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Electro-magnetic transport behavior of $La_{0.7}Ca_{0.3}MnO_3/SnO_2$ composites

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Abstract

The composites of $(1-x)La_{0.7}Ca_{0.3}MnO_3$ (LCMO) + $xSnO_2$ (x = 0.01, 0.05, 0.10, 0.30, 0.50, 0.60, 0.65 and 0.70) were synthesized by conventional solid-state reaction method. The results of X-ray diffraction (XRD) and scanning electronic microscopy (SEM) indicate that SnO_2 and LCMO coexist in the composites and SnO_2 mainly segregates at the grain boundaries of LCMO, which are in accordance with the results of the magnetic measurements. The detailed electrical characterizations for all the samples showed that a new metal–insulator (M–I) transition temperature (T_{P2}) appeared at a lower temperature compared with the intrinsic metal–insulator (M–I) transition temperature (T_{P1}) when $x < 0.50$ ($T_{P1} > T_{P2}$). When $x > 0.50$, T_{P1} disappeared, leaving only T_{P2}. The resistivity percolation threshold of the composites occurred at $x = 0.60$. Corresponding to the two M–I transition peaks, the curves of magnetoresistance against temperature also showed two peaks for all composites. These phenomena can be explained by the segregation of a new phase related to SnO_2 at the grain boundaries or surfaces of the LCMO grains.

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1. Introduction

Perovskite manganites such as $RE_{1-x}A_xMnO_3$ (RE = rare earth, A = Ca, Sr, Ba) have been the subject of intense research in the last few years since the discovery of the phenomenon of colossal magnetoresistance (CMR) in these systems. The CMR is usually explained with double-exchange (DE) mechanism [1] and the CMR materials have potential applications such as in magnetic switching or recording devices, etc. However, the intrinsic CMR effect is usually found in the condition of several teslas magnetic field and a narrow temperature range near the Curie temperature (T_C) [2]. This magnetic field and temperature range is incapable of practical application. Recently, another type of MR called the inter-grain MR (IMR) has also been a research focus found in polycrystalline half-metallic ferromagnets, which is associated with the spin-dependent charge transport across the grain boundaries [3–7]. Compared with the CMR in single crystals, the IMR in polycrystalline usually occurs over a wider temperature range

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and at a lower magnetic field below T_C, which is usually called low-field magnetoresistive (LFMR). Compared with CMR, LFMR may be more useful for practical application.

In order to comprehend the fundamental mechanism of the LFMR effect and obtain a higher LFMR, some attention have been paid to the granular manganite/insulator mixture in bulk form, such as the composites of $La_{0.67}Ca_{0.33}MnO_3/ZrO_2$ [8], $La_{0.67}Sr_{0.33}MnO_3/CeO_2$ [9], $La_{0.67}Ca_{0.33}MnO_3/SrTiO_3$ [10], $La_{0.67}Ca_{0.33}MnO_3/Al_2O_3$ [11], etc. In these systems, nonmagnetic insulating oxides as a second phase were introduced to the grain boundaries of manganites where to form local spin disorders. Generally speaking, the LFMR is closely related to the grain boundaries which have great effects on the spin-dependent scattering (SPS) and spin-dependent tunneling (SPT). But the mechanism of the LFMR and the electro-magnetic transport behaviors of such materials have not been understood clearly and need to be studied further.

In this paper, we have synthesized $(1-x)$LCMO/$x$$SnO_2$ homogeneous composites and introduced SnO_2 as the second phase to LCMO matrix which are mainly segregated at the grain boundaries of the LCMO grains by a special experimental procedure. We intend to modify the microstructure of grain boundaries and surfaces of the LCMO and obtain an obvious effect on the electrical transport properties of LCMO.

2. Experimental

$(1-x)$LCMO + $x$$SnO_2$ (x = 0, 0.01, 0.05, 0.1, 0.30, 0.60, 0.65 and 0.70) composites were prepared in three steps. First, the pure LCMO was prepared by the traditional ceramic reaction method. The powers of La_2O_3, $CaCO_3$ and MnO_2 were mixed with stoichiometry of LCMO. Ethanol was added into the agate vials as a milling medium with the powder. The mixture was milled by conventional planetary ball miller with agate vials and balls. The ratio of ball–powder weight was 5:1 and the rotating speed was set to 300 rpm. After milling for 24 h, the mixture was dried in air at 90 °C to remove the ethanol and then the dried stoichiometric mixture was sintered at 1400 °C for 10 h to crystallize. Second, SnO_2 power was obtained by decompounding H_2SnO_3 which was fabricated by the reactions of HNO_3 (the concentration is 69%) with Sn (the purity is higher than 99%) at 800 °C for 10 h. Finally the combinations $(1-x)$LCMO/$x$$SnO_2$ (x = 0, 0.01, 0.05, 0.1, 0.30, 0.60, 0.65 and 0.70) were mixed and grinded in a agate mortar for 2 h. The resulting homogeneous powder was pelletized into a form of rectangular rod (10 mm × 5 mm × 2 mm) at a pressure of 10 MPa and then sintered at 1100 °C for 2 h, which could avoid the reaction between LCMO and SnO_2.

The room temperature crystal structure was determined by X-ray diffraction (XRD, PANalytical company design) in the range of 20–80° with a step size of 0.0170° using Cu Kα radiation. The morphologies of samples (x = 0, 0.10 and 0.30) were analyzed by scanning electronic microscopy (SEM). Magnetic measurements were carried out using a vibrating sample magnetometer (VSM) in the temperature range from 80 to 290 K. The electro transport behaviors were measured by a standard four-probe technique in the temperature range from 80 to 300 K for all samples. A magnetic field of 3 kOe was applied to measure the MR effect.

3. Results and discussion

The XRD patterns of the samples with x = 0, 0.05, 0.10, 0.30 and 0.60 at room temperature are shown in Fig. 1. The results of XRD measurements show that all the composites of LCMO/SnO_2 include two sets of XRD patterns. One result is from LCMO, the other is from SnO_2. With increasing content of SnO_2, the intensity of pure LCMO phase decreases and that of SnO_2 increases. Compared with XRD pattern of pure LCMO (x = 0), the SnO_2 phase has no obvious effects on the crystal structure of LCMO phase. The XRD analysis suggests that SnO_2 and pure LCMO are coexistent in the $(1-x)$LCMO/$x$$SnO_2$ composites and no chemical reaction takes place between LCMO and SnO_2.

In order to analyze the effects of SnO_2 on the microstructure of LCMO grain boundaries and the distribution of SnO_2 in the LCMO matrix, the experiment of SEM has been carried out for the samples with x = 0, and 0.30. The morphologies of these two samples are shown in Fig. 2a and b, respectively. In Fig. 2a, grain boundary in LCMO (x = 0) can be clearly observed and all the particles are grey. For the samples with x = 0.30, many small bright regions appear. Based on the results of XRD, the bright regions stand for SnO_2. It is can be suggested that SnO_2 phase is mainly segregated at grain boundary of LCMO.

The temperature (T) dependence of the specific magnetic moment (σ_S) has been measured in an applied field of 4 kOe for the composites of x = 0, 0.05, 0.10, 0.30, 0.50 and 0.60. The measurement results are shown in Fig. 3. As can be seen, σ_S decreases with increasing content of the nonmagnetic SnO_2 and the T_C of all samples are almost the same.