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# Low-field transport properties of $(1-x)La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3+x(ZnO)$ composites

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ABSTRACT

Composite samples $(1-x)La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$(LCSMO)+$x$(ZnO) with different ZnO doping levels $x$ have been investigated systematically. The structure and morphology of the composites have been studied by the X-ray diffraction (XRD) and scanning electronic microscopy (SEM). The XRD and SEM results indicate that no reaction occurs between LCSMO and ZnO grains, and that ZnO segregates mostly at the grain boundaries of LCSMO. The magnetic properties reveal that the ferromagnetic order of LCSMO is weakened by addition of ZnO. The results also show that ZnO has a direct effect on the resistance of LCSMO/ZnO composites, especially on the low-temperature resistance. With increase of the ZnO doping level, $T_P$ shifts to a lower temperature and the resistance increases. It is interesting to note that an enhanced magnetoresisitance (MR) effect for the composites is found over a wide temperature range from low temperature to room temperature in an applied magnetic field of 3 kOe. The maximum MR appears at $x = 0.1$. The low field magnetoresistance (LFMR) results from spin-polarized tunneling. However, around room temperature, the enhanced MR of the composites is caused by magnetic disorder.



## 1. Introduction

The discovery of the colossal magnetoresistance (CMR) effect in manganites [1,2] has caused a renewed interest in these perovskites, which are known for more than 50 years [3,4]. Much research has been done on the manganites $Re_{1-x}A_xMnO_3$ (Re = rare earth, A = Ca, Sr, Ba). So far, two CMR effects have been found in these manganites, the intrinsic CMR and extrinsic CMR. The intrinsic CMR [5] is caused by the double exchange (DE) mechanism. The DE mechanism, which has been proposed by Zener in 1951 [6], is useful to explain the CMR phenomena observed near Curie temperature ($T_C$) at a relative high magnetic field (up to several kOe). The extrinsic CMR, which is related to the grain boundaries [7], can be explained by spin-polarized tunneling [5] or spin-dependent scattering [7]. Unfortunately, as temperature increases, the low field grain boundary magnetoresistance decreases rapidly, hindering the utilization of this effect in sensor application.

Much effort has been made to enhance the LFMR, such as synthesizing CMR–insulator composites. These extrinsic effects rely on the existence of an insulating tunneling barrier separating the ferromagnetic grains. Such attempts include LCMO/$Al_2O_3$ [8], LSMO/$CeO_2$ [9], LCMO/$SrTiO_3$ [10], LBMO/YSZ [11], and so on.

For practical application, we hope to realize CMR at a low magnetic field and at room temperature. As we know, the magnetic-ordering temperature $T_C$ of LCMO is about 270 K, which is below room temperature, while $T_C$ of LSMO is far above the room temperature. At the transition temperature, the MR value of LCMO is relatively bigger than that of LSMO. So we can make hypothesis that when we change the value of $x$ in $La_{0.7-}Ca_{0.3-x}Sr_xMnO_3$ we can get an intrinsic CMR at room temperature. In this paper, we select $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ (LCSMO) as the matrix phase.

The effects of $Zn^{2+}$ ions substituting for $Mn^{3+}$ ions by solid-state synthesis have been reported [12]. The electrical transport behavior of the composites has been investigated in a lower magnetic field through liquid phase method and solid state reaction [13], and the low-field magnetotransport properties of LSMO/ZnO nanocomposite films via pulsed laser deposition have also been studied [14,15]. But the maximum MR generally occurred at low temperature or the value of MR is not big in their work. Vijayanandhini and Kutty have reported the magnetically tunable nonlinear electronic properties for the composites

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of ZnO/$La_{0.6}Sr_{0.4}MnO_3$ [16]. In the present work, we select ZnO to investigate the effects of high resistance on LCSMO and intend to get an enhanced room temperature magnetoresistance.

## 2. Experiment

$La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$+$x$(ZnO) ($x = 0$, 0.01, 0.03, 0.05, 0.08, 0.1, 0.15, 0.25, 0.35, 0.5 and 0.6) composites were prepared by two steps. Firstly, the LCSMO powder was prepared using a solid-state reaction: stoichiometric mixtures of $La_2O_3$, $CaCO_3$, $SrCO_3$ and $MnO_2$ were ground for 12 h by using ball milling technology and presintered in the air at 800 °C for 10 h. After the second milling for 2 h, the powders were pressed into pellet form with the parameter $10 \times 5\ mm^2$ under the pressure about 10 MPa/$cm^2$ and sintered in the air at 1200 °C for 10 h. Thus the pure LCSMO was prepared successfully. Secondly, the series of ceramic samples of LCSMO+$x$(ZnO) composites were mixed thoroughly and sintered at 1000 °C for 3 h. The structure of the specimen was examined by XRD using Cu $K_\alpha$ radiation. The particle size and shape was studied by SEM together with energy dispersive analysis of X-rays (EDX). The DC magnetization was measured using a vibrating sample magnetometer (VSM) in an applied magnetic field of 6 kOe from 100 to 340 K. The temperature dependence of resistivity was measured by a standard four-probe technique in the temperature range from 110 to 340 K under a zero and 3 kOe magnetic field, respectively. We also measured the magnetic field dependence of magnetoresistance in a magnetic field from 0 to 20 kOe at 300 K for the composites (1−$x$)LCSMO+$x$(ZnO) with $x = 0$, 0.05, 0.08, 0.1, 0.15 and 0.25.

## 3. Results and discussion

The XRD patterns of the composites ($x = 0$, 0.01, 0.05, 0.08, 0.15 and 0.35) are shown in Fig. 1, and the inset shows the structure of ZnO. For all samples, the XRD analysis exhibits that the composites consist of two phases: one is LCSMO perovskite phase; the other is ZnO phase. The diffraction peaks of LCSMO do not shift. The peaks corresponding to ZnO are also observable. The

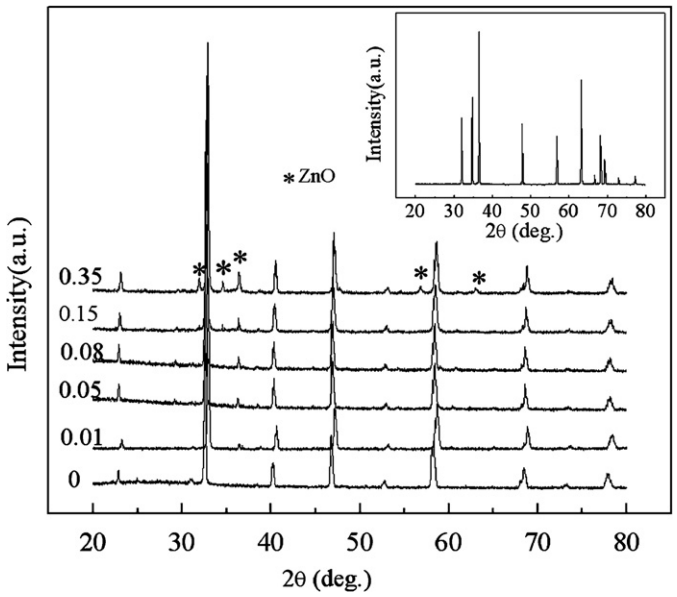


**Fig. 1.** XRD patterns for selected samples of (1−$x$)LCSMO+$x$(ZnO), with $x = 0$, 0.01, 0.05, 0.08, 0.15 and 0.35, from bottom to top; the inset shows XRD patterns for ZnO.

results show that there is no reaction between LCSMO and ZnO. With increasing ZnO content, the peak intensity of ZnO phase increases, which indicates that ZnO grains are mainly segregated at the grain boundaries or surfaces of LCSMO grains. The result of SEM (see Fig. 2) also supports this opinion.

Fig. 2 typically shows a SEM micrograph of (1−$x$)$La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$+$x$(ZnO) composites as well as the EDX patterns for the composite with ZnO content $x = 0.35$. There is a clear grain boundary in pure LCSMO (see Fig. 2(a)). The grain size of pure LCSMO is larger than that of composites, for the composites has been grounded for another 2 h. From Fig. 2(b), it can be observed that as the ZnO dopes into the matrix the grain boundaries become ambiguous, and the bright areas (ZnO) appears, which is confirmed by the EDX.

The temperature dependence of the specific magnetic moment ($\sigma_S$) for several selected samples of (1−$x$)$La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$+$x$(ZnO) in an applied field of 6 kOe is shown in Fig. 3. With the increase of ZnO content, the volume fraction of the ferromagnetic LCSMO phase in the composites decreases and the nonmagnetic ZnO phase increases, so $\sigma_S$ monotonously decreases. All the composites have almost the same behavior of the magnetization as a function of temperature and there is a shift in the paramagnetic (PM) to ferromagnetic (FM) phase around $T_C$, which moves towards lower values with ZnO content increasing. The embedding of ZnO into LCSMO matrices not only dilutes the magnetization but also results in additional magnetic disorder [17]. As observed by SEM, ZnO segregates at the grain boundaries or surfaces, which affects the doubling-exchange (DE) mechanism [17]. Consequently, it leads to the suppression of the PM–FM transition temperature towards lower values with increasing the ZnO concentration. In fact, the reduction in magnetization also suggests the suppression of the DE mechanism, because the ZnO at the grain boundaries blocks the alignment of Mn ions in neighboring pure LCSMO grains. This indicates that magnetic spin disorder is due to the grain boundaries in the composites.

Fig. 4 shows the temperature dependence of zero-field resistivity of the composites LCSMO/ZnO with $x = 0$, 0.01, 0.03, 0.05, 0.08, 0.1, 0.15, 0.25, 0.35, 0.5 and 0.6 measured at 110–340 K. Results show that: (1) When $x \leqslant 0.05$, a metal-insulator (M–I) transition is observed at the temperature $T_P$. With increasing ZnO doping level $x$, the transition temperature $T_P$ decreases and the resistivity increases. (2) When $x \geqslant 0.08$, two transition temperatures appear. One is the intrinsic metal–insulator transition temperature ($T_{P1}$) at a higher temperature and the other is a new transition temperature ($T_{P2}$) at a lower temperature. With increasing ZnO doping level $x$, $T_{P1}$ keeps the same, and the resistivity at $T_{P1}$ increases; however, the transition temperature $T_{P2}$ decreases, and the resistivity at $T_{P2}$ increases monotonously. At high doping level, $T_{P2}$ decreases very slowly, while the resistivity keeps increasing.

In order to understand the electrical properties of the composites, it is necessary to discuss the formation of two transition temperatures. $T_{P1}$, the intrinsic transition temperature, is related to the DE interaction between $Mn^{3+}$ and $Mn^{4+}$ ions. With the increase of ZnO doping level, the stoichiometry of LCSMO does not change, and the DE interaction in the core of LCSMO grains will not be affected, so $T_{P1}$ does not change. But as ZnO distributed at the grain boundaries of LCSMO, it has a direct impact on the DE interaction in LCSMO domain at the grain boundaries. It increases the disorder of the Mn ions spin orientation between the grain boundaries and decreases the ferromagnetic coupling, and then it leads to the decrease of $T_{P2}$. With increasing ZnO doping level $x$, the high resistivity of the composites should be related to the effect of insulator phase ZnO. In pure LCSMO, electrical transport occurs through a direct contact among LCSMO grains. However, there are two parallel conduction channels in LCSMO/ZnO