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Electrical Properties in the System $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$ $(0 \leq x \leq 0.4)$

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The electrical resistivity of $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$ $(0 \leq x \leq 0.4)$ was measured in the temperature range 80 to 700 K. At low temperature, manganates are *n*-type semiconductors, and the electrical resistivity follows Mott's $T^{-1/4}$ law, indicating the possible occurrence of variable range hopping of electrons due to Anderson localization. At high temperature, manganates exhibit a metal–insulator transition with no crystallographic change. The metal–insulator transition temperature linearly increased with increasing x. Since both the number of 4*f* electrons in rare earth ions and the Mn^{3+}/Mn^{4+} ratio are independent of x, the increase of the metal–insulator transition temperature depends on the cell constants.

Many investigations have been reported on the substitution of Ca^{2+} by rare earth ions in orthorhombic perovskite-type $CaMnO_3$. The electrical properties of $(Ln_{1-x}Ca_x)MnO_3$ (*Ln*: La, Nd, and Gd) were measured by Taguchi *et al.* (*1–3*). These manganates exhibit *n*-type semiconducting behavior below room temperature. At low temperature, the electrical resistivity follows Mott's $T^{-1/4}$ law, indicating the possible occurrence of variable range hopping of electrons due to Anderson localization (*4*). At high temperature, the resistivity of these manganates has a positive temperature coefficient, and the metal–insulator transition of these manganates occurs without any crystallographic change.

The metal–insulator transition temperature in each $(Ln_{1-x}Ca_x)MnO_3$ (*Ln*: La, Nd, and Gd) decreases with increasing x. At a particular value of x, in which the Mn^{3+}/Mn^{4+} ratio is constant, the metal–insulator transition temperature of these manganates increases with the increasing ionic radius of the rare earth ion.

In the perovskite-type $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{3-\delta}$, both the number of 4*f* electrons in the rare earth ion and the Mn^{3+}/Mn^{4+} ratio are independent of x. With increasing x, it is expected that the cell constants increase due to the difference of the ionic radius between Ca^{2+} and Sr^{2+} ions. In the present

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study, an attempt was made to synthesize $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{3-\delta}$ $(0 \leq x \leq 0.4)$ samples in order to study their electrical properties. These results provide some information for discussing the relationship between the metal–insulator transition temperature and the cell constants.

All $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{3-\delta}$ $(0 \leq x \leq 0.4)$ samples were prepared by standard ceramic techniques. Powders of Nd_2O_3, $CaCO_3$, $SrCO_3$, and $MnCO_3$ were weighed in the appropriate proportions and milled for 12 hr with acetone. After the mixed powders were dried at 373 K, they were calcined in air at 1073 K for 24 hr, then fired at 1623 K for 24 hr under a flow of pure oxygen gas. For measuring the electrical resistivity, the powder was pressed into a pellet form under a pressure of 50 MPa, and the pellet was sintered at 1623 K for 12 hr under the flow of pure oxygen gas. The oxygen-deficient materials obtained in this manner were annealed at 973 K under a flow of pure oxygen gas.

The phases of the samples were identified by X-ray powder diffraction with Ni-filtered Cu$K\alpha$ radiation. The cell constants of the samples were determined from high-angle reflections with Si as a standard.

The oxygen content in each sample was determined by the oxidation–reduction (redox) method. After sodium oxalate solution and perchloric acid were added to dissolve the sample in a flask, the solution was titrated with a standard potassium permanganate solution (*5*).

The electrical resistivity of the samples was measured by a standard four-electrode technique in the temperature range 80 to 700 K. Differential thermal analysis (DTA) and thermogravimetry (TG) of the samples were performed in the temperature range 300 to 1273 K.

The oxygen content of $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{3-\delta}$ $(0 \leq x \leq 0.4)$ annealed at 973 K under pure oxygen was determined to be 2.97 $(\delta = 0.03)$ by the chemical analysis, independent of x. X-ray powder diffraction patterns of all manganates were completely indexed as the orthorhombic perovskite-type structure. The relation between the cell constants and x is shown in Fig. 1. The cell constants (a-, b-, and c-axis) increased linearly with increasing x. The ionic radii of Ca^{2+} and Sr^{2+} ions with a coordination number(CN) of 12 are 0.135 nm and 0.144 nm, respectively (*6*); the Mn^{3+}/Mn^{4+} ratio of each manganate is constant. It is obvious that the increase of the cell constants does not depend on manganese ions, but on the average ionic radius of the A-site ion in the perovskite-type structure (ABO_3).

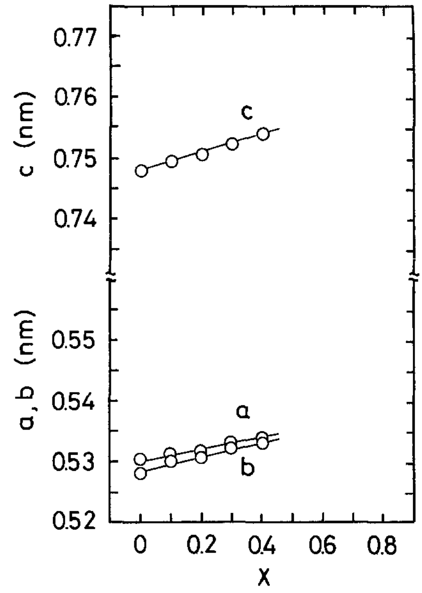

FIG. 1. Cell constants vs composition for the system $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$.

The electrical resistivity data of $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$ in the temperature range 80 to 700 K are shown in Fig. 2. Below room temperature, all manganates were n-type semiconductors and the electrical resistivity increased with increasing x. At low temperature, a plot of log ρ vs $1000/T$ was

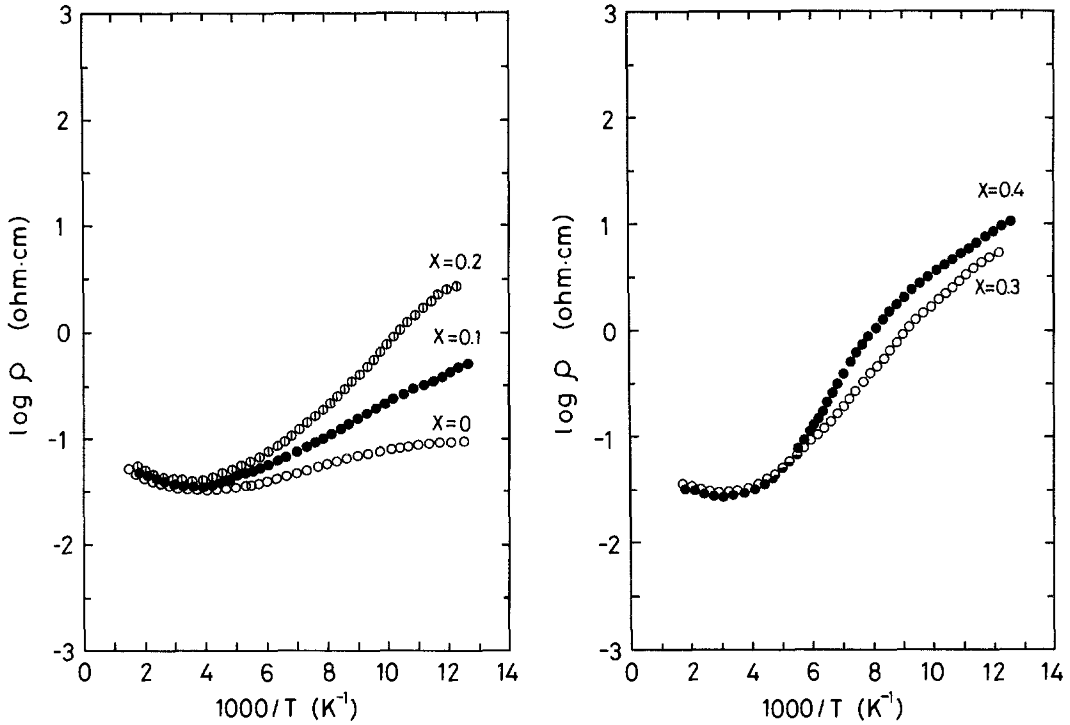

FIG. 2. Electrical resistivity vs 1000/T for the system $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$.

nonlinear. The relationship log ρ vs $T^{-1/4}$ in $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$ is shown in Fig. 3. The plot of log ρ vs $T^{-1/4}$ is linear in the temperature range ca. 80 to ca. 150 K, and at fixed T, log ρ increases with increasing x. The logarithm of ρ follows Mott's $T^{-1/4}$ law; the electrical properties of $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$ can be related to variable range hopping of electrons due to Anderson localization (*4*), which was also reported for other perovskite systems such as $(Eu_{1-x}Sr_x)FeO_3$ (*7*), $CaMnO_{3-\delta}$ (*8*), and $(Ln_{1-x}Ca_x)MnO_3$ (*Ln*: La, Nd, and Gd) (*1–3*).

Above 200 to 400 K, the electrical resistivity of $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$ had a slight positive temperature coefficient as shown in Fig. 2; this temperature coefficient is essentially independent of x. No exothermic and endothermic peaks were found in DTA measurement. This fact indicates that the changeover in $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$ occurs without a detectable transition, by analogy with $(Ln_{1-x}Ca_x)MnO_3$ (*Ln*: La, Nd, and Gd) (*1–3*). No loss or gain of weight was found in TG measurement in the temperature range 300 to 470 K. This fact indicates that the change of the temperature coefficient is not due to alteration in the oxygen content of all manganates. We define the metal-insulator transition temperature (T_t) as the temperature where the resistivity coefficient changes from negative to positive. The relation between T_t and x is shown in Fig. 4. T_t increased linearly with increasing x, and this increase is in good agreement with the case of $(Ln_{1-x}Ca_x)MnO_3$ (*Ln*: La, Nd, and Gd) (*1–3*); that is, T_t increases with

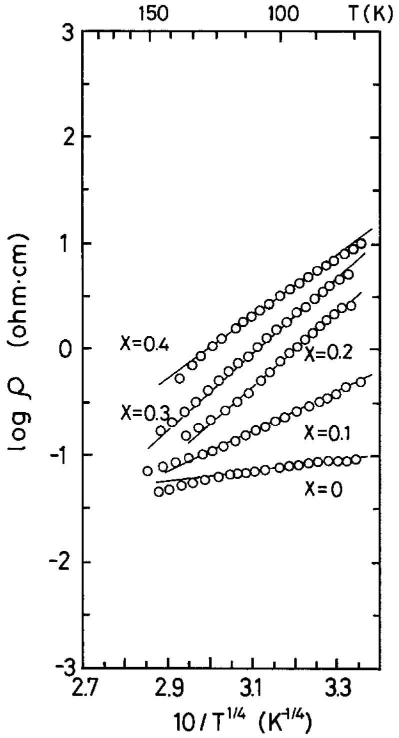

FIG. 3. Electrical resistivity vs $10\,T^{-1/4}$ for the system $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$.

the increasing ionic radius of the *A* site in the perovskite-type structure.

It is concluded that $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$ exhibits variable range hopping of electrons due to Anderson localization at low temperature. At high temperature, $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$ exhibits the metal–insulator transition without the phase transition, and the mechanism of the metal–insulator transition is considered in the same manner as for $(Ln_{1-x}Ca_x)MnO_3$ (*Ln*: La, Nd, and Gd) (*1–3*). Since both the number of 4*f* electrons in Nd^{3+} ion and the Mn^{3+}/Mn^{4+} ratio are independent of *x*, the value of T_t depends on the cell constants.

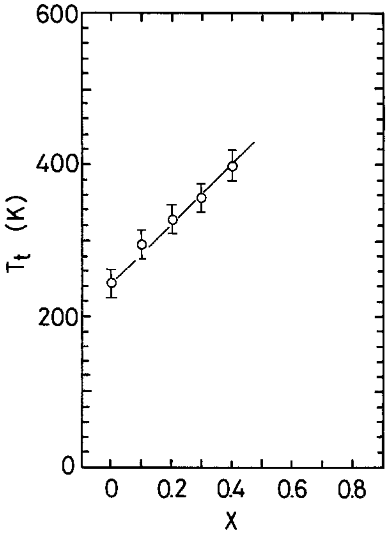

FIG. 4. Metal–insulator transition temperature vs composition for the system $(Nd_{0.1}Ca_{0.9-x}Sr_x)MnO_{2.97}$.

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References

1. H. TAGUCHI AND M. SHIMADA, *J. Solid State Chem.* **62,** 290 (1986).
2. H. TAGUCHI, M. NAGAO, AND M. SHIMADA, *J. Solid State Chem.* **76,** 284 (1988).
3. H. TAGUCHI, M. NAGAO, AND M. SHIMADA, *J. Solid State Chem.* **82,** 8 (1989).
4. N. F. MOTT, *Adv. Phys.* **21,** 785 (1972).
5. N. MIZUTANI, N. OKUMA, A. KITAZAWA, AND M. KATO, KOGYO KAGAKU ZASSHI **73,** 1103 (1970). [in Japanese]
6. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr., Sect. B* **25,** 925 (1969).
7. V. JOSHI, O. PARAKASH, G. N. RAO, AND C. N. R. RAO, *J. Chem. Soc., Faraday Trans.* **2,** 75 (1979).
8. H. TAGUCHI, *Phys. Status Solidi A* **88,** K79 (1985).