Magnetoresistance in La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ ($x = 0.15-0.30$) polycrystalline samples

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Abstract

Magnetoresistive properties of La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ ($x = 0.15-0.30$) bulk polycrystalline samples sintered at temperatures $T_S = 1300-1360^\circ$C have been investigated. As $T_S$ decreases, the low-temperature magnetoresistance has been found to increase, the effect reaching its maximum value at $x = 0.20$. © 1999 Elsevier Science B.V. All rights reserved.

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The recent observation of colossal magnetoresistance in the La$_{1-x}$A$_x$MnO$_3$ (A = Ba, Sr, Ca, etc.) has spurred renewed interest in studying these doped perovskites [1,2]. Large values of magnetoresistance (MR) have been achieved in thin films, polycrystalline bulk and single crystals at high fields of up to several Teslas. For the single crystals and epitaxial thin films of La$_{1-x}$A$_x$MnO$_3$, a large MR was observed within a narrow temperature range around the ferromagnetic transition [2–4]. An attractive feature for the polycrystalline samples of doped manganites is a large low-field MR component over wide temperature range from the ferromagnetic transition down to 4.2 K [3–6]. Comparing measurements among polycrystalline pellets, single crystals, and thin films with composition La$_{0.67}$A$_{0.33}$MnO$_3$ (A = Sr, Ca), Jeffrey Snyder et al. [7] have concluded that the low-temperature MR phenomenon is not intrinsic to the thermodynamically stable phases but rather caused by microstructure, strain, and/or compositional variations. In such situation, sample preparation conditions are expected to influence greatly the properties of the doped manganites. A series of work has been concentrated on the investigation of the effect of sample preparation technique on the transport and magnetoresistive properties of La$_{1-x}$A$_x$MnO$_3$ [3–8]. Most of them, however, have been devoted to the materials with a fixed concentration of the divalent element A, typically in the vicinity of 0.30. Our work focus attention on the details of the sintering temperature dependence of the magnetoresistive properties of bulk polycrystalline La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ samples in the range of strontium concentration $x = 0.15-0.30$.

The perovskite samples of La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ ($x = 0.15, 0.175, 0.20, 0.30$) were prepared through two-stage solid-state reaction processing in air. The
starting mixture of La$_2$O$_3$, Mn$_2$O$_3$ and SrCO$_3$ was at first calcined for 2 h at a temperature of 1100°C. After subsequent ball milling and uniaxial pressing in pellets, the obtained products were sintered for 2 h at various temperatures $T_s$ and then furnace cooled down to room temperature. Two sets of the polycrystalline samples have been studied in this work, the final sintering temperatures $T_s$ being 1300°C for set A and 1360°C for set B. X-ray diffraction study showed single-phase perovskite structure. DC resistance measurements were performed in the temperature range 77–370 K using standard four-probe method. The samples for resistivity measurements were cut into rectangular bars, with the typical dimensions of $2 \times 3 \times 10$ mm$^3$. The magnetoresistance was measured in fields up to 15 kOe and is defined as $(\rho_0 - \rho_H)/\rho_0$ where $\rho_0$ and $\rho_H$ are the resistivity in zero field and applied field, respectively.

The main features of the resistive behavior of our La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ samples are analyzed in Ref. [9]. Each $\rho_0(T)$ curve reaches maximum at a certain temperature $T_{MI}$, the values of $T_{MI}$ being almost equal for the corresponding samples of both sets. Both $T_{MI}$ and the resistivity at $T_{MI}$ depend on $x$. $\rho_0(T_{MI})$ drops from about 0.6 to 0.08 $\Omega$ cm as $x$ changes from 0.15 to 0.30 (set A). $T_{MI}$ increases with increasing $x$ from 212 K ($x = 0.15$) to 330 K ($x = 0.30$). For each strontium concentration $x$, the resistivity $\rho_0$ of the set A is higher than that of the set B over all temperature range investigated (77–370 K). Being almost coincident at higher $T$, corresponding $\rho_0(T)$ curves diverge, when going from high to lower temperatures, and show a marked difference at $T < T_{MI}$.

The temperature dependencies of the magnetoresistance $MR = (\rho_0 - \rho_H)/\rho_0$ in field $H = 10$ kOe are displayed in Fig. 1 for both La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ sets. In the samples with $x = 0.15$–0.30, the MR show a steady decline with increasing $T$, interrupted by an increase slightly below $T_{MI}$, before finally dropping to zero with a further rise of $T$. At $x = 0.15$, an increase in the magnetoresistance occurs over all low-temperature region before reaching maximum value at about 207 K. Two contributions in the magnetoresistance are clearly seen from the figure, one is the cusplike MR near the temperature $T_{MI}$, and the other is low-temperature MR, which is usually very small in single crystals and epitaxial films [3–7] but in our case reaches a value of 10–18% at $T = 77$ K. As $x$ increases from 0.15 to 0.30, the peak value of the first MR component drops from 23 to 7% (set A) and from 29 to 5% (set B).

As can be seen from the insets of Fig. 1, the low-temperature component of the magnetoresistance shows two regimes in the dependence MR versus $H$. A sharp drop in resistance is observed at small $H$ (< 1500 Oe) followed by a more gradual drop at higher values. In both the regions the magnetoresistance changes almost linearly with magnetic field. As clearly seen from the MR($H$) curves, both drop in resistance at low fields as well as that occurring at higher $H$ are more marked in the samples sintered at the lower temperature ($T_s = 1300^\circ$C). As a function of strontium concentration

![Fig. 1. Temperature dependencies of the magnetoresistance of the samples sintered at different temperatures $T_s$. The insets show MR versus $H$ dependencies at $T = 77$ K for $x = 0.20$ and 0.30.](image)
x, the difference between the magnetoresistance magnitudes of both sets reaches maximum at $x = 0.20$ ($\Delta MR_{\text{set A}}(77 \text{ K}, 10 \text{ kOe}) - \Delta MR_{\text{set B}}(77 \text{ K}, 10 \text{ kOe}) \approx 5\%$) and is around 2–3% for the other $x$ values.

The effect of the grain size as well as intergrain boundaries on the magnetoresistance of doped manganites has been studied both in thin film and bulk polycrystalline samples [3–8]. The low-temperature magnetoresistive component is generally believed to be closely related to the average grain size and the properties of grain boundaries, while the MR peak at higher temperatures seems to arise from the magnetoresistance contribution inside the grains [4–8]. Various explanations for the low-temperature MR have been proposed by Hwang et al. [3], Zhang et al. [8] (intergrain spin-polarized tunneling) and Gupta et al. [4,5] (spin-dependent scattering of polarized electrons at the grain boundaries). All these models predict an increase in this MR component as the grain size decreases. Since the average grain size $d$ of the samples prepared by bulk ceramic method is very sensitive to the value of the sintering temperature [10], it is reasonable to suppose that the lowering $T_s$ in our case gives rise to a decrease in the value of $d$. In such case, our results showing increase in low-temperature magnetoresistance with lowering sintering temperature are in general compliance with these models. Further structural and magnetic investigations are now in progress to elucidate the details of the compositional dependence of the magnetoresistance.

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References