Clean Synthesis of Low-Temperature Air-Sinterable Lanthanum Calcium Chromite Powders by the Citrate Method without using Nitrates

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Sintering characteristics of low-temperature air-sinterable calcium-doped lanthanum chromites, $La_{1-x}Ca_{x+0.02}CrO_3$ (x = 0.1, 0.2, 0.3), which were synthesized by the citrate method using starting materials of La_2O_3, $CaCO_3$ and chromium carbonate or chromium hydroxide, have been studied. After calcining at 800°C for 5 h, the powders using chromium carbonate showed much higher sintering characteristics, when compared to those using chromium hydroxide. A relative density of 94% was attained after firing at 1400°C within 20 h for $La_{0.9}Ca_{0.12}CrO_3$, within 10 h for $La_{0.8}Ca_{0.22}CrO_3$ and within 5 h for $La_{0.7}Ca_{0.32}CrO_3$ in air. All the calcined powders included second phases of $CaCrO_4$ and La_2CrO_6. These second phases in the powders using chromium hydroxide disappeared at 1000°C, on the other hand, the presence of the second phases was observed in the powders using chromium carbonate even at 1200°C. High sintering characteristics of the powder using chromium carbonate should be caused by existence of $CaCrO_4$ with low-melting point during the sintering process.

Key words: Lanthanum chromite, Sinterability, Citrate method, Solid oxide fuel cell

1. INTRODUCTION

Because of high chemical stability and good electronic conductivity in both oxidizing and reducing atmospheres at an operating temperature of around 1000°C, Ca-doped lanthanum chromites are expected to be interconnect materials in high-temperature solid oxide fuel cells (SOFC) with Y_2O_3 stabilized ZrO_2 electrolyte [1,2]. For gas tightness to be assured, the ceramic interconnect materials are desired to be good sintering characteristics in air. However, lanthanum chromites with stoichiometric compositions, $La_{1-x}Ca_xCrO_3$, have poor sintering characteristics in air. Recently, Sakai et al. [3] found that a slight chromium-deficiency enhances the sintering characteristics of the lanthanum chromites with A-site excess compositions, $La_{1-x}Ca_{x+y}CrO_3$ ($0 \le x \le 0.4$, y > 0). Especially, fine $La_{0.7}Ca_{0.32}CrO_3$ powder, which was synthesized by the pseudo-coprecipitation method using the nitrates as starting materials, showed excellent air-sintering characteristics [4,5]. The temperature, where the relative density of the sample reaches above 94%, is one of the lowest values for lanthanum chromites in the previous papers [6].

For the synthesis method using the nitrates, nitrogen oxides (NO_x) occur during the powder synthesizing process. Thus, a solution of this problem has an impact on environment and material fabrication cost. Although, for a usual ceramic powder preparation, NO_x does not occur in the process, it is known that the obtained powders are coarse. The sintering characteristics of $La_{1-x}Ca_{x+y}CrO_3$ powders with A site excess composition tend to lower remarkably with increasing particle size.

Therefore it is desirable to develop a new fine powder synthesis method without using the nitrates for the lanthanum chromites. In this study, fine powders of low-temperature air-sinterable lanthanum chromites, $La_{1-x}Ca_{x+0.02}CrO_3$ (x = 0.1, 0.2, 0.3), have been synthesized by the citrate method using La_2O_3, $CaCO_3$ and chromium carbonate or hydroxide as starting materials. In addition, air-sintering characteristics of these powders have been examined and their sintering mechanisms have been discussed.

2. EXPREMENTAL PROCEDURE

Sample powders of $La_{1-x}Ca_{x+0.02}CrO_3$ (x = 0.1, 0.2, 0.3) were prepared by the citrate method. La_2O_3 (99.96%, Jiangyin Jiahua Advanced Material Resouces Co. Ltd., China), $CaCO_3$ (99.9%, Ubematerial Industries Ltd., Japan) and chromium carbonate (32.63%, Seimi Chem. Ltd., Japan) or chromium hydroxide (35.75%, Kanto Chem. Ltd., Japan) were used as starting materials. Concentration of the aqueous solutions was confirmed by chelatometric titration. These starting materials were mixed and citric acid was added to the solution in equivalent molar proportions to the amount of metal cations presents.

In order to compare with the citrate method, fine powders of $La_{1-x}Ca_{x+0.02}CrO_3$ (x = 0.1, 0.2, 0.3) were synthesized by the pseudo-coprecipitation method [5]. The metal nitrates as starting materials $La(NO_3)_3 \cdot 6H_2O$ (99.99%, Rhodia, France), $Ca(NO_3)_2$ (99%, Wako Pure Chem. Ltd.) and $Cr(NO_3)_3 \cdot 9H_2O$ (95%, Wako Pure Chem. Ltd.) were used.

All the powders were fired at 800°C for 5 h to remove

any remaining organic materials. In this paper, $La_{1-x}Ca_{x+0.02}CrO_3$ powders using the chromium hydroxide, carbonate and nitrate as starting materials represent *samples A, B* and *C*, respectively. Sample powders were analyzed by powder X-ray diffraction (XRD) technique (RINT 2100, Rigaku Co., Ltd., Japan, CuKα).

The calcined powders were milled using zirconia balls and pressed into pellets at 50 MPa by cold isostatic press. They were sintered in the temperature range from 1100 to 1400°C in the holding time range of 0 - 20 h. Theoretical density (d_0) was calculated using the experimental lattice parameters of the perovskite phases. The density of the sintered specimens (d) was determined from observed values of size and weight of the specimens. Sintering characteristics of the powders were evaluated by relative density (d/d_0) of the sintered bodies. Theoetical densities used were $6.60g/cm^3$ for $La_{0.9}Ca_{0.12}CrO_3$, $6.34g/cm^3$ for $La_{0.8}Ca_{0.22}CrO_3$, and $6.08g/cm^3$ for $La_{0.7}Ca_{0.32}CrO_3$. The microstrucutes of the samples were investigated using scanning electron microscope (SEM, S-3500H, Hitachi Co., Ltd., Japan).

3. RESULT AND DISSCUSION

For poor air-sintering characteristics of doped lanthanum chromites with stoichiometric composition, Yokokawa *et al*. [7] have indicated the reason from the thermodynamic calculation; chromium-vapor component from the $LaCrO_3$ particles starts to evaporate as gaseous CrO_3 at temperatures above 1000°C and this disturbs the densification of the particles by an evaporation process, which in turn reduces the ability of producing a dense sintered body. A-site excess composition suppresses the evaporation of gaseous CrO_3 and the densification of the $LaCrO_3$ particles is remarkably promoted. Thus, the sintering characteristics of these materials have a tendency to increase with decreasing particle size. In addition, the lanthanum chromites with A-site excess compositions, $La_{1-x}Ca_{x+y}CrO_3$, are a composite material of the perovskite and second phases. In some cases, the second phases assist the densification of the perovskite particles,
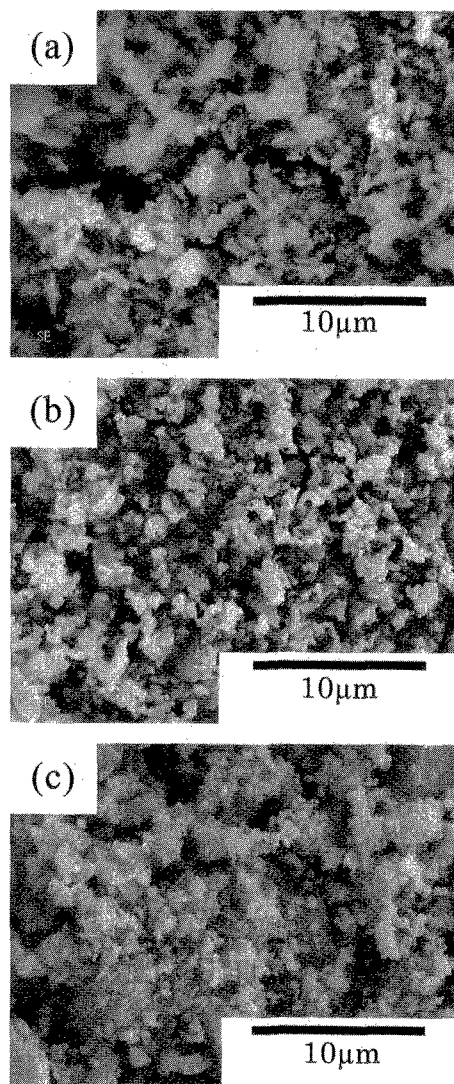

Fig.1. SEM images of $La_{0.9}Ca_{0.12}CrO_3$ powders for *samples A, B* and *C*. (a) *sample A*, (b) *sample B*, (c) *sample C*.

sample	x	D_{50} (μm)	SSA (m^3/g)	Second phases
sample A	0.1	1.2	3.6	La_2CrO_6, $La(OH)_3$, $CaCrO_4$, Cr_2O_3
	0.2	1.1	3.7	La_2CrO_6, $La(OH)_3$, $CaCrO_4$, Cr_2O_3
	0.3	0.96	3.9	La_2CrO_6, $La(OH)_3$, $CaCrO_4$, Cr_2O_3
sample B	0.1	1.0	3.4	La_2CrO_6, $CaCrO_4$
	0.2	0.97	3.4	La_2CrO_6, $CaCrO_4$
	0.3	0.87	3.2	La_2CrO_6, $La(OH)_3$, $CaCrO_4$, Cr_2O_3
sample C	0.1	2.9	3.9	La_2CrO_6, $La(OH)_3$, $CaCrO_4$
	0.2	4.8	4.2	La_2CrO_6, $La(OH)_3$, $CaCrO_4$
	0.3	2.9	4.6	La_2CrO_6, $CaCrO_4$

Table 1. Average particle size (D_{50}) and specific surface area (SSA) and second phases of *samples A, B* and *C*.

when they change into liquid phase during the sintering process [4,5]. Thus, the sintering characteristics for the lanthanum chromites with A-site excess compositions are strongly affected by the second phases. Median diameter (D_{50}) specific surface area and observed second phases of powders calcined at 800°C for 5h are summarized in Tables 1. With regard to the crystallographic properties of the perovskite phases after heating at 800°C, we observed that the GdFeO_3-type perovskite with orthorhombic symmetry (space group Pbnm). The lattice parameters obtained for $La_{0.9}Ca_{0.12}CrO_3$ (*sample A*) were a=5.478(1)Å, b=5.5134(4)Å, c=7.7576(6)Å. The lattice parameters of these calcined perovskites are independent of Ca content. This is due to same Ca substitutions in th e perovskite by the low calcination temperature of 800°C. XRD patterns of all the samples showed small amounts of La_2CrO_6, $La(OH)_3$, $CaCrO_4$ and Cr_2O_3 as second phases in the perovskite phase.

Figure 1 shows the SEM images of $La_{0.9}Ca_{0.12}CrO_3$ powders for *samples A, B* and *C*. For *samples A*, the crystallite size of the powders was about 0.1 – 0.2 μm diameter on average. It is seen that particles aggregated partly. *Samples B* showed the particle size of about 0.5 – 1.0 μm in diameter on average. These particles aggregate and form the secondary particles with the particle size of 2 – 5 μm. Although no significant change of the particle size and its distribution by Ca-doping was observed, the aggregations of the particles have a tendency to increase with increasing Ca content.
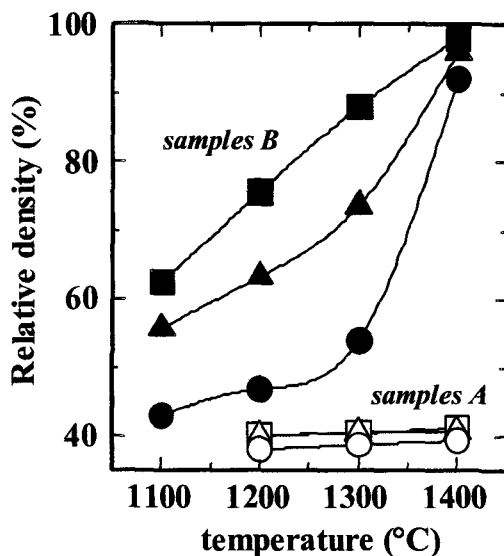

Fig.2. Relative density of sintered *samples A* and *B* as a function of sintering temperature, where the holding time at the highest temperature was 10 h.

Crystallite size and aggregation of *samples C* are almost similar to those of *samples A*.

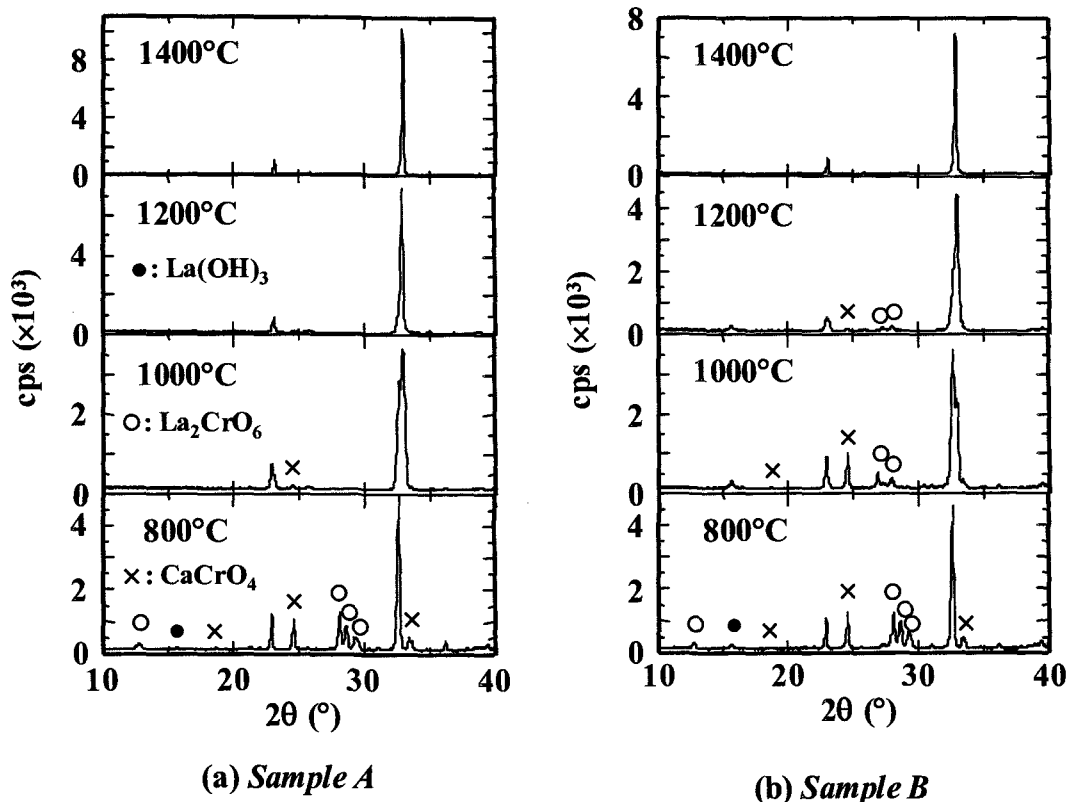Figure 2 shows the relative density of sintered *samples*

(a) *Sample A*

(b) *Sample B*

Fig.3. XRD patterns of $La_{0.7}Ca_{0.32}CrO_3$ powders for *samples A* and *B* after heating at selected temperatures for 5 h.

A and *B* as a function of sintering temperature, where the holding time at the highest temperature was 10 h. The relative densities of the perovskites are presented as the circles for the $La_{0.9}Ca_{0.12}CrO_3$, the triangles for the $La_{0.8}Ca_{0.22}CrO_3$, and the squares for the $La_{0.7}Ca_{0.32}CrO_3$ sample. The open and closed symbols represent *samples A* and *B*, respectively. The relative densities of *samples B* were much higher than those of *samples A*. Although the relative densities of *samples B* increased with increasing firing temperature, no temperature dependency of relative density was observed for *sample A*. Note that it was observed that cream color of the alumina plate, which *samples A* were placed on, turned reddish-black after sintering. This feature is usually observed when alumina plate reacts with chromium component in the lanthanum chromites. On the other hand, the sintering characteristics of *samples B* have a tendency to increase with increasing Ca content. Additionally, in the case of *sample B*, the sticking and coloring were not observed.

Figures 3(a) and (b) show the XRD patterns of $La_{0.7}Ca_{0.32}CrO_3$ powders for *sample A* and *B*. At 800°C for 5 h, both the calcined powders included second phases of $CaCrO_4$ and La_2CrO_6. These second phases in *sample A* disappeared at 1000°C, on the other hand, the presence of the second phases was observed in *sample B* even at 1200°C. $CaCrO_4$ is known to the decompose into $Ca_3Cr_2O_8$ and $CaCr_2O_4$ and then forms a liquid phase at approximately 1030°C and its related CaO rich compound, $Ca_3Cr_2O_8$, which melts incongruently around 1230 - 1330°C [8]. High sintering characteristics of *samples B* should be caused by existence of $CaCrO_4$ with low-melting point in the powders during the sintering process.
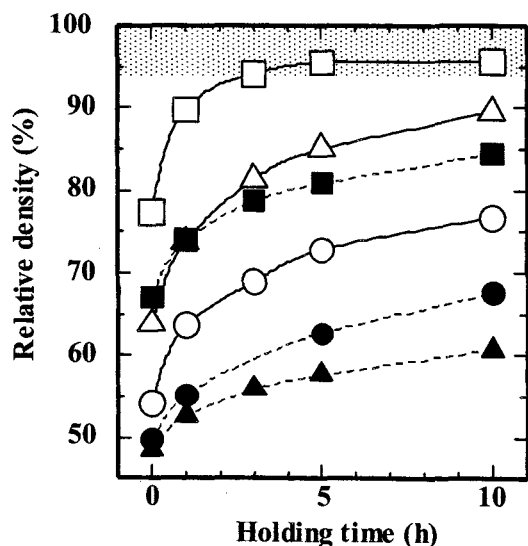

Fig. 4. Relative density of $La_{1-x}Ca_{x+0.02}CrO_3$ at 1400°C as a function of holding time.
○● : x = 0.1, △▲ : x = 0.2, □■ : x = 0.3
The open and closed symbols represent the powders of *samples B* and *C*, respectively.

Figure 4 shows the relative densities of *samples B* and *C* at 1400°C as a function of holding time. The shaded region in Fig. 4 represents relative densities of ≥ 94%; sintered ceramics in this region can provide gastightness, which required for SOFC interconnects. The relative densities of the perovskites are presented as the circles for the $La_{0.9}Ca_{0.12}CrO_3$, the triangles for $La_{0.8}Ca_{0.22}CrO_3$, and the squares for the $La_{0.7}Ca_{0.32}CrO_3$ samples. The open and closed symbols represent *samples B* and *C*, respectively. The relative densities of *samples B* were higher than those of *samples C*. A relative density of 94% was attained after firing at 1400°C within 20 h for $La_{0.9}Ca_{0.12}CrO_3$, within 10 h for $La_{0.8}Ca_{0.22}CrO_3$, and within 5 h for $La_{0.7}Ca_{0.32}CrO_3$.

4. CONCLUSION

Low-temperature air-sinterable calcium-doped lanthanum chromites with high sintering characteristics powders, $La_{1-x}Ca_{x+0.02}CrO_3$ (x = 0.1, 0.2, 0.3), have been synthesized by the citrate method using starting materials of La_2O_3, $CaCO_3$ and chromium carbonate. After calcining at 800°C for 5 h, these powders showed much higher sintering characteristics. A relative density of 94% was attained after firing at 1400°C within 20 h for $La_{0.9}Ca_{0.12}CrO_3$, within 10 h for $La_{0.8}Ca_{0.22}CrO_3$ and within 5 h for $La_{0.7}Ca_{0.32}CrO_3$ in air. The temperatures, where the relative density of sintered samples reaches above 94%, are one of the lowest values in the previous papers of lanthanum chromites. The present low-temperature sintering of the lanthanum chromites is quite useful in view of the fabrication method of interconnect materials in the SOFC, and the present citrate method is quite attractive as clean and low cost synthesis from the industrial viewpoint.

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