The Nd Doping Effect on the Room Temperature Magnetoresistance in Manganites (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ ($x \leq 0.3$)

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The Nd doping effect on the room temperature magnetoresistance in manganites (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ was investigated. With increasing Nd doping content in manganites (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ the room temperature magnetoresistance $\Delta R/R_0$ decreases for low Nd content $x < 0.1$, which may be mainly due to the sharp reduction of the room temperature saturation magnetization $M_S$. For $x > 0.1$, an enhancement of the room temperature magnetoresistance can be obtained. Such enhancement of the room temperature magnetoresistance is correlated with the shift of the Curie temperature to near room temperature and the slow change of the room temperature saturation magnetization $M_S$ induced by the appropriate Nd doping. The $\Delta R/R_0$ become small again at large Nd doping contents. The drop of $\Delta R/R_0$ may be attributed to their lower metal-insulator transition temperature $T_M$ far from the room temperature and the smaller $M_S$ value at room temperature. Values of the room temperature magnetoresistance $\Delta R/R_0$ for manganites (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ depend not only on the Curie temperature $T_C$ but also on the metal-insulator transition temperature $T_M$ and the room temperature saturation magnetization $M_S$.

1. Introduction

There has been great interest in perovskite manganites La$_{1-x}$A$_x$MnO$_3$ (A=Ca, Ba and Sr) due to the colossal magnetoresistance (CMR) effect which is potentially interesting for many applications. The double exchange interaction model [1] has been firstly adopted to explain the colossal magnetoresistance. However recent calculation showed that the double exchange alone can not explain all aspect of the CMR effect [4] and suggested that the electron-phonon coupling with the Jahn-Teller distortion also plays an important role in transport behavior of manganites. [5,6] The evidences of the polaron mechanisms have been provided by many theoretical and experimental works. [7-12] As we know, the colossal magnetoresistance depends on the temperature strongly, and its peak generally occurs near the Curie temperature. For the point of view of practical applications, it is essential to improve the magnetoresistance under low magnetic fields at room temperature. It was found that the substitution of Mn by Ti, [13] Fe, Ni, [14] Co, [15] Cu, [16] Cr [17] and Al [18] in La-Sr-Mn-O can enhance the room temperature magnetoresistance. Many works investigated the effect of rare earth substitution on the temperature dependence of magnetoresistance. [19-21] However, their attention were paid on the peak of magnetoresistance or the low temperature behaviors. For example, there are a lot of published papers on the Nd doping effects in (La, Nd)-(Ca, Sr)-Mn-O compounds [22-25] but up to now the work concentrated on the Nd doping effect on the room temperature magnetoresistance was not done yet. In the present work, the Nd doping effect on room temperature magnetoresistance in (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ manganites was investigated.

2. Experiments

Manganites (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ ($x = 0, 0.04, 0.08, 0.12, 0.16, 0.2, 0.25, 0.3$) were prepared by the traditional solid state reaction method. Mixed powders of La$_2$O$_3$, Nd$_2$O$_3$, MnO$_2$ and SrCO$_3$ were ground for 20 min, ball-milled for 30 min, and pressed into pellets, where a pressure of 6.8 MPa was used. The pellets were firstly heated at 800°C for 24 h and then subsequently pulverized. After milled for 20 min they were pressed into pellets again and then sintered at 1200°C for 24 h, followed by furnace cooling in atmosphere. Powder X-ray diffraction of manganites (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ were performed with Cu-K$_\alpha$ radiation at room temperature. Curie temperatures were determined from thermal magnetic curves measured with a thermal magnetic analyzer (TMA) under a low magnetic field of about 1.59 $\times$ 10$^4$ A/m. The room temperature saturation magnetization value was measured by a vibrating sample magnetometer (VSM). The magnetoresistance $\Delta R/R_0 = R(H) - R(0)/R(0)$ of manganites were measured using a four terminal method at $T = 293$ K. The metal-insulator transition temperatures of manganites were determined from the temperature dependence of resistance measured with a four terminal method under zero field.

3. Results and Discussion

Results of X-ray diffraction showed that manganites (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ ($x \leq 0.3$) form single phase with perovskite rhombohedral structure. X-ray diffraction patterns of typical samples (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ with $x = 0, 0.08, 0.25$ and 0.3 were shown in Fig. 1, respectively.

Figure 2 shows the Curie temperature $T_C$ dependence on the Nd doping content in (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ manganites. It can be seen that the Nd doping in LaSrMnO decreases the Curie temperature $T_C$ of the undoped manganite La$_{0.67}$Sr$_{0.33}$MnO$_3$ ($x = 0$) is about 436 K higher than the room temperature. It is possible to depress $T_C$ to the near room temperature by adjusting the appropriate content of Nd in (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$. The $T_C$ is 344 K for $x = 0.2$ and 333 K for $x = 0.3$ in (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$. As shown in Table 1, with Nd doping in (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$, the average A-site cation radius

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(rA) decreases due to the smaller ionic radii of Nd3+ (0.1163 nm) than that of La3+ (0.1205 nm). The Mn-O-Mn bond angle θ become small27 with Nd doping in La-Sr-Mn-O manganites, resulting in the reduction of electronic overlap and double exchange interaction, thus weakening the ferromagnetism.

The Nd doping content dependence of the metal-insulator transition temperature $T_{MI}$ for (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ is shown in Fig. 3(a). With increasing Nd doping, the transition temperature $T_{MI}$ decreases, accompanying the reduction of the Curie temperature $T_C$. The $T_{MI}$ is 357 K for the undoped sample La$_{0.67}$Sr$_{0.33}$MnO$_3$ and 263 K for (La$_{0.75}$Nd$_{0.25}$)$_{0.67}$Sr$_{0.33}$MnO$_3$. The metal-insulator transition temperature in manganites is dependent upon the mean A-cation radius $r_A$ and the A-site disorder quantified by the variance of the A-cation radius distribution $\sigma^2$.28 As shown in Table 1, there is a rise of the variance of the A-cation radius distribution $\sigma^2$, accompanying a reduction of the mean A-cation radius $r_A$, with Nd doping in (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$. As shown in Fig. 3(b), there exists a difference between the Curie temperature $T_C$ and metal-insulator transition temperature $T_{MI}$ for (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$. The value of difference $\Delta T = T_C - T_{MI}$ is only 5 K for the undoped LaSrMnO, which shows that $T_C$ and $T_{MI}$ are almost coincident. However, the $\Delta T$ becomes larger for the Nd doped samples. This difference may be attributed to the local inhomogeneities in magnetic and electronic transport behaviors, even though it is one single phase as viewed from crystalline structure. There may exist disorder and inhomogeneous occupations on A-site by rare earth ions La/Nd29 or the oxygen nonstoichiometry and various grain boundaries in the samples.25

Figure 4 shows the Nd doping content dependence of the room temperature saturation magnetization value $M_S$ for (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ manganites. It can be seen that with increasing Nd doping content the $M_S$ drops sharply for $x < 0.1$, and then changes slowly for $0.1 < x < 0.25$, and

![Fig. 1 X-ray diffraction patterns of typical samples (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ with $x = 0, 0.08, 0.25$ and $0.3$, respectively.](image)

![Fig. 2 The Curie temperature $T_C$ dependence on the Nd doping content in (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ manganites.](image)

<table>
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<th>$x$</th>
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Table 1 The Nd doping content dependence of the mean A-cation radius $r_A$ and the variance of the A-cation radius distribution $\sigma^2$ for (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$.28
reduces quickly again for $x > 0.25$.

Figure 5 shows the typical magnetic field dependence of the magnetoresistance ratio $\Delta R/R_0 = (R(H) - R(0))/R(0)$ at 293 K for $(La_{1-x}Nd_x)$_{0.67}Sr$_{0.33}$MnO$_3$ manganites. Negative magnetoresistance effect can be observed for various Nd doping manganites. The Nd doping content dependence of the magnetoresistance ratio $\Delta R/R_0$ at 293 K with $H = 9.55 \times 10^5$ A/m is shown in Fig. 6. The value $\Delta R/R_0$ is $-2.39\%$ for the undoped sample ($x = 0$). For $x < 0.1$, with increasing Nd doping the $\Delta R/R_0$ decreases, which may be mainly due to the sharp reduction of the room temperature saturation magnetization $M_S$. For $x > 0.1$, an enhancement of the room temperature magnetoresistance can be observed. The value $\Delta R/R_0$ is $-3.94\%$ for the sample ($x = 0.2$). Such enhancement of the room temperature magnetoresistance is correlated with the shifts of the Curie temperature to near room temperature and the slow change of the room temperature saturation magnetization $M_S$ induced by the appropriate Nd doping. The $\Delta R/R_0$ become small again at large Nd doping contents. For example, the $\Delta R/R_0$ is $-2.10\%$ for $(La_{0.2}Nd_{0.8})_{0.67}Sr_{0.33}$MnO$_3$ ($x = 0.3$). The drop of $\Delta R/R_0$ may be attributed to their lower metal-insulator transition temperature $T_{MI}$ far from the room temperature and the smaller $M_S$ value. Values of the room temperature magnetoresistance $\Delta R/R_0$ for manganites $(La_{1-x}Nd_x)$_{0.67}Sr$_{0.33}$MnO$_3$ depend not only on the $T_C$ but also on the $T_{MI}$ and the room temperature $M_S$.

4. Conclusions

Manganites $(La_{1-x}Nd_x)$_{0.67}Sr$_{0.33}$MnO$_3$ crystallize a perovskite rhombohedral structure for $x \leq 0.3$. With increasing
Nd doping, the Curie temperature and metal-insulator transition temperature decrease due to the reduction of $T_c$ and the increase of the $\sigma^2$. There is a difference between the Curie temperature $T_c$ and metal-insulator transition temperature $T_{MI}$ in Nd doping manganites, which may be attributed to the local inhomogeneities in magnetic and electronic transport behaviors within the doped samples. For low substitution content $x < 0.1$, the $\Delta R/R_0$ decreases with increasing Nd doping, which may be mainly due to the sharp reduction of the room temperature saturation magnetization $M_S$. For $x > 0.1$, an enhancement of the room temperature magnetoresistance can be obtained. The value $\Delta R/R_0$ under $H = 9.55 \times 10^5 \text{A/m}$ is $-3.94\%$ for the sample ($x = 0.2$). Such enhancement of the room temperature magnetoresistance is correlated with the shifts of the Curie temperature to near room temperature and the slow change of the room temperature saturation magnetization value $M_S$ induced by the appropriate Nd doping. The $\Delta R/R_0$ become small again at large Nd doping contents. For example, the $\Delta R/R_0$ under $H = 9.55 \times 10^5 \text{A/m}$ is $-2.10\%$ for (La$_{0.7}$Nd$_{0.3}$)$_{0.67}$Sr$_{0.33}$MnO$_3$ ($x = 0.3$). The drop of $\Delta R/R_0$ may be attributed to their lower metal-insulator transition temperature $T_{MI}$ far from the room temperature and the smaller $M_S$ value. Values of the room temperature magnetoresistance $\Delta R/R_0$ for manganites (La$_{1-x}$Nd$_x$)$_{0.67}$Sr$_{0.33}$MnO$_3$ depend not only on the $T_c$ but also on the $T_{MI}$ and the room temperature $M_S$.

REFERENCES