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Enhanced room-temperature magnetoresistance in high-temperature sintered La_{2/3}Sr_{1/3}MnO₃ doped with ZrO₂

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Abstract

Granular metal/insulator ($La_{2/3}Sr_{1/3}MnO_3$ doped with ZrO₂) composites were prepared by high-temperature sintering. The effects of sintered time on structure and grain size, as well as on magnetic and electric properties have been investigated. The XRD patterns of all doped samples show that the crystal structure is predominantly a perovskite phase with $R\bar{3}c$ symmetry, in addition to the minor secondary compounds (SrZrO₃, $La_2Zr_2O_7$ and ZrO₂). The microscopic studies show that the long-time sintered samples have excellent connectivity between grains. The analysis of XPS reveals that the loss of oxygen occurs during the high-temperature sintering in air. It is also found that with sintered time increasing the paramagnetic insulator–ferromagnetic metal transition temperature T_C (or T_P) decreases gradually and the room-temperature magnetoresistance increases significantly. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The compounds $\text{Re}_{1-x}A_x\text{MnO}_3$ have recently attracted much attention (where Re is a trivalent rare-earth ion and A is a divalent ion) [1,2]. They show a transition from a paramagnetic semiconducting to a ferromagnetic quasimetallic state at the Curie temperature (T_C). Many of these compounds also exhibit the colossal negative magnetoresistance (CMR), being most pronounced in the vicinity of T_C . So far many investigations on CMR materials have concerned some aspects relative to their application. To this aim, materials need to be tailored with great negative magnetoresistance in lower magnetic field and proper temperature range, since the magnetoresistance (MR) effect of single crystals and epitaxial films commonly

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occurs only at a high magnetic field and within a narrow temperature range around $T_{\rm C}$, much beyond the premise of application [1,3]. By tuning the composition of these compounds, e.g., doping A or B site with other ions of different sizes or charges, one can control the competitions among the double-exchange(DE), superexchange, and Coulomb interactions between Mn ions, and thus modify the magnetoresistive properties of these perovskite compounds [4,5]. As reported previously, the MR effect of polycrystalline compounds exhibit a low-field magnetoresistance (LFMR) in a broad temperature range [6,7]. The LFMR has been explained by the following two possible mechanisms. Firstly, the spin-polarized conduction electrons tunnel across grain boundaries and interfaces separated by an energy barrier, which is the so-called tunnel magnetoresistance (TMR) [6]. The second mechanism is the electrons spin-dependent scattering by barrier layers, which leads to giant magnetoresistance (GMR) of granular film [8]. Thus, tuning grain surfaces or barrier

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layers by altering the size of the ferromagnetic grains, making artificial boundaries or diluting with a nonmagnetic insulator will significantly influence the transport process [9–11]. In recent years, it was reported that introduction of a second phase into the ferromagnetic manganite matrix had resulted in an enhancement of MR [12–14]. These secondary phases include insulating oxide [11,12]; half-metallic ferromagnet [13] and polymer composite [14], etc. It was further pointed out that the conduction behavior and MR effect of the perovskite manganites are significantly influenced by the grain connectivity [15,16].

In this paper, we introduce ZrO_2 as the second phase into the manganite and investigate the effect of sintered time on magnetotransport properties and MR in $La_{2/3}Sr_{1/3}MnO_3$ (LSMO)+0.1 (the mole fraction) ZrO_2 granular composites. Firstly, the LSMO manganite is nearly 100% spin polarization [6], which may boost magnetoresistance associated with spin-dependent tunneling; and LSMO has high Curie temperature ($T_C \approx 360$ k) [2], being available to attain a large MR at room temperature. Secondly, due to the low solid solubility of Zr ions in $La_{2/3}Sr_{1/3}MnO_3$, only a small amount of Zr^{4+} ions go into the lattice of $La_{2/3}Sr_{1/3}$ MnO₃ [17] and most Zr^{4+} ions segregate as secondary at grain boundaries insulating compounds at higher Zr content [17,18], which will influence the transport process. Thirdly, the grain connectivity of samples can be improved by high-temperature sintering with long time [15,16].

2. Experimental

 $LSMO + 0.1(ZrO_2)$ samples were fabricated by three steps. Firstly, the LSMO powders were prepared by sol-gel method [17] and sintered at 1300 °C for 8 h. Secondly, the ZrO_2 particles were pre-prepared by a thermal decomposition method. $Zr(NO_3)_4 \cdot 5H_2O$ was sintered in air at 650 °C for 8 h. Thirdly, the above two pre-prepared powders in an appropriate mole ratio were completely mixed, ground carefully, and subsequently pressed into discs under 400 MPa. The final sintering process was carried out at 1400 °C in air for 1, 4, 8, 24, 48 h, respectively, and then furnace cooled in air, to obtain a series of granular samples (these samples are called Zr1h, Zr4h, Zr8h, Zr24h, Zr48h, respectively), as well as LSMO was carried out at 1300 and 1400 °C for 8 h in air. X-ray diffraction (XRD) was used to characterize the structure of the samples with Bruker D8-ADVANCE. The morphology was probed by FEG SEM Sirion. An X-ray photoelectron spectroscopy (XPS) spectrum was obtained with Kratos XSAM800. Mg Ka (1253.6 eV) X-ray source was used for excitation. The resistivity ρ and saturated magnetization Ms measurements were carried out by physical property measurement system (PPMS). The DC magnetization measurements were carried out with the vibrating sample magnetometer (VSM) of the IDE Corporation in the temperature region of 150-400 K. The paramagnetic-ferromagnetic transition temperature $(T_{\rm C})$ was taken as the minimum dM/dT. The resistivity measurements were performed by standard four-probe method in the temperature range from 380 to 20 K. The MR was defined as $MR = (\rho_0 - \rho_{3T})/\rho_0$, where ρ_{3T} and ρ_0 are the resistivities measured at 3 T magnetic field and zero field, respectively.

3. Results and discussions

Fig. 1 shows a series of powder XRD patterns of LSMO(1400 °C). Zr1h. Zr4h. Zr8h. Zr24h. and Zr48h. recorded at room temperature. The XRD pattern for the undoped sample shows a single-phase perovskite structure with $R\bar{3}c$ symmetry. But the impurity phases including SrZrO₃, La₂Zr₂O₇ and ZrO₂ occur in all Zr-doped samples investigated here. These impurity phases are still retained even after 48 h sintering at 1400 °C, indicating that only limited amount of Zr can go into the lattice of $La_{2/3}Sr_{1/3}$ ₃MnO₃. Although these impurity phases appear in all our doped samples, their contents are quite low (see the inset of Fig. 1). The lattice parameters of these samples are shown in Table 1. The lattice parameters of LaMnO_{3.15} in the JCPDSICDD (No. 32-0484) are a = 5.523 Å and c = 13.324 Å in a hexagonal system. The lattice parameters of our sample for LSMO are close to these values. The lattice parameters of LSMO $+ 0.1(ZrO_2)$ sets of samples increase slightly with the sintered time. This can be explained in terms of the different ionic radii of Zr⁴⁺ and Mn^{4+} ions (they are 0.72 and 0.53 Å, respectively [19]), or in terms of the oxygen vacancies as reported by Rojas et al. [20].

Fig. 2 shows the typical SEM micrographs for several samples. It can be seen that the size of grains gradually increases and the connectivity between grains becomes excellent with prolonging sintered time. One hour sintered sample is very porous with a small grain size of about $5 \,\mu\text{m}$ and contains a large number of weakly linked grain boundaries. By contrast, the 48 h sintered sample appears very dense with an excellent connectivity and melting



Fig. 1. X-ray powder diffraction patterns of LSMO(1400 °C), Zr1h, Zr4h, Zr8h, Zr24h and Zr48h. The inset shows the relative enlarged diffraction patterns.

Table 1				
The experimental	data	of	partial	samples

Samples	Temperature (°C)	Time (hours)	a (Å)	<i>c</i> (Å)	$T_{\rm C}$ (K)	$T_{\mathrm{P}}\left(\mathrm{K}\right)$	CMR (%)
LSMO	1400	8	5.523	13.332	377	373	8.5
Zrlh	1400	1	5.5.510	13.389	330	358	18.7
Zr4h	1400	4	5.515	13.391	323	354	21.5
Zr8h	1400	8	5.519	13.389	323	337	28.9
Zr24h	1400	24	5.520	13.391	297	336	32.3
Zr48h	1400	48	5.528	13.406	297	347	34.4



Fig. 2. SEM morphologies of samples: (a) Zr1h, (b) Zr4h, (c) Zr8h, (d) Zr48h.

occurs in the some parts of the surface, similar to the observed previously in partially melted polycrystalline [15,16].

Since the Mn⁴⁺ content is a crucial factor in controlling the magnetic and transport properties [21,22], we examined the valence states of the manganese ions in the LSMO(1300 °C) and LSMO $+ 0.1(ZrO_2)$ samples with XPS. The samples were ground with a mortar and pestle before the XPS measurement. Fig. 3 shows the XPS spectra and their corresponding fitting curves for the Mn 2p level of LSMO, Zr1h, Zr8h and Zr24h. The peak positions of Mn^{3+} are observed at 641.3, 641.6, 641, and 641.7 eV for LSMO, Zr1h, Zr8h and Zr24h, respectively. They are close to the binding energy value 641.9 eV of the Mn $2p_{3/2}$ level in α -Mn₂O₃ [23]. The peak positions of the Mn⁴⁺ are observed at 642.8, 643.3, 643 and 643.7 eV, respectively. They are close to the binding energy value 643.35 eV of the $Mn^{4+}2p_{3/2}$ level in La_{0.9}Te_{0.1}MnO₃ [24]. It can be obtained from their fitting areas in Fig. 2 that the ratios of $Mn^{4+}/$ $Mn^{3+} + Mn^{4+}$ are 36.7%, 36%, 34.5%, 32.4% for LSMO, Zr1h, Zr8h and Zr24h, respectively, indicating that some of Zr⁴⁺ into Mn⁴⁺ site, meanwhile, a certain amount of the oxygen is lost during sintering at high temperature in air.

Fig. 4 shows curves of the magnetization versus temperature at applied field 0.02 T for the various samples.

The Curie temperatures are 377, 330, 323, 323, 297 and 297 K for LSMO(1400 °C), Zr1h, Zr 4h, Zr 8h, Zr 24h and Zr 48h, respectively, as shown in Table 1, Obviously, the $T_{\rm C}$ values for LSMO + 0.1(ZrO₂) samples decrease gradually with increasing sintered time. It is also noticed that the pure LSMO sample shows the sharpest transition, but the transition for the LSMO $+ 0.1(ZrO_2)$ samples becomes very broader and a residual tail is observed until 365 K. The magnitude of low-temperature magnetization under a magnetic field of 0.02 T for the short-time sintered samples is not remarkably different, while it decreases for long-time sintered samples. One of the possible reasons for the lower magnetization of 48 h is due to the presence of a large number of strong-link boundaries between domains. The domain walls at the strong-link grain boundaries enhance the interaction between domains in each strong-link grain. Therefore, alignment of spins in each domain is hardly enhanced at a low field than other samples below $T_{\rm C}$ [16]. The inset shows the magnetic field dependence of magnetization (M-H) of all samples recorded at 10 K. For the undoped sample, the experimental saturated magnetization of 89.3 emu/g agrees well with the theoretically expected the M_s of 91 emu/g for pure La_{2/3}Sr_{1/3}MnO₃ (assuming spin-only moment). For the samples doped with Zr, the saturated magnetization M_s is almost identical, say, e.g., $M_s \sim 83 \,\mathrm{emu/g}$.



Fig. 3. The Mn 2p spectra and the fit curves (a) LSMO(1300 °C), (b) Zr1h, (c) Zr8h, (d) Zr24h.



Fig. 4. The magnetization versus temperature curves for partial samples. The inset shows the relative magnetization versus applied field measured at 10 K.

Fig. 5 shows the temperature dependence of the resistivity ρ on cooling. For all samples, the resistance at zero field increase with decreasing temperature until insulator-metal transition temperature $T_{\rm P}$. Below $T_{\rm P}$, the resistance decreases on further cooling down to 20 K. With increasing sintered time, the resistivity ρ increases markedly for all samples except for Zr48h one. Meanwhile, the insulator-metal transition temperature $T_{\rm P}$ decreases gradually (seen Table 1), from 370 K for LSMO(1400 °C) down to 336 K for Zr24h. The Zr48h sample exhibit a



Fig. 5. Temperature dependence of resistivity of partial samples without the field.

decrease in resistivity and a slight increase in $T_{\rm P}$ value (see Table 1) by comparing with Zr24h. It is also noted that the resistivity of Zr48h drops quickly as the temperature is lowered and becomes smallest among all LSMO+0.1(ZrO₂) samples at T < 205 K. The lower resistivity appearing in the Zr48h sample may result from its good inter-grain connectivity produced by prolonging sintered time. A good connectivity between grains may open up many new conduction channels and thus reduce the effective contact resistance between grains [25].

Fig. 6 shows the MR as a function of temperature under an applied magnetic field of 3T. Clearly, every $LSMO + 0.1(ZrO_2)$ sample exhibits a MR peak around room temperature and the CMR peak gradually increases with prolonging sintered time. The CMR peak values are 9.5%, 18.7%, 21.5%, 28.9%, 32.3%, 34.5% for LSMO(1400 °C), Zr1h, Zr4h, Zr8h, Zr24h and Zr48h, respectively, as shown in Table 1, For the Zr1h and Zr4h samples, the MR peaks are lower and wider, but for Zr8h, Zr24h and Zr48h, the CMR peaks become higher and sharper. These CMR peaks may be interpreted in terms of the intrinsic MR component related to DE interaction. In the low-temperature ferromagnetic metallic regime, a marked MR effect can still be seen far below $T_{\rm C}$ and it increases with decreasing temperature. In Fig. 6, it is also noticed that the samples showing the higher CMR peak exhibits lower low-temperature MR. It is worth pointing out that the CMR for long-time sintered samples (i.e., for Zr24h, Zr48h) have very high CMR values around room temperature. Such a large MR effect in room temperature could be useful for future applications in MR device.

Summarizing the above experimental results, the electric and magnetic properties change with sintered time. The $T_{\rm C}$ (or $T_{\rm P}$) decreases gradually and the resistivity (ρ) increases with increasing sintered time. Correspondingly, the CMR peaks become higher and narrower. Generally, larger resistivity and lower $T_{\rm C}$ are associated with a higher MR ratio. The increase in CMR peak height by prolonging sintered time can be explained in terms of the intrinsic DE interaction and the effect of grain boundaries. As the sintered time increases, more Zr^{4+} ions enter into the $La_{2/}_{3}Sr_{1/3}MnO_{3}$ lattice to replace $Mn^{4+}.$ The appearance of Zr^{4+} ions in the La_{2/3}Sr_{1/3}MnO₃ lattice demolishes the DE interaction and causes the local magnetic disorder around doped Zr sites, thus leading to the decrease in $T_{\rm C}$ and to the increases in both resistance and MR around $T_{\rm C}$ [26,27]. Simultaneously, the distribution of Zr ions becomes more homogeneous, which leads to the higher and sharper CMR



Fig. 6. Temperature dependence of MR of partial samples under a magnetic field of 3 T.

peaks. Moreover, the defects on the grain boundaries decrease due to the strong-link boundaries between grains and to the increased grain size, also enhancing the room temperature MR. These results are similar to those observed previously in LCMO polycrystalline [15,16].

It should be mentioned that the MR at low temperatures decreases with the prolonging sintered time. This results from that disorder magnetization of grain boundaries is dramatically reduced in the long time sintered samples due to improved connection between the domains [16], which leads to reduce the spin-dependent tunneling across the grain boundaries [6,12] or spin-dependent magnetic domain scattering at boundary regions [8,28]. This indicates that prolonged sintered time increases the effective channels for metallic conductivity at low temperature, which coincides with the change of resistivity.

Noticeably, in our studied samples, the effect of sintering time on electrical transport and magnetic transport properties show a difference at 24 h. At the sintering time of 24 h, a good connectivity between grains is obtained, so the magnetization becomes smaller [16], but no good electrical transport path (percolation) is obtained. As the sintering time increase, the magnetization decrease further, and a good electrical transport path is formed at the sample, so a lower resistivity is observed in the sample sintered 48 h.

4. Conclusions

The effect of sintered time on structure, grain size, magnetic and electric properties in $La_{2/3}Sr_{1/3}MnO_3 + 0.1(Z-rO_2)$ composites have been investigated systematically. It has been found that the long-time sintered samples show an excellent connectivity between grains. Significantly enhanced room-temperature CMR effect has been achieved in the Zr-doped samples, especially for the long time sintered samples, which profits for the potential application of MR materials.

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