Thermoelectric Properties of (La\textsubscript{x}Ca\textsubscript{1-x})CrO\textsubscript{3}

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Abstract: The thermoelectric properties of perovskite-type La\textsubscript{1-x}Ca\textsubscript{x}CrO\textsubscript{3} were investigated. The electrical conductivity (\(\sigma\)) of La\textsubscript{1-x}Ca\textsubscript{x}CrO\textsubscript{3} exhibited semiconducting behavior, and increased with increasing Ca content. Ca-doping increased both the carrier concentration and carrier mobility. The Seebeck coefficient (S) was positive, and decreased with increasing Ca content. The doping level dependence of S was explained by the valence state of Cr ion. The thermal conductivity (\(\kappa\)) was about 2 W m\textsuperscript{-1} K\textsuperscript{-1} for 0 \(\leq x \leq 0.5\), and the temperature dependencies were slight. The figure of merit (Z) was positive, and decreased with increasing Ca content. The doping level dependence of Z was explained by the valence state of Cr ion. The thermal conductivity (\(\kappa\)) was about 2 W m\textsuperscript{-1} K\textsuperscript{-1} for 0 \(\leq x \leq 0.5\), and the temperature dependencies were slight. The figure of merit (Z = \(\sigma S^2/\kappa\)) increased with temperature, and reached 5.6\times10\textsuperscript{-5} K\textsuperscript{-1} for \(x = 0.5\) at 1100 K.

Keywords: Thermoelectric, Oxides, Perovskite

1. INTRODUCTION
Thermoelectric materials have attracted attention since they can convert waste heat into electrical energy. The energy conversion efficiency of thermoelectric materials is evaluated using the figure of merit (Z) defined as Z = \(\sigma S^2/\kappa\) (\(\sigma\) is the electrical conductivity, S is the Seebeck coefficient, and \(\kappa\) is the thermal conductivity).

In perovskite-type oxides, several 3d transition-metal oxides have been reported to show high thermoelectric performances; p-type (La\textsubscript{1-x}M\textsubscript{x})CrO\textsubscript{3} [1], n-type (Sr\textsubscript{1-x}Ca\textsubscript{x})TiO\textsubscript{3} [2] and (Ca\textsubscript{1-x}Sr\textsubscript{x})MnO\textsubscript{3} [3] (M shows metals). In (La\textsubscript{1-x}M\textsubscript{x})CrO\textsubscript{3}, having perovskite-type structure, several studies have reported that (La\textsubscript{1-x}M\textsubscript{x})CrO\textsubscript{3} exhibits a high Seebeck coefficient [4-6]. However, the thermoelectric properties have not been well investigated.

In this study, we investigated the electrical conductivity, Seebeck coefficient, and thermal conductivity of polycrystalline La\textsubscript{1-x}Ca\textsubscript{x}CrO\textsubscript{3} in the temperature range of 300 to 1100 K to estimate its potential as thermoelectric materials.

2. EXPERIMENTAL
La\textsubscript{1-x}Ca\textsubscript{x}CrO\textsubscript{3} was prepared by a conventional solid state reaction. La\textsubscript{2}O\textsubscript{3}, CaCO\textsubscript{3}, and Cr\textsubscript{2}O\textsubscript{3} powders were used as starting materials. These powders were mixed in the appropriate proportion (the molar ratios of metals were La:Ca:Cr = 1−\(x\):1) in an agate mortar with ethanol and pressed into a pellet form. The pellets were heated at 1673 K for 20 h in air. After heating, the samples were ground, re-pressed into a pellet form, and sintered at 1673 K for 20 h in air.

Powder X-ray diffraction (XRD) data was collected by a diffractometer (RIGAKU, RINT2200) using CuK\textalpha\ radiation with a pyrolytic graphite monochromator. The electrical conductivity was measured by the direct-current four-probe method in the temperature range of 300 \(\leq T \leq 1100\) K in air. The Seebeck coefficient was determined by the least squares method from a plot of thermal e.m.f. (\(\Delta\epsilon\)) vs. temperature difference (\(\Delta T\)), and the contribution of lead wires (Pt) was subtracted. The thermal conductivity was calculated from the bulk density, heat capacity, and thermal diffusivity measured by a laser flash technique (ULVAC-RIKO, TC-7000).

3. RESULTS AND DISCUSSION
A single phase of La\textsubscript{1-x}Ca\textsubscript{x}CrO\textsubscript{3} was obtained for \(x = 0, 0.1, 0.3\), and 0.5. The unit cell volume linearly decreased with increasing Ca content as shown in Fig. 1. Since ionic radii are 1.36 (La\textsuperscript{3+}), 1.34 (Ca\textsuperscript{2+}), 0.615 (Cr\textsuperscript{3+}), and 0.55 Å (Cr\textsuperscript{4+}) [7], the decrease in the cell volume results from both the substitution of Ca\textsuperscript{2+} and formation of Cr\textsuperscript{4+} by charge compensation.

Figure 2 shows the Seebeck coefficient (S) of La\textsubscript{1-x}Ca\textsubscript{x}CrO\textsubscript{3}. S of La\textsubscript{1-x}Ca\textsubscript{x}CrO\textsubscript{3} exhibited a positive value, and decreased with increasing Ca content. The temperature dependencies of Ca-doped samples were very slight, whereas S of non-doped LaCrO\textsubscript{3} decreased with increasing temperature. According to Chaikin and Beni [8], Seebeck coefficient of a system of localized carrier at high-temperature state was described as follows,

\[
S = -\frac{k_B}{e} \ln \left(\frac{x}{2-x}\right),
\]

where \(k_B\) is the Boltzmann constant and \(e\) is the elemen-

For Ca-doped samples, the experimental values agreed well with the calculated values (Table I). The carrier concentration \(n\) can be estimated using experimental value of \(S\) as follows,

\[
n = N \cdot \frac{2 \exp(-eS/k_B)}{1 + \exp(-eS/k_B)},
\]

where \(N\) is the number of available sites per unit volume. As shown in Table I, \(n\) increased with increasing Ca content. Since \(n\) were almost consistent with Ca concentration (the number of Ca atoms per unit volume) in \(\text{La}_{1-x}\text{Ca}_x\text{CrO}_3\), Ca doping seems to successfully yield conductive carrier for \(0.1 \leq x \leq 0.5\).

Figure 3 shows the electrical conductivity \(\sigma\) of \(\text{La}_{1-x}\text{Ca}_x\text{CrO}_3\). \(\sigma\) increased with increasing Ca content, and exhibited semiconducting behavior. For all samples, \(\log(\sigma T)\) were proportional to \(1/T\), indicating that hopping conduction was dominant. As shown in Table I, the carrier mobility \((\mu = \sigma e / n)\) at 1100 K increased with increasing Ca content. In hopping conduction, conductive carrier hops between Cr sites with different valence state, e.g., \(\text{Cr}^{3+}\) and \(\text{Cr}^{4+}\). Thus, the increase in \(\mu\) is attributable to the increase in conduction pass arising from the increase in \(\text{Cr}^{3+}/\text{Cr}^{4+}\) ratio. The activation energy \((E_a)\), estimated from the slope of the least-squares fitting using the equation \(1/(\sigma T) = A \exp(E_a/k_B T)\) \((A\) is a constant and \(T\) is temperature), were 0.11–0.18 eV (Table I).

The power factor \((\sigma S^2)\) of \(\text{La}_{1-x}\text{Ca}_x\text{CrO}_3\) increased with increasing temperature, and reached \(1 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}\) at 1100 K for \(x = 0.5\). Although the value was about ten times larger than that of non-doped \(\text{LaCrO}_3\), it was still low compared to a standard value of \(1 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}\) for practical materials. This is due to the low electrical conductivity that can be attributed to the small carrier mobility of \(\text{La}_{1-x}\text{Ca}_x\text{CrO}_3\).

Figure 4 shows the thermal conductivity \((\kappa)\) of \(\text{La}_{1-x}\text{Ca}_x\text{CrO}_3\). The temperature dependencies of Ca-doped samples were relatively slight, whereas \(\kappa\) of \(\text{LaCrO}_3\) decreased with temperature. For Ca-doped samples, \(\kappa\) increased with increasing Ca content. In many cases, thermal conductivity is sum of \(\kappa_l\) and \(\kappa_c\) \((\kappa = \kappa_l + \kappa_c)\), where \(\kappa_l\) and \(\kappa_c\) are the thermal conductivities by phonon and conductive carrier, respectively. \(\kappa_c\) can be

Table I Calculated Seebeck coefficient, carrier concentration \((n)\), carrier mobility \((\mu)\), and activation energy \((E_a)\) for \(\text{La}_{1-x}\text{Ca}_x\text{CrO}_3\).

<table>
<thead>
<tr>
<th>Ca content, (x)</th>
<th>(- (k_B/e) \ln \left[ x/(2-x) \right] / \mu \text{V K}^{-1})</th>
<th>(n / 10^{21} \text{ cm}^{-3})</th>
<th>(\mu / \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1})</th>
<th>(E_a / \text{ eV})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>(0.11)</td>
<td>(0.022)</td>
<td>0.18</td>
</tr>
<tr>
<td>0.10</td>
<td>254</td>
<td>2.2</td>
<td>0.031</td>
<td>0.12</td>
</tr>
<tr>
<td>0.30</td>
<td>150</td>
<td>6.2</td>
<td>0.058</td>
<td>0.17</td>
</tr>
<tr>
<td>0.50</td>
<td>95</td>
<td>9.3</td>
<td>0.081</td>
<td>0.11</td>
</tr>
</tbody>
</table>
evaluated from the Wiedemann-Franz law ($\kappa_c = \sigma L T$; $L$ is the Lorenz number (2.45×10^{-8} V^2 K^{-2})). $\kappa_l$ is generally reduced by substitutions of other elements due to the enhancement of phonon-point defect scattering. However, such a reduction of $\kappa_l$ was not observed in Ca-doped La-CrO$_3$. The differences in $\kappa_l$ among the samples were slight after density correction.

Figure 5 shows the figure of merit ($Z$) of La$_{1-x}$Ca$_x$CrO$_3$. For all samples, $Z$ increased with increasing temperature. This mainly arises from $\sigma$ that increased with temperature as shown in Fig. 3, since the temperature dependencies of $S$ and $\kappa$ were not significant compared to that of $\sigma$. As shown in Fig. 5, $Z$ was improved by Ca-doping, and reached 5.6×10^{-5} K^{-1} (ZT = 0.062) for $x = 0.5$ at 1100 K.

4. CONCLUSIONS

The thermoelectric properties of perovskite-type La$_{1-x}$Ca$_x$CrO$_3$ were investigated. The carrier concentration and carrier mobility increased by Ca-doping, resulting in an increase in the electrical conductivity. It was found that Ca-doping was efficient in improving the thermoelectric properties of LaCrO$_3$. However, its performance was still low compared to those of practical materials. This is mainly attributed to the lower electrical conductivity caused by its small carrier mobility.

REFERENCES