

Defect structure and electrical conductivity of

$\text{La}_{0.9}\text{Ca}_{0.1}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3-\delta}$  ( $y = 0 - 0.9$ )

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## 1. Introduction

Perovskite-type oxides, ( $\text{ABO}_3$ ) comprise with various compounds and have various applications. B-site ion is strongly bounded 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  $\text{La}_{0.9}\text{Ca}_{0.1}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3-\delta}$ , changing the dopant content from 0 to 0.9.

## 2. Experimental

$\text{La}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Al}_{0.1}\text{O}_{3-\delta}$  powder was provided by Central Research of Electric Power Industry.  $\text{La}_{0.9}\text{Ca}_{0.1}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3-\delta}$  ( $y = 0.2, 0.4, 0.6, 0.8, 0.9$ ) 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,  $P_{\text{O}_2}$ , by thermogravimetry using a microbalance (Cahn D200). Electrical conductivity of the specimens were measured as a function of  $P_{\text{O}_2}$  by using an a.c. four-probe method.

## 3. Result

Figure 1 shows the oxygen nonstoichiometry,  $\delta$ , of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3-\delta}$  (LCCA) ( $y = 0 - 0.9$ ) at 1273K. With increase in Al content, The deviation from stoichiometry becomes obvious at higher  $P_{\text{O}_2}$ .

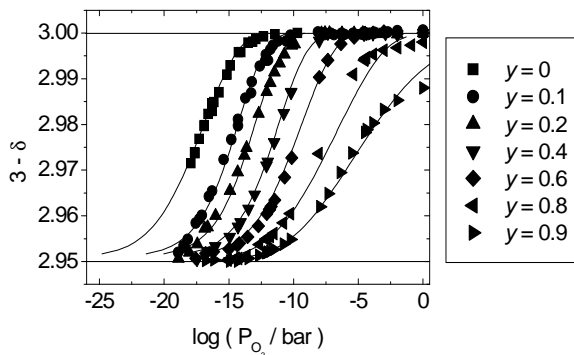
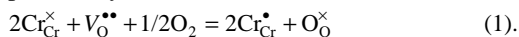


Fig. 1 Oxygen nonstoichiometry of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3-\delta}$  ( $y = 0 - 0.9$ ) at 1273K

The same model applied to lanthanum chromites [1] was used for defect chemical analysis of LCCA.

Using the Kröger-Vink notation, the oxygen formation can be expressed by



Considering the conditions of charge neutrality, and the site balance, the equilibrium constant,  $K$ , for this reaction can be written as

$$K = \frac{(x-2\delta)^2(3-\delta)}{(1-x-y+2\delta)^2 \cdot \delta} \cdot \frac{\gamma_3^2 \gamma_4}{\gamma_1^2 \gamma_2} \cdot P_{\text{O}_2}^{-1/2} \quad (2)$$

where  $\gamma$  is activity coefficient of each defect species. Here, applying the regular solution model, excess free energy can be assumed as a linear function,  $b\delta$ , and we obtain

$$P_{\text{O}_2} = (1/K)^2 \left( \frac{3-\delta}{\delta} \right)^2 \left( \frac{x-2\delta}{1-x-y+2\delta} \right)^4 \left( \exp\left(\frac{b\delta}{RT}\right) \right)^{-2} \quad (3)$$

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

Table 1 Thermodynamic parameters

	$K$	$b / \text{kJ mol}^{-2}$
$y = 0$	$750 \pm 3.8 (\times 10^5)$	$382 \pm 31$
$y = 0.1$	$93 \pm 13 (\times 10^5)$	$27 \pm 53$
$y = 0.2$	$27 \pm 7.7 (\times 10^5)$	$11 \pm 91$
$y = 0.4$	$5.6 \pm 2.8 (\times 10^5)$	$59 \pm 16$
$y = 0.6$	$1.3 \pm 3.9 (\times 10^5)$	$227 \pm 78$
$y = 0.8$	$0.14 \pm 0.054 (\times 10^5)$	$593 \pm 136$
$y = 0.9$	$0.064 \pm 0.019 (\times 10^5)$	$661 \pm 86$

Fig. 2 shows the electrical conductivity,  $\sigma$ , of LCCA ( $y = 0.9$ ) at 1173K. The conductivity is  $P_{\text{O}_2}$  independent in low  $P_{\text{O}_2}$  region and increases with increasing  $P_{\text{O}_2}$  in high  $P_{\text{O}_2}$  region.

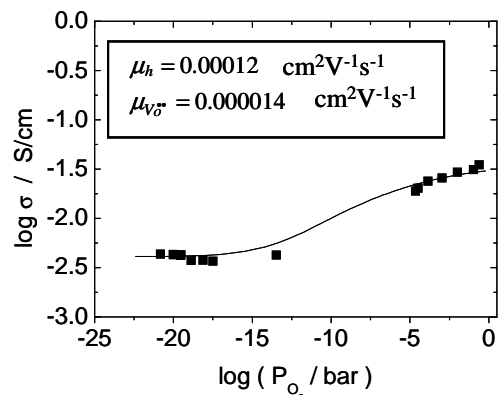


Fig. 2 Electrical conductivity of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{Cr}_{1-y}\text{Al}_y\text{O}_{3-\delta}$  ( $y = 0.9$ ) at 1173K

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

$$\sigma = e\mu_h N_A [h^{\bullet}] / V_M + 2e\mu_{\text{V}_{\text{O}}^{\bullet\bullet}} N_A [\text{V}_{\text{O}}^{\bullet\bullet}] / V_M \quad (4)$$

where,  $e$ ,  $\mu_i$ ,  $N_A$ ,  $V_M$  are elementary charge, mobility of carrier  $i$ , Avogadro's number, and molar volume of LCCA, respectively. The concentrations of hole and oxygen vacancy were estimated from TG data.

## 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

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## 6. References

[1] J. Mizusaki et al., *Solid State Ionics* **12**, 119-124 (1984)