Thermoelectric properties of p-type perovskite $\text{La}_{0.95-x}\text{Sr}_x\square_{0.05}\text{CoO}_3$ systems containing the A-site vacancy

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Thermoelectric properties of Sr-doped $\text{LaCoO}_3$ system such as $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{0.95-x}\text{Sr}_x\square_{0.05}\text{CoO}_3$ ($\square$: A-site vacancy) were investigated. The effects of A-site vacancy on electrical conductivity, Seebeck coefficient, and thermal conductivity were discussed. It was found that the thermoelectric properties of $\text{La}_{0.95-x}\text{Sr}_x\square_{0.05}\text{CoO}_3$ containing the A-site vacancy showed the higher values than those of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ at 873K.

Key words: p-type perovskite, thermoelectric property, A-site vacancy, electrical conductivity, thermal conductivity

1. INTRODUCTION

Recently, thermoelectric materials have been investigated extensively because of the environment-friendly energy conversion systems. The thermoelectric performance of a material is appraised by the figure of merit, $Z=S^2\sigma/\kappa$, where $S$, $\sigma$ and $\kappa$ represent the Seebeck coefficient, the electrical conductivity and the thermal conductivity, respectively. Oxide materials are paid attention for high temperature use because of various advantages such as excellent thermal stability, oxidation resistance, low costs, and weak toxicity, compared with alloy materials, [1].

Perovskite-type oxides have been paid attention more and more due to the various interesting thermoelectric properties. For example, several perovskite-type oxides such as $\text{LaCoO}_3$ [1], $\text{SrTiO}_3$ [2, 3] and $\text{CaMnO}_3$ [4, 5] have been reported to show the high performance of thermoelectric properties. Teraoka et al. [6] reported that $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ is good electronic and ionic conductors. They can be good candidates as thermoelectric materials if the Seebeck coefficient and the thermal conductivity are favorable. Androulakis et al. [1] have also studied the low temperature thermoelectric properties of $\text{La}_{0.95}\text{Sr}_{0.05}\text{CoO}_3$ and found that the $Z$ value was $6 \times 10^{-4}$ /K at 300 K.

In the present study, we investigated the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{0.95-x}\text{Sr}_x\square_{0.05}\text{CoO}_3$ ($\square$: A-site vacancy) in order to clarify the effect of the A site vacancy in the perovskite structure on the thermoelectric properties at high temperature.

2. EXPERIMENTAL

All the samples used in the present study are prepared by conventional solid-state reaction. $\text{La}_2\text{O}_3$ (99.99%, Kojundo chemical), $\text{SrCO}_3$ (99.99%, Wako pure Chemical) and $\text{Co}_3\text{O}_4$ (99.9%, Kojundo chemical) powders were used as starting materials. These powders in the stoichiometric ratio were ball milled and then calcined at 1273 K for 10 h in air. After the calcination, the samples were pressed into a rectangular-shaped specimen, and then sintered at 1473 K for 10 h in air. Furthermore, $\text{LaCoO}_3$ and $\text{La}_{0.95-x}\square_{0.05}\text{CoO}_3$ were prepared in $\text{O}_2$ atmosphere. The samples that include 6%, 7% and 10% A-site vacancy were also prepared.

The crystal structure of the synthesized powders were determined using X-ray powder diffraction (Multiflex, Rigaku) with CuK$\alpha$ radiation at room temperature.

The electrical conductivity of the sintered specimens was measured by the DC four-probe method in the temperature range from room temperature to 1173 K in air. Relative densities of sintered samples were calculated to be 89-98%. The Seebeck coefficient was measured by the handmade apparatus at 873 K. The thermal conductivity was measured by the comparison method under the same conditions. The figure of merit $Z$ was calculated using the observed electrical conductivity, Seebeck coefficient and thermal conductivity.

3. RESULTS AND DISCUSSION

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{0.95-x}\text{Sr}_x\square_{0.05}\text{CoO}_3$ ($0 \leq x \leq 0.4$) were obtained as single phase of a rhombohedral perovskite-type structure. However, it was found that all the samples that contain 6%, 7% and 10% A-site vacancy were mixed phases which include $\text{Co}_3\text{O}_4$ as impurity. Therefore, it was found that the $\text{LaSrCoO}_3$ system can contain 5% A-site vacancy as the maximum amount.

Figure 1 shows the lattice volumes as a function of the Sr content ($x$) in the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{0.95-x}\text{Sr}_x\square_{0.05}\text{CoO}_3$ systems. The lattice volumes increased with increase in the Sr content and also increase in the A-site vacancy. The increase of the lattice volume due to the Sr content can be ascribed to the larger ionic radius of Sr than that of La. However, it is interesting that the existence of A-site vacancy also enlarges the lattice volume. The reason of lattice expansion may be ascribed to the decrease in the bond strength due to A-site vacancy.
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Figure 2 shows the Arrhenius plots of electrical conductivity of La$_{1-x}$Sr$_x$CoO$_3$ system. The electrical conductivity increased with increasing the Sr content. It can be speculated that the occurrence of hole in the La$_{1-x}$Sr$_x$CoO$_3$ system can increase the electrical conductivity, as shown by following equation.

$$\text{null} = \text{Sr}^{1+} + h^+$$ \hspace{1cm} (1)

Furthermore, the temperature dependence of the electrical conductivity showed the change to metallic behavior by doping of Sr. The compositional dependences of the electrical conductivity of La$_{1-x}$Sr$_x$CoO$_3$ and La$_{0.95-x}$Sr$_x$CoO$_3$ at 873 K are presented in Fig. 3. The electrical conductivity of La$_{0.95-x}$Sr$_x$CoO$_3$ showed the higher values than those of La$_{1-x}$Sr$_x$CoO$_3$. We can speculate that the presence of A-site vacancy can generate holes by following equation.

$$\text{null} = V_{La}^{1-} + 3h^+$$ \hspace{1cm} (2)

Figure 4 shows the Seebeck coefficient (S) at 873 K as a function of the composition in both La$_{1-x}$Sr$_x$CoO$_3$ and La$_{0.95-x}$Sr$_x$CoO$_3$ systems. The positive S value suggests that the dominant electrical carriers are holes for all the samples. The S value decreased with increase in the Sr content. It is known generally that the Seebeck coefficients are inverse proportion to carrier concentration. Therefore, the decrease in the S values can be ascribed to the increase in the charge carrier due to the increase of Co$^{4+}$ content, which can contribute to the increase in the electrical conductivity. Furthermore, as seen in Fig.4, it is clear that the S value of La$_{0.95-x}$Sr$_x$CoO$_3$ systems are higher than that of La$_{1-x}$Sr$_x$CoO$_3$ systems. This fact means that the A-site vacancy can increase the electrical conductivity without decreasing the S value.

Thermal conductivity is given by lattice thermal conductivity ($\kappa_L$) and carrier contribution ($\kappa_c$) by following equation.

$$\kappa = \kappa_L + \kappa_c$$ \hspace{1cm} (3)

On the other hand, $\kappa_c$ is related to the electrical conductivity ($\sigma$) by Wiedemann-Franz law,
\[ \kappa_e = \frac{L \sigma}{T} \quad (4) \]

where \( L \) and \( T \) represent the Lorenz number \((2.45 \times 10^{-8} \text{ V}^2 \text{ K}^{-2})\) and the absolute temperature, respectively. Usually, the \( \kappa \) value of metal oxides is determined by \( \kappa_L \). However, for the samples having the high electrical conductivity, we must consider a contribution of \( \kappa_e \).

Figure 5 shows the thermal conductivity for the La\(_{1-x}\)Sr\(_x\)CoO\(_3\) systems at 873K. The \( \kappa \) value increased with increasing the Sr content. This result suggests that the increase in \( \kappa_L \) may be due to the substitution of Sr, which is lighter than La. On the other hand, the \( \kappa_e \) value, which was estimated using Eq. (4), increased with increasing the electrical conductivity. Although the \( \kappa_e \) also increased with increase of the Sr content, the contribution to the total thermal conductivity was small.

Figure 6 shows the relationship between \( \kappa_L \) and the composition \( x \) \((0 \leq x \leq 0.3)\) of both La\(_{1-x}\)Sr\(_x\)CoO\(_3\) and La\(_{0.95-x}\)Sr\(_x\)CoO\(_3\) systems. At \( x=0 \) and 0.1, the \( \kappa_L \) value of La\(_{0.95-x}\)Sr\(_x\)CoO\(_3\) was lower than that of La\(_{1-x}\)Sr\(_x\)CoO\(_3\). This fact suggests that the introduction of A-site vacancy restrains the lattice vibration. Especially at \( x=0.1 \), \( \kappa_e \) decreased from 5.2 Wm\(^{-1}\)K\(^{-1}\) to 2.7 Wm\(^{-1}\)K\(^{-1}\) by the introduction of A site vacancy. In the composition range, \( 0.2 \leq x \leq 0.3 \), the substitution effect of Sr was superior to that of the A-site vacancy.

The figure of merit (Z) thus obtained is shown in Fig. 7. The Z values of both La\(_{1-x}\)Sr\(_x\)CoO\(_3\) and La\(_{0.95-x}\)Sr\(_x\)CoO\(_3\) showed the maximum values at \( x=0.1 \), and then decreased with increase in \( x \) because of the decrease in the Seebeck coefficient and the increase in the thermal conductivity. The maximum value of Z was \( 0.03 \times 10^{-3} \) K\(^{-1}\) for La\(_{0.85-x}\)Sr\(_{0.1}\)CoO\(_3\). The figure of merit estimated in the present study was low in comparison with reported value \([1]\) at room temperature.

4. CONCLUSIONS

The thermoelectric properties of La\(_{1-x}\)Sr\(_x\)CoO\(_3\) and La\(_{0.95-x}\)Sr\(_x\)CoO\(_3\) containing A-site vacancy at 873 K were investigated. The A-site vacancy of La\(_{0.95-x}\)Sr\(_x\)CoO\(_3\) system, in comparison with La\(_{1-x}\)Sr\(_x\)CoO\(_3\) system, showed various effects such as the increase of electrical conductivity, the increase of Seebeck coefficient and the decrease of lattice thermal conductivity. The figure of merit showed the maximum value of \( 0.03 \times 10^{-3} \) K\(^{-1}\) for La\(_{0.85-x}\)Sr\(_{0.1}\)CoO\(_3\), and thermoelectric property was improved about 300% in comparison with La\(_{1-x}\)Sr\(_x\)CoO\(_3\) system. The introduction of A-site vacancy was effective on the improvement of thermoelectric property.

ACKNOWLEDGMENT

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

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(Received December 31, 2009; Accepted May 12, 2010)