Thermoelectric properties of perovskite-type oxide system having A-site vacancy, $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$

Hiroshi Kawakami, Mayuka Anzai, Mina Sugimoto, Toshio Takayama
and Hiroshi Yamamura,

Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University
3-37-1 Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686, Japan
Fax: 81-045-413-9770, e-mail: hiroshikawakami627@yahoo.co.jp

The orthorhombic perovskite-type oxides having A-site vacancy, $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$, were synthesized by a standard ceramic technique. The thermoelectric properties such as Seebeck coefficient (S), thermal conductivity (κ) and electrical conductivity (σ) were investigated as functions of temperature and composition. The effects of insertion of A-site vacancy to the perovskite-type structure on the thermoelectric properties were investigated.

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

1. 1. INTRODUCTION

In the recent energy supply systems, thermal power generation and nuclear power generation are typical power generation systems that harness thermal energy. These power generation systems convert the thermal energy into kinetic energy, and then convert into electric energy. In this process, most thermal energies are abandoned as waste heat. On the other hand, as thermoelectric power generation systems which occur by the difference in temperatures can convert directly thermal energy into electric energy, the use of the exhaust heat could be available. High-temperature thermoelectric materials need high thermal and chemical stability for long time use at high temperatures in various atmospheres. Therefore, the metal oxides which have both high thermal and chemical stability are one of suitable candidate for the thermoelectric materials at high temperatures.

The performance of thermoelectric materials is given by the figure of merit Z as follows,

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

where S , σ and κ is the Seebeck coefficient, the electrical conductivity and the thermal conductivity, respectively. Otaki et al.¹⁾²⁾ reported $Z = 0.14 \times 10^{-3} \text{ K}^{-1}$ ($ZT = 0.16$ at $T = 1173 \text{ K}$) for the polycrystalline CaMnO_3 based material having a perovskite-type structure. Further decrease in the thermal conductivity is necessary for the enhancement of the figure of merit³⁾. In the previous study⁴⁾⁵⁾, we paid attention to perovskite-type compounds which have Ruddlesden-popper structure⁶⁾ with a general formula of $\text{AO} \cdot n(\text{ABO})_3$, or which have the A-site vacancy in perovskite structure with a general formula of $\text{A}_{1-x}\text{BO}_{3-x}$. Ruddlesden-popper structure includes lock salt layers (We called it heat resistance layers (HRL)) which could decrease the thermal conductivity, but they also decreased the electrical conductivity. On the other hand, the insertion of A-site vacancy into

$\text{Ca}_{1-m}\text{Nd}_m\text{MnO}_3$ could improve the figure of merit due to both the decrease in thermal conductivity and the increase in electrical conductivity. In the present study, the thermoelectric properties of the systems, $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ (Fig.1(a)) and $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ having A- site vacancy for electroneutrality (Fig.1(b)), were investigated.

2. EXPERIMENTAL

All of the present samples were prepared by a solid state reaction. CaCO_3 (99.99%, Kojundo chemical), La_2O_3 (99.99%, Kojundo chemical) and MnO_2 (99.99%, Kojundo chemical) were used as starting materials. Weighed powders were mixed for 24 h using ball mill. After sieving to under $53 \mu\text{m}$, the mixed powders were pressed into a rectangular shape under the pressure of 50 kgf cm^{-2} and then subjected to rubber pressing under 2000 kgf cm^{-2} . These samples were sintered at 1573 K for 10 h or 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 $\text{Cu K}\alpha$ radiation at room temperature.

The electrical conductivity of sintered specimen was measured by the DC four-probe method at various constant temperatures in the temperature range from 873 to 1273 K . The thermal conductivity of sintered sample was measured by the comparison method at 873 K , and the Seebeck coefficient was also measured at the same temperature.

Fig.1 Schematic representation of crystal structures of perovskite-type compounds; perovskite-type structure of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ (a), and perovskite-type structure having A site vacancies of $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ (b), where $\square$ shows lattice vacancies.

Fig.2 XRD patterns of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ (a) and $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ (b).

3. RESULTS AND DISCUSSION

The powder XRD patterns of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ ($0 \leq x \leq 0.2$) and $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ ($0 \leq x \leq 0.2$) were completely indexed according to the orthorhombic CaMnO_3 -type structure (Fig. 2). The thermoelectric properties were investigated as functions of temperature and composition. Figure 3 shows the electrical conductivity of both $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ and $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ systems as a function of temperature. The electrical conductivities of the $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ systems increased with increasing x . Moreover, the temperature dependences of the electrical conduction showed a metallic behavior. The increase in the electrical conductivity of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ system may originate from the increase in carrier concentration due to the occurrence of Mn^{3+} by substitution of La^{3+} into Ca^{2+} site.⁷⁾ On the other hand, though the composition of the $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ system was controlled to maintain the electroneutrality by the introduction of the A-site vacancy, the electrical conductivity was larger than that of the $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ system. Here, we speculated that the carrier generation mechanism in both $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ and $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ systems are given by the following equations, respectively.

Fig.3 Electrical conductivity of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ (a) and $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ (b).

The larger electrical conductivities of $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ system than that of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ system may originate from the increase in the carrier concentration according to Eq. (3). Furthermore, there may be the change of the conduction pass or a change of the effective electron mass or a change of the mobility due to the A-site vacancy. In both $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ and $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ systems, the increase in the electric conductivity lead to the decrease in the absolute Seebeck coefficient (S). In order to clarify this origin, the plots of the S value to $\ln \sigma$ which are called as Jonker plot are shown in Fig. 4. When the electrical conductivity of both systems show metallic behavior, the Jonker plot ought to show a linear relationship, as shown in Fig. 4. We can discuss about the relationship between electrical conductivity and Seebeck coefficient in the based on a simple theoretical model of Boltzmann statistics, that are given by the following equations⁸⁾:

$$S = p(q - \ln \sigma) \dots \dots \dots (4)$$

$$p = k / e \approx 86.14 \mu\text{V} / \text{K} \dots \dots \dots (5)$$

$$q = 5/2 + s + \ln N \mu / e$$

$$\approx s + \ln \left[T^{3/2} (m^* / m_0)^{3/2} \mu \right] - 4.66 \dots \dots \dots (6)$$

where k is the Boltzmann constant, e : the electronic charge, m^* : the effective mass, m_0 : the free electron mass and μ : the carrier mobility. p and q are fixed numbers which can be calculated from the linear relationship between S and $\ln \sigma$. The Jonker plot of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ system was represented by a single dotted line in Fig. 4, even if the composition and temperature changed at the same time, while that of the $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ system shifted to the right side from the dotted line. This result shows that the relationship between the electric conductivity and the Seebeck coefficient of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ system is independent on the composition x , but shows that the relationship in the $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ system is

Fig.4 Jonker plot of (Ca,La)-Mn-O system.

strongly dependent on the composition x . From this result, it is speculated that the quantity $T^{3/2}(m^*/m_0)^{3/2}\mu$ changes by A-site vacancy. The electrical conductivity of $\text{Ca}_{0.85}\text{La}_{0.1}\square_{0.05}\text{MnO}_3$ (193 S cm^{-1}) were larger than that of $\text{Ca}_{0.9}\text{La}_{0.1}\text{MnO}_3$ (113 S cm^{-1}), when they were compared for the sample having the same Seebeck coefficient value of $S = -80 \mu\text{V K}^{-1}$. This result shows that the parameters of p and q improved by an A site vacancy. The electrical conductivity and the Seebeck coefficient of $\text{Ca}_{0.9}\text{La}_{0.066}\square_{0.033}\text{MnO}_3$ were larger than those of $\text{Ca}_{0.9}\text{La}_{0.1}\text{MnO}_3$, when they were compared for the sample having the same Ca content. The power factor ($S^2\sigma$) estimated from the observed S and σ was shown in Fig.5. The power factor showed the maximum value at La content 0.1, and more increased by the insertion of the A-site vacancy. Figure 6 shows thermal conductivity (κ) of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ and $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ systems at 873 K. Here, the electronic thermal conductivity (κ_e) is given by the following equation:

$$\kappa_e = L\sigma T \dots \dots \dots (7)$$

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

$$\kappa_L = \kappa - \kappa_e \dots \dots \dots (8)$$

Although κ_e value increased with increasing electrical conductivity, the influence of κ_e to the total κ may be very small because of small value in comparison with κ . For all samples, the phonon contribution is more important than the electronic one. Therefore, the total κ is mainly ascribed to the lattice contribution. The thermal conductivities of the both systems decreased with the increase in the La content. Additionally, the insertion of A-site vacancy into the $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ system was further lowered the κ value.

Fig.5 Power factor ($S^2\sigma$) of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ (a) and $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ (b).

Fig.6 Thermal conductivity of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ (a) and $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ (b) at 873 K.

For example, $\text{Ca}_{0.85}\text{La}_{0.1}\square_{0.05}\text{MnO}_3$ reduced the κ value from $3.8 \text{ Wm}^{-1}\text{K}^{-1}$ to $2.5 \text{ Wm}^{-1}\text{K}^{-1}$ by the insertion of A-site vacancy into the $\text{Ca}_{0.9}\text{La}_{0.1}\text{MnO}_3$. Therefore, we can suggest that the A-site vacancy which lowered the thermal conductivity plays a role of the heat resistance points (HRP).

Figure 7 represents the figure of merit (Z) as a function of the La content (x). The Z values of $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ was larger than those of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$. This reason may originate from that the insertion of A-site vacancy can decrease the thermal conductivity and also increase the electrical conductivity of $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$. We considered that the insertion of A-site vacancy into perovskite-type structure could improve the figure of merit due to the decrease in thermal conductivity and the increase in power factor. Consequently, we obtained the maximum figure of merit Z of $0.05 \times 10^{-3} \text{ K}^{-1}$ at 873 K. Thus, the insertion of A-site vacancy into the perovskite-type structure could be the new method for the enhancement of thermoelectric performance. The decrease in the Z value after showing the maximum value may be owing to the

Fig.7 Figure of merit for (Ca, La)-Mn-O system at 873 K.

4. CONCLUSION

The orthorhombic perovskite-type oxide systems, $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ and $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$, were synthesized by a standard ceramic technique. All samples showed a n-type semiconductor from the measurement of Seebeck coefficient (S), the thermal conductivity (κ) and the electrical conductivity (σ). The insertion of A-site vacancy into the perovskite-type structure lowered the thermal conductivity. The larger electrical conductivities of $\text{Ca}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{MnO}_3$ system than that of $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ system may originate from the increase in the carrier concentration according to Eqs. (3) and (4). Furthermore, there may be the change of the conduction pass or a change of the effective electron mass or a change of the mobility by the A-site vacancy. The insertion of A-site vacancy improved the thermoelectric performance. We obtained the maximum figure of merit Z of $0.05 \times 10^{-3} \text{ K}^{-1}$ at 873 K.

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. Conf. Thermo., 224 (1997)
- 2) D. Flahaut, T. Mihara, R. Funahashi, J. APPLIED PHYSICS, 100, 084911(2006)
- 3) G. A. Slack, "CRC Handbook of Thermoelectrics" (1995) p.407.
- 4) H. Kawakami, K. Kakinuma, H. Yamamura, Trans. Mater. Res. Soc. Japan 33[4](2008)
- 5) H. Kawakami, H. Noda, M. Sugimoto, T. Takayama and H. Yamamura, Trans. Mater. Res. Soc. Japan, 34 [2](2009)
- 6) S. N. Ruddlesden, P. Popper, Acta Crystallogr. 11, 54 (1958)
- 7) B. M. Ferreira, M. E. Melojorge, M. E. Lopes, et al., Electrochimica Acta 54 (2009)
- 8) D. M. Rowe, G. Min, J. Mater. Scien. Lett. 14 (1995)

(Received January 31, 2010; Accepted May 7, 2010)