Study of magnetoresistance in nanostructured La$_{2/3}$Sr$_{1/3}$MnO$_3$ powder compacts

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Abstract

The magnetotransport properties in nanostructured La$_{2/3}$Sr$_{1/3}$MnO$_3$ powder compacts prepared under different pressure (0.4–4 GPa) have been examined. For all samples, high field magnetoresistance (HFMR) effect weakens at $T < 130$ K, and there exists Coulomb blockade at $T < 60$ K. An increase in the preparation pressure results in systematic changes in the various features. These include a decrease in grain size, a reduction in low-field magnetoresistance (LFMR) within the whole experimental temperature, an enhancement of HFMR at $T > 200$ K, and a decrease of HFMR at $T < 200$ K. The surface phase and the link condition in grain boundaries are suggested to be responsible for the present observations.

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1. Introduction

Magnetoresistance (MR) effect has been extensively applied in electronic devices such as magnetic read heads, storage devices and sensors, and it brings innovative impacts to information storage field. Since von Helmolt et al. [1] observed MR of 150% in La$_{2/3}$Ba$_{1/3}$MnO$_3$ at ambient temperature in 1993 with field being 50 kOe, colossal magnetoresistance (CMR) effect of perovskite manganites Re$_{1-x}$A$_x$MnO$_3$ (Re and A are rare earth ions and alkaline ions, respectively) has attracted intense research activity in recent years.

The MR response of polycrystalline CMR manganites has been reported in detail for bulk...
and thin films, and a different MR behavior from single crystals was observed. The variation shows a low field MR and a characteristic linear variation of resistivity with field at high fields with normalized slope [2]. It was found that grain boundaries play an important role for the LFMR [2–5]. Some models such as spin polarized tunnelling, spin-dependent scattering and nearest neighbor hopping have been applied successfully for specific situation [2,6,7]. However, a final consensus on the basic physical mechanism behind the LFMR has not yet been reached and less work has been done on the origin of HFMR. In addition, reports on pressure effects about the MR in doped manganese perovskites indicated that pressure decreases resistivity ρ and drives the Curie temperature $T_c$ up. Structural modifications, such as the variation of Mn–O–Mn bond distance and bond angle, are suggested to be responsible for these effects [8–10]. In order to shed some light on the applications of the polycrystalline perovskite manganites and enhance our knowledge of the MR mechanism of these materials, more detailed investigations are still required. In this paper, we present a careful study on the MR of nanostructured La$_{2/3}$Sr$_{1/3}$MnO$_3$ powder compacts formed at different pressure (0.4–4 GPa). It is found that grain size, LFMR and HFMR have some regular changes with the variation of briquetting pressure.

2. Experiment

Using the sol–gel method, powder La$_{2/3}$Sr$_{1/3}$MnO$_3$ was synthesized. The as-formed powder was cold-compacted at 0.4, 1, 2, 3 and 4 GPa for 30 min, respectively, with a dihedral anvil high-pressure apparatus in which hydrostatic pressure was applied using mineral oil as the pressure transmitting medium. After pressure release, compacted samples were obtained. X-ray powder diffraction (XRD) measurements were performed at the Bede D1 X-ray diffractometer with Cu Kα radiation. Resistance $R$ was measured using the standard four probe technique in a Physics Property Measurement System (PPMS, Quantum Design).

3. Results and discussion

Our XRD study indicated that all the compacted samples are of single phase with rhombohedral perovskite structure. However, differences of peak width can be clearly observed in these samples. There are two factors including residual stress and grain size which are possibly responsible for the change of peak width in our study. It was found that all peak widths among the experimental $θ$ range from 20° to 60° become wide. Also, after annealing at 773 K for 2 h in order to relieve stress, the XRD patterns of these samples were remeasured. They showed no systematic variation, especially of peak width. Thus, residual stress could be ruled out as the origin of the present observation. Through small step-scanning measurement of X-ray pattern, in which the step is 0.005° and the stop time is 3 s, the normalized XRD profiles of (0 2 4) for the different samples were obtained. Profile of (0 2 4) was selected to measure just because it does not overlap with other profile. Then the forming pressure dependence of the average grain size $D$, which was evaluated from the conventional Scherrer method, is clear, as shown in Fig. 1. We noted that grain size decreases with the increasing of forming pressure. However,
the origin of crystallite breaking induced by pressure is unclear at present.

In Fig. 2 (main panel) we show the resistance of $P = 0.4$ GPa sample at zero field. It is clear that the resistance decreases with increasing temperature over the whole experimental temperature, and it is also found that the rate of change at $T \leq 60$ K is obviously larger than that at $T > 60$ K. Despite the difference in forming pressure, the shape of the $R(T)$ curves of the other samples are similar to the one of $P = 0.4$ GPa sample and the value of resistance varies little, so the other curves are not included for clarity. For polycrystalline cold-pressed compacts, the resistance can be divided into body resistance and interface resistance. The latter is dominant for our samples because of their small grain size, thus an intrinsic metallic-like behavior is not observed. At low temperature ($T < 60$ K), the resistance of the cold-pressed samples is found to be proportional to $\exp(T^{-1/2})$ (inset in Fig. 2), which is suggested to be associated with spin-dependent Coulomb blockade. The intergranular resistance as a function of temperature is given by [11–13]

$$R(T) = R_0 \exp[(\Delta/T)^{1/2}],$$

where $\Delta$ is proportional to the Coulomb charging energy $E_c$ and barrier thickness. The $\Delta$ can be determined from the slopes of linear part for $T < 60$ K of inset in Fig. 2. It is found that $\Delta = 52$, 46, 44, 42 and 40 K for samples of $P = 0.4, 1, 2, 3$ and 4 GPa, respectively. According to the charging energy $E_c = e^2/2C$ [14], the reduction of grain size due to the augmentation of pressure leads to the increment of $E_c$, so $\Delta$ increases. However, the contact between grains becomes tighter and the barrier thickness reduces under higher forming pressure, which causes the value of $\Delta$ decrease. Our analysis of the data shows that the variation of barrier thickness makes the main contribution to value of $\Delta$.

Fig. 3 shows the MR for different temperature corresponding to our smallest forming pressure compact ($P = 0.4$ GPa). The same basic features are observed for all of our samples: a sharp drop in the MR at low fields, and then a slow decrement at high fields. The former is more prominent as temperature decreases. This is consistent with previous reports [2,15]. However, as already observed in ceramic samples of the same composition [2], in the high field regime the variation of MR is almost linear with a slope $S = dMR/dH$ which remains constant with temperature. In contrast, the value of $S$ is invariant below 150 K, but rises considerably with temperature above this range in our observation. This phenomenon is also common to all of our samples. To the best of our

![Fig. 2. Temperature dependence of resistance for the $P = 0.4$ GPa sample of La$_{2/3}$Sr$_{1/3}$MnO$_3$. Inset shows LnR versus $T^{-1/2}$ for the samples of La$_{2/3}$Sr$_{1/3}$MnO$_3$ with different forming pressures.](image)

![Fig. 3. Field dependence of magnetoresistance under different temperatures in the $P = 0.4$ GPa sample of La$_{2/3}$Sr$_{1/3}$MnO$_3$.](image)
knowledge, this is the first experimental observation of a large temperature dependence of $S$ in polycrystalline manganites.

Although there are less systematic studies on high field effect and no general agreement on the microscopic mechanism of the effect, suppression of spin fluctuation in single crystal [2] and spin disorder in grain boundaries of polycrystalline [7] are proposed to be responsible for the HFMR. For nanoparticles, experimental evidences for surface spin disorder have been reported in previous studies and a nanoparticle can be divided into a body phase and a surface phase in which the Curie temperature ($T_{cs}$) is lower than the one ($T_c$) in the body phase [16,17]. Contrary to our results, in the case of single crystal $La_{2/3}Sr_{1/3}MnO_3$, $S$ value decreases with the growth of temperature [2], indicating that surface phase plays an important role in the HFMR of our samples. For $T < T_{cs}$, it is easy to accept that $S$ is almost a constant because it is not so difficult to change spin disorder into spin alignment through high field. With $T$ increasing near $T_{cs}$, a transition from ferromagnetism to paramagnetism gradually proceeds in the surface phase; accordingly spin alignment can be hardly obtained, so the contribution of surface phase to HFMR becomes weak step by step, leading to the enhancement of $S$ value. As $T > T_{cs}$, surface phase is completely paramagnetic and it does negligible work to HFMR; $S$ value becomes more large.

We present the effect of preparation pressure on LFMR in Fig. 4. It can be seen that LFMR increases with reduction of preparation pressure. A stronger LFMR in lower preparation pressure sample than in higher preparation pressure sample is reminiscent of the observation of a larger LFMR in weak-link sample than in strong-link sample [18]. As discussed above, the contact between grains becomes more tight and barrier thickness reduces with increase of preparation pressure. Therefore, the magnetic interaction has been strengthened and alignment of spin is difficult to attain between neighboring grains, which leads to a weak LFMR effect.

An interesting phenomenon is observed through making a comparison between the HFMR of samples with different forming pressure. Fig. 5 shows the temperature dependence of $dMR/dH$ ($S$) for the 0.4–4 GPa samples, in which $S$ is obtained from linear fitting of MR vs. $H$ curves for 15 000 Oe $\leq H \leq 50$ 000 Oe. It appears that $S$ in the sample with higher forming pressure is less than the one with lower forming pressure for $T < 200$ K, and it is almost the same value at $T = 200$ K for all samples, and it then reverses from the low-temperature behavior for $T = 300$ K. The
difference of $S$ may reflect the difference among ratios between surface phase and body phase. In contrast to samples with low-forming pressure, a sample with high-forming pressure has smaller grains and the proportion of surface is bigger. Since the HFMR attributed to surface phase is dominant for $T \ll T_{cs}$, and it becomes weak for $T$ near $T_{cs}$, and body phase plays an important role for HFMR at $T > T_{cs}$, it is reasonable that the HFMR effect of the sample with high-forming pressure is stronger at low temperature and is weaker at high temperature than the one with low-forming pressure.

4. Conclusions

We have investigated the magnetoresistance of nanostructured La$_{2/3}$Sr$_{1/3}$MnO$_3$ powder compacts prepared under different pressures. It is found that preparation pressure induces the reduction of grain size and causes variations in both LFMR and HFMR. The present study suggests that spin disorder in surface phase of ferromagnetic oxides with nano grain size plays an important role in the HFMR, and LFMR is sensitive to link condition at the grain boundaries.

References