Research Article

The Effect of Reducing Time on the Magnetoresistance of Manganite $\text{La}_{0.67}\text{Sr}_{0.20}\text{Cu}_{0.10}\square_{0.03}\text{MnO}_3$ at a Temperature of 30°C

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$\text{La}_{0.67}\text{Sr}_{0.20}\text{Cu}_{0.10}\square_{0.03}\text{MnO}_3$ (“ $\square$ ” representing cation vacancy) polycrystalline manganite powder was synthesized by sol-gel method, which we used as parent materials. After reduced in hydrogen atmosphere for 30 and 60 minutes at a temperature of 400°C , the series bulk samples were obtained by sintering in argon atmosphere for 12 hours at 1100°C . The structure, electrical and magnetic properties, and colossal magnetoresistance of samples were researched in detail. Experiment results indicate that under an applied magnetic field of 1.8 T, the two bulk samples sintered in Ar atmosphere for 12 hours at 1100°C , with the powder reduced for 30 and 60 minutes in 400°C hydrogen atmosphere for $\text{La}_{0.67}\text{Sr}_{0.20}\text{Cu}_{0.10}\square_{0.03}\text{MnO}_3$ parent powders, respectively, have the stable MR $(11.0 \pm 0.3)\%$ and $(10.0 \pm 0.5)\%$ in temperature region from 270 K to 330 K. This is important for the potential application of this kind of magnetoresistance materials.

1. Introduction

Manganite $\text{R}_{1-x}\text{T}_x\text{MnO}_3$ with ABO_3 perovskite structure, where R and T are rare earth and alkaline earth ions, respectively, has been extensively studied due to its abundant physics related to colossal magnetoresistance (CMR) and its potential application in magnetic devices [1–4]. In general, the MR magnitude of a perovskite manganite reaches the maximum only at the Curie temperature (T_C), which is beyond the room temperature region generally. And the MR changes abruptly with the temperature approaching the Curie temperature. These properties severely limit the practical applications of these materials [5–8]. Many researchers have thus been concentrated on making new material system that provides low-field magnetoresistance (LFMR) around room temperature. On the other hand, recent efforts to broaden the CMR temperature range have been made by means of the Mn-site substitution or oxygen deficiency [9–12]. Brando et al. [11] studied the dependence of oxygen deficiency on electrical and magnetic properties of $\text{La}_{0.85}\text{Na}_{0.15}\text{MnO}_{3-\delta}$ ($\delta = 0; 0.04; 0.10$), they found that when the δ increased, the Curie temperature of the samples decreased. Liu et al. [12] studied the electrical

properties and magnetoresistance effect and found that for $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$, Sr-site substituted by Cu and leading to vacancy could both change the peak temperature (TMR) of MR to room temperature and improve the peak value of MR.

In this paper, we chose $\text{La}_{0.67}\text{Sr}_{0.20}\text{Cu}_{0.10}\square_{0.03}\text{MnO}_3$ as parent materials because its TMR is higher than room temperature, and its MR value is a little bigger. By means of reducing the powders in different temperature hydrogen atmosphere and changing the oxygen content of the parent materials, both the stabilization of MR and the peak value of MR are improved.

2. Experiment

$\text{La}_{0.67}\text{Sr}_{0.20}\text{Cu}_{0.10}\square_{0.03}\text{MnO}_3$ polycrystalline manganite powder was prepared by sol-gel method [12], which we used as parent powder materials. After reduced in hydrogen atmosphere for 30 and 60 minutes at a temperature of 400°C , the series bulk samples were obtained by sintering in argon atmosphere for 12 hours at 1100°C .

The phase identification of samples at room temperature has been carried out by the X-ray diffraction (XRD) with an

FIGURE 1: X-ray diffraction patterns for bulk samples B1 (a), B2 (b), and B3 (c).

TABLE 1: The lattice parameters and unit cell volume for bulk samples B1, B2, and B3.

Sample ID	Lattice parameters		Crystal cell volume $V/\text{\AA}^3$
	$a/\text{\AA}$	$c/\text{\AA}$	
B1	5.5273	13.371	353.77
B2	5.5158	13.356	351.92
B3	5.5160	13.366	352.19

18 kW Rigaku Max-RB diffractometer with $\text{CuK}\alpha$ radiation in the 2θ range of 20° – 80° . The magnetization measurements were carried out with a Lake Shore vibrating sample magnetometer (VSM) in the temperature region of 120–370 K. All the Curie's temperature measurements were performed at an applied field 0.05 T. The morphology was obtained by S-570 scanning electron microscopy (SEM). The temperature and magnetic field dependences of the resistivity were measured (using Oxford Maglab Exa Measurement System) with the standard DC four-probe method, and the applied field was parallel to the direction of current.

3. Results and Discussion

3.1. X-Ray Characterization. The structural characterization of the powder samples grinding from the bulk samples was determined. Figure 1 shows the X-ray diffraction patterns for bulk samples B1–B3. (B1: parent materials; B2: reduced for 30 min; B3: reduced for 60 min). The results indicate that the materials are a single phase with $R\bar{3}c$ perovskite phase without any other secondary or impurity phase.

We use a Rietveld refinement software Fullprof Suite to calculate the lattice parameter and crystal cell volume. The results are given in Table 1. It can be seen from Table 1 that the lattice parameter and crystal cell volume of reduced samples B2 and B3 are slightly lower comparing to parent sample B1, thus causing the Mn–O bond length of the unit cell to be slightly lower.

3.2. Morphology of the Powder Sample. Figure 2 shows the scanning electron microscopy (SEM) morphology of powder

TABLE 2: The Curie temperature T_C (K) and special saturation magnetization σ (Am^2/kg) for samples B1 (a), B2 (b), and B3 (c).

Sample ID	T_C (K)	σ (Am^2/kg)
B1	337.6	9.5
B2	307.3	4.3
B3	305.2	3.2

samples B1, B2, and B3. From Figure 2, we can see that the $\text{La}_{0.67}\text{Sr}_{0.20}\text{Cu}_{0.10}\text{MnO}_3$ parent sample B1 prepared by sol-gel method possesses homogeneously globular shape grains, and the grain size is about 100 nm. After being reduced by hydrogen, the phenomenon of conglomeration in particles was improved.

3.3. Magnetization versus Temperature of Power Samples. Figure 3(a) shows curves of the special magnetization σ versus temperature T for the power samples, under an applied magnetic field of 0.05 T. Figure 3(a) shows that in the temperature region measured, the samples experienced a shift from ferromagnetic to paramagnetic; the changes have gone through a transition region, because samples still in the transition zone show varying degrees of ferromagnetism, so we define $d\sigma/dT$ which tends to zero corresponding to the temperature as the Curie temperature T_C .

Figure 3(b) shows curves of the $d\sigma/dT$ calculated from Figure 3(a) versus temperature, in which the Curie temperature (T_C) of the samples is determined by $d\sigma/dT$ tending to zero. Figure 3(b) indicates that reducing treatment can decrease Curie temperature T_C of the sample obviously, and the more reducing time, the more Curie temperature T_C decreases. Abdelmoula et al. [13] studied the dependence of oxygen deficiency on electrical and magnetic properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ ($0 \leq \delta \leq 0.15$), they found that when the δ increased, the Curie temperature of the samples decreased, which was the same as our conclusion. This phenomenon can be explained by the weakness of double exchange theory. Reducing treatment could result in the deficiency of oxygen. With oxygen deficiency increased, Mn^{4+} ion is reduced, Mn^{3+} ion increased, and R_n (the ratio of Mn^{4+} and Mn^{3+} ion) decreased quickly, causing T_C to lower temperature.

Figure 4 shows the magnetic hysteresis loop of the powder samples at room temperature (300 K).

As shown in Figure 4, at room temperature (300 K), our samples are in the transition region from ferromagnetic to paramagnetic; the Curie temperature is higher than room temperature; magnetization has not yet reached saturation under an applied magnetic field of 500 mT.

Table 2 shows the special saturation magnetization σ (Am^2/kg) under an applied magnetic field 500 mT. It can be seen from Table 2 that: Reducing treatment could reduce the special magnetization σ significantly, as the reducing time longer, σ decreases more.

3.4. Colossal Magnetoresistance of Samples. The temperature dependence of the resistivity measured in zero field and in an applied field (1.8 T) for the samples B1 (a), B2 (b), and

FIGURE 2: SEM morphology of powder samples B1, B2, and B3.

FIGURE 3: (a) Curves of special magnetization σ versus temperature T for samples B1 (a), B2 (b), and B3 (c). (b) Curves of $d\sigma/dT$ calculated from Figure 3(a) versus temperature T for samples B1 (a), B2 (b), and B3 (c).

FIGURE 4: The magnetic hysteresis loop for samples B1 (a), B2 (b), and B3 (c) at room temperature (300 K).

B3 (c) is plotted in Figure 5. From Figure 5, we know that with the increase of temperature, the conductivity of the samples experienced a metal-semiconductor transition. The definition of metal-semiconductor transition temperature TMI for resistivity and temperature curve of resistivity maximum point corresponds to the temperature. For sample B1 (a), as in the temperature deviation TMI, its resistivity decreases rapidly, similarly to most of what is reported in the reference. But for samples B2 (b) and B3 (c), their resistivity changes a little near TMI.

Define the magnetoresistance by $MR(\%) = [(\rho_0 - \rho_H)/\rho_0] \times 100\%$, where ρ_0 and ρ_H stand for the resistivities at 0 and 1.8 T, different from most of the reports in the past; as the temperature decreases, the changes in samples B2 and B3 can be divided into three stages: in the high temperature area, MR increases as the temperature decreases; in near room temperature, MR is basically unchanged; in the low-temperature area, with decreasing temperature MR continues to increase.

For B2 and B3 samples at room temperature (300 K), their MR was 11.0% and 10.0%, not only higher than the sample B1 (9.5%), but also the temperature stability of MR is better; in the temperature range from 270 K to 330 K, their MR was maintained at 11.0% ($\pm 0.3\%$) and 10.0% ($\pm 0.5\%$) almost flat with temperature, which is important for the potential application of this kind of magnetoresistance materials.

4. Conclusions

By using reducing treatment, we can improve the MR of $\text{La}_{0.67}\text{Sr}_{0.20}\text{Cu}_{0.10}\text{□}_{0.03}\text{MnO}_3$ polycrystalline manganite. The reduced samples B2 and B3 have the stable MR ($11.0 \pm 0.3\%$)

FIGURE 5: Temperature dependence of the resistivity measured in zero field and in an applied field (1.8 T) for samples B1 (a), B2 (b), and B3 (c). The corresponding magnetoresistances are also indicated.

and ($10.0 \pm 0.5\%$) in a temperature range between 270 K and 330 K. this is important for the potential application of this kind of magnetoresistance materials.

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