

Formation and sinterability of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ powder by a complex polymerization method

Ho-Sik Shin^{a,*}, Masato Uehara^b, Naoya Enomoto^b and Junichi Hojo^b

^aDepartment of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University

^bDepartment of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812-8581, Japan

Calcium-doped lanthanum chromite powders were prepared by a complex polymerization method and their sintering behavior was investigated. The mixture solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, citric acid and ethylene glycol was heated at 200°C to form a polymerized gel. When the precursor was heat-treated at 300°C, a lanthanum chromite phase was detected by XRD. The XRD peak of lanthanum chromite became sharp by heat treatment at 800°C. $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powder exhibited the single phase of lanthanum chromite. However, CaCrO_4 was detected besides lanthanum chromite in $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$ powder. When carbon black powder was used as inert filler, the fine powder of submicrometre size was obtained. The fine powder of calcium-doped lanthanum chromite had a high sinterability. The relative density of a $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ sintered body was $\geq 96\%$ at 1700°C in an Ar atmosphere.

Key words: lanthanum chromite, complex polymerization method, fine powder, sinterability.

Introduction

Lanthanum chromite has been used as heating elements in electric furnaces because of its high electrical conductivity, high melting point ($>2400^\circ\text{C}$) and stability in air and reducing atmospheres. Now, its application has been developed as an interconnector for solid oxide fuel cells (SOFCs) [1]. The electrical conductivity of lanthanum chromite can be increased by doping with alkaline earth ions (Ca^{2+}) [2]. The addition of calcium ions to lanthanum chromite enhances the p-type semi-conductivity [3]. One of the important factors is the homogeneous distribution of the dopant. Another is the improvement of sinterability because lanthanum chromite has a poor sinterability under ambient atmosphere due to the high vapor pressure of chromium oxide [4]. Sammes *et al.* prepared calcium-doped lanthanum chromite powder by a solid state reaction and a complex polymerization method, but required the milling of powders and a long sintering time to achieve a high sintered density [5].

In the present work, we tried to synthesize submicrometre powder of calcium-doped lanthanum chromite by a complex polymerization method and investigated its sinterability.

Experimental

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

*Corresponding author:

Tel : +81-92-642-3543

Fax: +81-92-642-3547

E-mail: jhojotcf@mbox.nc.kyushu-u.ac.jp

were used as material sources. The nitrates were dissolved in an ethylene glycol solution including citric acid at 80°C stirring in air. The molar ratio of total metal ions to citric acid was 1:5. In some experiments, carbon black powder was added to the reaction system as an inert filler. The solution mixture was heated at about 200°C to form a gel of a polymerized complex compound. The gel was crushed and pyrolyzed at 300°C for 2h. The powder was calcined at 800°C for 2h in air. The calcined powders of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ ($x=0.2, 0.3$) were uniaxially pressed into pellets at 50 MPa and then isostatically cold-pressed at 350 MPa. The green body was sintered using a lanthanum chromite powder bed for 3h at 1500°C-1700°C in Ar and air atmospheres.

The thermogravimetry (TG) of the synthesized powders was performed in air at a heating rate of $10 \text{ K} \cdot \text{minute}^{-1}$. The composition of metallic elements was measured by energy dispersive X-Ray spectrometry (EDX). The crystalline phases in the powder and the sintered body were identified by X-ray diffraction (XRD). The particle morphology and the fracture surface of the sintered body were observed by scanning electron microscopy (SEM). The sintered densities were determined by Archimedes method.

Results and Discussion

Formation of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ powder

Figure 1 shows a TG curve of the synthesized powder after pyrolysis at 300°C. The powder was heated up to 1200°C. The TG curve exhibited a small weight loss up to 300°C. The initial weight loss may be assigned to evaporation of adsorbed water. After then, the weight

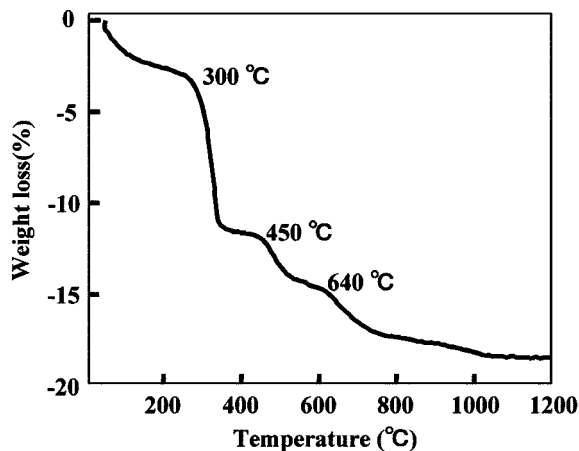


Fig. 1. TG curve of synthesized powder after pyrolysis at 300°C.

decreased stepwise at the temperatures above 300°C, 450°C and 640°C. These weight losses may be ascribed to oxidation and the decomposition of organic species remaining in the powder.

XRD patterns of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ powders are shown in Fig. 2. The XRD peaks were indexed to the orthorhombic perovskite. The powder of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ was calcined in air at different temperatures for 2h (Fig. 2a). After heat treatment at 300°C, the $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ phase was detected by XRD. The peak height increased with elevating temperature, showing the formation of the $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ phase from the amorphous precursor mixture. These results indicate that the $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ phase forms at low temperatures in this complex poly-

merization method. Calcination above 800°C is enough to prepare pure $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ powder as seen in Fig. 1. The change of the XRD pattern with the content of calcium dopant is shown in Fig. 2b. Calcination was carried out at 800°C in air for 2h. When the calcium content $x \leq 0.2$, the powder produced exhibited the single phase of lanthanum chromite. When $x=0.3$ and 0.4, a second phase, CaCrO_4 , was detected besides the lanthanum chromite. This means that the higher valence chromium ions are formed in the oxidizing atmosphere. From these results, we conclude that the solid solubility limit of the calcium content in lanthanum chromite is around $x=0.2$.

Particle morphology

Figure 3a shows SEM images of the $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ powder ($x=0.2$) after calcination for 2h at 800°C in air. The calcined powders were strongly agglomerated (Fig. 3a). This is caused by sintering between the particles during calcination. Figure 3(b, c) shows SEM images of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ powders ($x=0.2, 0.3$) prepared using carbon black as an inert filler. Fine powders of sub-micrometre size were obtained by this method. The particle size was about 0.1–0.3 μm . Thus the addition of carbon black powder is effective in preventing agglomeration between the particles. The quantity of carbon black was 8–16 wt% to the $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$. The particle size of the powder produced did not change in this range of carbon black content. The carbon black filler was easily eliminated during the calcination at 800°C in air.

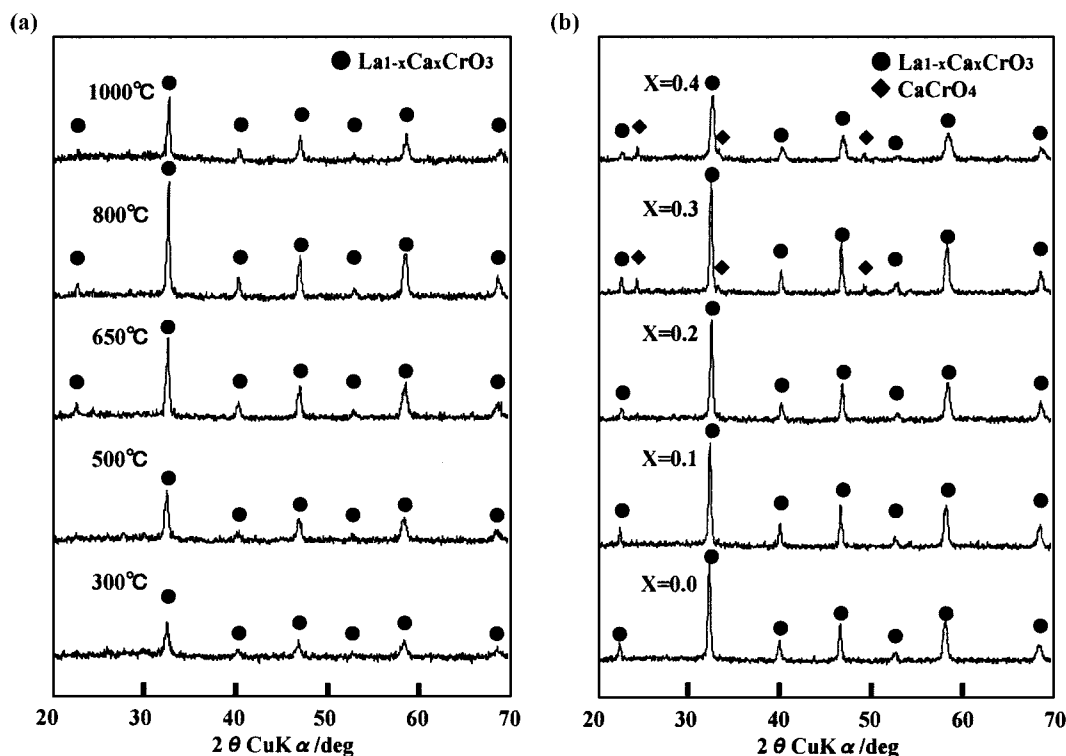
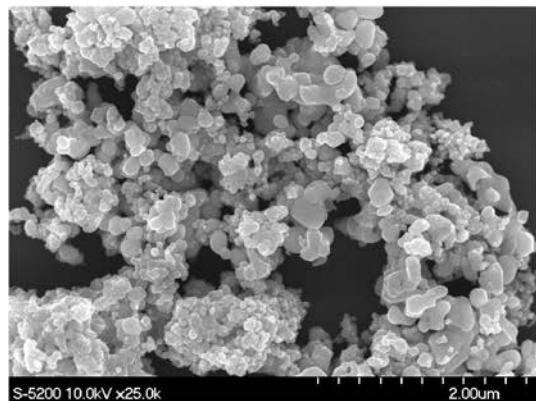


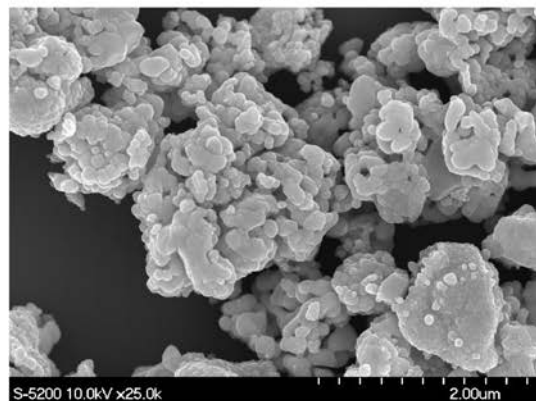
Fig. 2. XRD patterns of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ (a) $x=0.2$, calcined at different temperatures, (b) $x=0.0$ –0.4, calcined at 800°C in air.



(a)



(b)



(c)

Fig. 3. SEM images of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ powders calcined at 800°C in air. (a) $x=0.2$, carbon black 0 wt%, (b) $x=0.2$, carbon black 8 wt%, (c) $x=0.3$, carbon black 8 wt%.

Sinterability of the powders

Figure 4 shows the relative density of the sintered body as a function of sintering temperature. The sintering was conducted for 3h in Ar and air atmospheres at a range of temperature. A powder bed of commercial LaCrO_3 was used in order to prevent the evaporation of chromium oxide. Large agglomerated powder was difficult to sinter under these conditions. On the other hand, fine powders prepared using the carbon black filler had a high sinterability. The relative density of the sintered body increased with an increase in sintering

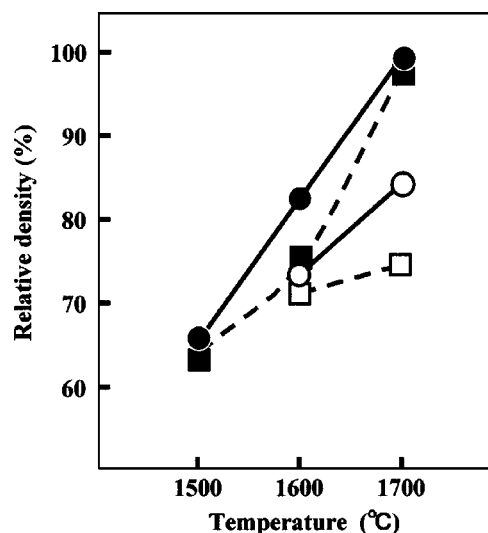
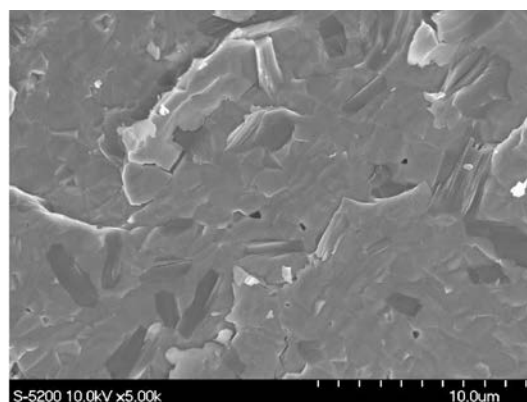
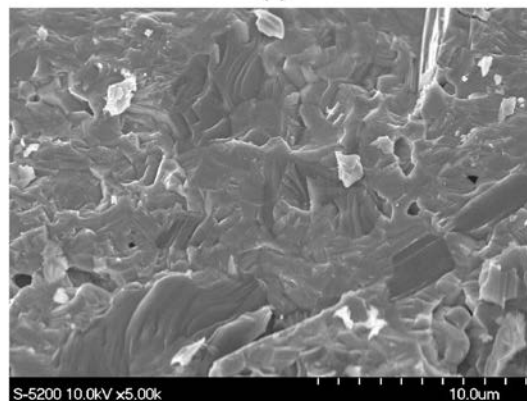


Fig. 4. Relative density of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ sintered for 3h in air and Ar atmospheres as a function of temperature. ● : $x=0.2$ in Ar, ○ : $x=0.2$ in air, ■ : $x=0.3$ in Ar, □ : $x=0.3$ in air.



(a)



(b)

Fig. 5. SEM images of fracture surfaces of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ bodies sintered at 1700°C in Ar. (a) $x=0.2$, (b) $x=0.3$.

temperature. When sintered in Ar, high densities were achieved: 99.5% of theoretical for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ and 98.2% of theoretical for $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$ at 1700°C. On the other hand, the relative densities of sintered bodies in air were low: 84.3% for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ and 74.7% for $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$ even at 1700°C. Figure 5 shows

SEM images of the fracture surfaces of bodies sintered at 1700°C in Ar. The sintered bodies were highly densified for both $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$. These results mean that fine $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ powder has a high sinterability in an inert atmosphere. The low sinterability of lanthanum chromite powder in air has been explained by the evaporation of CrO_3 in an oxidizing atmosphere [5].

Conclusions

Calcium-doped lanthanum chromite powder was prepared by a complex polymerization method. The solid solubility limit of calcium in lanthanum chromite was around $x=0.2$. When carbon black powder was used as an inert filler in the reaction system, a fine powder of

submicrometre size free from agglomeration was obtained. The relative density of sintered bodies of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$ reached above 98% at 1700°C in an Ar atmosphere. Fine $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ powder has a high sinterability in an inert atmosphere.

References

- [1] N.Q. Minh, J. Am. Ceram. Soc. 76 (1993) 563-588.
- [2] F.X. Jin, T. Endo, H. Takizawa and M. Shimada, J. Solid State Chem. 113 (1994) 138-144.
- [3] S. Kose, Kagakukogyo 12 (1974) 1384-1391.
- [4] N. Sakai, T. Kawada, H. Yokokawa, M. Dokiya and T. Iwata, J. Mater. Sci. 25 (1990) 4531-4534.
- [5] N.M. Sammes, R. Ratnaraj and M.G. Fee, J. Mater. Sci. 29 (1994) 4319-4324.