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Substituting effects of Sm in polycrystalline La–Ca–Mn–O

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Abstract

The Sm substituting effects for La in $La_{0.67}Ca_{0.33}MnO_3$ have been studied systematically. With increasing Sm doping amount, the metal–isolator phase transition temperature for the samples decreases monotonically, the corresponding peak resistivity increases dramatically and the Curie temperature decreases monotonically. The substitution of La–Ca–Mn–O with 0.13% Sm for La improved the magnetoresistance ratio by an order of magnitude. The effects of doping with Sm can be explained in terms of the lattice effects. An irreversible MR behaviour was observed in the Sm-doped compound. This effect was enhanced with increasing Sm doping amount.

1. Introduction

In recent years, there has been much attention paid to the rare-earth manganites due to the discovery of colossal magnetoresistance (CMR) [1–4]. The physics of the CMR effect so far has been focused on the double exchange of carriers between the Mn^{3+} and Mn^{4+} ions. Millis *et al* suggested that double exchange alone cannot explain the dramatic change of the resistivity and proposed that strong electron–phonon coupling arising from the Jahn–Teller effect plays a crucial role [5]. This coupling has been experimentally demonstrated by anomalous thermal expansion and magnetostriction measurements in yttrium doped La–Ca–Mn–O [6], unconventional magnetostriction in La–Sr–Mn–O [7] and other evidences [8, 9]. These results indicate that there exist strong charge–lattice and spin–lattice coupling in these compounds. In the doped rare-earth manganites, the Mn^{3+}/Mn^{4+} ratio is the key factor attributed for the physical properties of the compounds, especially the transport properties. However, some experiments have showed that the properties of the compounds can also be strongly influenced by the internal pressure generated by A-site substitution with ions of different radii while keeping the Mn^{3+}/Mn^{4+} ratio fixed [2, 10, 11]. This is known as the lattice effect. In this paper, we report the magnetic and magnetoresistive properties of polycrystalline La–Sm–Ca–Mn–O. Our results showed that Sm doping is an important factor to influence the properties of the compound.

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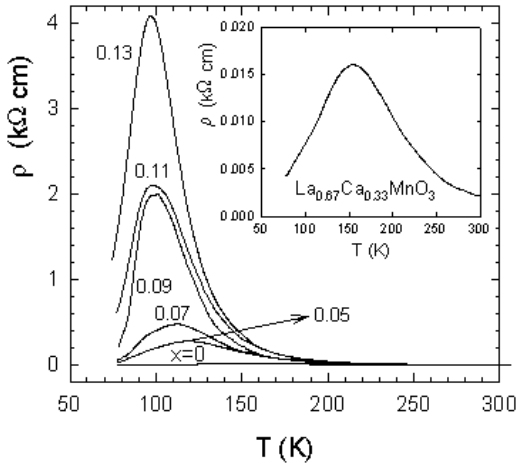

Figure 1. Temperature dependences of the resistivity ρ for $(La_{1-x}Sm_x)_{0.67}Ca_{0.33}MnO_3$ with x as a parameter. Numbers on the curves indicate the values of x. The inset is a magnified curve for the sample with $x = 0$.

2. Experiment

The polycrystalline samples with nominal composition of $(La_{1-x}Sm_x)_{0.67}Ca_{0.33}MnO_3$ were prepared by the conventional solid state reaction. Stoichiometric amounts of La_2O_3, Sm_2O_3, $CaCO_3$ and $MnCO_3$ were mixed, ground and pressed into plates. The plates were calcined at 900 °C for 8 h in air. Then they were sintered at 1400 °C for 10 h and furnace cooled in air. Six sets of samples with $x = 0$, 0.05, 0.07, 0.09, 0.11 and 0.13 were obtained for our study. The magnetic properties of the samples were measured by the vibrating sample magnetometer (VSM). VSM was also used to measure the resistance and magnetoresistance of the samples at low magnetic field up to 10 kOe in the temperature range from 77 K to 300 K. The resistance and magnetoresistance of the samples in the temperature range from 5 K to 300 K were measured by a commercial superconducting quantum interference device (SQUID) magnetometer with magnetic field up to 50 kOe. Transport measurements were performed by using the standard four- point technique. The dimension of the samples used in the electrical measurements was about $6 \times 2 \times 2$ mm^3. A constant current of 0.1 mA was used and parallel to the long direction of the sample. The magnetic field was parallel to the current direction.

3. Results and discussion

X-ray diffraction analysis indicates that all samples have a perovskite-type cubic structure with single phase. The cubic lattice parameter of the samples decreases from 0.3868 nm for $x = 0$ to 0.3855 nm for $x = 0.13$. Figure 1 shows the temperature dependences of the resistivity ρ for six $(La_{1-x}Sm_x)_{0.67}Ca_{0.33}MnO_3$ samples. Numbers on the curves indicate the values of x. The inset to figure 1 is a magnified curve for the sample with $x = 0$, so one can see it in detail. Figure 1 was obtained as follows: the samples were cooled down to 77 K and then the resistivity measured with increasing temperature. Our experiments showed that a different behaviour of resistivity versus temperature was obtained when the measurement was performed during the decrease of temperature, i.e., a hysteretic effect in temperature exists for the resistivity, especially for a larger doping amount of Sm. This hysteresis was observed in the doped

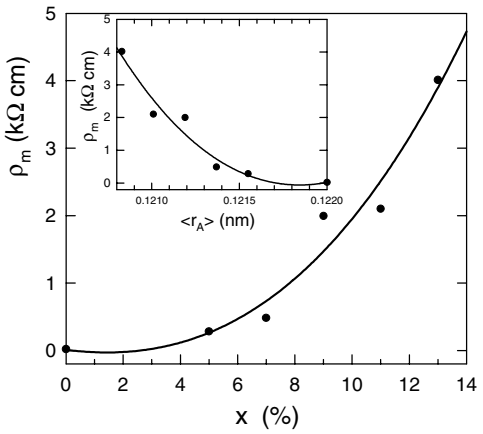

Figure 2. Dependence of the maximum resistivity ρ_m at the transition points for La–Sm–Ca–Mn–O on the Sm content x. The inset is the dependence of ρ_m on the average radius $\langle r_A \rangle$ of the rare-earth ions. The lines in the figure are guides for the eyes.

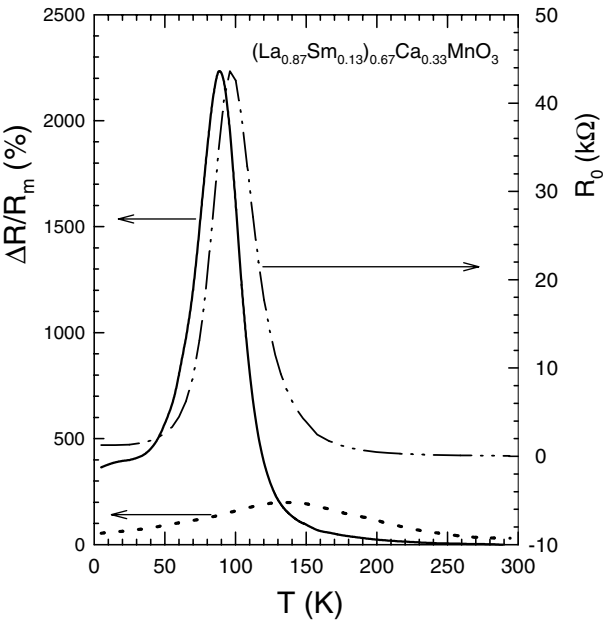

Figure 3. Temperature dependences of the resistance R_0 and the MR ratio $\Delta R/R_m$ for $(La_{0.87}Sm_{0.13})_{0.67}Ca_{0.33}MnO_3$ at 50 kOe field. The dotted line is obtained from $La_{0.67}Ca_{0.33}MnO_3$.

manganites with other rare-earth elements, such as Y or Pr [10]. One can see from figure 1 that a transition temperature T_P from metal to insulator exists for all samples. With the increase of x, T_P decreases from 155 K for $x = 0$ to 96 K for $x = 0.13$ monotonically, and the corresponding peak resistivity increases dramatically from 16 Ω cm for $x = 0$ to 4 k Ω cm for $x = 0.13$. The incremental amount of resistivity is as large as two orders of magnitude. Dots in figure 2 shows the dependence of the maximum resistivity ρ_m at the transition points for La–Sm–Ca–Mn–O on the Sm content x. The transition temperature obtained in the warming process is

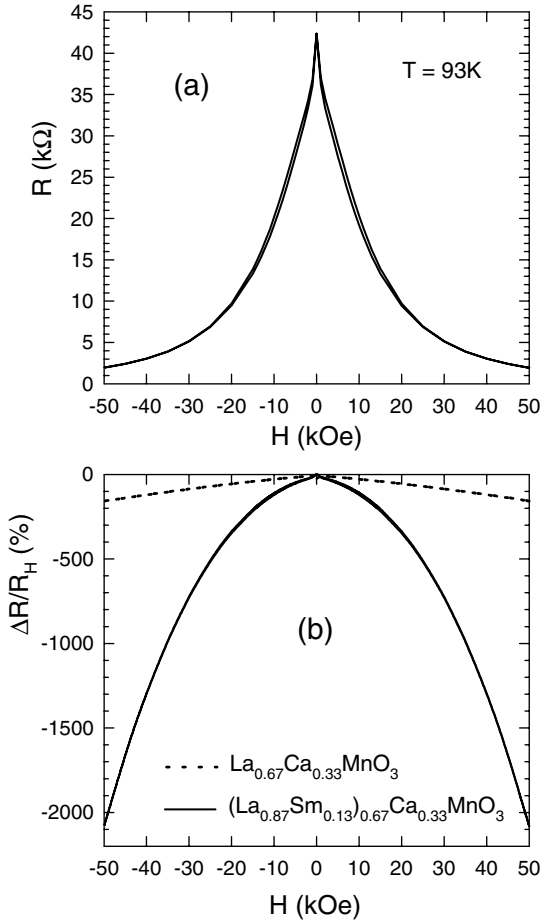

Figure 4. Dependences of the resistance R (a) and MR ratio $\Delta R/R_H$ (b) on the applied magnetic field H for $(La_{0.87}Sm_{0.13})_{0.67}Ca_{0.33}MnO_3$ at 93 K. The dotted line in (b) is the result obtained at 155 K from $La_{0.67}Ca_{0.33}MnO_3$.

always higher than that obtained in the cooling process, and the corresponding peak resistivity obtained in the warming process is always lower than that obtained in the cooling process.

Figure 3 shows the temperature dependences of the resistance R_0 and the MR ratio for $(La_{0.87}Sm_{0.13})_{0.67}Ca_{0.33}MnO_3$. A result obtained from $La_{0.67}Ca_{0.33}MnO_3$ is also given in figure 3 for comparison (denoted by the dotted line). The MR ratio is defined as $\Delta R/R_m = (R_0 - R_m)/R_m$, where R_0 and R_m are the resistances in zero and in 50 kOe applied magnetic field, respectively. The undoped sample has a maximum MR ratio of about 200% at 140 K. The Sm-doped sample shows a maximum MR ratio as high as 2230% at 88 K, which is 8 K lower than the metal–insulator transition temperature (96 K) of the sample in zero field. The doping of Sm makes MR ratio increase by more than one order of magnitude at the maximum MR ratio. However, the temperature with maximum MR ratio for doped sample is 59 K lower than that for the undoped one. When the temperature is higher than 130 K, the MR ratio for the Sm-doped sample is lower than that for the undoped one.

Figure 4 shows the dependences of the resistance R (figure 4(a)) and MR ratio $\Delta R/R_H$ (figure 4(b)) on the applied magnetic field H for the $(La_{0.87}Sm_{0.13})_{0.67}Ca_{0.33}MnO_3$ sample. The

result obtained at 155 K from the $La_{0.67}Ca_{0.33}MnO_3$ sample is also given in figure 4 (b) (denoted by the dotted line) for comparison. The MR ratio is defined here as $\Delta R/R_H = (R_0 - R_H)/R_H$, where R_0 and R_H are the resistances of the sample in zero and in H applied magnetic field. Figure 4 (a) is obtained as following: the sample is first cooled down to 5 K in zero field, and then warmed up to 93 K. When the temperature is stable, 50 kOe magnetic field is applied. After that, we measure the dependence of R on H when the magnetic field decreases and goes through a cycle. As we will show later, a different measuring process results in a different behaviour. This is because there exist thermal hysteresis and irreversible magnetoresistance effects. One can see from figure 4(a) that when H is less than 1 kOe, R falls quickly with increasing magnetic field and an approximately linear relationship between R and H is obtained. R decreases more slowly when $H > 1$ kOe and it cannot saturate until $H = 50$ kOe. A small magnetic hysteresis of R can be seen in figure 4(a). The resistance of the Sm-doped sample decreases from 42 kΩ in zero field to 2 kΩ in 50 kOe field giving rise to a large negative MR ratio of 2100%, while the maximum MR ratio in 50 kOe field for the undoped sample at 155 K is only 158%. The doping effect of Sm is dramatic.

The reason for the dramatic changes in the resistance and magnetoresistance on Sm doping can be explained in terms of the lattice effects. The experiments reported by Hwang showed that when La is partially substituted by Y or Pr in the $La_{0.7}Ca_{0.3}MnO_3$ compound, significant changes in resistance, magnetoresistance and Curie temperature occur [10]. It is indicated that substituting smaller rare-earth ions for La with fixed carrier concentration in La–Ca–Mn–O reduces the average ionic radius of the A site $\langle r_A \rangle$. The principal effect of decreasing $\langle r_A \rangle$ is to decrease the Mn–O–Mn bond angle, and cause the Mn ions to get closer to each other. This must change the electron hopping between the Mn sites. In our case, the radii of La^{3+} and Sm^{3+} are 0.122 nm and 0.113 nm, respectively[12]. With increasing Sm substitution, the average radius of the rare-earth ions, $\langle r_A \rangle = 0.122(1 - x) + 0.113x$, decreases monotonically. The properties of the compound changes thereby. The inset to figure 2 is the dependence of ρ_m on the average radius $\langle r_A \rangle$ of the rare-earth ions. ρ_m increases with decreasing $\langle r_A \rangle$ dramatically. One can see the close relationship between ρ_m and $\langle r_A \rangle$.

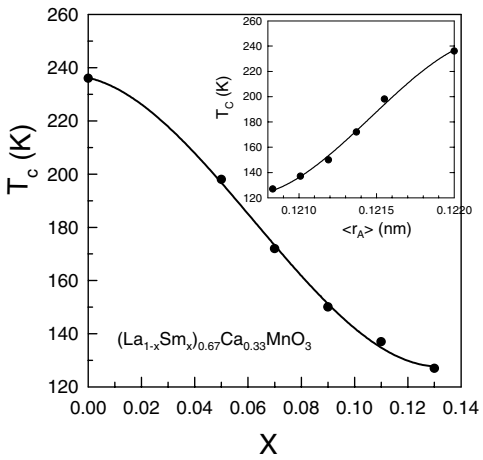

Figure 5. Curie temperature T_C versus x curve for $(La_{0.87}Sm_{0.13})_{0.67}Ca_{0.33}MnO_3$. The inset is the T_C versus $\langle r_A \rangle$ curve. The lines in the figure are guides for the eyes.

Shown in figure 5 is the Curie temperature T_C versus x curve for all samples. The inset to figure 5 is the T_C–$\langle r_A \rangle$ curve. Lines in figure 5 are guides for the eyes. T_C decreases

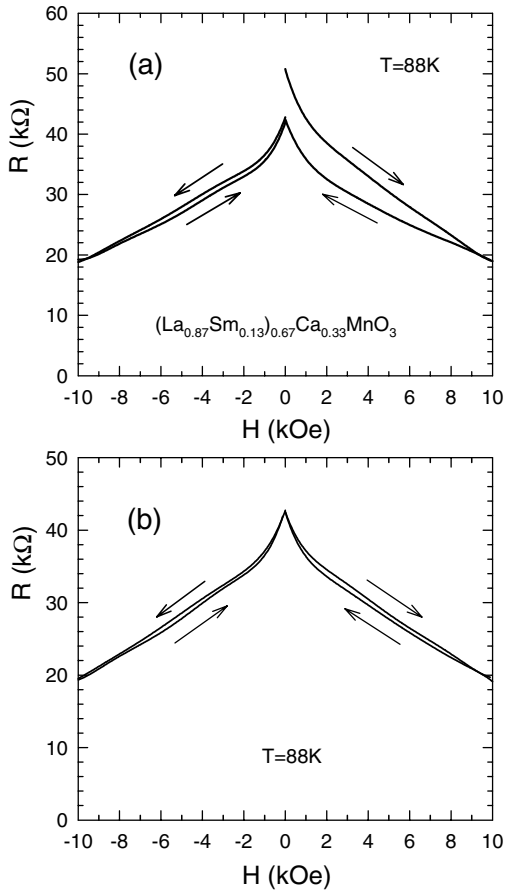

Figure 6. Dependences of the resistance R for $(La_{0.87}Sm_{0.13})_{0.67}Ca_{0.33}MnO_3$ on the magnetic field H at 88 K. (a) was obtained from the first measuring cycle, and (b) from the second cycle.

with increase of x, and with decrease of $\langle r_A \rangle$ monotonically. The close relationship between magnetic properties of the samples and average radius $\langle r_A \rangle$ of the rare-earth ions is obvious. It is indicated from figures 2 and 5 that with decreasing $\langle r_A \rangle$, the electron hopping between the Mn sites gets more and more difficult. As a result, the resistivity of the samples increases and the double exchange decreases with decreasing $\langle r_A \rangle$. These two effects are coincident, and they fit the basic concept of double exchange. We suggest that a key reason giving rise to the enhancement of MR effect in the rare-earth substituted compounds is the field-induced deformation of the lattice, which is more serious than that for the unsubstituted compounds because of the compressive effect of the lattice. When a magnetic field is applied, the lattice of the compound deforms by means of magnetostriction. This results in the increase of the space between the Mn sites, and enhances the charge motion determined by the Mn–Mn electron hopping rate. Accordingly, the resistivity of the compound decreases dramatically and the Curie temperature increases because the double exchange is strengthened. Because the magnetostriction in the manganese perovskites is much larger near the transition temperature T_P than far away from T_P, the CMR appears mainly around T_P.

In our measurements on the MR, an irreversible MR effect was observed. figure 6(a) and (b) show the dependences of resistance R for $(La_{0.87}Sm_{0.13})_{0.67}Ca_{0.33}MnO_3$ on the magnetic

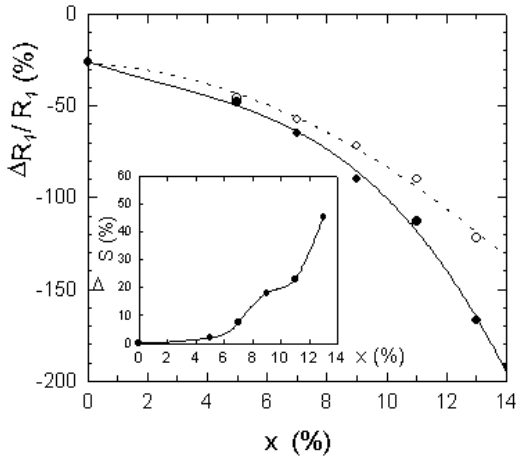

Figure 7. MR ratios $\Delta R_1/R_1$ of the samples versus x at the transition temperatures obtained during cooling of the samples. Dots and circles were obtained from the irreversible and reversible MR ratios. The inset is the dependence of the irreversible increment ΔS of the MR on x. The lines in the figure are guides for the eyes.

field H at 88 K. This temperature of 88 K locates at about the phase transition temperature obtained during cooling the sample. The arrows in the figures indicate the scan direction of the field. In figure 6(a), the sample was cooled down from room temperature to 88 K in zero field first. When the temperature was stable, the measurement was performed with increasing magnetic field from zero, and went through a measuring cycle. In figure 6(b), the sample experienced a second measuring cycle after the first turn. The appearances of the curves in figures 6(a) and (b) are quite different in the branch from the beginning zero field to +10 kOe, but the other branches are similar. Our experiments showed that the R versus H curve does not change any more after the second turn, i.e. the irreversible phenomenon of MR disappears after the sample is magnetized. If the sample is warmed up to room temperature and measured again at the transition temperature obtained during cooling process, the R versus H curve is as the same as that shown in figure 6(a). The irreversible effect of the R–H curve appears again. figure 6 indicates that the magnetoresistance behaviour of the sample is field-history dependent in the measuring process. In other words, the sample can keep the magnetic field in memory. When the sample was warmed up from low temperature to the phase transition temperature, and then the R versus H curve measured, the irreversible behaviour disappeared. This indicates that the irreversible MR effect and the thermal hysteresis of the resistivity may be caused by the same reason. Perhaps it is related to the lattice compression because we did not observe these phenomena in the undoped La–Ca–Mn–O. Figure 7 shows the MR ratio $\Delta R_1/R_1$ of the samples versus x at the transition temperatures obtained during cooling the samples, where $\Delta R_1/R_1 = (R_0 - R_1)/R_1$; R_0 and R_1 are the resistances of the samples in zero and in 10 kOe applied magnetic field, respectively. Dots and circles in figure 7 were obtained from the irreversible and reversible MR ratio at 10 kOe field. The inset to figure 7 is the dependence of the irreversible increment ΔS of the MR on x, where $\Delta S = S_i - S_r$; S_i and S_r are the irreversible and reversible MR ratio at 10 kOe field, respectively. Lines in figure 7 are guides for the eyes. The MR ratios and the irreversible effect increase with increasing Sm doping amount. An irreversible increment of MR ratio as large as 45% is obtained when the Sm doping amount is 13%.

In summary, we have studied the Sm doping effects in $La_{0.67}Ca_{0.33}MnO_3$ with fixed carrier concentration. With increasing Sm doping amount, the metal–isolator phase transition

temperature for the samples decreases from 155 K for $x = 0$ to 96 K for $x = 0.13$. The corresponding peak resistivity increases dramatically from 16 Ω cm for $x = 0$ to 4 k Ω cm for $x = 0.13$. The incremental amount of resistivity is as large as two orders of magnitude. The Curie temperature decreases from 238 K for $x = 0$ to 128 K for $x = 0.13$ monotonically. The doping of La–Ca–Mn–O with 0.13% Sm for La improved the magnetoresistance ratio by an order of magnitude. The effects of doping Sm can be explained in terms of the decrease in the lattice parameter. With increasing doping amount of Sm, the average radius of the rare-earth ions in A sites decreases. This changes the electron transportation properties and the exchange interaction between the Mn ions. An irreversible MR behaviour was observed in the Sm-doped compound. This effect is enhanced with increasing Sm substitution amount.

Acknowledgments

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