective way to improve their MRs. The addition of the insulator ZrO_2 introduces intensive spin-dependent domain scattering and other barriers to the system, which makes the composites become more sensitive to the external magnetic field and results in the remarkable increase of MR. It should be pointed out that the improvement of MR in the $LTMO/ZrO_2$ system in various temperature regions differs to those in p-manganate / insulator composites. In $La_{2/3}Ca_{1/3}MnO_3/Cr_2O_3$ [11] and $La_{2/3}Ca_{1/3}MnO_3/Sb_2O_5$ [12] systems, the introduction of an insulator enhances the MRs in the metal transporting ($T < T_{MI}$) zone and transition zone (around T_{MI}), whereas it decreases the MR in the insulator region sharply. By comparison, the $LTMO/ZrO_2$

system in the present work exhibits an enlargement of the MRs in the insulator zone ($T > T_{\rm MI}$) and the transition zone (around $T_{\rm MI}$). It is well known that in the insulator zone of a polycrystalline composite, small polarons need to hop against a longer space length between the manganate grains. From the experimental data, it can be deduced that small polarons maintain effective transport in the n-manganate/insulator composites, and the system shows an increase of MR. By contrast, in p-manganate/insulator system, the long-range hopping of small polarons is weakened by the insulator grains, and the system loses its sensitivity to the external magnetic field in the insulator zone gradually.

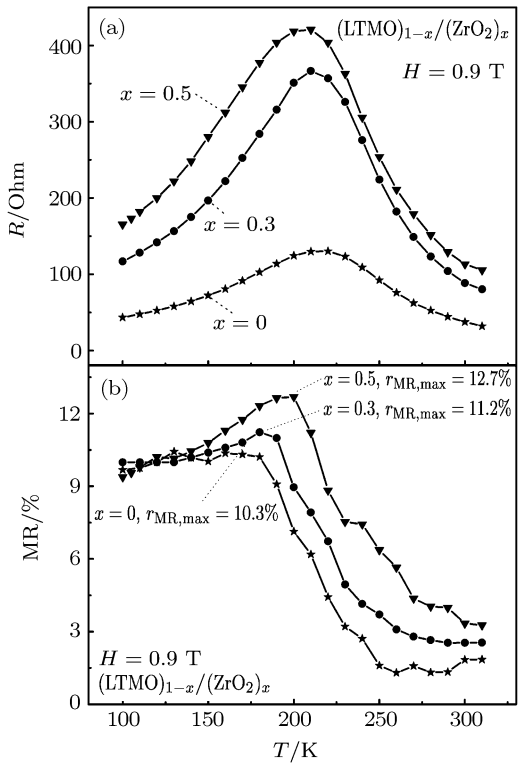


Fig. 4. (a) Resistance; (b) magnetoresistance of $(LTMO)_{1-x}/(ZrO_2)_x$ ($x = 0$, 0.3 and 0.5) under 0.9 T versus temperature.

4. Conclusions

The transport properties and magnetoresistance of electron-doped manganate / insulator $(La_{0.8}Te_{0.2}MnO_3)_{1-x}/(ZrO_2)_x$ ($x = 0$, 0.3 and 0.5) are investigated. The metal–insulator transitions of the three composites take place at 214, 209 and 202 K respectively, which lower monotonically with the increase of ZrO_2 content. In the temperature region in which the LTMO/ZrO_2 systems present metallic conductivity, the introduction of ZrO_2 strengthens not only the domain scattering, but also the electron–electron, electron–phonon and electron–magnon scatterings. In the region in which the systems show insulator characteristics, the relationships between resistance and temperature agree well with the SPH model. Besides, the thermal activation energy of small polarons seems invariable in the systems with different ZrO_2 contents. When a magnetic field is applied, the magnetoresistance of the LTMO/ZrO_2 systems are effectively enhanced as ZrO_2 content rises. This change could be ascribed to the remarkable promotion in magnetic ordering of the composites compared to pure LTMO induced by the magnetic field.

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