

Preparation of calcium doped LaCrO_3 fine powders by hydrothermal method and its sintering

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Abstract

The synthesis of fine powders of LaCrO_3 and its solid solutions doped with calcium under hydrothermal conditions and the sintering of these powders were investigated. Precursor alkaline coprecipitated lanthanum chromite gels with three different compositions: LaCrO_3 , $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$, were processed under hydrothermal conditions at low temperatures (350–425 °C), for a reaction time between 30 and 120 min. Powders of a single phase with orthorhombic structure of LaCrO_3 , $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ were obtained at a temperature as low as 350, 400 and 425 °C, respectively, for a short reaction interval of 1 h. SEM and TEM micrographs showed that particles with an irregular morphology and an average particle size of 300 nm, were mainly obtained under hydrothermal conditions. The powders were pressed by cold isostatic pressing at 200 MPa, and then sintered in air at a temperature range of 1200–1500 °C for various intervals (1 to 5 h). A maximum apparent density of 97.7% was achieved on specimens with high calcium content, $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$, at 1400 °C for 5 h. The average grain size measured on the sintered specimens was 6 μm.

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1. Introduction

Lanthanum chromite powders substituted with alkaline metals (Ca or Sr) have been widely accepted as the candidate for interconnection materials in the present generation of Solid Oxide Fuel Cells (SOFCs).¹ The interconnector in SOFCs must be stable under reducing and oxidizing atmospheres, and must possess an adequate electronic conductivity in both atmospheres, as well as, thermochemical compatibility with other cell components under operating conditions^{1,2} and have high density (typically >94% of the theoretical).³

It has been found that a partial substitution of lanthanum ions with an alkaline metal ions, such as: Ca or Sr, is likely to increase chemical stability and electric conductivity of pure lanthanum chromite.⁴ Recently, various chemical routes

have been used to process lanthanum chromite powders such as glycine nitrate process,⁵ oxalic salt method,⁶ hydrazine,⁷ coprecipitation⁸ and sol-gel.⁹ These chemical processes, however, involve a heat treatment which is normally conducted at temperatures between 700 and 800 °C, in order to obtain the crystalline phase. Furthermore, a milling stage is required in order to disperse the agglomerated particles formed during the heat treatment.

On the other hand, the sintering of LaCrO_3 powders assisted by the presence of a liquid phase has been the main focus of investigation. It was found that the incorporation of $\text{Ca}(\text{CrO}_4)$ particles allows the sintering to proceed at temperatures between 1300 and 1500 °C in air, because this compound forms a transient liquid phase at above 1076 °C.¹⁰ High dense Ca-doped lanthanum chromite specimens with a relative density of 97% of the theoretical value, were obtained by heat treatments in air at 1550 °C for 20 h. However, the sintering is also difficult due to a significant

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volatilization of chromium oxide at high temperatures in oxidizing atmosphere.¹

Hitherto, it was found that sinterability of LaCrO_3 and its solid solution doped with Ca might be achieved by several factors of the raw powder, such as: high purity, controlled particle morphology, and nanometric particle size.¹¹ Thus, among the conventional or other non-conventional chemical synthesis processes, the hydrothermal technique is considered as a single step process that allows the synthesis of a wide variety of raw oxide powders, which fit more of the particular characteristics mentioned above.¹² Indeed, the first evidence of the synthesis of the LaCrO_3 pure compound under hydrothermal conditions was reported by Yoshimura et al.¹³ They prepared LaCrO_3 powders with a grain size of 0.7 μm , at 700 °C with a confining pressure of 100 MPa, the crystallization process of the stable perovskite phase was conducted in a platinum capsule by dissolving stoichiometric amount of the compounds $\text{La}(\text{OH})_3$ and Cr_2O_3 . In contrast, pure LaCrO_3 powders were prepared by the same ordinary hydrothermal treatment at lower temperature (260 °C). The powders were synthesized from La_2O_3 powder and CrCl_3 dissolved in an alkaline solution of KOH (8.5 M).¹⁴ The particles obtained under these conditions, had a cubic morphology with an average particle size of 3 μm . Although the crystallization of the single LaCrO_3 have been widely investigated by the hydrothermal method, neither the crystallization of alkaline metal doped lanthanum chromite under hydrothermal conditions nor its sintering have been investigated as yet. Therefore, we aimed to study the synthesis of pure lanthanum chromite (LaCrO_3) and its solid solution doped with calcium ($\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$) under hydrothermal conditions by employing a coprecipitated gel containing the raw constituents (La and Cr) and the dopant element (Ca), at lower temperatures (300–425 °C). In addition, the sintering of the powders obtained during the hydrothermal treatments was studied by conventional heat treatment in air. The differences on the microstructure of the specimens sintered under these conditions are discussed on base of the size and the morphology of the hydrothermally synthesized powders. The sinterability of these powders was compared with that reported in the former literature for doped lanthanum chromite powders prepared by different chemical methods.

2. Experimental

2.1. Hydrothermal synthesis

Precursor lanthanum chromite gel was prepared by the alkaline coprecipitation method reported by Inagaki et al.,¹⁵ employing reagent grade chemicals of: $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (99.9%), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (99%) and NaOH (99.998%) (Wako Pure Chemical Industries, Ltd., Japan). Aqueous solutions with a concentration 0.05 M of LaCl_3 , $\text{Cr}(\text{NO}_3)_3$ and CaCl_2 were prepared with deionized water, and a solution of 0.5 M of NaOH was employed as coprecipitation media.

In a typical procedure, a volume of 475 ml of the precipitating solution (NaOH) was poured in a biker, and the solution of chromium (500 ml) was then mixed, which results in the formation of an opaque whitish green precipitate. The vigorous stirring of the mixed solutions leads to the dissolution of the preliminary precipitated gel of $\text{Cr}(\text{OH})_3$. Finally, the coprecipitation of the complex gel was carried out by the addition of the same volume (500 ml) of the solution containing the other elements, La or the mixture of La + Ca. The solutions were mixed in three different volumetric ratios, La:Ca:Cr, 1:0:1, 0.9:0.1:1 and 0.8:0.2:1; which matches the compositional stoichiometric of the solid solutions, LaCrO_3 , $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$. The coprecipitated gel was centrifuged and a volume of 20 ml was then poured into a hydrothermal Hastelloy C-lined microautoclave (40 ml capacity). The vessel was heated at a constant rate of 20 °C/min up at various temperatures (350–425 °C) for a reaction interval between 0.5 and 2 h. After the treatments, the precipitates were well washed with distilled water, decanted and then dried in an oven at 100 °C overnight.

2.2. Sintering

The sintering of the powders was conducted by a conventional firing in air. The powders (0.5 g) were poured into a tungsten carbide die (10 mm diameter) and pressed by hand, the formed pellets were then cold isostatic pressed at 200 MPa for 5 min. The green compacts were heated at a constant heating rate of 10 °C/min up to the desired temperature. The sintering was conducted in air at a temperature range between 1200 and 1500 °C for several reaction intervals from 1 to 5 h.

2.3. Characterization

Powder X-ray diffraction analyses were carried out to determine the crystalline phases and the lattice parameter constants of the synthesized powder. Measurements were made by an X-ray diffractometer (Rigaku Rotaflex) with graphite-monochromatized $\text{Cu K}\alpha$ radiation at 40 kV and 100 mA. Diffraction patterns were taken from 10 to 70° at a scanning speed of 4°/min. The lattice parameters were calculated by the least square method from the diffraction peaks collected in the 2θ range from 20 to 60° at a scanning speed of 0.4°/min and step sampling interval of 0.006°, using Si as an internal standard. The theoretical densities of the hydrothermally synthesized powders were calculated from the lattice parameters data. Moreover, morphological aspects of the powders were examined by scanning electron microscopy (SEM, Philips XL30 ESEM) equipped with an energy dispersive X-ray (EDX) analyzer. In addition, the particle size was measured by transmission electron microscopy (TEM, Phillips CM200).

In addition, the sintered specimens were polished to mirror like surface, followed by a thermal etching, which was conducted at 1020 to 1275 °C for 2 h in order to reveal the microstructure. The apparent density of the sintered

specimens was determined by Archimedes' principle using a helium pycnometer (Multipycnometer Quantachrome). Apparent density measurements were carried out at a constant helium pressure of 0.117 MPa.

3. Results and discussion

3.1. Hydrothermal synthesis of LaCrO_3 , $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders

Fig. 1 shows the effect of the reaction interval and temperature on the crystallization of pure LaCrO_3 and its solid solutions doped with calcium under hydrothermal conditions. X-ray diffraction pattern (Fig. 1a) showed that the formation of pure LaCrO_3 phase from coprecipitated gel occurred for an interval as short as 0.5 h. The increase in the reaction time up to 1 h resulted in the complete transformation of the gel to the perovskite structure ABO_3 type. The presence of secondary phases, such as $\text{La}(\text{OH})_3$, was only observed on the samples treated at earlier stages of the hydrothermal treatment (0.5 h).

Fig. 1b shows the typical X-ray diffraction patterns of the LaCrO_3 , $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders, prepared at the lowest temperature to obtain a single phase, 350, 400, and 425 °C, respectively. Thus, these results depict that the crystallization temperature under hydrothermal conditions, depends on the amount of Ca doping the site A of the perovskite structure. In each case, below this temperature the crystallization of the perovskite phase did not proceed. The X-ray diffraction patterns of the powders obtained by hydrothermal treatments show that LaCrO_3 and its solid solutions, $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$, belongs to the LaCrO_3 single phase with orthorhombic structure (JCPDS 33-701). In addition, the gradual shifting to high angle observed on the X-ray diffraction pattern peaks for doped calcium lanthanum chromite powders, is associated with the formation of the lanthanum chromite solid solutions, due to the incorporation of Ca ions with a small ionic radius (0.99 Å) in comparison with La (1.15 Å). Indeed, the decrease on the lattice parameters of Ca-doped powders (Table 1) from that of the pure LaCrO_3 powder crystallized under hydrothermal conditions, agrees with the inference proposed above.

SEM images of the LaCrO_3 , $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ solid solutions powders obtained after hydrothermal treatments conducted at 350, 400 and 425 °C for 1 h, respectively, are shown in Fig. 2. SEM observations revealed that clusters of particles resembling raspberry-like

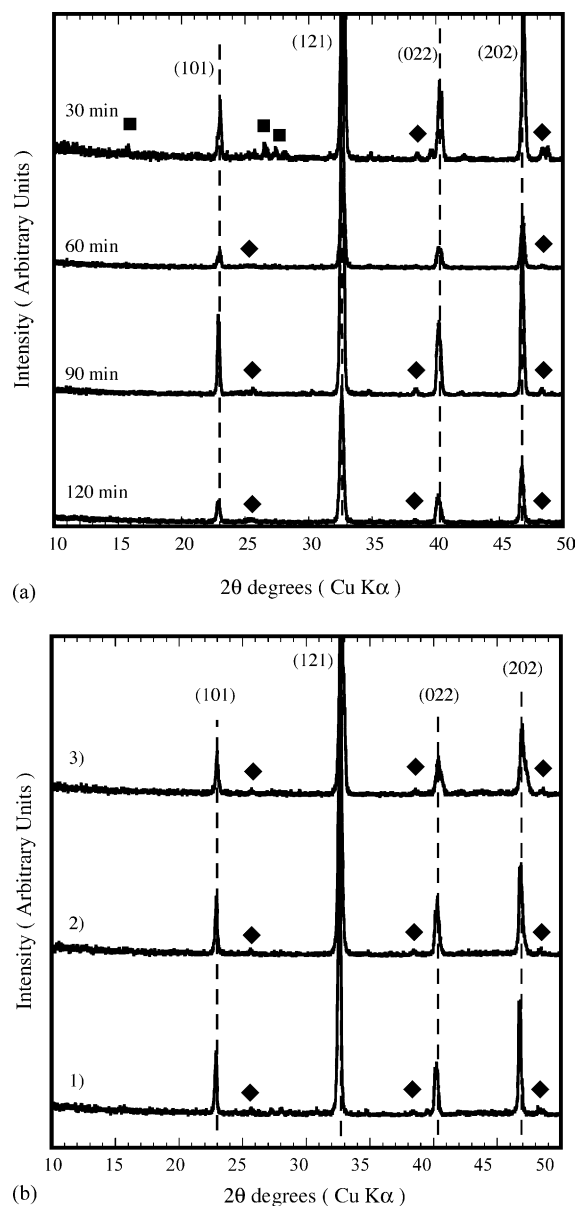


Fig. 1. (a) X-ray diffraction patterns of coprecipitated complex La-Cr gels hydrothermally treated at 400 °C for different reaction times. (b) X-ray diffraction patterns of (1) pure LaCrO_3 , (2) $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and (3) $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders obtained under hydrothermal conditions for 1 h at 350, 400 and 425 °C, respectively. Dotted line: main diffraction pattern lines and (◆) minor intensity lines of LaCrO_3 with orthorhombic structure, (■) $\text{La}(\text{OH})_3$.

Table 1

Theoretical density calculated from lattice parameters obtained by X-ray diffraction patterns

Composition	Lattice parameter (Å)			Cell volume (Å ³)	Theoretical density (g/cm ³)
	a (Å)	b (Å)	c (Å)		
LaCrO_3	5.4759 (4)	5.5113 (4)	7.7761 (4)	234.58	6.7605
$\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$	5.4615 (9)	5.4956 (9)	7.7559 (9)	232.79	6.5336
$\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$	5.4529 (3)	5.4845 (9)	7.7394 (9)	231.46	6.2875

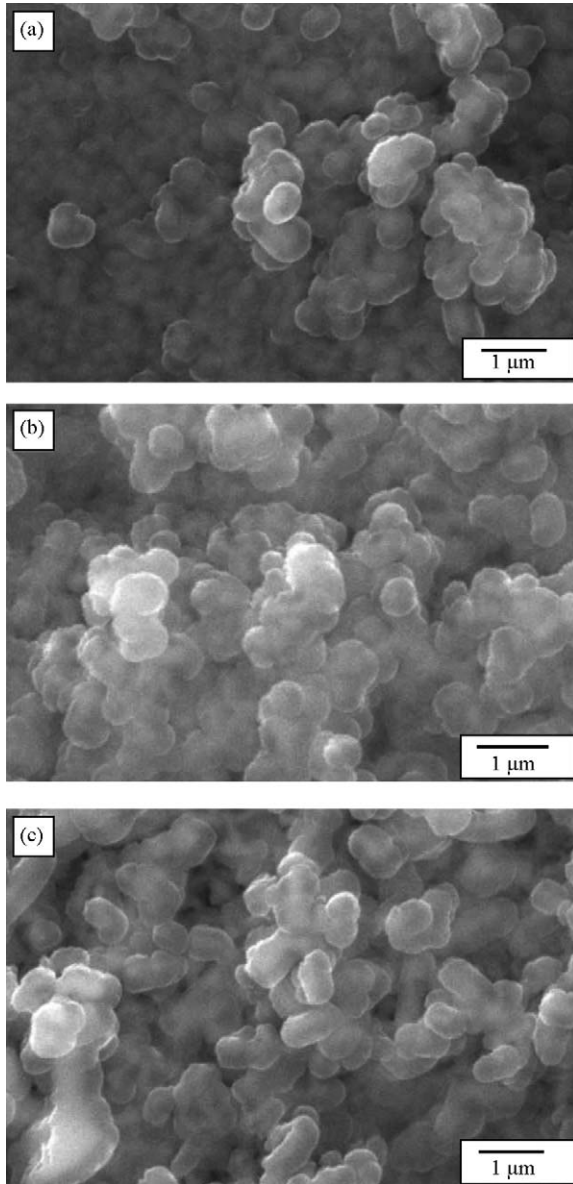


Fig. 2. SEM micrograph of Ca-doped lanthanum chromite powders obtained under hydrothermal conditions for 1 h at several temperatures. (a) LaCrO_3 at 350°C , (b) $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ at 400°C and (c) $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ at 425°C .

shapes with nanometric size were preferentially crystallized under hydrothermal conditions. It is well known that the control of particles size and morphology depends on the reaction interval, temperature, pH of the mineralizer under hydrothermal conditions. Recently, it was found that LaCrO_3 particles with controlled cubic shape (average size of $3\ \mu\text{m}$) were obtained under hydrothermal conditions at 250°C for 1 week by using high concentrated ($>8.5\ \text{M}$) alkaline solutions of KOH .¹⁴ In contrast, with the previous results, we surmise that the peculiar morphology of the particles obtained during hydrothermal treatment of the complex coprecipitated gel, depends on the crystallization mechanism. Under ordinary hydrothermal crystallization process, the stable oxide phase proceeds by a dissolution-crystallization mechanism, simi-

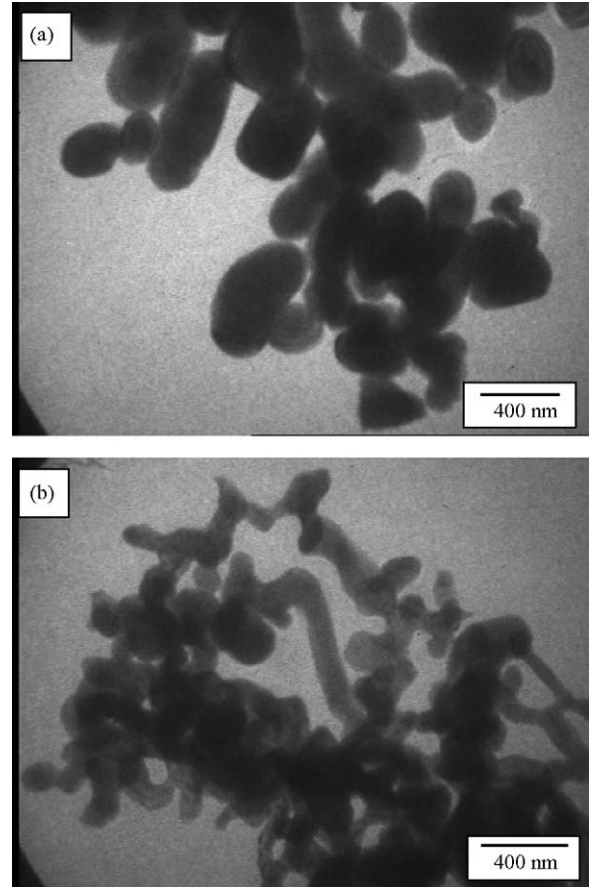


Fig. 3. TEM micrograph of lanthanum chromite powders obtained under hydrothermal conditions at 400°C for a time interval of 1 h. (a) LaCrO_3 and (b) $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$.

lar to that observed in previous studies.^{12–14,16} However, we surmise that the crystallization of the amorphous precursor gel of LaCrO_3 and its solid solutions doped with Ca, proceeds simultaneously with the gel dehydration.¹⁷ We suggest that during dehydration process, the nucleation of the oxide particles starts from the surfaces of the dehydrated gel due to a presence of high content of OH^- ions, which resulted from the hydrolysis of the in situ solvent formed during the hydrothermal treatment.¹⁸ This inference is supported by the fact that on preliminary experiments, we found that during the heating stage of the hydrothermal treatment, a great amount of the precursor gel was remained without no reaction. At present, additional experiments under different hydrothermal conditions are being conducted in order to develop more control of the particle morphology.

More aspects of the particles were revealed by TEM micrographs on LaCrO_3 and $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ particles (Fig. 3). Both powders were synthesized hydrothermally at 400°C for 1 h. It is clear that the LaCrO_3 particles exhibit a regular morphology consisting in platelets with round edges and a homogeneous size distribution, the average particle size was $\sim 300\ \text{nm}$. In contrast, the incorporation of dopant Ca (Fig. 3b) seems to produce particles with irregular shapes

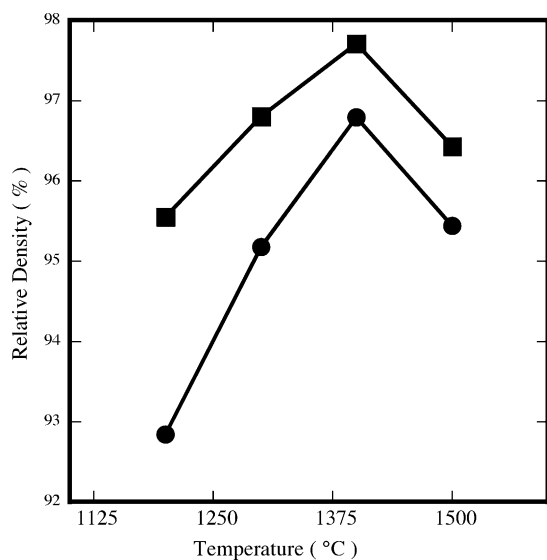


Fig. 4. Effect of the sintering temperature on the relative density of La_{0.9}Ca_{0.1}CrO₃ (●) and La_{0.8}Ca_{0.2}CrO₃ (■) pellets sintered for 5 h in oxidizing atmosphere, respectively.

connected each other; and the average particle size is less than that measured in the undoped LaCrO₃ powders. The bonding of some particles might be due to a partial dissolution-precipitation mechanism of the particles during crystallization by gel dehydration.¹⁹ Furthermore; the particles of LaCrO₃ and La_{0.9}Ca_{0.1}CrO₃ prepared under hydrothermal conditions were irregular on morphology and have an average grain size of 300 nm. The results above mentioned show clear evidences that under hydrothermal conditions pure and Ca-doped lanthanum chromite fine powders could be prepared at lower temperatures (375–425 °C) in a single processing stage, thus, no calcination and milling stages are required as in the case of other chemical processing routes. In addition, we also expect that these fine powders should might a better sinterability even in oxidizing atmospheres.

3.2. Sintering of LaCrO₃, La_{0.9}Ca_{0.1}CrO₃ and La_{0.8}Ca_{0.2}CrO₃ powders

Fig. 4 shows the variation of relative density for samples of La_{0.9}Ca_{0.1}CrO₃ and La_{0.8}Ca_{0.2}CrO₃ powders sintered in air at various temperatures for 5 h. These results were determined from the apparent density values measured by helium pycnometry and the theoretical density determined from the lattice parameter of the pure LaCrO₃ phase and its solid solutions. In general, the relative density of the La_{0.9}Ca_{0.1}CrO₃ and La_{0.8}Ca_{0.2}CrO₃ samples increase gradually with increasing the sintering temperature up to 1400 °C. However, beyond this temperature, a marked decrease on the relative density occurred on the pellets of La_{0.9}Ca_{0.1}CrO₃ and La_{0.8}Ca_{0.2}CrO₃. This phenomenon might be associated with the loss of chromium during the sintering stage. In fact, this is supported by the microstructural variations observed on the sintered pellets of La_{0.8}Ca_{0.2}CrO₃ at 1400 °C (Fig. 5c) and

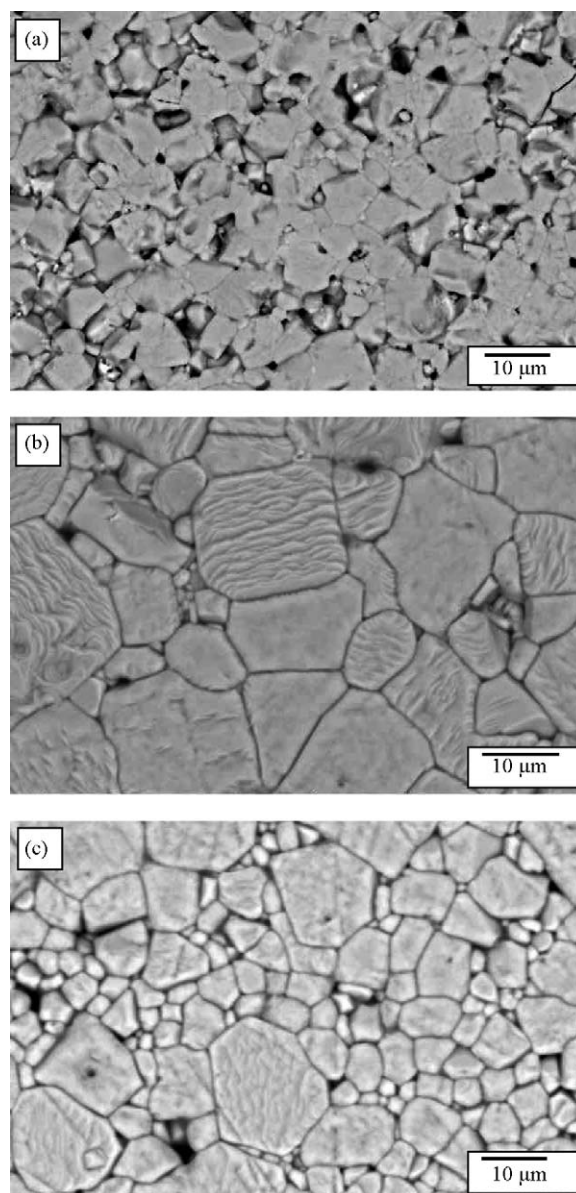


Fig. 5. SEM micrograph of samples (a) LaCrO₃, (b) La_{0.9}Ca_{0.1}CrO₃ and (c) La_{0.8}Ca_{0.2}CrO₃ sintered at 1400 °C for 5 h in air.

1500 °C (Fig. 6d), where a large amount of pores remaining on the pellet sintered at 1500 °C, was observed. The maximum density obtained on La_{0.9}Ca_{0.1}CrO₃ pellet was 96.8%, and the maximum densification value of 97.7% was obtained on the pellet of the solid solution doped with 20 mol% of Ca. Hence, the above mentioned results depict that the hydrothermally prepared calcium doped lanthanum chromite powders exhibit good sinterability in comparison with the pure LaCrO₃ powders which were densified to a relative density of 85%.

The sinterability of calcium-doped lanthanum chromite powders has been found to vary significantly with the material stoichiometry and the processing route, although, much work has been aimed to sinter Ca substituted LaCrO₃ powders prepared by several chemical routes. Fine powders obtained for

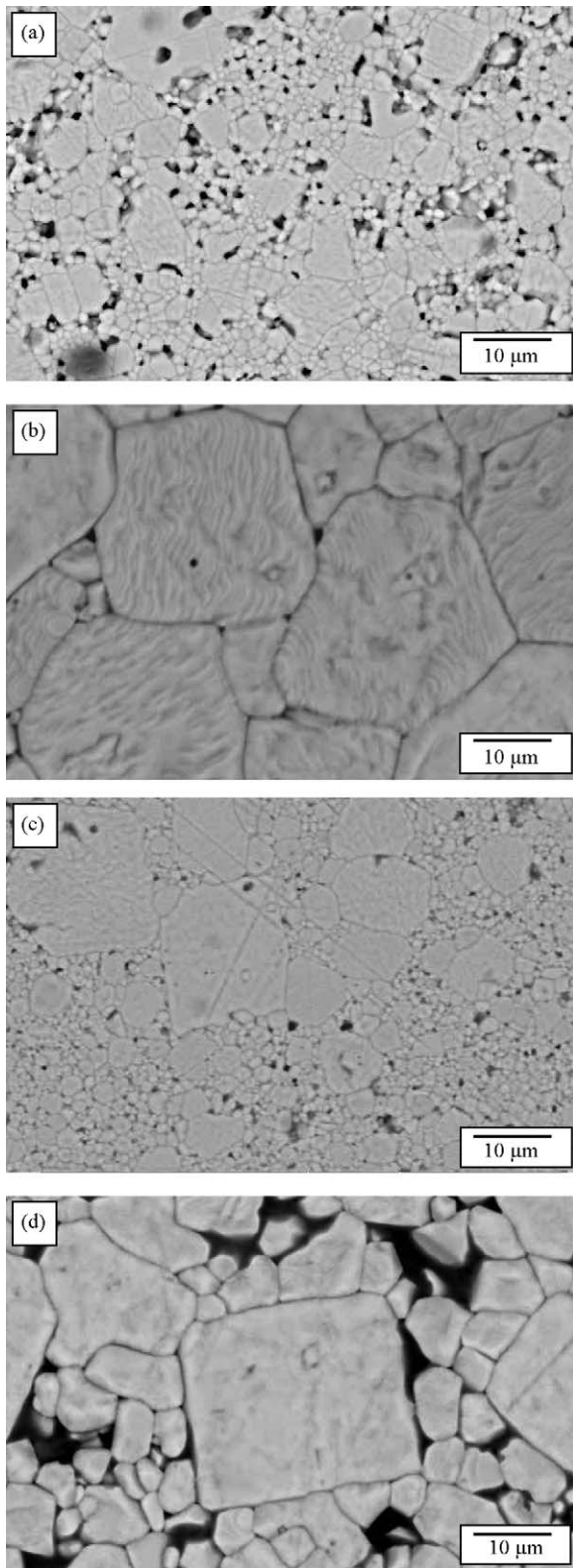


Fig. 6. SEM micrograph of pellets of $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ sintered at (a) 1200°C and (b) 1500°C ; $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ at (c) 1200°C and (d) 1500°C .

most of these routes, namely Pechini,^{11,20} coprecipitation,^{8,11} and autoignition processes,¹ were sintered at high relative density values in the range of 94–97%. These high density values have been obtained at relatively low temperature ($1300\text{--}1400^\circ\text{C}$) for sintering intervals of 5–20 h, for powders doped with 20 or 30 mol.% Ca.^{1,8,11} However, in all cases the processing route involved the use of prolonged calcination stages (10 h) at 1000°C , as well as a milling step for 20 h.¹¹ In contrast, both $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders prepared hydrothermally at very low temperature ($400\text{--}425^\circ\text{C}$), in a single step, seem to be attractive for industrial proposes in the manufacturing of SOFCs separator material, because they can be sintered at high relative density ($\sim 98.0\%$); at 1400°C for an interval as short as 5 h, without any appreciable loss of Cr^{6+} associated with the powder sintering. Indeed, in recent data reported by Valadez-Farias,²¹ it was found that coprecipitated $\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Al}_{0.1}\text{O}_3$ powders achieved a relative density of 92% after sintering at 1400°C for 5 h in air, this relative density is lower than that obtained by the hydrothermally derived fine $\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Al}_{0.1}\text{O}_3$ powders (97.0 wt.%).

3.3. Microstructural aspects of sintered LaCrO_3 , $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ pellets

The microstructure was examined on the surface of the sintered specimens after thermal etching by a SEM. Fig. 5 shows the variation of the microstructure of the compacts of LaCrO_3 , $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ powders sintered at 1400°C in air. In general, the microstructure of the sintered sample of LaCrO_3 consisted of equiaxial grains with an average grain size of $4\ \mu\text{m}$ (Fig. 5a). However, this powder showed low sinterability because of the presence of a large amount of remaining pores, which is in accordance with the maximum relative density achieved in the sintered body (85%). In contrast, the samples of lanthanum chromite doped with 10 and 20 mol.% Ca exhibited more dense microstructures formed by equiaxed grains, and a small amount of pores were visible (Fig. 5b and c). Furthermore, it was found that the incorporation of Ca in the A site of the lanthanum chromite affects the microstructure of the samples during sintering. An abnormal grain growth was observed in the specimens prepared with 20 mol.% Ca, which resulted in a heterogeneous microstructure with some faceted grains. However, it often occurs that disproportional large grains are present in the ceramic body, formed through a discontinuous grain growth. It is well known that grains with a large size and more than six walls are more stable and grow rapidly, and a phenomena that achieves the discontinuous grain growth in ceramics materials is associated with the formation of liquid phases during the sintering stage.²² Hence, the microstructural differences determined on the pellets prepared with Ca-doped lanthanum chromite powders, must be associated to the morphology of original powders and the sintering which is assisted by the liquid phase produced by a partial decomposition of the lanthanum chromite solid solution.

Additional experiments were conducted to determine the effect of temperature on the microstructural changes and densification of solid solutions of $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$. The SEM micrographs of these specimens sintered at 1200 and 1500 °C are shown in Fig. 6. At 1200 °C, the samples of $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ (Fig. 6a) showed no significant microstructural differences when compared to $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ (Fig. 6c), which showed a peculiar microstructure formed by a bimodal grain size, in which very large grains (10 μm) coexisted with smaller grains with a size $<2\ \mu\text{m}$. In particular, a more densified microstructure was obtained in the specimen doped with 20 mol.% of Ca even at 1200 °C, in comparison with that doped with 10 mol.% Ca which also exhibited a great amount of residual porosity. The densification of the hydrothermal lanthanum chromite solid solution doped with the large Ca content (20 mol.%) at low sintering temperatures, might be assisted by the liquid phase sintering process which promotes the atomic motion through grain boundary¹¹ as well as the abnormal grain growth.²³ The present results also suggest that, the abnormal grain growth might be associated with the differences on the morphology of the hydrothermally prepared $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ powders (Fig. 3b), because this phenomena was not detected on LaCrO_3 powders which have a more regular morphology (Fig. 3a). Moreover, the increase on the sintering temperature up to 1500 °C resulted in limiting the abnormal grain growth, thus, a more homogeneous equiaxial grain microstructure was obtained on the sintered pellet of $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ (Fig. 6b), and the average grain size measured on low magnification micrographs by linear intersection was approximately 20 μm . However, a marked abnormal grain growth was observed on the pellet of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ sintered at 1500 °C for 5 h shows a great amount of porosity, which might be due to the partial decomposition of the lanthanum chromite solid solution at high temperatures. It is well known that under oxidizing conditions at high temperature, the sintering of LaCrO_3 is limited at high temperatures due to the loss of Cr^{6+} ions, as CrO_3 molecules.²⁴

4. Summary

Pure fine LaCrO_3 powders were obtained under hydrothermal conditions at a temperature as low as 350 °C for 1 h. In our case, the processing route allows to form the crystalline single orthorhombic LaCrO_3 phase during the hydrothermal treatment, in comparison with the hydroxide complex that was reported in the former literature. The incorporation of Ca dopant increased the temperature for crystallization of lanthanum chromite solid solutions under hydrothermal conditions. SEM and TEM observations revealed that the particles of $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ solid solutions were preferentially crystallized as clusters with irregular shapes, and the average size of the particles was approximately 300 nm. The powder of LaCrO_3 prepared under hydrothermal conditions has a poor sinterability in air, but highly dense

Ca-doped lanthanum chromite pellets were obtained by firing at 1400 °C for 5 h from the hydrothermally synthesized Ca-doped lanthanum chromite powders. The maximum densification obtained in pellets of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ by sintering at 1400 °C was 97.7% of the theoretical density, and the average grain size was of 6 μm . A marked abnormal grain growth was observed mainly in the Ca-doped lanthanum chromite due to the heterogeneity on the distribution of particle size. In addition, we surmise that the hydrothermally derived fine Ca-doped lanthanum chromite powders might have an industrial interest for processing SOFC separators due to their good sinterability and limited processing stages.

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