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Electrical transport of $(1-x)La_{0.7}Ca_{0.3}MnO_3+xAl_2O_3$ composites

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ABSTRACT

We report the resistivity (ρ)–temperature (T) patterns in $(1-x)La_{0.7}Ca_{0.3}MnO_3+xAl_2O_3$ composites ($0 \le x \le 0.05$) over a temperature regime of 50–300 K. Al_2O_3 addition has increased the resistivity of these composites. The Curie temperature (T_C) is almost independent on the Al_2O_3 content and is about 250 K for all the samples, while the metal–insulator transition temperature (T_{MI}) decreases with increasing Al_2O_3 content. Based on the phenomenological equation for conductivity under a percolation approach, which is dependent on the phase segregation of ferromagnetic metallic clusters and paramagnetic insulating regions, we fitted the experimental data ($\rho-T$) from 50 to 300 K and find that the activation barrier increases as Al_2O_3 content increases.

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1. Introduction

Since the discovery of "colossal magnetoresistance" (CMR) in perovskite-based rare-earth manganites, intensive research activities have been focused on the materials of $Ln_{1-x}A_xMnO_3$ (where Ln = La, Pr, Nd, etc. and A is a divalent doping cation). However, the intrinsic CMR effect in the perovskite manganites can only be triggered at high magnetic fields of several teslas, disqualifying them from practical applications. Recently, growing attention has been paid to polycrystalline manganites in which the grain boundary effect dramatically modifies their physical properties. It is well known that the grain boundary effect of the perovskite manganites can be further improved by introducing a second phase. For instance, Hueso et al. [1] have reported that an enhanced low-field magnetoresistance in $(1-x)La_{0.67}Ca_{0.33}MnO_3+xAl_2O_3$ (LCMO/Al_2O_3) (with $x = 0\%$; 5.5%; 8%; 15% and 25% in volume) composite can be achieved by the sol–gel technique. The insulator–metal transition temperature (T_C) of the LCMO/Al_2O_3 composites decreases as a result of the introduction of Al_2O_3 and it further reduces with the increasing of Al_2O_3. In addition to the shift of the T_{MI} value to the low temperature, the peak resistance of the LCMO/Al_2O_3 composites also increases with increasing Al_2O_3. Similar results were also observed in other systems of manganite–insulator composites [2–8]. Although these behaviors of the manganite composites have been extensively studied, their physical origins remain unknown. Andres et al. [9] have proposed a phenomenological model considering two parallel conduction channels for explaining the electronic transport and magnetoresistance in polycrystalline manganites. Also, Li et al. [10] have suggested the phenomenological percolation model based on phase segregation to explain the electronic transport in polycrystalline manganites.

In the previous work [11], we have investigated the crystalline structures and the magnetoresistance properties of the LCMO/Al_2O_3. In this study, we have prepared $(1-x)La_{0.7}Ca_{0.3}MnO_3+xAl_2O_3$ (with $x = 0$; 0.01; 0.02; 0.03; 0.04 and 0.05 in weight) polycrystalline composites via conventional solid-state reaction method combine with a high-energy milling method. By considering the phenomenological percolation model based on phase segregation, we propose an expression for the temperature dependency of the resistance. It is in good agreement with the experimental data measured in LCMO/Al_2O_3 polycrystalline composite samples.

2. Experiment

The LCMO/Al_2O_3 ($x = 0$; 0.01; 0.02; 0.03; 0.04; 0.05) composites were prepared by three steps. First, the LCMO powder was synthesized by a conventional solid-state reaction method combining with a high-energy milling method. High-purity (9999%) La_2O_3, $CaCO_3$ and MnO powders were mixed in the appropriate stoichiometric ratio and ground. The well-mixed powders were preheated at a temperature of 1250 °C for 15 h. Subsequently, it was heated at 1300 °C for 10 h. Next the LCMO and Al_2O_3 powders were ground by the energy milling machine for 2 h. Finally, the appropriate amounts of LCMO nano-powder and Al_2O_3 powder were mixed and a homogenous powder was pressed in pellets at a pressure of 10 MPA/cm^2 and sintered at 900 °C for 3 h.

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The structural characterization was done by employing the X-ray diffraction (XRD) technique at room temperature in the 2θ range (20–75°) with a step size of 0.03° using Cu$K\alpha$ ($\lambda = 1.5406$ Å) radiation and the surface morphology was observed by scanning electron microscopy (SEM). The magnetic measurements were performed by utilizing a vibrating sample magnetometer (VSM) in the temperature range from 100 to 300 K. The magnetization of the samples was examined in a physical properties measurements system (PPMS). The electrical resistance is measured using a four-probe method with a PPMS.

3. Results and discussion

The XRD patterns of the composites ($x = 0$; 0.01; 0.02; 0.03; 0.04 and 0.05) are displayed in Fig. 1. The perovskites phase of LCMO is maintained for all the x weigh fractions of Al_2O_3 considered, which would be an indicative of the coexistence of the two phases in the composite. Besides, the addition of the Al_2O_3 almost did not change position of the peaks of LCMO phase, which implies that Al_2O_3 is probably distributed at the grain boundaries and on the surfaces of the LCMO grains. The direct evidence of two phases also comes from SEM micrographs. The representative SEM micrographs of LCMO/Al_2O_3 composites with $x = 0.01$ and 0.04 are shown in Fig. 2, respectively. The interfaces between LCMO and Al_2O_3 can be distinguished clearly. Moreover, energy-dispersive X-ray (EDX) spectra of the doped composite for $x = 0.01$ and 0.04 shows the aluminum peak along with La, Ca, Mn and O peaks, which also supports the presence of Al_2O_3 in the doped composites.

The temperature dependence of magnetization at 100 Oe for LCMO/Al_2O_3 is shown in Fig. 3. The paramagnetic (PM) to ferromagnetic (FM) phase-transition temperature (T_C) determined

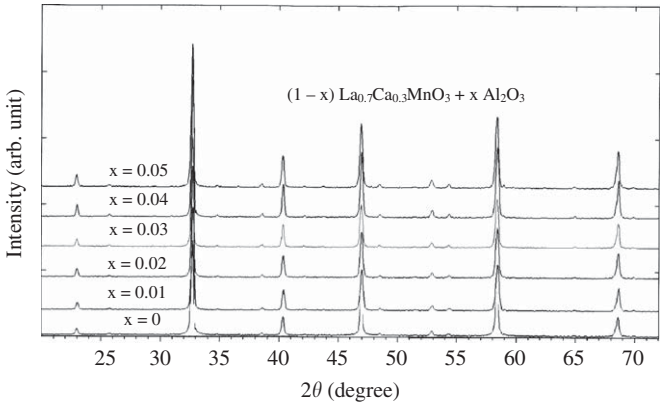

Fig. 1. XRD patterns of $(1-x)$LCMO+$x$$Al_2O_3$ composites.

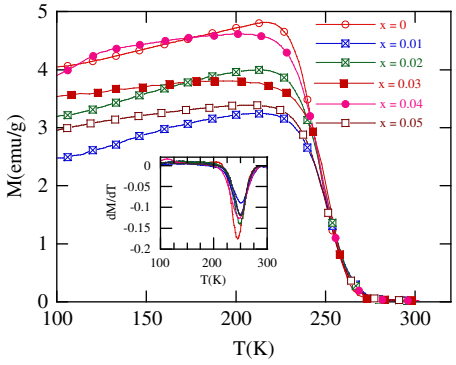

Fig. 3. Temperature dependence of magnetization at 100 Oe for LCMO/Al_2O_3 composites. Inset shows T_C of the samples.

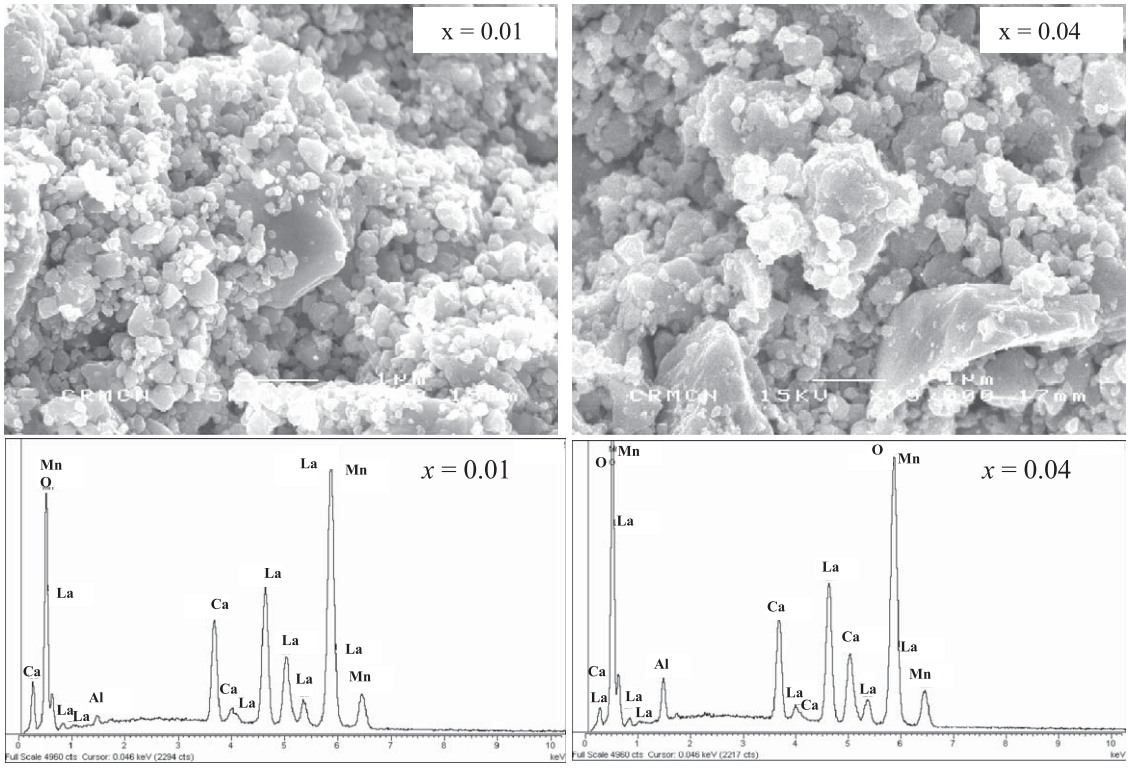

Fig. 2. Scanning electron micrographs and EDX spectra of LCMO/Al_2O_3 composite samples with $x = 0.01$ and 0.04.