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Magnetotransport Property of Layered Manganites $(La,Sr,Ca)_3Mn_2O_7$

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Abstract

We report the magnetotransport properties of two series of $Sr_3Ti_2O_7$ type manganites, $La_{2-2x}Sr_{1+2x}Mn_2O_7$ and $La_{1\cdot4}Sr_{1\cdot6-x}Ca_xMn_2O_7$. The former manganites show magnetotransport properties, which depend on x*, that is, the carrier number. They show insulator to metal transition, when reducing temperature. The transition temperature increases with* x *up 0·4 and decreases with* x *exceeding 0·4. Around their transition temperature, they also show giant magnetoresistance, which decreases monotonically with increasing* x*. The latter manganites also show the electric transition temperature, which decreases with increasing* x*, that is, decreasing lattice constants. The giant magnetoresistance around transition temperature decreases monotonically with decreasing lattice constants. The magnetotransport properties of $Sr_3Ti_2O_7$ type manganites are sensitive to carrier number and lattice constants. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

Recently, perovskite type manganites[1–4] with various chemical compositions have been studied extensively, since they show giant magnetoresistances (GMR), which is applicable to sensitive magnetic sensors. Related structures can be derived from perovskite type structure $AMnO_3$, that is, Ruddlesden–Popper (RP) type structure,[5] $A_{n+1}Mn_nO_{3n+1}$ (A = lanthanide ions and alkaline earth ions). For example, the $n=1$ RP structure is derived as K_2NiF_4 type structure and the $n=2$ RP structure is derived as $Sr_3Ti_2O_7$ type structure. The K_2NiF_4 type manganites, $La_{1-x}Sr_{1+x}MnO_4$, show insulating behavior below room temperature and do not show GMR.[6] The $Sr_3Ti_2O_7$ type manganite, $La_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$ shows insulator to metal transition at 127 K with reducing temperature and shows GMR below the temperature.[7] Especially around the transition temperature, the manganite shows colossal magnetoresistance (CMR), which reaches ~20 000% at 129 K under a magnetic field of 7 T, when MR is defined by $\rho(0)/\rho(H)$.

Magnetoresistive materials are required to have large MR as possible for designing sensitive magnetoresistive devices. For this reason, $La_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$ is a useful material for application. However, it is necessary to raise the temperature at which the CMR occurs. The CMR in $La_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$ relates to the electric transition. The temperature, at which the CMR occurs, should rise by raising the electric transition temperature. The electric transition temperature is realized to rise by improvement of electric conductivity. We have two ideas for the improvement of electric conductivity. First is carrier doping, which has often been used to raise superconducting transition temperatures in cuprate superconductors. Second is shrinking Mn–O bond length so that Mn $3d$ orbitals and O $2p$ orbitals overlap well to lead to the improvement of electric conductivity. In the present study, we prepared two series of manganites, $La_{2-2x}Sr_{1+2x}Mn_2O_7$ and $La_{1\cdot4}Sr_{1\cdot6-x}Ca_xMn_2O_7$. We investigated the relation between magnetotransport properties and carrier doping in the former series and the relation between the magnetotransport properties, especially the electric transition temperature, and lattice constants in the latter series.

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2 Experimental

The samples were prepared by a solid state reaction method. The raw materials, La_2O_3 (99·9%), $SrCO_3$ (99·9%), $CaCO_3$ (99·9%) and Mn_3O_4 (99·9%) were weighed and were mixed thoroughly with an agate mortar and ethanol. The mixed materials were calcined in air atmosphere at 1400°C for 12 h. The calcined samples were pulverized and were pressed into pellets under isostatic pressure of 1 GPa. The pellets were sintered in N_2 gas (99·5%) at 1500°C for 12 h.

The lattice constants were calculated from the X-ray diffraction angles by a least square method. The diffraction angles were measured with an X-ray diffractometer (RINT2500VHF, Rigaku, Japan) and were calibrated using the diffraction angles of Si. The electric resistivity was measured by dc four-probe method under applied magnetic field of 0–1·5 T. The magnetoresistance is defined as the reduction rate of the electric resistivity under a magnetic field.

3 Results and Discussion

3.1 Properties of $La_{2-2x}Sr_{1+2x}Mn_2O_7$

Figure 1 shows the temperature dependence of electric resistivity under no magnetic field. The manganites with $0{\cdot}3\leq x\leq 0{\cdot}45$ have negative temperature coefficients of resistivity near room temperature and they have positive ones in the lower temperature range. They have electric transitions from insulator to metal. The transition temperature increases monotonically with x up to 0·4. The sample with $x=0{\cdot}45$ shows a further transition from metal to insulator at 41 K. On the other hand, the sample with $x=0{\cdot}5$ shows insulating behavior below room temperature. It is noteworthy that a hump is found around 120 K in the temperature dependence of resistivity. It has been reported that the $x=0{\cdot}5$ manganite, that is, $LaSr_2Mn_2O_7$, shows an insulator–metal transition and simultaneously shows a magnetic transition to weak ferromagnetism at 132 K.[8] The hump may relate to the electric and magnetic transition, though no magnetic transition has been found in our present study.

Figure 2 shows the temperature dependence of magnetoresistance measured under a magnetic field of 1·5 T. The samples with $0{\cdot}3\leq x\leq 0{\cdot}45$ have peak values at low temperatures, which are close to their electric transition temperatures. With increasing Sr content x, the temperature, at which the peak value of magnetoresistance is found, shifts toward higher temperature.

For the present manganites and two perovskite-type manganites, $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xMnO_3$,[9] the insulator—metal transition temperature, T_{IM}, is plotted in Fig. 3(a) as a function of averaged valence of manganese ion, p, which is measured by an iodometric titration. The T_{IM}s of the present manganites are much lower than those of perovskite-type manganites. However, the T_{IM}s increase with increasing p up to 3·35 and suddenly decrease when the p exceeds 3·35 for all manganites. The relation between the peak value of the magnetoresistance and the value of p is shown in Fig. 3(b). The magnetoresistance of the present manganites correspond to those of the perovskite-type manganites, though the latter magneto-

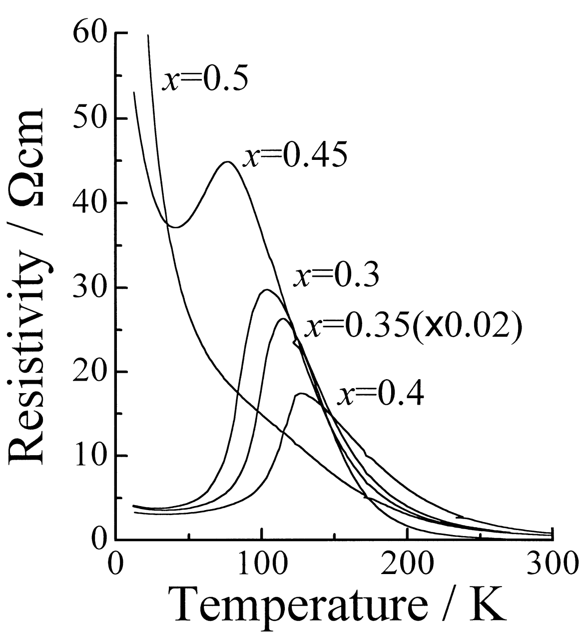

Fig. 1. Temperature dependence of electric resistivity of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ under no magnetic field.

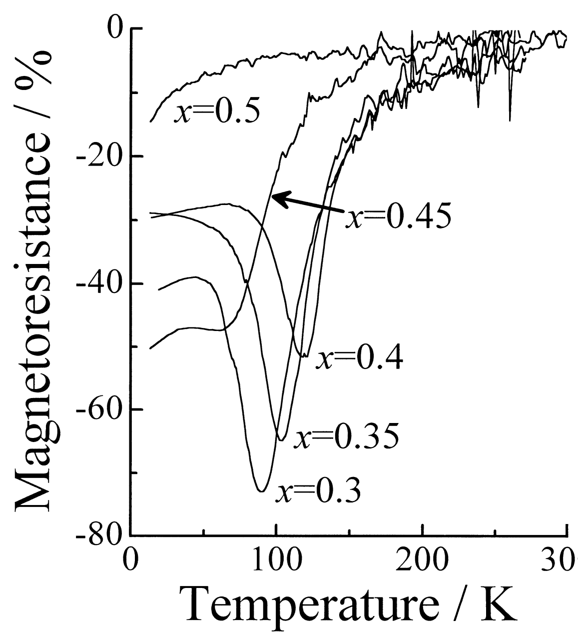

Fig. 2. Temperature dependence of magnetoresistance of $La_{2-2x}Sr_{1+2}Mn_2O_7$ under a magnetic field of 1·5 T.

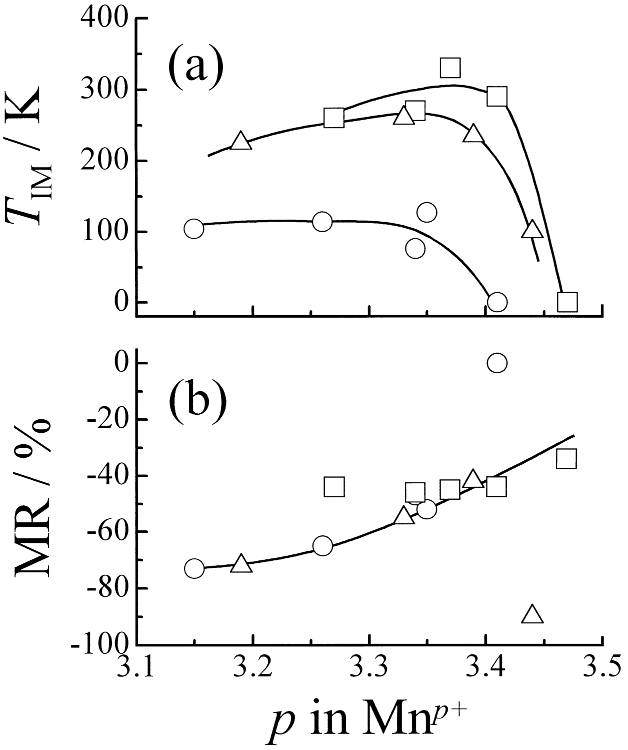

Fig. 3. Carrier number dependence of (a) the insulator–metal temperature T_{IM}. and (b) peak value of magnetoresistance MR. Circles, triangles and squares indicate the T_{IM}s and MRs of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (the present work), $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xMnO_3$,[9] respectively, in both panels.

Table 1. Lattice constants of $La_{1\cdot4}Sr_{1\cdot6-x}Ca_xMn_2O_7$

x	a *(nm)*	c *(nm)*	c/a
0·0	0·38780(2)	2·0395(8)	5·26
0·2	0·38659(2)	2·0301(4)	5·25
0·4	0·38625(5)	2·0236(3)	5·24
0·6	0·38550(2)	2·0091(2)	5·21

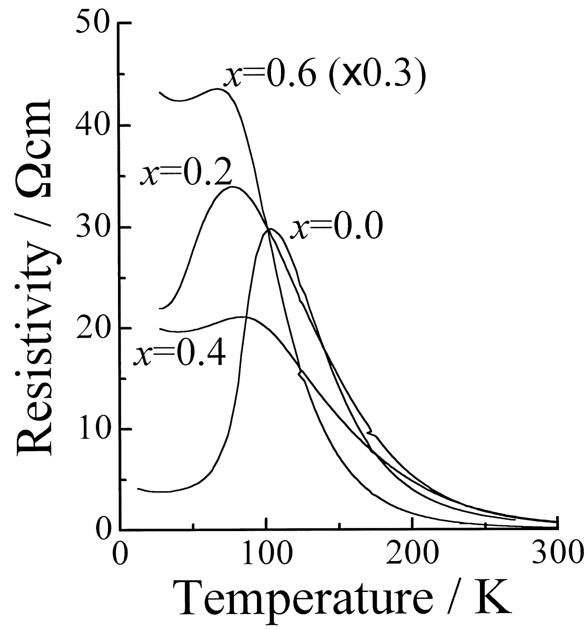

Fig. 4. Temperature dependence of electric resistivity of $La_{1\cdot4}Sr_{1\cdot6-x}Ca_xMn_2O_7$ under no magnetic field.

resistances were measured under higher magnetic field (6 T). The peak value of magnetoresistance tends to decrease with increasing p for all manganites.

3.2 Properties of $La_{1\cdot4}Sr_{1\cdot6-x}Ca_xMn_2O_7$

Single phase samples can be prepared with the composition of $0\cdot0 \leq x < 0\cdot8$ in the present study. The lattice constants of the samples are summarized in Table 1. Both a axis and c axis decrease monotonically with increasing Ca content x. The c axis shrinks preferably rather than the a axis through the cationic substitution. The ratio of c/a, thus, decreases with increasing x.

The temperature dependence of electric resistivity under no magnetic field is shown in Fig. 4. The manganite with $x = 0\cdot0$ shows insulating behavior down to 104 K and shows metallic behavior below the temperature. The remaining manganites show similar electric conduction. The insulator–metal transition temperature T_{IM} tends to decrease with increasing x.

Figure 5 shows the temperature dependence of magnetoresistance under a magnetic field of 1·5 T. We abbreviate the temperature, at which the maximum magnetoresistance occurs, to T_{MR} hereafter. All manganites show similar temperature dependence from room temperature to 150 K. The $x = 0\cdot0$ manganite shows the maximum magnetoresistance of -73% at 90 K, which is close to its T_{IM}. For the manganite with $x = 0\cdot2$, the magnetoresistance begins to increase below 100 K and shows the maximum value of -61% at 30 K, which is the lowest temperature during the measurement. The T_{MR} of the $x = 0\cdot2$ manganite is considered to be lower than 30 K. There is no abrupt change in the magnetoresistance for the $x = 0\cdot4$ and 0·6 manganites. The temperature T_{MR} decreases more drastically than the temperature T_{IM} through the Ca substitution.

From the above results, the temperatures T_{IM} and T_{MR} decrease with reducing lattice constants in $La_{1\cdot4}$,$Sr_{1\cdot6-x}$,$Ca_xMn_2O_7$. The lattice constants and magnetotransport properties of $(La_{1-z}Nd_z)_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$[10] and $Sr_{1\cdot6}R_{1\cdot4}Mn_2O_7$($R$ = La, Pr, Nd, Gd),[11] which are also $Sr_3Ti_2O_7$ type manganites, have also been measured. Their lattice constants, a and c axes, have been reported to decrease through the ionic substitution for these manganites. Figure 6(a) and (b) indicate the lattice constant dependence of the T_{IM} for the three $Sr_3Ti_2O_7$ type manganites including the present manganites. The T_{IM} tends to be raised with increasing a axis and c axis in these manganites. However, the T_{IM} is raised

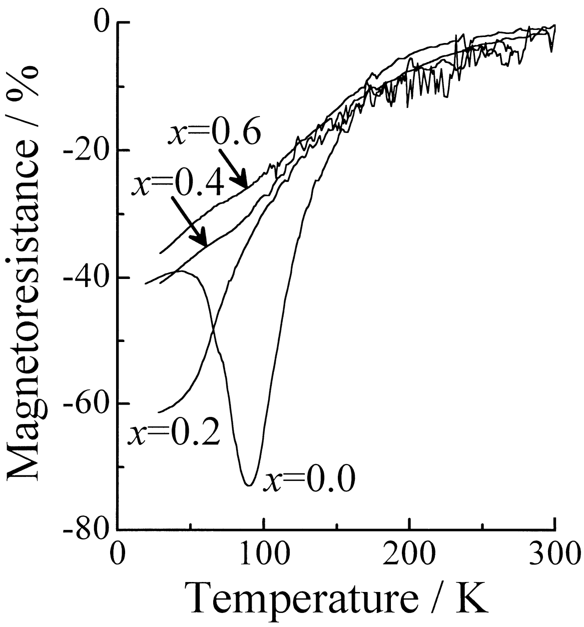

Fig. 5. Temperature dependence of magnetoresistance of $La_{1\cdot4}Sr_{1\cdot6-x}Ca_xMn_2O_7$ under a magnetic field of 1·5 T.

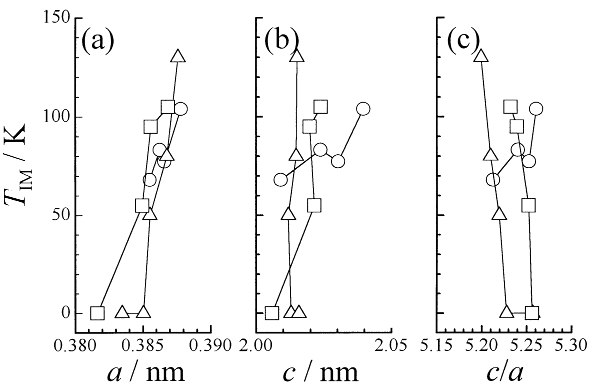

Fig. 6. Lattice constants dependence of the insulator–metal temperature T_{IM}: (a) *a* axis, (b) *c* axis and (c) *c*/*a* ratio. Circles, triangles and squares indicate the T_{IM}s of $La_{1\cdot4}Sr_{1\cdot6-x}Ca_xMn_2O_7$ (the present work), $(La_{1-z}Nd_z)_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$[10] and $Sr_{1\cdot6}R_{1\cdot4}Mn_2O_7$ (R = La, Pr, Nd, Gd),[11] respectively.

gradually with increasing *c* axis in the present manganites. The ratio of *c* and *a* axes, *c*/*a*, has been reported to increase for $(La_{1-z}Nd_z)_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$ and $Sr_{1\cdot6}R_{1\cdot4}Mn_2O_7$ (R = La, Pr, Nd, Gd) through the substitution. The change in *c*/*a* is considered to indicate the Jahn–Teller distortion in MnO_6 octahedrons. The conducting e_g electrons have dz^2-like character rather than $d_{x^2-y^2}$-like character due to the distortion so that the electronic transfer is suppressed and the T_{IM} is considered to be reduced.[10] Figure 6(c) shows the relation between the T_{IM} and the *c*/*a* ratio. The T_{IM} surely decreases with increasing the ratio of *c*/*a* in $(La_{1-z}Nd_z)_{1\cdot2}$ $Sr_{1\cdot8}Mn_2O_7$ and $Sr_{1\cdot6}R_{1\cdot4}Mn_2O_7$ (R = La, Pr, Nd, Gd). However, it increases with the *c*/*a* for the present manganite. It may be suggested that the Ca content dependence of T_{IM} cannot be explained by the Jahn–Teller distortion in MnO_6 octahedron for the present manganite. Refinement of local structure around Mn ion in the $Sr_3Ti_2O_7$ type manganites is necessary to discuss the relation between magnetotransport properties and lattice constants in detail.

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