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Electrical resistivity and Seebeck coefficient of $La_{1-x}M_xMnO_3$ (M = Ca, Sr) single crystals

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The temperature dependence of the electrical resistivity and Seebeck coefficient was measured on single crystals of $La_{1-x}Ca_xMnO_3$ $(0 < x \leqslant 0.3)$ and $La_{1-x}Sr_xMnO_3$ $(0 < x \leqslant 0.4)$ grown by the arc-image floating zone method. The electrical conduction for $La_{1-x}Ca_xMnO_3$ crystals with $x \geqslant 0.2$ was of the activation type above T_c and of the degenerate type below T_c, while that for the crystal with $x = 0.1$ was of the activation type over the whole measured temperature range between −170 and 400° C. The conduction behaviour of $La_{1-x}Sr_xMnO_3$ was essentially the same as that of $La_{1-x}Ca_xMnO_3$ except that the conduction of the crystals with $x = 0.3$ and 0.4 was of the degenerate type above T_c. A distinct difference in Seebeck data was observed between the calcium and the strontium compounds.

1. Introduction

In the $La_{1-x}M_xMnO_3$ (M = Ca and Sr) system, the end members $LaMnO_3$ and $CaMnO_3$ are antiferromagnetic, while the compounds in the range $0.2 \leqslant x \leqslant 0.4$ are ferromagnetic. The electrical properties closely correlate with the magnetic interaction and the metal–semiconductor transition is believed to accompany the ferromagnetic phase transition. Although extensive studies, including experimental and theoretical, have been carried out [1–9], the conduction mechanism is not fully clarified.

When a system consists of a number of components or includes multivalent cations, the stoichiometry and homogeneity of the sample are greatly affected by the preparation of samples. As a result, the physical properties, such as the electrical conduction, often become diffused and ambiguous. Use of carefully prepared single crystals rather than a sintered specimen may relieve the problems in most cases. In this paper, the electrical resistivity and the Seebeck coefficient are reported for single crystals grown in an arc-image furnace using the floating zone method.

2. Experimental techniques

Single crystals of $La_{1-x}Ca_xMnO_3$ (x = 0.1, 0.2 and 0.3) and $La_{1-x}Sr_xMnO_3$ (x = 0.1, 0.2, 0.3 and 0.4), with approximate dimensions of 3 mm diameter and 40 mm long, were grown from the melt in the xenon arc-image furnace using the floating zone method. Chemical analysis of the crystals indicated that the compositions differed from that intended by 4 at. % at the most. Details of the growth procedure and the crystallographic data for the crystals have already been reported by us [10]. For the electrical measurements, specimens were cut from the crystal rod and shaped into specimens of dimensions $1.5 \times 1.5 \times 8\,mm^3$ using no. 600 and no. 3000 abrasive wheels.

Polycrystalline specimens were also prepared as described by Tanaka *et al.* [11] using the coprecipitation method for comparison. Starting materials of La_2O_3, $CaCO_3$ (or $SrCO_3$), $MnCO_3$ were dissolved in 7 N HCl at 70° C. The precipitate was obtained by adding excessive 6 N $(NH_4)_2CO_3$ to the solution, calcining at 600° C for 1 h, pulverizing and calcining again at 1000° C for 10 h. The product was pulverized again and pressed isostatically at $1000\,kg\,cm^{-2}$ into dimensions of $3 \times 4 \times 30\,mm^3$ with a green density of 50%, and sintered at 1250° C for 24 h in an oxygen flow. The sintered specimens with an apparent density of 94% were polished to the same dimensions as those of the single crystals.

A conventional four-probe direct current method was used to measure electrical conductivities in the temperature range −170 to 400° C. Platinum wires, 0.1 mm diameter, were wound around the specimen with platinum paste as electrodes and annealed at 700° C in a muffle furnace. Seebeck coefficients were measured using a microvoltmeter (Ohkura Electric Co., Japan, AM1001) in the temperature range −170 to 200° C. Both ends of the specimen were coated with platinum paste and then placed in contact with thin copper plates. Copper–constantan thermocouples were welded on to the reverse side of each copper plate to measure both the temperature and the Seebeck voltage. All the measurements were carried out in an atmosphere of dry air flowing at $500\,cm^3\,min^{-1}$.

3. Results and discussion

3.1. $La_{1-x}Ca_xMnO_3$

The temperature dependence of the electrical

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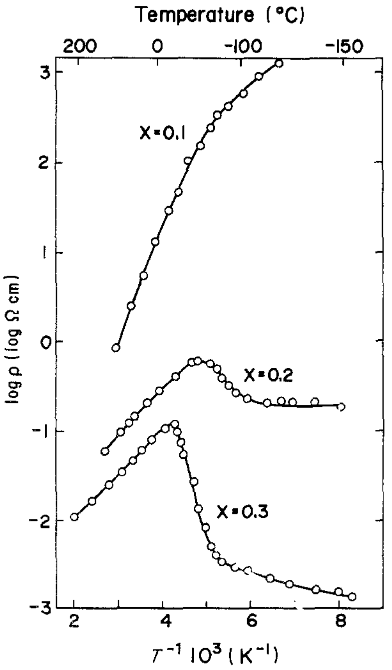

Figure 1 Temperature dependence of electrical resistivities for $La_{1-x}Ca_xMnO_3$ single crystals.

resistivities for $La_{1-x}Ca_xMnO_3$ crystals is shown in Fig. 1. Data for the crystal with $x = 0.1$ might have slightly lower quality for the quantitative discussion, because the crystal contains very fine cracks due to the phase transition which occurs during crystal growth. The resistivity becomes lower for the crystals with $x = 0.1$, 0.2 and 0.3, in that order. The Curie temperatures for these compounds were reported by Jonker [1], as approximately 185, 240 and 273 K, respectively. The resistivity below T_c markedly decreases as x increases, resulting in the formation of a resistivity maximum around T_c. As the temperature increases towards T_c, the resistivities of the specimens with $x = 0.2$ and 0.3 gradually increase, and then decrease almost linearly above T_c. The electrical conduction of these compounds is of the degenerate type below T_c and of the activation type above T_c. On the other hand, the conductivity of the specimen with $x = 0.1$ is activated over the whole temperature region studied. All these features are essentially the same as in the previous study on $La_{0.8}Ca_{0.2}MnO_{3-y}$ polycrystals [6].

In the $La_{1-x}Ca_xMnO_3$ system, holes are considered to be the main carrier for the electrical conduction. The positive Seebeck coefficient, as described later, is experimental evidence which supports this consideration. On substituting Ca^{2+} cations for La^{3+}, an equal amount of Mn^{3+} is required to become Mn^{4+} for charge compensation if the stoichiometry is maintained. These Mn^{4+} ions could be regarded as Mn^{3+} ions plus holes. Thus, the hole concentration increases in proportion to the Ca^{2+} concentration, giving a higher electrical conduction to the substance. This explains qualitatively the observed decrease of electrical resistivity with x in $La_{1-x}Ca_xMnO_3$ compounds.

Negative ($T > T_c$) and positive ($T < T_c$) temperature coefficients of the resistivity curves with $x = 0.2$ and 0.3 indicate the semiconducting and metallic behaviour above and below T_c, respectively. On the other hand, the crystal with $x = 0.1$ is still semiconductive even below T_c near 185 K [1]. Such a difference seems to have a close relation to the crystal structure: $La_{0.9}Ca_{0.1}MnO_3$ is orthorhombic, $a = 0.5531(2)$ nm, $b = 0.5613(2)$ nm, $c = 0.7719(2)$ nm, $Z = 4$, while $La_{0.8}Ca_{0.2}MnO_3$ is monoclinic, $a = 0.77828(6)$ nm, $b = 0.77695(9)$ nm, $c = 0.77832(5)$ nm, $\beta = 90.096(4)°$, $Z = 8$ [10]. The former symmetry is the same as that of $LaMnO_3$ which is electrically insulative and has no magnetic transition. The compound with $x = 0.1$ is supposingly located near the border between the antiferromagnetic and ferromagnetic structures.

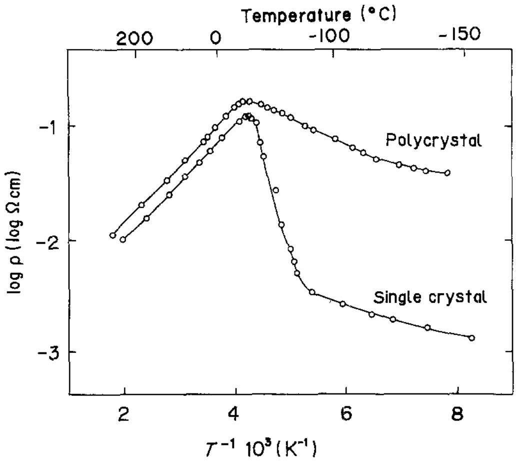

Figure 2 Temperature dependence of electrical resistivities for $La_{0.7}Ca_{0.3}MnO_3$ single and polycrystals.

Electrical resistivity of polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ is shown in Fig. 2 compared with the single crystal data. The resistivity of the polycrystalline specimen below T_c is higher than that of the single crystal by one order of magnitude and gives a diffuse maximum around T_c. This will be due to the random crystallographic orientation among the grains, which causes the scattering of holes on the grain boundaries.

The temperature dependence of the Seebeck coefficients for $La_{1-x}Ca_xMnO_3$ is shown in Fig. 3. All these data have positive values indicating that holes are responsible for the electrical conduction. The coefficients in specimens with $x = 0.2$ and 0.3 have maxima around T_c but not in the specimen with $x = 0.1$. These maxima become sharp with increasing x, being similar to the resistivity data shown in Fig. 1. Activation energies, ΔE_ϱ and ΔE_α above T_c are estimated

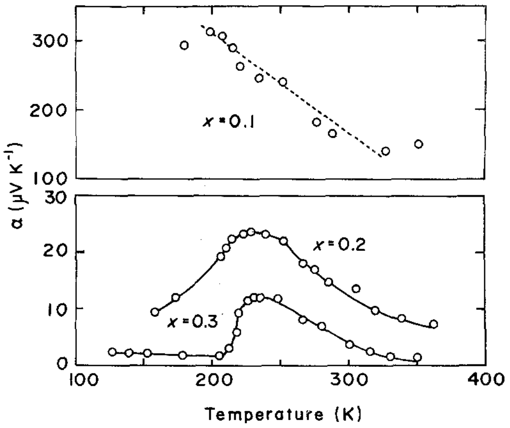

Figure 3 Temperature dependence of Seebeck coefficients for $La_{1-x}Ca_xMnO_3$ single crystals.

TABLE I Activation energies calculated from the resistivity data (ΔE_ϱ) and Seebeck data (ΔE_α) above T_c of $La_{1-x}Ca_xMnO_3$ single crystals

x	ΔE_ϱ (eV)	ΔE_α (eV)
0.1	0.183	0.071
0.2	0.106	0.012
0.3	0.104	0.010

from the temperature dependence of resistivity and Seebeck data, respectively, and given in Table I. The values measured by Tanaka *et al.* [6] for $La_{0.8}Ca_{0.2}MnO_3$ polycrystal were $\Delta E_\varrho = 0.116\,eV$ and $\Delta E_\alpha = 0.035\,eV$. The former value is approximately the same while the latter is three times larger than that given in Table I. Generally speaking, however, both studies agree in that ΔE_α is much smaller than ΔE_ϱ.

The resistivity, ϱ, is expressed as

$$\varrho = ce\mu \qquad (1)$$

where c, e and μ represent the concentration, electric charge and drift mobility of the carrier, respectively. The Seebeck coefficient, α, for the activation-type semiconductor is expressed as

$$\alpha = \pm(k/e)[\ln(n/c) + A] \qquad (2)$$

where n is the effective density, k is the Boltsmann constant, and A is a constant concerning the kinetic term and its sign depends on the type of carrier. Among these terms, those which are temperature-activated are c and μ in Equation 1, but only c in Equation 2. As ΔE_ϱ is much larger than ΔE_α in this system, the drift mobility, μ, of holes may largely contribute to the activation energy. Therefore, the conduction mechanism above T_c could be explained by the hopping mechanism, rather than the band model, which is consistent with the previous study [6].

3.2. $La_{1-x}Sr_xMnO_3$

The temperature dependence of the resistivity of $La_{1-x}Sr_xMnO_3$ is shown in Fig. 4. The resistivity of $La_{0.9}Sr_{0.1}MnO_3$ changes with temperature in a similar way to that of $La_{0.9}Ca_{0.1}MnO_3$ shown in Fig. 1. Resistivity curves of $La_{1-x}Sr_xMnO_3$ with $x \geqslant 0.2$ below T_c are similar to those of $La_{1-x}Ca_xMnO_3$ with $x \geqslant 0.2$, though their values are rather small in $La_{1-x}Sr_xMnO_3$, approaching $10^{-4}\,\Omega\,cm$ at low temperatures. The resistivity data of the compound with $x = 0.4$ are slightly larger than those with $x = 0.3$ due to the decrease of T_c, in agreement with the study of Santen and Jonker [2]. On the other hand, the resistivities of $La_{1-x}Sr_xMnO_3$ with $x = 0.3$ and 0.4 above T_c still have positive temperature coefficients, which have not been observed before. It seems that the resistivities of the specimens of this system in general converge to a value between 10^{-2} and $10^{-3}\,\Omega\,cm$ at elevated temperatures, though the reason is not fully understood. This phenomenon always appeared for the compounds with $x = 0.3$ and 0.4 in repeated measurements using various electrodes (such as silver or In–Ga amalgam) and various shapes of specimens.

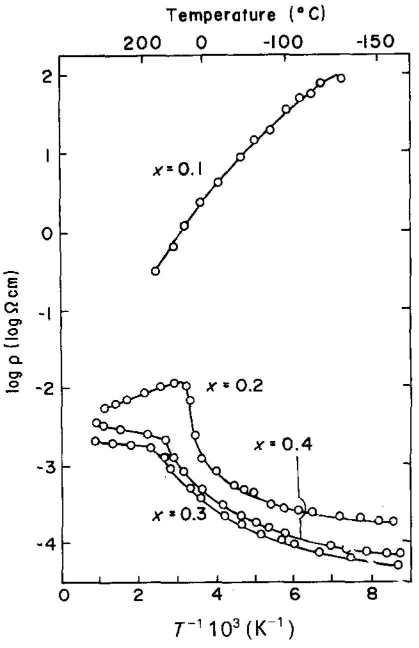

Figure 4 Temperature dependence of electrical resistivities for $La_{1-x}Sr_xMnO_3$ single crystals.

Because holes are believed to transfer along Mn–O–Mn bonds by the double-exchange interaction [7, 8] or other mechanisms [3, 5, 6], they could move easier in the MnO_6 octahedral network with higher symmetries. Although the structures of the orthorhombic ($x \leqslant 0.1$) and monoclinic ($x \geqslant 0.2$) modifications of $La_{1-x}M_xMnO_3$ (M = Ca, Sr) have not yet been determined precisely, it is believed that (a) the MnO_6 octahedra in the orthorhombic form are highly distorted because of the Jahn–Teller effect, and (b) the unit cell deformation of the monoclinic forms with respect to the orthorhombic form is relatively small [10]. Therefore, the monoclinic modifications with $x \geqslant 0.2$ are supposed to have smaller resistivities than the orthorhombic one. Furthermore, the Ca–O bonding is more covalent than Sr–O, because the calcium atom has a larger electronegativity than the strontium atom. This means that calcium atoms tend to attract oxygen atoms and contribute to deform MnO_6 octahedra. The smaller resistivity of $La_{1-x}Sr_xMnO_3$ with respect to $La_{1-x}Ca_xMnO_3$ could be thus understood.

The temperature dependence of the Seebeck coefficients of $La_{1-x}Sr_xMnO_3$ ($0.2 \leqslant x \leqslant 0.4$) is shown in Fig. 5. The curves are quite different from those of

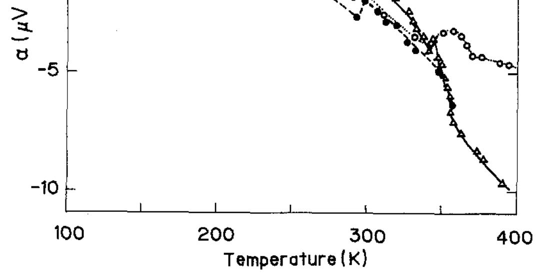

Figure 5 Temperature dependence of Seebeck coefficients for $La_{1-x}Sr_xMnO_3$ single crystals. (○) $x = 0.2$, (△) $x = 0.3$, (●) $x = 0.4$.

$La_{1-x}Ca_xMnO_3$. First, the values are 2 to 4 $\mu V K^{-1}$ in $La_{1-x}Sr_xMnO_3$, which are as small as those of metals. Secondly, these values change their sign at about room temperature and the absolute values increase with temperature. A similar tendency was also reported by Volger [9] for polycrystalline $La_{1-x}Sr_xMnO_3$, and could be explained by the phonon drag effect occurring at relatively high temperature.

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