Magnetic and electrical transport properties on \((\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3)_{1-x}/(\text{CuFe}_2\text{O}_4)_x\) composites

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Abstract. The magnetic and electrical properties of \((\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3)_{1-x}/(\text{CuFe}_2\text{O}_4)_x\) have been investigated. The \((\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3)_{1-x}/(\text{CuFe}_2\text{O}_4)_x\) composites with \(x = 0, 0.01, 0.03, 0.06\) and 0.09 wt.% were prepared by conventional solid state reaction method, respectively. The structures, morphology, magnetic and electrical properties of the samples have been studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and physical property measurement system (PPMS). The resistance measured as a function of temperature demonstrates that the pure LSMO samples display metal to semiconductor transition. On the other hand, the others indicated semiconductor/insulator behaviors. The MR was measured in an applied magnetic field of 0.5T. The results clearly show that the magnetoresistance (MR) effect is enhanced at a wide temperature range with CuFe\(_2\)O\(_4\) composition. It may be helpful to improve the low-field magnetoresistance (LFMR) under the influence of the spin-polarized tunneling and the spin-dependent scattering.

1. Introduction

Perovskite manganites \(\text{Re}_{1-x}\text{A}_x\text{MnO}_3\) (Re: rare earth, A= Ca, Sr, Ba) have attracted a lots of interest due to the colossal magnetoresistance (CMR) [1-4]. These manganites have found two CMR effects: one is intrinsic CMR [5]; the other is extrinsic CMR. The intrinsic CMR is caused by the Zener’s double exchange (DE) mechanism [6] and the cooperative Jahn-Teller effect [7]. However, the intrinsic CMR effect in the perovskite manganites is normally restricted to a magnetic field of several teslas and a narrow range of the metal-insulator (M-I) transition temperature \(T_p\). So, this is far from the practical applications. The extrinsic CMR can be explained by spin-polarized tunneling or spin-dependent scattering at grain boundary of charge carriers [8-9]. The extrinsic CMR can be found at low fields, this behavior is the low-field magnetoresistance (LFMR) effect. The existence of an insulating phase such as \(\text{Al}_2\text{O}_3\) [10], \(\text{NiO}\) [11], \(\text{SiO}_2\) [12], \(\text{CeO}_2\) [13] and \(\text{ZnO}\) [14] in grain boundary improves low field magnetoresistance (LFMR) in a wide temperature range. Many researchers have attempted to synthesize CMR-insulators composites in order to reduce the required magnetic fields of the CMR effects at room temperature.

In this present work, we attempt to introduce the insulating CuFe\(_2\)O\(_4\) into the manganites and investigate the structure, magnetic and electrical transport properties of ferromagnetic/insulator (1-
La$_{0.7}$Sr$_{0.3}$MnO$_3$/xCuFe$_2$O$_4$ composites (referred as LSMO/CFO). We choose CFO as second phase because it is good insulator and nonmagnetic material, thus it can enhance the LFMR effects.

2. Experimental

The (1-x)La$_{0.7}$Sr$_{0.3}$MnO$_3$/xCuFe$_2$O$_4$ samples (x = 0 ~ 0.09) were prepared as follows: First, the pure polycrystalline LSMO was prepared by the traditional ceramic reaction method. The stoichiometric amount of La$_2$O$_3$, Sr$_2$O$_3$ and Mn$_2$O$_3$ (the high purity 99.9%, Aldrich) were ground completely to achieve the homogeneity of the mixed powder for 12h by using a ball milling technology and then pre-calcinated in air at 1000°C for 12h. The pre-calcinated materials were again ground and pre-sintered at 1200°C for 24h. Secondly the prepared LSMO powder was mixed with CFO of high purity and then the mixed LSMO/CFO powders were re-processed, according to the above experimental system to get the expected composites powder. Finally, the LSMO/CFO composites were ground to fine powder and palletized at 5 tons. Finally the samples were sintered at 1300°C for 24h followed by slow cooling, as is an essential and important process to favor the required oxygen content in the material. The structural properties of the LSMO/CFO composites were analyzed by X-ray diffraction (Cu Ka1, λ = 0.154 nm) and the scans were performed with 0.02° step size in the 2θ range of 20 - 80°. The surface morphologies of the LSMO/CFO composites were observed by a JSM 5610 scanning electron microscope (SEM). The M-T curves and resistance (Ω) was measured by using a Quantum Design Physical Properties Measurement System (PPMS) over a temperature range of 100 – 400K.

3. Results and discussion

The XRD patterns of a series of (1-x)La$_{0.7}$Sr$_{0.3}$MnO$_3$ + xCFO (x = 0, 0.03, 0.06, 0.09 and 1) samples are shown in Fig. 1. For the composite samples, the XRD patterns can be indexed to two set of diffraction peaks corresponding to LSMO and CFO phases. As it can be seen, pure LSMO has a rhombohedral structure, and CFO has a single inverse spinel structure and no new phase appeared in the composites. Compared with the XRD pattern of pure LSMO, CFO with low doping level has no effects on the structure of LSMO. In the composite with x=0.09, small diffraction peak at 20 of 35.39° related to CFO appears.

![Figure 1. Room temperature X-ray diffraction patterns of (1-x)La$_{0.7}$Sr$_{0.3}$MnO$_3$/xCuFe$_2$O$_4$ composite with x=0, 0.03, 0.06, 0.09 and 1, respectively.](image)

To confirm the coexistence of both phases in the composites, all samples were examined by SEM.
Fig. 2 shows the back scattering SEM image of pure LSMO and the CFO doped composites of $x=0.03$, 0.06 and 0.09, respectively. From the image of Fig. 2, grain boundaries in pure LSMO ($x=0$) can be clearly observed. While for the compositions, as shown in Fig. 2 ($x=0.03$, 0.06 and 0.09), two phases (LSMO and CFO) are clearly distinguishable from each other. Fig. 2(a, b) show that the main composition at the bright regions (a) are LSMO and the dark regions (b) are CFO with iron. It is obvious that cubic type structure CFO grains are exists between LSMO grains and CFO grain size increases with increasing the CFO contents. The shape of LSMO grains transform from a hexagon to a quadrangle as composition change from $x=0.03$ to $x=0.09$. It is expected that the cause of transition behavior is due to the inter-substitution between manganese in LSMO grains and iron in CFO grains which can transform the shape and volume of LSMO grains.

![Image of SEM micrographs](image)

**Figure 2.** SEM micrographs of (1-$x$) La$_{0.7}$Sr$_{0.3}$MnO$_3$/xCuFe$_2$O$_4$ composites with $x=0 \sim 0.09$.

The temperature dependence of magnetization measured at 0.5T is shown in Fig. 3. All samples have a similar behavior of the magnetization and there is the paramagnetic (PM) to ferromagnetic (FM) transition around Curie temperature ($T_c$). The values of magnetization (M) at 60K are 16.1, 12.8, 11.4 and 4.8 emu/g for $x=0$, 0.03, 0.06 and 0.09, respectively. This decrease in M with increasing CFO concentrations is due to the dilution effect of CFO on the magnetism of the composites and result in additional magnetic disorder. The transition temperature ($T_c$) is decreased from 372K ($x=0$) to 147K ($x=0.09$) and $T_c$ is defined as the temperature where dM/dT reaches minimum. The cause of $T_c$ decrease can be seen that the DE interaction of the compounds will be destructed. We can suggest that the CFO do not react with LSMO, and only located in the interface or surface of LSMO grains.

The temperature dependent of resistivity in magnetic field of 0.5T and with the temperature from 90K to 400K for the LSMO/CFO composites is shown in Fig. 4. We can see that the samples ($x=0$, 0.03 and 0.06) exhibit an insulator to metal (I-M) transition behavior at the transition temperature ($T_p$) and with increasing LSMO content $x$, $T_p$ decreases from 345K to 190K and resistivity increases. While only sample with $x=0.09$ show fully insulator behavior. The transition behavior can be explained by the DE mechanism in LSMO grains [15-17] and the disappearance of I-M transition and increase of resistivity are due to the enhanced grain boundaries. Massive interfaces and boundaries between LSMO and CFO grains may play the role of additional barriers, as results in increase in the carrier scattering causing enhancement in the resistivity.
Figure 3. Temperature dependence of magnetization at 0.5T for (1-x) La_{0.7}Sr_{0.3}MnO_3/x CuFe_2O_4 combined samples.

Figure 4. Temperature dependence of the resistivity at magnetic field of 0.5T for (1-x) La_{0.7}Sr_{0.3}MnO_3/x CuFe_2O_4 combined samples. The inset shows the resistivity for the composites with x=0, 0.03.

Fig. 5 shows the temperature dependence of MR for all samples in the magnetic field of 0.5T and 1T. In this paper, the MR is defined as MR (%) = [ρ(T, 0)−ρ(T, H)]/ρ(T, 0)×100, where ρ(T, 0) and ρ(T, H) are resistivity at zero field and an applied field, respectively. It is found that the MR exhibits a
maximum near the transition temperature and a rising part at low temperatures for all the samples. The MR compared with pure LSMO is enhanced at low temperatures for the composites. Besides, the maximum MR moves to lower temperatures with increment of CFO contents. The values of MR peak are 4.52, 5.12, 6.48 and 11.9% for $x=0$, 0.01, 0.03 and 0.06 at 0.5 T, respectively. The MR% increases for all samples (Fig. 5b) as we increase the magnetic field from 0.5 T to 1 T. There is one MR peaks in pure LSMO and composites with $x=0.03$, 0.06 have two peaks except for the sample with $x=0.09$. The composition $x=0.03$ shows the enhanced MR at room temperature. The low MR peak as the inter-grain magnetoresistance which was explained by the spin polarized tunneling at the grain boundaries and the high MR peak as the intrinsic CMR [1–3] were classified to compare the two MR peaks.

![Figure 5](image_url)  
**Figure 5.** Temperature dependence of MR for the composite with $x=0$, 0.01, 0.03, 0.06 and 0.09, measured at (a) $H_{dc}=0.5T$ and (b) $H_{dc}=1T$
4. Conclusions
In summary, we have studied the magnetic and electrical transport properties of LSMO/CuFe$_3$O$_4$ composition system. The XRD and SEM results show that there is no reaction between LSMO and CFO grains, and CFO is distributed at the grain boundaries or surfaces of the LSMO grains. We have observed that with increasing CFO contents, resistivity increases but magnetization and transition temperature decreases. We can conclude that to form the composites using LSMO as matrix and CFO as dopants can enhance the LFMR in wide temperature range, which is encouraging as regards the practical application of MR materials.

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