MAGNETIC PROPERTIES AND COLOSSAL MAGNETORESISTANCE OF $La_{1-x}Sr_xMn_{0.88}Fe_{0.12}O_3$ ①

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ABSTRACT $La_{1-x}Sr_xMn_{0.88}Fe_{0.12}O_3$ compounds ($0.15 \leq x \leq 0.5$) was prepared by the sol-gel technique. The effect of Fe doping on the magnetic properties, conductivity and magnetoresistance for $La_{1-x}Sr_xMnO_3$ was investigated. Experimental results indicated that the Fe doping leads to a decrease in the ferromagnetic ordering temperature, an increase in the resistance, and an enhancement of magnetoresistance for the $La_{1-x}Sr_xMnO_3$ system.

Key words LaSrMnFeO compound magnetic properties colossal magnetoresistance sol-gel technique

1 INTRODUCTION

The ABO_3 oxides with perovskite-based structure of Mn series which have CMR effects have been the subjects of intensive research efforts recently[1-9]. These oxides $La_{1-x}Sr_xMnO_3$ change from AFI to FM due to the double exchange interaction between the Mn^{3+} and Mn^{4+} ions when the content of Sr(x) is tuned[10, 11]. For $x \approx 1/3$, the maximal ferromagnetism is obtained[7, 9]. There is no reports about the research in which Mn is partly substituted by Fe. This article relates to the relation about the content of Sr(x) and the magnetic property, conductivity and magnetoresistance when Mn is substituted by a certain content of Fe(12%) in $La_{1-x}Sr_xMnO_3$.

2 EXPERIMENTAL PROCEDURE

The micropowders of $La_{1-x}Sr_xMn_{0.88}Fe_{0.12}O_3$($0.15 \leq x \leq 0.5$) are prepared by the sol-gel technique. The crude materials include La_2O_3 (99.99%), $Mn(NO_3)_2$ (50% sol, AR), $Sr(NO_3)_2$(AR), $Fe(NO_3)_3 \cdot 9H_2O$ (AR) etc. La_2O_3 are dissolved in the diluted nitric acid, and $Fe(NO_3)_3 \cdot 9H_2O$ and $Sr(NO_3)_2$ in water, therefore we can get three kinds of nitrate sols. The mixed sols of nitrates are made according to formula $n(La):n(Sr):n(Mn):n(Fe) = (1-x):x:0.88:0.12$. The gel powders are made by adding citric acid of tuned amount to the sol and evaporating off the water on the stirring apparatus.

The oxides $La_{1-x}Sr_xMn_{0.88}Fe_{0.12}O_3$ micropowders are obtained as the gel is fired. The mircropowders of oxides are calcined in the cased furnace at 1 073 K for 2 h, then they are pressed into circular slices with a size of d 10 mm × 2 mm in the squeezer. The slices are sintered in the cased furnace in the air at 1 473 K for 24 h, at last we get the flake samples.

The structure is determined by the X-ray diffractometer with steering target of RK-D/Max-RA type. The temperature dependence of resistivity (curve of temperature vs resistivity) was measured by the method of four-probe electrodes from 78 to 350 K at zero and 10 kOe field. The Curie temperature is determined by the measurement of ac susceptibility with the varying temperature. And the state of Fe ion is de-

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termined by Mössbauer.

3 RESULTS AND DISCUSSION

The experimental results are presented in Figs. 1, 2 and 3 and Table 1.

Fig. 1 illustrates the spectrums of XRD for $x = 0.2$ and $x = 0.5$, which are respectively of typical rhombohedral structure and cubic structure. The X-ray patterns show that the structures are the same as those of the oxides $La_{1-x}Sr_xMnO_3$ without doping Fe. Mössbauer spectrums of $La_{1-x}Sr_xMn_{0.88}Fe_{0.12}O_3$ samples indicate from g factor that Fe ions are trivalent. Because the radius of Fe^{3+} ion is almost equal to that of Mn^{3+}, the doping of Fe has no obvious effect on the symmetry of the crystal structure of the system, therefore there is no influence on the experimental results caused by the transition in structure. The probation of the components by XRD indicates that all the samples are single phases. For $x < 0.45$, the samples have the rhombohedral structures. On the other hand, the samples are of cubic structures for $x \geq 0.45$[12].

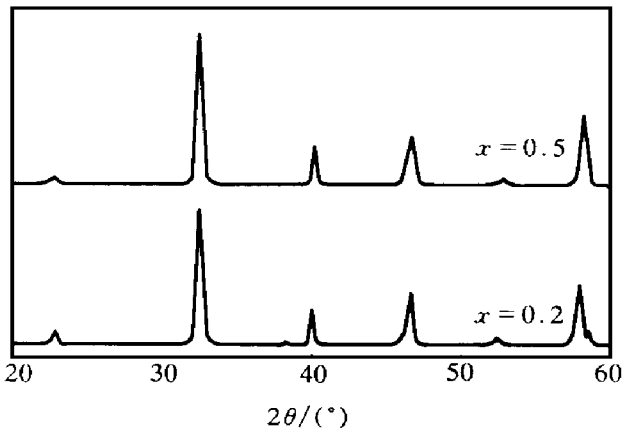

Fig. 1 X-ray diffraction patterns of $La_{1-x}Sr_xFe_{0.12}Mn_{0.88}O_3$

Fig. 2 shows the R-T curves of oxides $La_{1-x}Sr_xMn_{0.88}Fe_{0.12}O_3$. For $0.25 \leq x \leq 0.45$, the samples exhibit a phase transition similar to the metal-insulator (M-I) transition above the temperature limit of liquid nitrogen. T_P is maximal at $x = 0.4$, and then it decreases with the increase of x. For $x \leq 0.2$ or $x \leq 0.5$, the samples are always insulating, so there is no M-I transition above the temperature limit of liquid nitrogen. The extent at which the materials can become metallic narrows significantly when a certain amount (12%) of Mn is substituted by Fe. The oxides $La_{1-x}Sr_xMnO_3$ without doping Fe are metallic below the Curie temperature for $0.175 \leq x \leq 0.6$[7], and the M-I transitions can not be observed. The effects caused by doping Fe indicates that the doping of Fe is helpful to the turn-up of a kind of mechanism which reduces the double exchange interaction leading the system to become insulating which reduces the double exchange interaction.

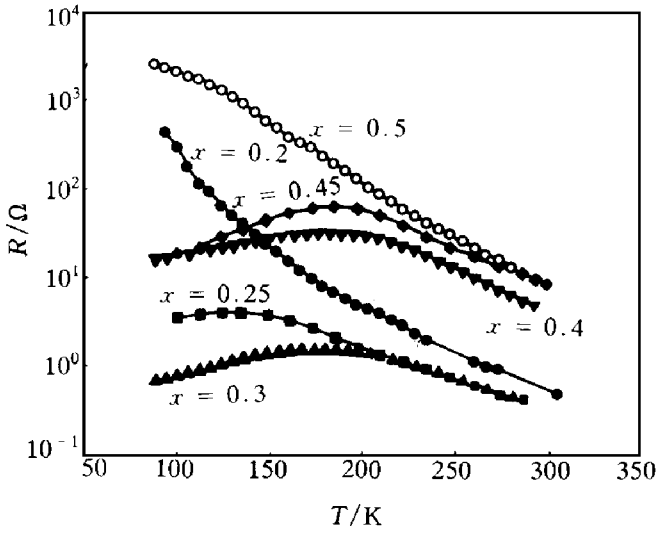

Fig. 2 R-T curves of $La_{1-x}Sr_xFe_{0.12}Mn_{0.88}O_3$

Table 1 lists the Curie temperature T_C and M-I transition temperature T_P. For comparison, the T_C of $La_{1-x}Sr_xMnO_3$ without doping are

Table 1 T_C and T_P of $La_{1-x}Sr_xFe_{0.12}Mn_{0.88}O_3$

x	T_C(non-doped Fe) / K	T_C / K	T_P / K
0.15	238[7]	190	–
0.2	309[7]	209	–
0.25	342[7]	225	130
0.3	369[7]	243	175
0.4	371[7]	249	185
0.45	367[7]	225	180
0.5	364[7]	197	–

also listed in Table 1[1]. From the data of Table 1, the doping of Fe leads to a significant decrease of Curie temperature of the samples, and the magnitudes of the decrease are different because of the different contents of Sr(x). For $0.25 \leq x \leq 0.4$, the change of magnitude of decreasing is about 120 K. The magnitude of decrease of T_C due to the doping of Fe increases with the increase of x for $x \geq 0.45$. The magnitude decreases slowly with the decrease of x for $x \leq 0.2$ than with the increase of x for $x \geq 0.45$. The T_P of the samples with the content of x between 0.25 and 0.45 are 50~ 100 K lower than the corresponding Curie temperatures. When $x < 0.25$ or $x > 0.45$, T_P rapidly decreases to below the liquid nitrogen temperature (78 K), while

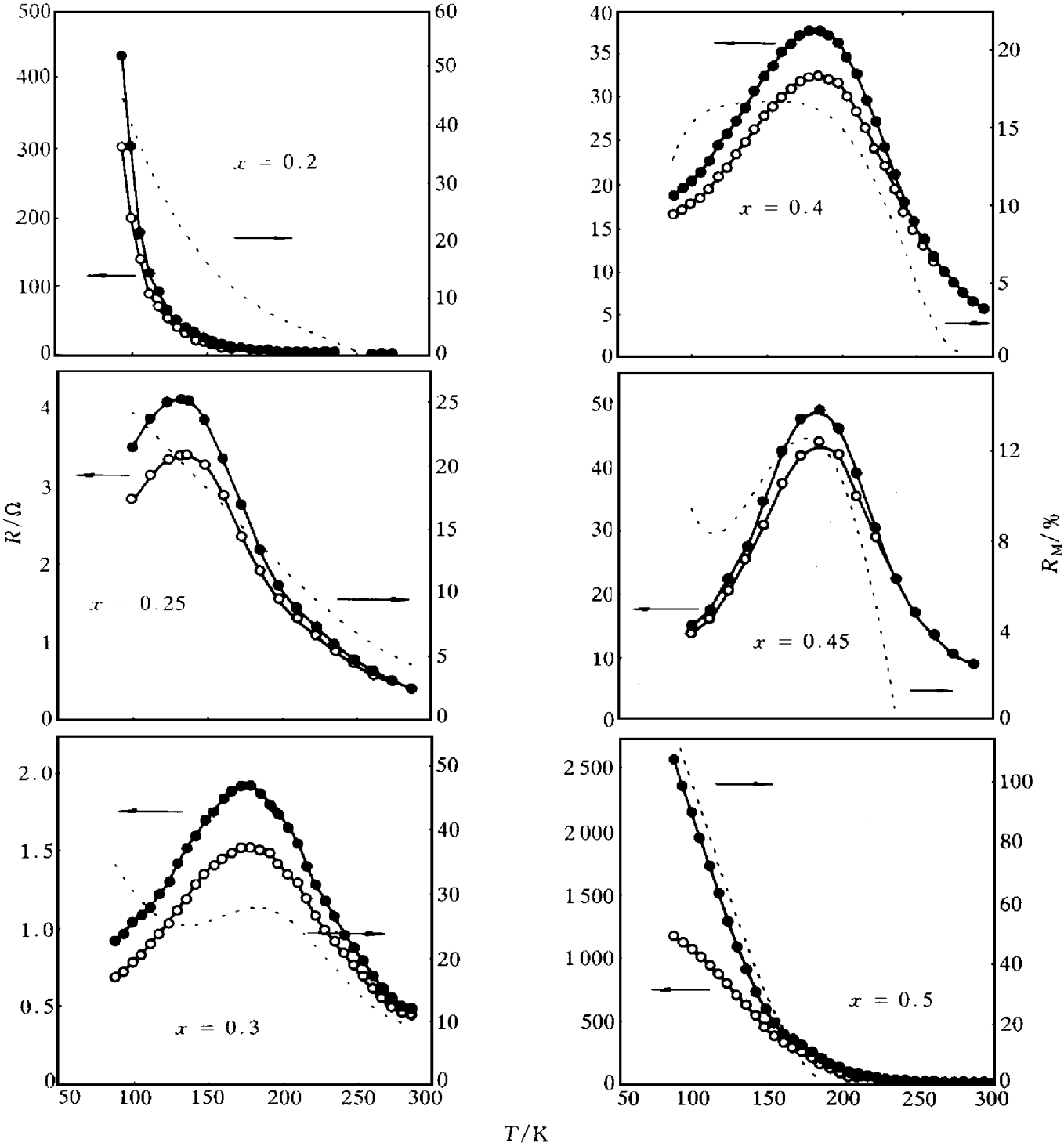

Fig. 3 R-T curves of $La_{1-x}Sr_xFe_{0.12}Mn_{0.88}O_3$ and R_M – T curves
● —H = 0; ○—H = 10 kOe)

above 78 K, the samples are always insulating. This is due to the fact that when $x \geq 0.45$ or $x \leq 0.25$, the Curie temperatures of the samples are very lower, therefore the ferromagnetism is weak and the antiferromagnetism is enhanced. In fact, the former itinerant e_g electrons become more localized, thus the materials are more insulating. That the doping of Fe weakens the ferromagnetism is mainly due to the reduction of double exchange interaction. When the trivalent Fe ions substitute the Mn ions, the transitions of electrons in Fe-Fe and Fe-Mn are much more difficult to occur than those in $Mn^{3+} - O^{2-} - Mn^{4+}$ because there are 5 electrons in 3d orbit which can just fill the orbit by half leading to a stable structure, thus the double exchange interaction was weakened. The antiferromagnetism turns up due to the exchange interaction in Fe-Fe and Fe-Mn, so the Curie temperature decreases and the resistivity increases.

Fig. 3 shows the R-T curves (real line) and R_M-T curves (dotted line) at zero and 10 kOe external magnetic field, the magnetoresistance (MR) is obtained according to $R_M = -[R(H) - R(0)]/R(H)$. All the samples demonstrate the negative MR effect because all of their magnetoresistances decrease with different extents under external magnetic field. Although there is no (M-I) transitional peak in the curves of samples for $x = 0.2$ and $x = 0.5$ which are insulators above temperature limit of liquid nitrogen, the R_M effect is magnificent, e. g., the MR of sample is up to 120% at 100K for $x = 0.5$ under 10kOe field. So obvious MR effect is likely to occur for FI material at a lower temperature. All of the four samples with x between 0.25 and 0.45 have M-I transitional peaks. The R_M tends to increase with the decrease of the temperature and a peak turns up near the T_P in R_M-T curve.

4 SUMMARY

The doping of Fe leads the Curie temperature of CMR materials $La_{1-x}Sr_xMnO_3$ to decrease, so it is helpful for the materials to become insulating. Unlike the R-T curves of $La_{1-x}Sr_xMnO_3$ compounds without doping Fe, those of materials with doping Fe indicate the metal-insulator (M-I) transitions. From the curves of $La_{1-x}Sr_xMn_{0.88}Fe_{0.12}O_3$ with $x = 0.2$ and $x = 0.5$, the great CMR effects are likely to turn up in FI materials at a lower temperature. With different contents of Sr, doping Fe affects the material to different extents.

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