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Anomalous transport effects for the metal and insulator doped $La_{0.833}K_{0.167}MnO_3$ systems

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ABSTRACT

The $La_{0.833}K_{0.167}MnO_3$:Ag_2O and the $La_{0.833}K_{0.167}MnO_3$:$SrTiO_3$ samples are fabricated by the sol–gel method. The microstructure, magnetic and transportation properties have been systematically studied. X-ray diffraction patterns show that the $La_{0.833}K_{0.167}MnO_3$:Ag_2O (abbreviated as LKMO/Ag) sample is a two-phase composite and consists of a magnetic $La_{0.833}K_{0.167}MnO_3$ (abbreviated as LKMO) perovskite phase and a nonmagnetic Ag metal phase, while the structure of the $La_{0.833}K_{0.167}MnO_3$:$SrTiO_3$ (abbreviated as LKMO/STO) sample is a homogeneous solid solution phase. Comparing with the pure LKMO sample, the room temperature magnetoresistance (MR) effect for the LKMO/Ag sample is enhanced significantly due to the addition of Ag metal. The MR ratio increases from ~25% for the pure LKMO sample to 65% for the LKMO/Ag sample under a higher field of 5.5 T at 300 K. For the LKMO/STO sample, however, the room temperature MR effect is weakened dramatically and is almost close to zero due to the addition of $SrTiO_3$ insulator. In the low temperature regime below the Curie temperature, the MR behaviors are different from that of the room temperature; that is, the MR effect is decreased for the LKMO/Ag sample and increased for the LKMO/STO sample with temperature decrease. In fact, the low-field ($\mu_0 H = 0.5$ T) MR decreases from 32% to 5% for the LKMO/Ag sample, while increasing from 0.07% to 25% for the LKMO/STO sample with decreasing temperature from 300 to 4 K. The relative change between the intrinsic and the extrinsic MR, and varied roles of the spin-polarized-tunneling and the spin-dependent scattering mechanisms in different temperature regimes are employed to interpret the anomalous transport behaviors.

1. Introduction

The perovskite-type compounds have been extensively investigated due to the colossal magnetoresistance (CMR) effect and a variety of transport and magnetic properties that sensitively depend on the doping ions and contents [1–4]. For perovskite manganites $R_{1-x}A_x(Mn^{3+}_{1-x}Mn^{4+}_x)O_3$, in general, the mechanism of the magnetoresistance (MR) effects is divided into two classes, namely the intrinsic and extrinsic MR [5,6]. The former is referred to intragrain MR, which has a maximum near the Curie temperature (T_C), and is well explained by the combination of the double exchange model [7] and the electron–phonon interaction [8]. The latter is intergrain MR observed over a wider temperature range below T_C and is characteristic of a large low field MR. As found by Hwang [9] and Gupta [10], the manganite single crystals or epitaxy-grown films do not exhibit MR effect, but the manganite polycrystalline ceramics or films exhibit apparent MR effect of ~20% in the magnetic field of several hundred Gauss at the low temperature below T_C. The low field MR effect has drawn widespread attention because not only it has application prospect in practical spintronic devices, but also the physical mechanism is still to be more investigated. In previous literatures, several models have been proposed for their theoretical explanation, and some of them are discussed controversially. Hwang et al. [9] propose a model based on spin-polarized tunneling between ferromagnetic grains through an insulator. Gupta et al. [10] report that the switching of magnetic domains in the grains and disorder-induced canting of Mn spins in the grain boundary region play an important role in low field MR. Ziese et al. [11] suggest a description of the transport characteristic of the grain boundary based on tunneling via magnetically ordered states in the barrier. Guinea et al. [12] propose that probably tunneling via paramagnetic impurity states in the grain boundary barrier is also an important factor. Srinitiwarawong et al. [13] point out that the suppression of magnetic frustration contributes to the MR effect. Pin et al. [14] show the variation of the electronic spin polarization and the inelastic intergrain tunneling induced by the collective excitations of local spins at the grain boundaries are simultaneously responsible for the rapid decay of the low field MR ratio with increasing temperature.

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In order to get a clearer picture of the mechanism of the grain boundary MR effect, we produce the $La_{0.833}K_{0.167}MnO_3$:$SrTiO_3$ (abbreviated to LKMO/STO) and the $La_{0.833}K_{0.167}MnO_3$:Ag_2O (abbreviated to LKMO/Ag) systems. The Ag_2O oxide is decomposed at 300–400 °C, and the Ag metal will be mixed with $La_{0.833}K_{0.167}MnO_3$ (abbreviated to LKMO), leading to a metal doped system. The Ag metal does not interact with the perovskite phase, which has been reported by other research groups [15–17], and is known to segregate among the grain boundaries. The $SrTiO_3$ insulator, however, is easily interacted with the LKMO system due to the fact that they are both the similar perovskite structures. When the Ag metal and the $SrTiO_3$ insulator are doped into the perovskite manganites respectively, they result in a great change of the barriers of grain boundaries among the LKMO manganites. The $SrTiO_3$ insulator will increase the potential of the barriers, while the Ag metal contrarily decreasing it.

2. Experimental

Polycrystalline LKMO powders are prepared by the sol–gel method. An appropriate amount of citric acid (as a complex agent) and glycol (as a dispersing agent) are added into a solution which is previously obtained by dissolving the high-purity oxides La_2O_3, K_2CO_3 and $Mn(NO_3)_2$ in dilute nitric acid. The gel is decomposed slowly at 200 °C in air. The precursor is decarbonated at 700 °C for 6 h, and the powder obtained is ground, pelletized, and sintered at 1100 °C for 10 h to form stable LKMO phase. For the LKMO/Ag sample, the Ag_2O powders are added directly according to the appropriate ratio to the LKMO powders (The molar ratio of Ag_2O: LKMO is 0.25:1). Then the mixtures are ground carefully, pressed into disks with a radius of 10 mm and a thickness of 5–6 mm and sintered at 1200 °C for 10 h. In order to get the LKMO/STO sample, the LKMO powders are put into $SrTiO_3$ precursive solution that is prepared by the sol–gel method, and mixed together for about 3 h. The mixtures are filtered to removal the redundant $SrTiO_3$ precursive solution (The molar ratio of $SrTiO_3$: LKMO is 0.13:1, which can be calculated from the weight loss of precursive solution.). After this, the mixtures are dried in the furnace, pressed into disks with a radius of 10 mm and a thickness of 5–6 mm and sintered at 1200 °C for 10 h.

The structure of the sample is characterized by x-ray diffraction (XRD) using Cu K_α radiation and measured at room temperature. Resistivity is measured by the standard four-probe technique. The MR ratio is defined as

$$\frac{\Delta\rho_H}{\rho_0} = \frac{\rho_0 - \rho_H}{\rho_0}, \quad (1)$$

where ρ_0 and ρ_H are the resistivities in the zero and applied field H, respectively. Resistivity is measured by a standard dc four-probe technique with the electrical current parallel to the magnetic field in a physical property measurement system (PPMS, quantum design). The magnetic measurements are carried out with a vibration sample magnetometer (Lakeshore Cryotronics, Inc.).

3. Results

The XRD patterns for the LKMO, LKMO/Ag and LKMO/STO samples at 300 K are shown in Fig. 1, respectively. From the figure, we can see that the LKMO and LKMO/STO samples are homogeneous rhombohedral perovskite structures (space group $R\bar{3}c$) which show double peaks and indicated by the diamond symbol (♦) in Fig. 1. The LKMO/Ag sample is inhomogeneous system containing an Ag metal phase which is indicated by the circle symbol (●) and an orthorhombic perovskite phase (space group *Pbnm*) which shows

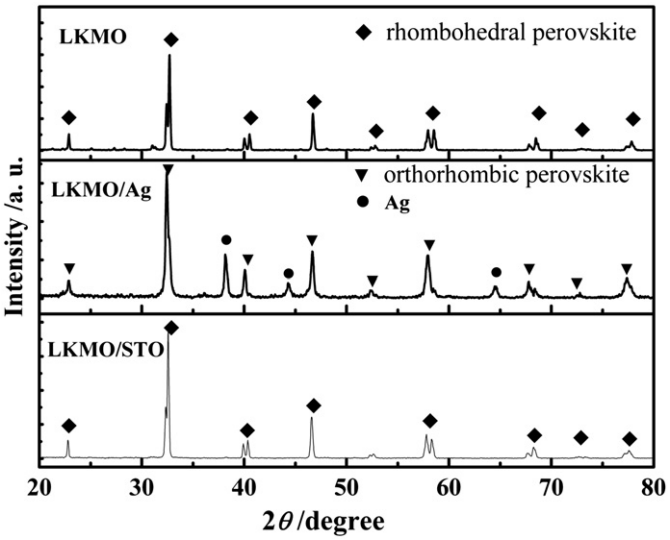

Fig. 1. XRD patterns for LKMO, LKMO/Ag and LKMO/STO.

single peak and indicated by the inversed triangle symbol (▼) in Fig. 1. The lattice parameters, refined by the Rietveld method, are $a=0.5467(3)$ nm and $c=1.3349(8)$ nm for the LKMO sample and slight less than that of the LKMO/STO sample with $a=0.5490(2)$ nm and $c=1.3391(3)$ nm. This phenomenon can be attributed to the following two reasons. On one hand, we know that LKMO crystallites are enclosed by the precursive solution of $SrTiO_3$, which can be seen from the producing process of the LKMO/STO sample. When they are dried and sintered, the thin films of $SrTiO_3$ formed on the surface of LKMO crystallites make potassium atoms be evaporated difficultly during the sintering process. The K^+ ion in $\langle A \rangle$ site has larger radius (0.133 nm) than La^{3+} (0.122 nm), therefore, resulting in the LKMO/STO sample having larger lattice constants than the LKMO sample in which some potassium atoms are evaporated. On the other hand, the effect of substitution of Ti^{4+} for Mn^{4+} in the $La_{0.7}Sr_{0.3}Mn_{1-x}Ti_xO_3$ system has been researched by Kallel et al. [18]. They find that the Ti^{4+} ions can enter into the lattice of perovskite and form homogeneous solid solutions after sintering at 1200 °C. As for our LKMO/STO sample, the Sr^{2+} and Ti^{4+} ions will also enter into the LKMO perovskite structure, diffuse into grains of LKMO along the interface gradually, and replace the Mn^{4+} ions in the $\langle B \rangle$ sites, forming a homogeneous solid solution phase in the sintering process with temperature as high as 1200 °C. The radius of Ti^{4+} (0.064 nm) is larger than Mn^{4+} (0.052 nm), so the LKMO/STO sample has larger lattice constants than the LKMO sample.

The non-magnetic Ti^{4+} ions that enter into the lattice of the LKMO sample and replace the Mn ions in the $\langle B \rangle$ sites reduce the exchange interaction between Mn^{3+} and Mn^{4+}, herewith T_C, which can be proved by the ac susceptibility versus temperature curves in Fig. 2. The T_C that is defined as the inflexion point of the χ–T curve are 277, 287 and 142 K for the LKMO, LKMO/Ag, and LKMO/STO samples, respectively. We can see that the T_C of the LKMO/Ag sample is slightly increased in comparison with the pure LKMO sample. The similar result has also been reported by Joly et al. [19], and is attributed to Ag_2O releasing oxygen. The LKMO is oxygenated by the additional oxygen incorporating in the structure, which increases Mn^{4+} content and reducing the Mn^{3+}/Mn^{4+} ratio. The T_C of the LKMO/STO sample, however, is dramatically lower than that of the pure LKMO sample. In consideration of the fact that the doped $SrTiO_3$ insulator has the similar structure with the LKMO matrix and is easy of entering into the surface structure of the LKMO grains, we believe that the final LKMO/STO sample is a system with the inner pure LKMO grains wrapped by a LKMO/STO surface layer. The magnetic