

Thermoelectric properties of the layered perovskite system $\text{Ca}_{3-m}\text{Ln}_m\text{Mn}_2\text{O}_{7-\delta}$ ($\text{Ln} = \text{Nd}, \text{La}$).

Hiroshi Kawakami, Katuyoshi Kakinuma, Hiroshi Yamamura

Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University

3-37-1 Rokkakubashi, Kanagawa-ku, Yokoham, 221-8686, Japan

Fax: 81-045-413-9770, e-mail: hirosikawakami627@yahoo.co.jp

Thermoelectric properties of the tetragonal perovskite-type oxide system $\text{Ca}_{2.73-m}\text{Ln}_m\text{Mn}_2\text{O}_{7-\delta}$ ($\text{Ln} = \text{Nd}, \text{La}$) ($0 \leq m \leq 0.18$) were investigated. The a-axis in the tetragonal phase increased with increasing m, while the c-axis decreased with increasing m. It was found that $\text{Ca}_{2.73-m}\text{Ln}_m\text{Mn}_2\text{O}_{7-\delta}$ system shows a n-type semiconductor in the range $0 \leq m \leq 0.18$ from the measurements of Seebeck coefficient (S), the thermal conductivity (κ) and the electrical conductivity (σ) and that the lattice thermal conductivity (κ_L) increases with increasing m. The relationship between the change in the c-axis due to the Ln content (m) and κ_L was linear. From these results, it was speculated that the c-axis plays an important role in the thermal properties. $\text{Ca}_{2.63}\text{Ln}_{0.09}\text{Mn}_2\text{O}_{7-\delta}$ showed the maximum figure of merit of $0.07 \times 10^{-3} \text{ K}^{-1}$ at 873 K among the $\text{Ca}_{2.73-m}\text{Ln}_m\text{Mn}_2\text{O}_{7-\delta}$ systems.

Key words: thermoelectric, layered perovskites, thermal conductivity, oxide semiconductor, electrical conductivity.

1. INTRODUCTION

Thermoelectric power generation, which is the useful energy supply system, occurs by the difference in temperature. The performance of thermoelectric materials is given by figure of merit Z as follows,

$$Z = S^2\sigma/\kappa, \quad (1)$$

where S, σ and κ is the Seebeck coefficient, the electrical conductivity and the thermal conductivity, respectively. Otaki et al.¹⁾ reported $Z = 0.14 \times 10^{-3} \text{ K}^{-1}$ ($ZT = 0.16$ at $T = 1173 \text{ K}$) for the polycrystalline sample of CaMnO_3 which has a perovskite-type structure. Further decrease in the thermal conductivity is necessary for the enhancement of the figure of merit. In this study, we paid attention to layered perovskite-type oxides having Ruddlesden-popper structure with a general formula of $\text{AO} \cdot n(\text{ABO})_3$, which includes heat resistance layers. We synthesized both $\text{Ca}_{2.73-m}\text{Ln}_m\text{Mn}_2\text{O}_{7-\delta}$ ($\text{Ln} = \text{La}, \text{Nd}$), in which the Ca site was partially reduced from the composition of $n = 2$, and CaMnO_3 of $n = \infty$, and compared the thermoelectric properties among them.

2. EXPERIMENTAL

Samples of the $\text{Ca}_{2.73-m}\text{Ln}_m\text{Mn}_2\text{O}_{7-\delta}$ ($\text{Ln} = \text{La}, \text{Nd}$) systems were prepared by solid state reaction. The starting materials of CaCO_3 (99.99%, Kojundo chemical), Nd_2O_3 (99.99%, Kojundo chemical), La_2O_3 (99.99%, Kojundo chemical), and MnO_2 (99.99%, Kojundo chemical) were mixed for 24 h using ball mill. The obtained powders, which were sieved to under 53 μm , were pressed at 50 kgf cm^{-2} into a rectangular shape and then subjected to rubber pressing at 2000 kgf cm^{-2} . These samples were sintered at 1673 K for 10 h in air.

The identification of the samples and the determination of lattice constant were performed by X-ray diffractometry using Cu K α radiation at room temperature. The electrical conductivity of sintered sample was measured at various constant temperatures by the D.C four-probe method in the temperature range from 873 to 1273 K. The thermal conductivity of sintered sample was measured at 873 K by the comparison method, and the Seebeck coefficient was also measured.

3. RESULT AND DISCUSSION

The powder XRD patterns of $\text{Ca}_{2.73-m}\text{Nd}_m\text{Mn}_2\text{O}_{7-\delta}$ ($0 \leq m \leq 0.18$) were completely indexed according to the tetragonal $\text{Ca}_3\text{Mn}_2\text{O}_7$ -type structure. Figure 1 shows the relationship between the cell constants (a and c) and the Nd content (m) of the $\text{Ca}_{2.73-m}\text{Nd}_m\text{Mn}_2\text{O}_{7-\delta}$ ($0 \leq m \leq 0.18$) system. The a-axis increased with increasing the content (m), while the c-axis decreased with

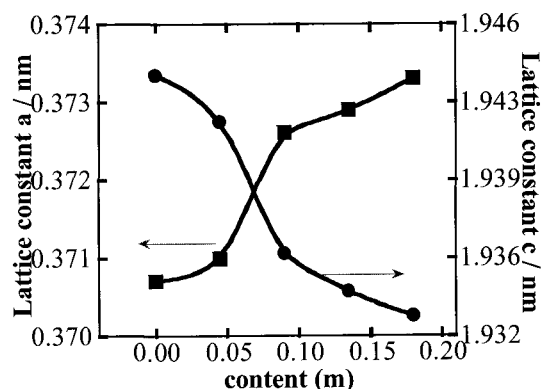


Fig.1 Lattice constant as a function of content (m) for $\text{Ca}_{2.73-m}\text{Nd}_m\text{Mn}_2\text{O}_{7-\delta}$.

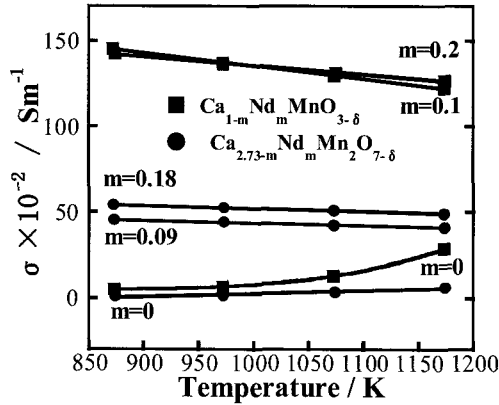


Fig.2 Electrical conductivity of $Ca_{1-m}Nd_mMnO_{3-\delta}$ and $Ca_{2.73-m}Nd_mMn_2O_{7-\delta}$.

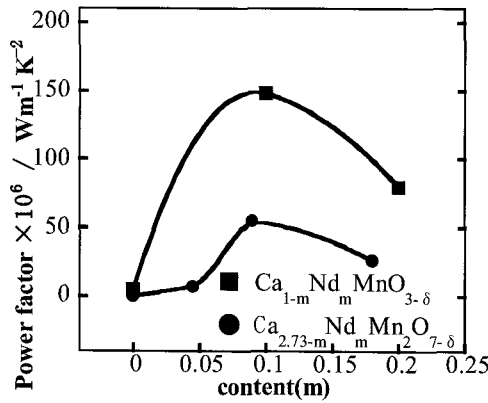


Fig.3 Power factor for $Ca_{1-m}Nd_mMnO_{3-\delta}$ and $Ca_{2.73-m}Nd_mMn_2O_{7-\delta}$ at 873K.

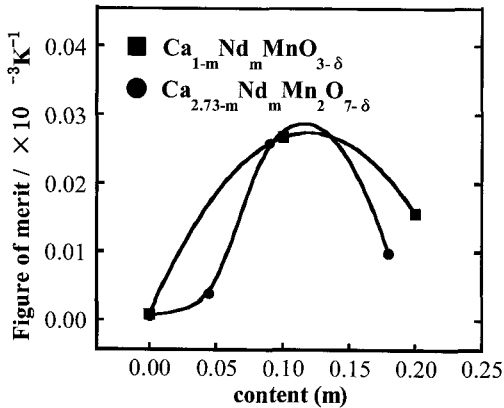


Fig.4 Figure of merit for $Ca_{2.73-m}Nd_mMn_2O_{7-\delta}$ and $Ca_{1-m}Nd_mMnO_{3-\delta}$ at 873K.

increasing m . Figure 2 shows the electrical conductivity of both $Ca_{2.73-m}Nd_mMn_2O_{7-\delta}$ and $Ca_{1-m}Nd_mMnO_{3-\delta}$ systems. The electrical conductivities of both systems increased with increasing m . This reason seems to be due to the increase of carrier by the change of Mn^{4+} into Mn^{3+} . In addition, the electrical conductivities of $Ca_{2.73-m}Nd_mMn_2O_{7-\delta}$ was lower than that of $Ca_{1-m}Nd_mMnO_{3-\delta}$. This result suggests that the heat resistance layer consisting of the rock salt structure may disturb electrical conduction. The Seebeck coefficient measurements showed that the all samples were n-type

semiconductor. Figure 3 shows the relationship between the power factor and the Nd content (m). The power factor of $Ca_{2.73-m}Nd_mMn_2O_{7-\delta}$ was lower than that of $Ca_{1-m}Nd_mMnO_{3-\delta}$. This origin may be due to the difference in the electrical conductivity. Figure 4 represents the calculation results of figure of merit (Z). The Z of $Ca_{2.73-m}Nd_mMn_2O_{7-\delta}$ and $Ca_{1-m}Nd_mMnO_{3-\delta}$ were similar level with each other. This reason may originate from the smaller κ value of $Ca_{2.73-m}Nd_mMn_2O_{7-\delta}$ than that of $Ca_{1-m}Nd_mMnO_{3-\delta}$ due to the effect of the heat resistance layer. Figure 5 represents the thermal conductivity as a function of the Nd content. Here, the electronic thermal conductivity (κ_e) is given by the following equation:

$$\kappa_e = L\sigma T, \tag{2}$$

where L represents the Lorenz number ($2.44 \times 10^{-8} \text{ W S}^{-1} \text{ K}^{-2}$). On the other hand, κ_L represents the lattice thermal conductivity which was given by following equation:

$$\kappa_L = \kappa - \kappa_e. \tag{3}$$

The κ value of $Ca_{1-m}Nd_mMnO_{3-\delta}$ decreased with increasing m , while that of $Ca_{2.73-m}Nd_mMn_2O_{7-\delta}$ increased with increasing m . Fig.5 shows that the κ

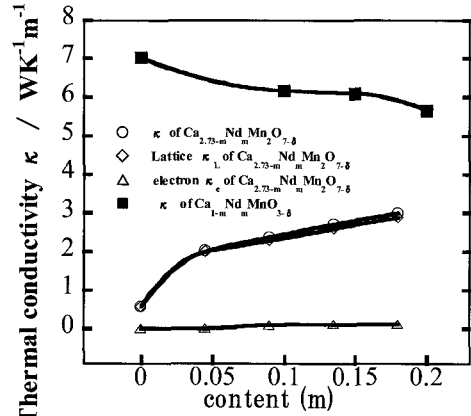


Fig.5 Thermal conductivity of $Ca_{1-m}Nd_mMnO_{3-\delta}$ and $Ca_{2.73-m}Nd_mMn_2O_{7-\delta}$ as a function of m .

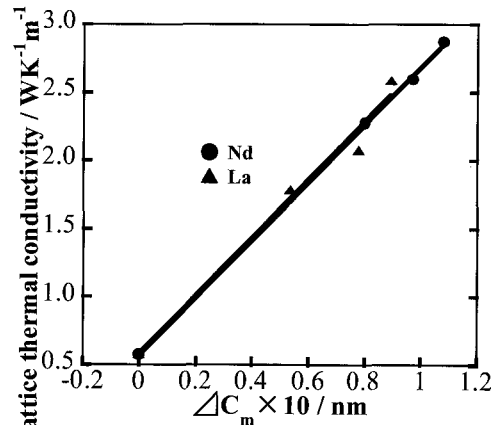


Fig.6 ΔC_m vs lattice thermal conductivity for $Ca_{2.73-m}Ln_mMn_2O_{7-\delta}$ ($Ln=Nd, La$).

value of $\text{Ca}_{2.73-m}\text{Nd}_m\text{Mn}_2\text{O}_{7-\delta}$ increases according to the increase in the κ_L value. This result suggests that the increase in κ_L as well as κ corresponds to the decrease in the effect of the heat resistance layer. Therefore, we paid attention to the c-axis which decreased with increasing m. We defined ΔC_m according to the following equation:

$$\Delta C_m = C_0 - C_m, \quad (4)$$

where C_0 and C_m represent the c-axes for $m = 0$ and m in the $\text{Ca}_{2.73-m}\text{Ln}_m\text{Mn}_2\text{O}_{7-\delta}$ system ($\text{Ln} = \text{Nd}, \text{La}$), respectively. Figure 6 shows that the relationship between ΔC_m and κ_L . The κ_L value of $\text{Ca}_{2.73-m}\text{Nd}_m\text{Mn}_2\text{O}_{7-\delta}$ is proportional to ΔC_m . Therefore, we can get the following expression:

$$\kappa_{Lm} \doteq \kappa_{L0} (\alpha \Delta C_m + 1), \quad (5)$$

where κ_{Lm} , κ_{L0} and α represent the lattice thermal conductivity for the sample with m and with $m = 0$, and the proportional constant, respectively. Eq. (5) shows that the κ_L can be suppressed by the decrease in the ΔC_m . Therefore, we also investigated ΔC_m of $\text{Ca}_{2.73-m}\text{La}_m\text{Mn}_2\text{O}_{7-\delta}$ system, where the Ca site was substituted by La ion having larger ionic radius (1.36 \AA) than that of Ca ion (1.34 \AA)²⁾. As a result, the κ_L of La-dope system also decreased in proportional to the decrease in the ΔC_m (Fig.5). From these results, it is speculated that the c-axis of layered perovskite structure plays an important role in the thermal properties. $\text{Ca}_{2.63}\text{Ln}_{0.09}\text{Mn}_2\text{O}_{7-\delta}$ showed the maximum figure of merit of $0.07 \times 10^{-3} \text{ K}^{-1}$ at 873 K among the $\text{Ca}_{2.73-m}\text{Ln}_m\text{Mn}_2\text{O}_{7-\delta}$ systems.

4. CONCLUSION

Tetragonal perovskite-type oxide systems $\text{Ca}_{2.73-m}\text{Ln}_m\text{Mn}_2\text{O}_{7-\delta}$ ($0 \leq m \leq 0.18$) were synthesized by a standard ceramic technique. The a-axis of the tetragonal phase increased with increasing m, while the c-axis decreased with increasing m. The $\text{Ca}_{2.73-m}\text{Ln}_m\text{Mn}_2\text{O}_{7-\delta}$ system showed a n-type semiconductor in the range $0 \leq m \leq 0.18$ from the measurement of Seebeck coefficient (S), the thermal conductivity (κ) and the electrical conductivity (σ). The lattice thermal conductivity (κ_L) increased with increasing m. The relationship between the change in the c-axis due to the Ln content (m) and lattice κ_L is linear. We got the expressions $\kappa_{Lm} \doteq \kappa_{L0} (\alpha \Delta C_m + 1)$. Therefore, it is speculated that the c-axis plays an important role in the thermal properties. $\text{Ca}_{2.63}\text{Ln}_{0.09}\text{Mn}_2\text{O}_{7-\delta}$ showed the maximum figure of merit of $0.07 \times 10^{-3} \text{ K}^{-1}$ at 873 K among the $\text{Ca}_{2.73-m}\text{Ln}_m\text{Mn}_2\text{O}_{7-\delta}$ systems.

ACKNOWLEDGMENT

This study was supported by Scientific Frontier Research Project of the Ministry of Education, Sports, Science, and Technology, Japan.

REFERENCES

1)M. Ohtaki, T. Tokunaga, K. Eguchi, H. Arai, 16th

Inter. Confe. Thermo., 224 (1997)

2)R. D. Shannon: Acta Cryst., A32, 751 (1976)

(Received December 9, 2007 ; Accepted September 1, 2008)