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Chemically controlled properties of layered perovskites

$\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$

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Abstract. The magnetic and magnetotransport properties of $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ have been investigated. In the low doping region $x < 0.5$, the samples show similar properties to $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($x = 0$), but magnetic transition temperature T_C , insulator–metal transition temperature T_p and the temperature of magnetoresistance (MR) maximum T_{MR} all decrease with x increasing. When $x \geq 0.6$ the samples resemble $\text{Nd}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($x = 1.2$), without spontaneous magnetization and being insulating. The MR maximum of $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ increases with Nd doping, and the highest MR ratio, $\Delta\rho/\rho_0 = 98\%$, is observed in the transition region $x = 0.5$ and 0.6. It is shown that the properties of $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ change gradually with Nd doping and can be chemically controlled by tuning the La/Nd ratio.

1. Introduction

Mixed valent manganites with perovskite structure, $(\text{Ln}, \text{M})\text{MnO}_3$ (Ln is lanthanide ions and M is divalent cations), have attracted great attention in scientific research and technology applications, for the observation of colossal magnetoresistance (CMR) in them. Recently the CMR effect has also been found in the layered perovskites $(\text{Ln}, \text{M})_3\text{Mn}_2\text{O}_7$ [1–5]. The perovskites $(\text{Ln}, \text{M})\text{MnO}_3$ and layered perovskites $(\text{Ln}, \text{M})_3\text{Mn}_2\text{O}_7$ are the $n = \infty$ and $n = 2$ members of the series of Ruddlesden–Popper (RP) phases $A_{n+1}B_nO_{3n+1}$, respectively. The layered structure, and the corresponding two-dimensional Mn–O–Mn network of the layered perovskites make them show some interesting properties different from the well known perovskites.

Previous studies have shown that the properties of the layered perovskites are very sensitive to the element composition. For $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ [1, 2, 6, 7], when $x = 0.3$ and 0.4, it is ferromagnetic (FM) and metallic, with an M–I transition close to T_C and an intermediate magnetic state (two-dimensional or short-range magnetic ordering) above T_C , but FM phase and antiferromagnetic (AFM) phase coexist for $x = 0.5$. $\text{Nd}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.3$ –0.5) [4, 8, 9] are insulating, and show no FM ordering, but also have the CMR effect. So there are great differences between the properties of the La-based system and Nd-based system. The difference should be attributed to the different sizes and ordering occupying the (Ln, M) site of La^{3+} and Nd^{3+} , and the influence of the Nd^{3+} moment. An investigation of the $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ system will be helpful to clearly understand the difference. More recently Battle *et al* [10] have reported that doping $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ with Nd leads to magnetization behaviour reminiscent of $\text{Nd}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ for $x \geq 0.7$. In this paper

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we investigated the effect of Nd doping on the magnetic and magnetotransport properties of $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ in detail, and found both magnetic properties and the MR effect can be chemically controlled by tuning the ratio of La/Nd.

2. Experiment

Bulk samples of $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($x = 0-0.6, 1.0, 1.2$) were prepared by a standard ceramic process. Stoichiometric amounts of La_2O_3 , Nd_2O_3 , SrCO_3 and MnCO_3 were mixed, ground and calcined at 1100°C for 24 h in air. The resulting powders were ground again, then pressed into pellets and sintered at 1250°C for 36 h with an intermediate grinding. The samples were characterized by x-ray diffraction with Cu $K\alpha$ radiation. Magnetization measurements were performed on a SQUID magnetometer (Quantum Design) or extracting sample magnetometer. Resistivities were measured as functions of temperature and magnetic field using a standard four-probe method. The magnetoresistance (MR) ratio is defined here as $\Delta\rho/\rho_0 = (\rho_0 - \rho_H)/\rho_0$, where ρ_0 and ρ_H denote resistivities at zero field and an applied field respectively.

3. Results and discussion

The x-ray diffraction study reveals that all the samples of $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ crystallize with $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type tetragonal structure ($I4/mmm$). As shown in table 1, the unit cell volume decreases with x increasing, which is consistent with the fact that the size of Nd^{3+} is smaller than that of La^{3+} . The crystal structure was further refined by the Rietveld technique (only the apical Mn–O(2) bond length will be discussed later in this paper and the detailed results will be presented in another publication).

Table 1. The unit cell volume v , the Curie point T_C , the upper transition temperature T^* , the I–M transition temperature T_p , the temperature of MR maximum T_{MR} and the maximum MR ratio MR_{max} of $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$.

	$x = 0$	$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.4$	$x = 0.5$	$x = 0.6$	$x = 1.0$
v (\AA^3)	302.98	301.43	301.72	300.90	300.42	300.20	299.67	297.49
T_C^a (K)	125	94	87	60	52	49		
T^{*a} (K)	245	224	220	205	197			
T_p (K)	130	107	100	74	63			
T_{MR} (K)	120	109	100	70	20	< 20	< 20	15
MR_{max} (%)	80	77	81	90	94	98	98	64

^a T_C and T^* are defined as the temperature where dM/dT is maximum.

The temperature dependence of magnetization measured at 1000 Oe is shown in figure 1. Many differences between the results of the two end compounds, $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ and $\text{Nd}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, are observed, consistent with the previous reports [1, 6, 9, 11]. The Nd-based sample does not show long-range magnetic ordering, but the La-based sample is FM below the Curie point 125 K (T_C), and above T_C there is another upper transition at $T^* \sim 245$ K which has been ascribed to short-range or two-dimensional ordering in the layered structure. As La^{3+} is substituted by Nd^{3+} , both T_C and T^* decreases with x increasing from 0 to 0.5, as shown in figure 1(a) and table 1. It is clear that the samples with low Nd doping show similar magnetization behaviour to the La-based sample, except a rise in magnetization below 20 K, especially for $x = 0.2$ and 0.3 . From $x = 0.4$, the ZFC magnetization value decreases apparently on cooling and a large difference between FC and ZFC data occurs at

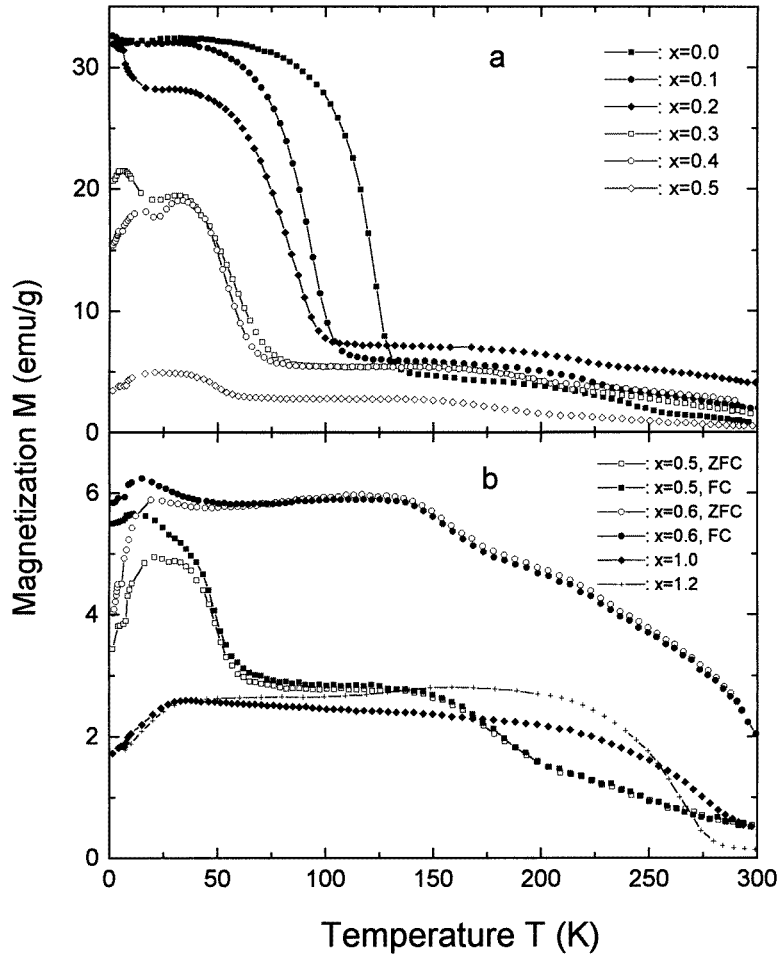


Figure 1. Temperature dependence of magnetization for $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ measured at 1000 Oe. (a) $x = 0-0.5$; (b) $x = 0.5, 0.6, 1.0, 1.2$, solid squares and circles represent the FC data.

low temperature (the FC data are shown only for $x = 0.5$ and 0.6 in figure 1(b)), indicating the presence of magnetic disorder frozen in a spin-glass-like fashion at low temperature. The sample with $x = 0.6$ begins to show similar behaviour to $\text{Nd}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, not showing long-range magnetic ordering, although the upper transition (short-range ordering) is still present. Moreover the magnetization behaviour of the sample with $x = 1.0$ is nearly the same as that of $\text{Nd}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. The field dependence of magnetization at 4.2 K plotted in figure 2 also shows the same gradual changing tendency with Nd doping. For the samples with $x = 0.3$ and 0.4 , besides the initial jump resulting from spontaneous magnetization, there is another slow jump in magnetization when the applied field is higher than 3 T. For $x = 0.5$ and 0.6 , the jump is also observed at 4 T and 5 T, and the magnetization does not reach saturation even at 6 T. From the Arrot plot in figure 3 it can be found that when $x > 0.4$, no net spontaneous magnetization is observed. So $x = 0.5-0.6$ is the transition region, below and above which $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ resembles $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ and $\text{Nd}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, respectively.

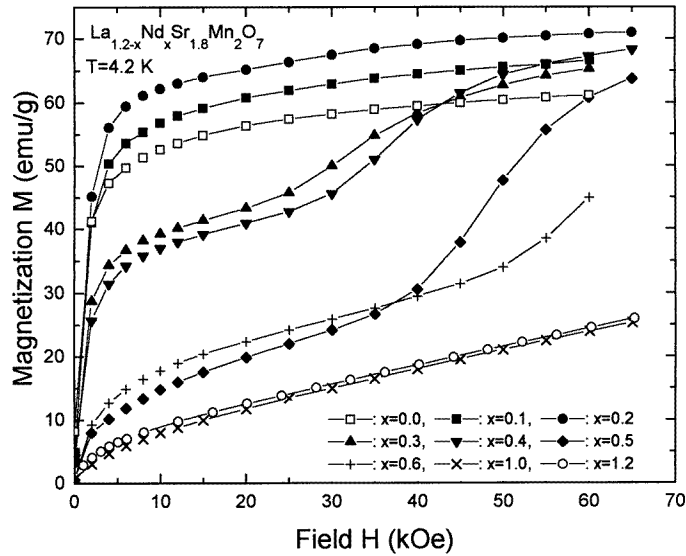


Figure 2. Field dependence of magnetization for $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ at 4.2 K.

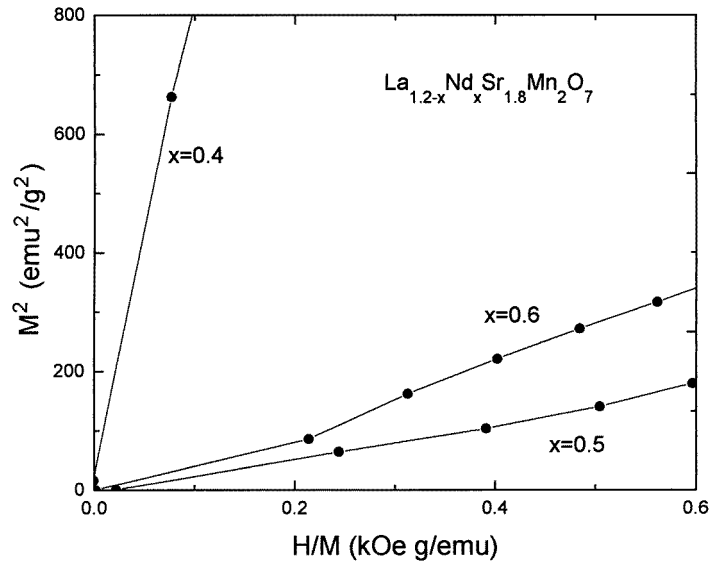


Figure 3. Arrot plot for $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($x = 0.4-0.6$) at 4.2 K.

The magnetotransport properties of $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ are also very sensitive to Nd doping x . As seen in figure 4, when $x = 0-0.4$ an insulator-metal (I-M) transition is observed, with the resistivity peak temperature T_p near to or a little higher than the corresponding T_C and decreasing as x increases (see table 1). For $x = 0.3$ and 0.4 , below the I-M transition, the insulating behaviour reemerges at low temperature. With Nd doping the I-M transition is suppressed, and the samples with $x \geq 0.5$ are insulating below 300 K, similar to $\text{Nd}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. An application of 6 T field leads to a reduction in resistivity for all samples,

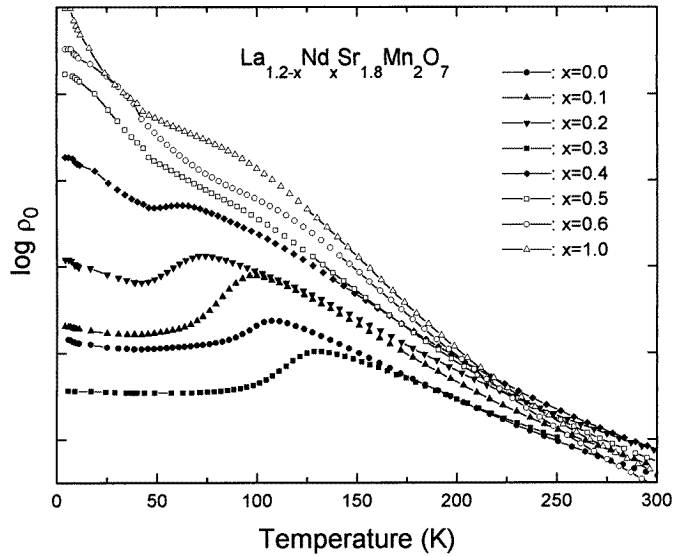


Figure 4. Resistivities as function of temperature without field for $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. Considering the polycrystalline samples, the absolute resistivity values are not shown. In order to show all curves clearly, the positions of some of the curves have been adjusted and the curve of $x = 1.2$ is not plotted.

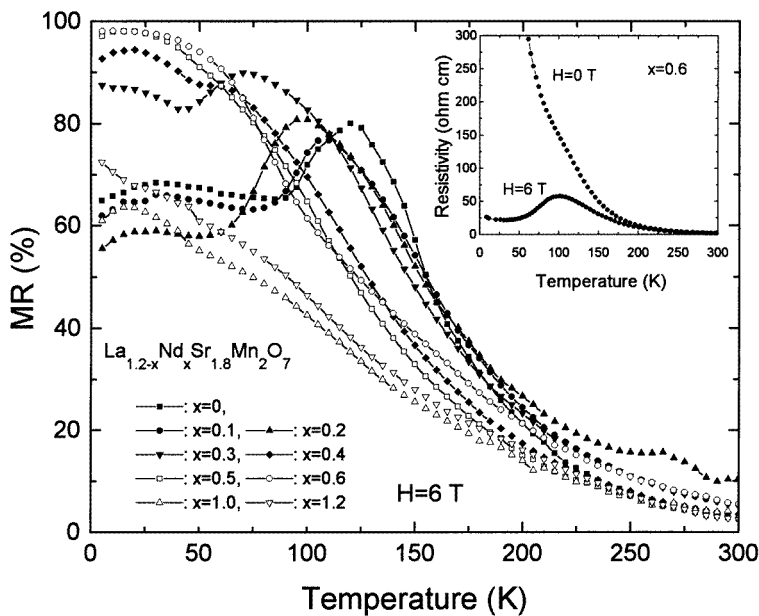


Figure 5. MR ratio at 6 T as function of temperature for $\text{La}_{1.2-x}\text{Nd}_x\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. Inset: Temperature dependence of resistivities at zero field and 6 T for $x = 0.6$.

giving rise to a large MR effect (figure 5). It is notable that for $x = 0-0.3$, near T_C and T_p , an MR maximum MR_{max} is observed at a peak temperature designated as T_{MR} (see table 1). With

increasing of x , T_{MR} decreases, the MR peak becomes broader and lower, then forming a step as $x = 0.4$. For the samples with $x = 0.5$ and 0.6 which are insulating, no MR peak is observed, but a large MR effect occurs during a broad low-temperature range. With x increasing, MR_{max} increases firstly and then decreases as $x > 0.6$ (table 1). The highest MR ratio of 98% is observed in the samples with $x = 0.5$ and 0.6 below 20 K. It is interesting that the two samples are insulating at zero field and have no spontaneous magnetization, apparently different from other CMR materials for which ferromagnetism and I–M transition are necessary for the CMR effect. As seen in the inset of figure 5, for $x = 0.5$ and 0.6 (only shown for $x = 0.6$), a field-induced I–M transition occurs at 6 T, which must be responsible for their low-temperature CMR effect, i.e., the field suppression of spin scattering results in large reduction of resistivity at low temperature.

The results provided above suggest that Nd doping in $La_{1.2-x}Nd_xSr_{1.8}Mn_2O_7$ weakens the strength of FM interaction and destroys the long-range FM ordering. Previous reports [11–13] show that the apical Mn–O(2) (unshared O) bond length ($d_{Mn-O(2)}$) in $Nd_{1.2}Sr_{1.8}Mn_2O_7$ is longer than in $La_{1.2}Sr_{1.8}Mn_2O_7$. Our structure refinement results from x-ray diffraction also indicate the same tendency. The $d_{Mn-O(2)}$ of $La_{1.2-x}Nd_xSr_{1.8}Mn_2O_7$ for $x = 0$ ($La_{1.2}Sr_{1.8}Mn_2O_7$), 0.3, 1.0 and 1.2 ($Nd_{1.2}Sr_{1.8}Mn_2O_7$) are 1.95(1), 1.98(1), 1.99(1) and 2.09(1) respectively. So it is clear that Nd doping in $La_{1.2-x}Nd_xSr_{1.8}Mn_2O_7$ leads to the lengthening of the Mn–O(2) distance, which will in turn weaken the coupling between the bilayers and result in the frustration of three-dimensional magnetic ordering and the formation of FM clusters. Another possible reason is that Nd doping will possibly change the magnetic structure (neutron diffraction is necessary for a direct proof) for Nd^{3+} cations have moments. Nd^{3+} will interact with Mn^{3+}/Mn^{4+} and influence the alignment of Mn moments, which also could result in the weakening of FM interaction, spin canting of Mn moments and the frustration of long-range magnetic ordering. These effects are negligible at low doping level, but become stronger gradually with x increasing. As $x < 0.3$, long-range FM ordering is still strong, and the increasing of saturation magnetization with x increasing (figure 3) could result from the contribution of ordering Nd^{3+} moments at low temperature. The jump in magnetization at high field above 3 T for $x = 0.3$ – 0.6 possibly results from the field suppression of the frustration of magnetic ordering. The facts that the field necessary for the jump increases and no saturation magnetization is observed at $x = 0.6$ suggest the frustration becomes more serious with x increasing. The low-temperature spin-glass state for $x > 0.3$ could also be attributed to the presence of the clusters and the frustration of magnetic ordering. At high Nd doping level ($x = 1.0$), the long-range magnetic ordering is no longer present, and the sample shows almost the same properties as $Nd_{1.2}Sr_{1.8}Mn_2O_7$. The change of magnetotransport properties with Nd doping, which is parallel to that of magnetic properties, could also be understood in a similar way. With x increasing, the weakening of FM interaction makes the electrons more localized, resulting in the disappearing of I–M transition and the occurrence of insulating behaviour. The frustration of magnetic ordering can be suppressed by applying a field, giving rise to the CMR effect. With x increasing, the frustration becomes serious, and, therefore, the restored ordering component by field also increases, resulting in the increasing of MR ratio.

4. Conclusion

The magnetic and magnetotransport properties of $La_{1.2-x}Nd_xSr_{1.8}Mn_2O_7$ can be well chemically controlled by tuning the La/Nd ratio, and vary with the same tendency with Nd doping. $x = 0.5$ – 0.6 is a transition region, below which the title samples are similar to $La_{1.2}Sr_{1.8}Mn_2O_7$, showing FM ordering and I–M transition, and above which they do not show long-range magnetic ordering and are insulating, resembling $Nd_{1.2}Sr_{1.8}Mn_2O_7$. All the

magnetic transition temperatures T_C and T^* , resistivity peak temperature T_p and MR maximum temperature T_{MR} decrease and the MR maximum increases as x increases. It is interesting that the highest MR ratio is observed in the transition region of $x = 0.5$ and 0.6 where the samples are insulating and have no spontaneous magnetization. By considering that Nd doping weakens the FM interaction and destroys the long-range magnetic ordering, which results in the formation of FM clusters, we can understand the gradual changes in magnetic and magnetotransport properties.

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