1. Introduction
Perovskite-type oxides, \((\text{ABO}_3)\) comprise with various compounds and have various applications. B-site ion is strongly bonded with oxygen ion as \(\text{BO}_6\) octahedron. It means that B-site metal ion mainly determines the character of the perovskite-type oxide.

In this study, we focused the effect of B-site doping on the defect structure and electrical conductivity of \(\text{La}_{0.6}\text{Ca}_{0.4}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3.9}\) changing the dopant content from 0 to 0.9.

2. Experimental
\(\text{La}_{0.6}\text{Ca}_{0.4}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3.9}\) powder was provided by Central Research of Electric Power Industry. \(\text{La}_{0.6}\text{Ca}_{0.4}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3.9}\) \((y = 0.2, 0.4, 0.6, 0.8, 0.9)\) powders were synthesized via combustion of the mixtures of nitrate solution and citric acid.

Oxygen nonstoichiometry of the specimens were measured as a function of oxygen partial pressure, \(P_{O_2}\), by thermogravimetry using a microbalance (Cahn D200). Electrical conductivity of the specimens were measured as a function of \(P_{O_2}\) by using an a.c. four-probe method.

3. Result
Figure 1 shows the oxygen nonstoichiometry, \(\delta\), of \(\text{La}_{0.6}\text{Ca}_{0.4}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3.9}\) (LCCA) \((y = 0 \cdot 0.9)\) at 1273K. With increase in Al content, the deviation from stoichiometry becomes obvious at higher \(P_{O_2}\).

\[
\delta \approx \left( \frac{3 - \delta}{x - 2\delta} \right)^{3/2} \left( 1 - \frac{x}{1 + 2\delta} \right)^{1/2} \exp \left( \frac{h\delta}{RT} \right)
\]

Using this equation, thermodynamic parameters, \(K\) and \(h\), for LCCA \((y = 0 \cdot 0.9)\), were determined as Table 1. The fitting results were shown as the solid lines in Fig. 1.

![Fig. 1 Oxygen nonstoichiometry of \(\text{La}_{0.6}\text{Ca}_{0.4}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3.9}\) (LCCA) \((y = 0 \cdot 0.9)\) at 1273K](image)

### Table 1 Thermodynamic parameters

<table>
<thead>
<tr>
<th>(y)</th>
<th>(K) (kJ mol(^{-1}))</th>
<th>(h) (kJ mol(^{-1}) bar(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>750 ± 3.8 ((10^2))</td>
<td>382 ± 31</td>
</tr>
<tr>
<td>0.1</td>
<td>93 ± 13 ((10^2))</td>
<td>27 ± 53</td>
</tr>
<tr>
<td>0.2</td>
<td>27 ± 3.7 ((10^2))</td>
<td>11 ± 9</td>
</tr>
<tr>
<td>0.4</td>
<td>5.6 ± 2.8 ((10^2))</td>
<td>50 ± 16</td>
</tr>
<tr>
<td>0.6</td>
<td>1.3 ± 3.9 ((10^2))</td>
<td>227 ± 78</td>
</tr>
<tr>
<td>0.8</td>
<td>0.14 ± 0.054 ((10^2))</td>
<td>593 ± 133</td>
</tr>
<tr>
<td>0.9</td>
<td>0.064 ± 0.019 ((10^2))</td>
<td>661 ± 861</td>
</tr>
</tbody>
</table>

Fig. 2 shows the electrical conductivity, \(\sigma\), of LCCA \((y = 0.9)\) at 1173K. The conductivity is \(P_{O_2}\) independent in low \(P_{O_2}\) region and increases with increasing \(P_{O_2}\) in high \(P_{O_2}\) region.

![Fig. 2 Electrical conductivity of \(\text{La}_{0.6}\text{Ca}_{0.4}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3.9}\) (LCCA) \((y = 0.9)\) at 1173K](image)

The solid line in Fig. 2 is \(\sigma\) which was calculated by the following equation

\[
\sigma = \frac{\epsilon \mu \nu}{V_A^2} \left| V_A \right| + 2\epsilon \mu \nu \frac{|V_{M-}|}{V_A} \quad (4)
\]

where, \(\epsilon\), \(\mu\), \(\nu\), \(V_A\), \(V_M\) are elementary charge, mobility of carrier i, Avogadro’s number, and molar volume of LCCA, respectively.

4. Conclusion
Thermogravimetry measurement revealed that Al doping affected redox behavior of LCCA, i.e. the higher Al content is, the easier LCCA is reduced.

From the result of electrical conductivity, it was shown that the valence variation of Cr ions controlled the behavior of electrical conductivity, even in the composition in which Al ions occupied as high as 90% of B-site.

Acknowledgement
The authors express thanks to Dr. Mori of Central Research of Electric Power Industry for providing sample powders.

6. References