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Magnetoresistance properties of $0.99La_{0.7}(Ca_xSr_{1-x})_{0.3}MnO_3/0.01CuZnFe_4O_4$ composites

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Abstract

The composites of $0.99La_{0.7}(Ca_xSr_{1-x})_{0.3}MnO_3/0.01CuZnFe_4O_4$ (LCSMO/CZF) ($x = 0$, 0.1, 0.2, 0.3, 0.5, 0.7 and 1) were fabricated by conventional solid state reaction method, and their electrical transport and magnetoresistance (MR) properties were investigated by physical property measurement system (PPMS). The result of X-ray diffraction (XRD) and scanning electronic microscopy (SEM) indicated that no new phase appeared in the composites except LCSMO and CZF phases. CZF is mainly distributed at the grain boundaries and surfaces of the matrix. The resistivity of all the composites was measured in the range 100–350 K at 0 T, 0.5 T and 1 T magnetic field. Room temperature MR peak appears for the composites $x = 0.03$. The observed variation of MR with varying Ca and Sr concentration has been qualitatively.

Keywords: B. Grain boundaries; C. Magnetic properties; Magnetoresistance; Electrical transport

1. Introduction

Perovskite manganites $L_{1-x}A_xMO_3$ (A = Ca, Sr, Ba) [1] have attracted much attention due to its colossal magnetoresistance (CMR) [2] which has potential application in high speed electronic, magnetic and recording devices, etc. However, the intrinsic CMR in perovskite manganites only can be found within a narrow temperature range around the ferromagnetic–paramagnetic transition temperature at high magnetic field of several teslas, which is incapable for practical application. Since many investigations have been studied, another type of MR effect which is called extrinsic MR effect in polycrystalline manganites has been found. This extrinsic MR is larger and can be found over a wide temperature range at only very low magnetic field. Spin polarized tunneling [3] or spin dependent scattering among neighboring grains seems to be responsible for this kind of MR effects. The introduction of high resistivity second phase in the manganites has a barrier effect to the tunneling process and also causes the magnetic disorder [4] near the grain boundary [5,6]. Hence as the tunneling process is influenced, an enhancement of the magnetoresistance is obtained.

Recently, some attempts have been made to study this enhancement in MR through the formation of composites of $La_{0.7}Ca_{0.3}MnO_3$ (LCMO)/$NiFe_2O_4$, LCMO/$CuFe_2O_4$, $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)/CeO_2, LCMO/$SrTiO_3$, etc. [7–10]. In these systems, nonmagnetic insulators as a second phase were introduced to the perovskite manganites matrix where to form local spin disorder.

LCMO and LSMO are two well-studied manganites among the large number of pure CMR material studied so far. In the present work, we select $La_{0.7}(Ca_xSr_{1-x})_{0.3}MnO_3$ (LCSMO) as the matrix which is a mixture of LCMO and LSMO. According to our research, the Curie temperature (T_c) of LCMO and LSMO are 250 K and 360 K, respectively. When the Ca content x changes, MR at a different transition temperature T_c will be obtained, including room temperature MR. $CuZnFe_4O_4$ (CZF) is selected to be the second phase which has large resistivity and strong ferromagnetic property. The investigation on magnetic properties of LCSMO/CZF has been done. We intend to obtain enhanced MR at room temperature.

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2. Experimental

The $0.99La_{0.7}(Ca_xSr_{1-x})_{0.3}MnO_3/0.01CuZnFe_4O_4$ ($x = 0$, 0.1, 0.2, 0.3 0.5, 0.7 and 1) composites were prepared by two steps. Firstly, LCSMO powders were fabricated by a two step heating process. The stoichiometric amount of La_2O_3, CaO, SrO and Mn_2O_3 raw powders were mixed completely by ball-milling and grinding process and then pre-calcinated at 1000 °C for 10 h. After calcination the powders were again ball-milled and grinded, and finally sintered at 1250 °C for 24 h. Secondly, the obtained LCSMO fine powders were mixed with high purity CZF. Then the above procedure was done again to obtain the expected composites. Finally, the obtained homogenous LCSMO/CZF composites powders were pelletized into rectangular blocks at the press of 10 MPa. For the final sintering temperature we also chose 1250 °C which is a little higher than the melting temperature of LCSMO and lower than that of CZF.

The distribution of CZF in the matrix was analyzed with a JSM-5610 scanning electron microscopy (SEM). The crystal structure of the resulting samples was checked by a Lab centre XRF-1800 X-ray diffraction (XRD) equipment using Cu Kα radiation at room temperature. The electrical transport behaviors were measured by standard four-probe method by using a quantum design physical property measurement system (PPMS) over a temperature range of 100–350 K.

3. Results and discussion

Fig. 1 shows the XRD patterns of the composites LCSMO/CZF at room temperature. With increasing x from 0.1 to 0.7, it shows that the peak intensity of LSMO phase decreases systematically. At $x = 0.1$ the LSMO peak appears as the main peak of the composite, however when the Ca content gets high to $x = 0.7$, LSMO peaks almost disappear and LCMO peak becomes to be the main peak. Except the LCMO and LSMO patterns, there is also another phase which is CZF. Due to the content of CZF 0.01 is too low that the peaks are not obvious. The results indicate that CZF and LCSMO co-exist in the studied composites. There was no chemical interaction during the sintering process. Considering our experimental procedure, before mixing with CZF, a LCSMO-perovskite structure has been formed. Then during the mixing process, the introduced CZF is preferentially segregated from the LCSMO matrix grains.

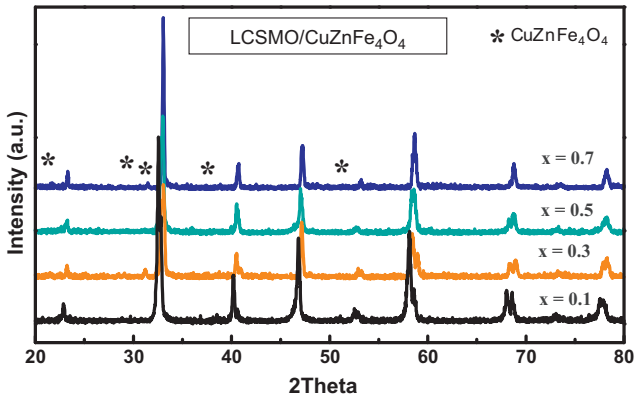

Fig. 1. XRD patterns for selected samples of LCSMO/CZF with $x = 0.1$, 0.3, 0.5 and 8.7.

Fig. 2 gives four representative SEM photographs for pure LCMO, LSMO and LCSMO/CZF $x = 0.3$ and 0.5 composites, respectively. From the images the pure LCMO and LSMO only

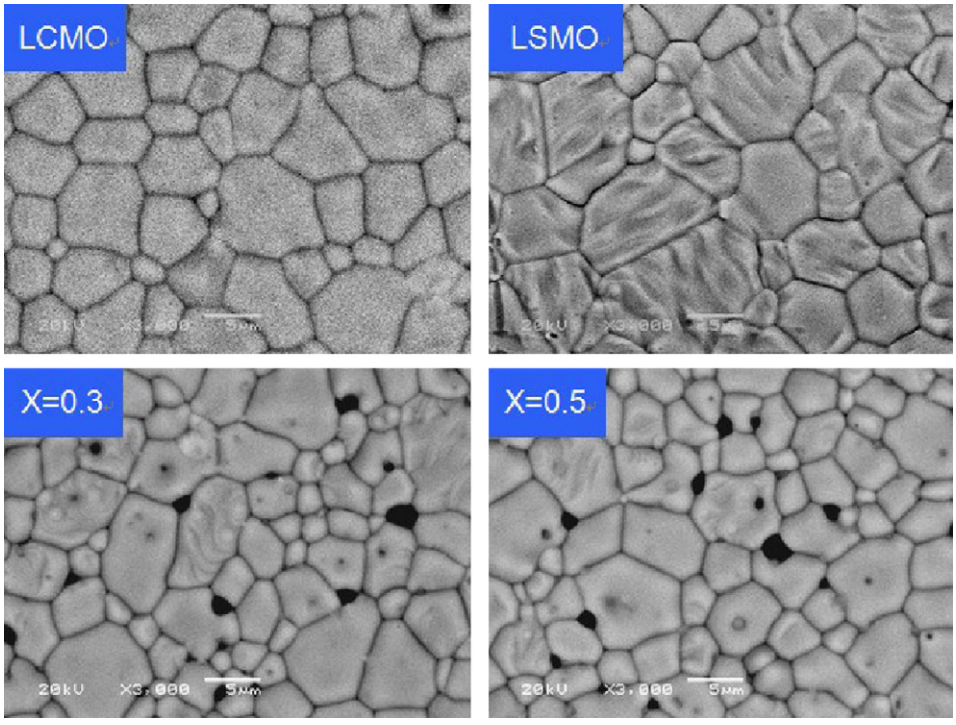

Fig. 2. Scanning electron micrographs of pure LCMO, LSMO and LCSMO/CZF $x = 0.3$ and 0.5.

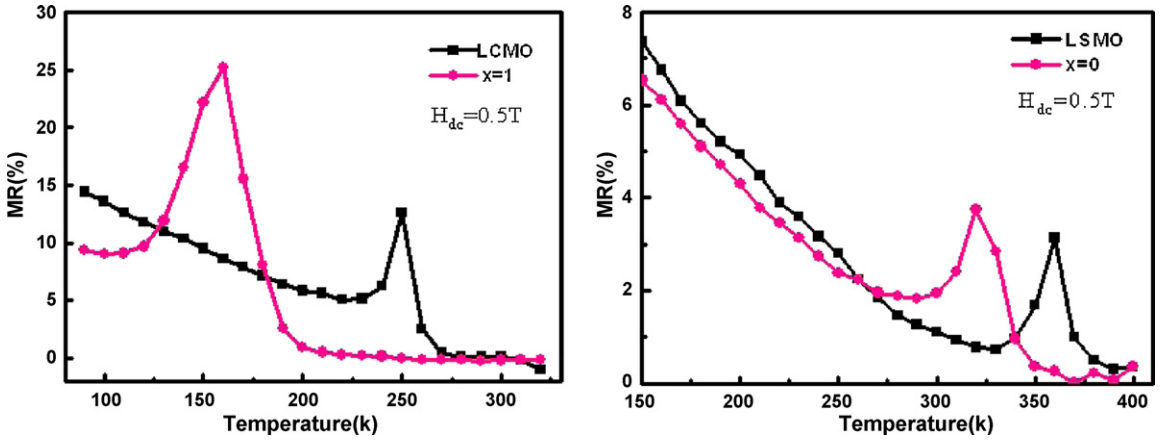

Fig. 3. Temperature dependence MR of pure LCMO, LSMO and LCSMO/CZF ($x = 0$ and 1) at 0.5 T magnetic field.

one single observed. For LCSMO/CZF composites, an obvious second phase embedded into the matrix can be observed which is considered to be CZF phase. The CZF grains present mainly at the boundaries of LSMO grains and each CZF grain is surrounded by adjacent LCSMO grains without forming cluster-like structure which indicates that the LSMO and CZF phase exist independently in the composites. The result is corresponding to the XRD analysis.

The MR of pure LCMO, LSMO and LCSMO/CZF ($x = 0$ and 1) at 0.5 T magnetic field are shown in Fig. 3. MR is defined as MR (%) = $[\rho(T, 0) - \rho(T, H)]/\rho(T, 0)$, where $\rho(T, 0)$ and $\rho(T, H)$ are resistivity at zero magnetic field and an applied magnetic field, respectively. Compare with pure LCMO and LSMO, after introduced by 0.01 content CZF an obvious enhanced MR at lower temperature was obtained. For LCMO composite, MR increases from 12.6% at 250 K to 25.2% at 160 K, and for LSMO composite from 3.1% at 360 K to 3.8% at 320 K. This enhancement of MR originates from the spin-dependent tunneling and scattering process at the interfaces of the grains [3]. As CZF is distributed at the grain boundaries that the structural disorder interfaces play an important role in the energy barrier. When the carriers pass through the interfaces of the grains, the tunneling process which is related to the misorientation of the magnetization in the grains at each side of the grain boundaries should happen. The coexistence of broken bonds and symmetry breaking leads the atoms at the interfaces of magnetic particles to be in disorder state and the magnetic coupling of the interfacial atoms to be weaker. This magnetic disorder increases the spin-dependent scattering and spin-dependent tunneling of conducting electrons, which contributes to the enhanced MR. Due to the large resistivity of CZF that very low content (0.01) can cause great magnetic disorder at the grain boundaries. As a consequence, an obvious enhanced MR is obtained when introduce 0.01 content CZF to LCMO and LSMO.

By comparing the above MR data, LCSMO/CZF $x = 0$ sample has a high MR at low temperature and $x = 1$ sample has a low MR at high temperature. According to this result, we intend to find the room temperature enhanced MR by changing the content of Ca and Sr in the composites. Fig. 4 shows the MR dependence of temperature of LCSMO/CZF ($x = 0.1$–0.7) composites at 0.5 T and 1 T magnetic field. With increasing the Ca content, MR of the composites shows an increasing trend and T_c shows a decreasing trend. Room temperature MR peak is observed by the sample $x = 0.3$, and the value is 5.1% and 10% at 0.5 T and 1 T magnetic field, respectively. MR of the $x = 0.3$ LCSMO/CZF composite at 300 K has also been investigated at different magnetic fields which is shown in Fig. 5. As can be

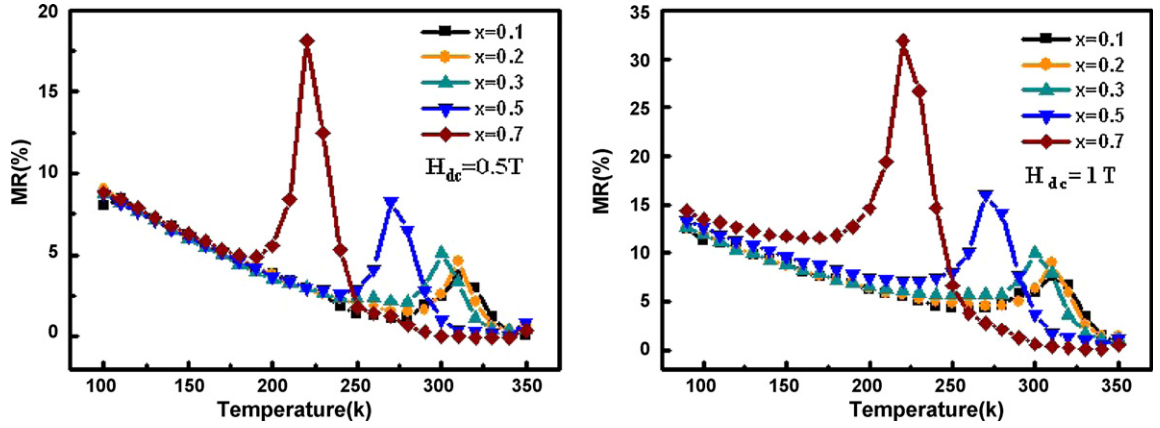

Fig. 4. Temperature dependence of MR of LCSMO/CZF ($x = 0.1$–0.7) composites at 0.5 T and 1 T magnetic field.

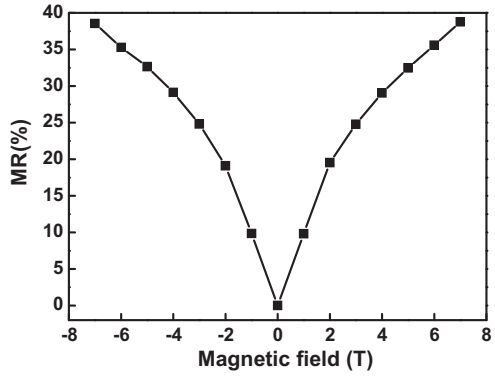

Fig. 5. MR% dependence of magnetic field of LCSMO/CZF $x = 0.3$ composite.

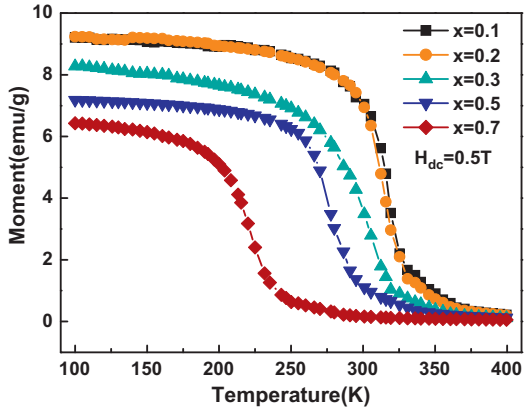

Fig. 6. Specific moment dependence of temperature of the LCSMO/CZF composites.

seen, a group of MR in increasing trend is obtained with increasing the magnetic field.

In order to testify the statement above, we have measured the magnetic properties of the samples with $x = 0.1$–0.7. The temperature dependence of magnetic moment in an applied field of 0.5 T is shown in Fig. 6. The decrease of T_c also can be observed in the M–T curve which is corresponding to the MR analysis. The magnetic interaction between neighboring LCMO ferromagnetic domains is weaker than that of LSMO which can explain the both decrease of magnetization and T_c when Ca content increases.

4. Conclusions

LCSMO/CZF composites have been fabricated carefully and characterized by several experimental techniques. SEM and XRD analyses show the distribution of introduced CZF second phase in the composites and the co-existence of CZF and LCSMO. By introducing the CZF secondary phase to the manganite matrix, the enhancement effect of MR was observed. By changing the Ca content x of the composites 0.99LCSMO/0.01CZF, a group of enhanced MR within a wide temperature range was obtained, including room temperature MR by $x = 0.3$ sample with the value 5.1% and 10% at 0.5 T and 1 T magnetic field, respectively.

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