Spark plasma sintering of hydrothermally derived ultrafine Ca doped lanthanum chromite powders

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Lanthanum chromite nano-particles, with a composition of $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$, were produced by 1 h of hydrothermal reaction at 400 and 425°C respectively. The sintering of the powders was conducted using a spark plasma apparatus over the temperature range 1300-1550°C for 1 min with a constant loading pressure of 45 MPa. Additional sintering experiments using conventional firing were carried out for comparison. Fully densified (98 % r.d.) lanthanum chromite pellets with fine equiaxial grains 2.3 μm in size were obtained using the SPS (spark plasma sintering) method. In contrast, a maximum relative density of 97 % was produced using $La_{0.8}Ca_{0.2}CrO_3$ sintered conventionally at 1400ºC for 300 min, and the average grain size of the resulting sintered sample was 6 μm.

Keywords: Lanthanum Chromite; Sintering, Solid Solution, Hydrothermal Treatment, Interconnector, Perovskites.

Sinterización por plasma de particulas ultrafinas de cromita de lantano dopado con clacio obtenidas por síntesis hidrotermal

Partículas ultrafinas de cromita de lantano, con una composición de $La_{0.9}Ca_{0.1}CrO_3$ y $La_{0.8}Ca_{0.2}CrO_3$ se obtuvieron después de 1 hora de síntesis hidrotermal a las temperaturas de 400 y 425°C respectivamente. Los compuestos obtenidos, con un tamaño de partícula de ~ 200 nm, se caracterizaron utilizando las técnicas de DRX, MEB y MET. La sinterización de estos polvos se efectuó en un equipo de chispa de plasma en el rango de temperatura de 1300-1500°C durante 1 min, y a una presión de compactación de 45 MPa. Ambos polvos también se sinterizaron siguiendo un tratamiento térmico convencional, en aire, con el propósito de comparar ambos métodos de sinterización. Las muestras de cromita de lantano sinterizadas por plasma presentaban una densidad relativa del 98 % (ρ/ρ$_t$); y una microestructura monofásica con granos equiaxiales con un tamaño medio de grano menor de 2.3 μm. En contraste, la composición $La_{0.8}Ca_{0.2}CrO_3$ sinterizada a 1400°C/300 min, por métodos convencionales alcanzó una densidad relativa máxima del 97 % y su microestructura estaba formada por una sola fase con un tamaño medio de grano de 6 μm.

Palabras clave: Cromita de Lantano; Sinterización, Solución Sólida, Síntesis Hidrotermal, Interconector, Perovskitas.

1. INTRODUCTION

Lanthanum chromite and their related solid solutions are the most suitable materials for use as an interconnector in solid oxide fuel cells (SOFC's), because these satisfy the requirements of the operating conditions for high electronic conductivity, chemical stability in both oxidizing and reducing atmospheres, thermo-mechanical compatibility with other cell components, also the interconnect must be impermeable to prevent gas cross leakage (1,2). Stoichiometric lanthanum chromite ($LaCrO_3$) and alkaline element-doped lanthanum chromites are well known for having poor sinterability in air (3), because the evaporation of the chromium component as gaseous CrO_3 at temperatures above 1000°C disrupts the sintering of the $LaCrO_3$ particles (4). The preparation of high density LC ceramics at firing temperatures below 1600ºC in air has been investigated by considering morphological and chemical compositional aspects of the raw powders (5-7).

The preparation of lanthanum chromite fine powders has been recently carried out by using chemical methods such as sol-gel (8), coprecipitation (9), hydrazine (10) and complex solution synthesis (11). These processing techniques are likely to be useful for the synthesis of fine alkaline earth (Ca or Sr)-doped lanthanum chromite powders at relatively low temperatures (700-800ºC). The hydrothermal technique allows us to produce a wide variety of ceramic powders with controlled chemical composition and low distribution of particle size (12). The first evidence for the hydrothermal formation of fine LC powders (average particle size 700 nm) was reported by Yoshimura et al (13), they prepared powders under hydrothermal conditions at 700ºC for 3 h in de-ionized water under a pressure of 100 MPa.

Over the last decade, more advanced techniques have been under development for ceramic powder consolidation. The Spark Plasma Sintering method (hereafter referred to as SPS) is a process developed to produce mainly high quality

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structural ceramics. This process resembles the uniaxial hot pressing process in as much as the precursor powder is placed in a die and uniaxially loaded during sintering. In the case of the SPS process, however, the sintering is promoted by applying a high DC pulse voltage to the graphite die, and in appropriate cases to the powder itself. The high DC pulse voltage produces spark discharges at particles contact points providing a more homogeneous heating of the sample than in the conventional firing (14). Under SPS conditions powder compacts with high density are produced because of uniform heating at relatively lower temperature for shorter sintering times, typically few minutes, compared with the conventional hot isostatic pressing (HIP) method (14). The short sintering time required for the SPS process is advantageous in suppressing exaggerated grain growth in ceramics for electrical applications (15,16). In the present study, we have attempted to study the sintering behavior of fine Ca doped lanthanum chromite (LCC) powders by means of the SPS process, because it is well known that Ca doping achieves a liquid sintering process at relative low temperatures (1076°C) which allows to produce high dense doped LC materials at sintering temperatures below 1550°C (7), and details regarding the sintering behavior of hydrothermally derived Ca-doped lanthanum chromite powders have not been reported yet. In addition, these powders were also sintered by conventional firing in air, to evaluate the microstructural differences with those LCC pellets prepared by SPS. The microstructural differences determined on the sintered bodies were discussed based on the morphological aspects of the hydrothermally produced LCC powders.

2. EXPERIMENTAL PROCEDURE

2.1. Powder synthesis

Precursor lanthanum chromite gel was prepared by using an alkaline coprecipitation method reported elsewhere (17), employing reagent grade chemicals of $LaCl_3 \cdot 7H_2O$ (99.9%), $Cr(NO_3)_3 \cdot 9H_2O$ (99.9%) and $CaCl_2 \cdot 2H_2O$ (99%) (Wako Chemical Industries, Ltd. Japan). Aqueous solutions of $LaCl_3$, $Cr(NO_3)_3$ and $CaCl_2$ with a concentration of 0.05 M were prepared with de-ionized water, and a 0.5 M solution of NaOH was employed as co-precipitation media. The solutions were mixed in two different volume ratios, La:Ca:Cr, 0.9:0.1:1 and 0.8:0.2:1, which correspond to the compositional stoichiometry of the solid solutions, $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$. The co-precipitated gel was centrifuged and a volume of 20 ml was then poured into a Hastelloy C-lined microautoclave (40 ml capacity). The autoclave was heated at a constant rate of 20 °C/min up to a desired temperature. Based on preliminary experimental results conducted by the present authors (18), the synthesis of the powders of $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$ was carried out at 400°C and 425°C, for reaction times of 1 h in both cases. After the treatment, the precipitates were well washed with ethanol, decanted and then dried in an oven at 100°C overnight.

2.2. Sintering

The dried powder (4 g) was placed in a cylindrical graphite die with an inner diameter of 20 mm, lined with graphite foil, and preloaded at 1 MPa. All the spark plasma sintering experiments were conducted (model SPS 1040,

Sumitomo Coal Co. Ltd) in vacuum (~ 10^{-3} Torr, to prevent a contamination by carbon diffusion) under a confining uniaxial pressure of 45 MPa, these conditions were kept constant during the heating and sintering stages. The powder was heated at a constant rate of 330 °C/min up to the desired temperature (1300 - 1550°C), and the sintering was carried out at each temperature for 1 min. After sintering, the sample was rapidly cooled down to room temperature by shutting off the electric power. In addition, conventional firing of the hydrothermally synthesized powder was also carried out for comparison. Green compacts were prepared by isostatic pressing at 200 MPa for 5 min, and sintered at various temperatures (1300 – 1500°C) up to 300 min in air. The heating rate was 10 °C/min, and the specimens were cooled down slowly inside the furnace.

2.3. Characterization

Powder X-ray diffraction analyses were used to determine the crystalline phases and the lattice constants of the hydrothermally synthesized powder. Measurements were made on an X-ray diffractometer (Rigaku, Rotaflex) with graphite-monochromatized CuKα radiation at 40 kV and 100 mA. Diffraction patterns were taken in the 2θ range from 10° to 70°. The thermal behavior of both powders of lanthanum chromite $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$; was determined by DTA analyses using a Perkin Elmer (Pyris-Diamond). The lattice parameters were determined by the least-squares 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. Morphological aspects of the powder were examined by scanning electron microscopy (SEM, Philips XL30 ESEM) equipped with an energy dispersive X-ray (EDX) device. The sizes of the powder particles were measured by transmission electron microscopy (TEM, Hitachi H-800).

The densities of the specimens were determined by the Archimedes' principle using a helium pycnometer (Multipycnometer Quantachrome) at a helium gas pressure of 0.117 MPa, and the theoretical densities of the powders were calculated from the lattice parameter data. Microstructural observations were made on dense specimens, which were ground and polished to a mirror like surface, the microstructure being revealed by thermal etching conducted between 1025 - 1275°C for 120 min.

3. RESULTS AND DISCUSSION

3.1. Characterization of hydrothermally derived $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$ powders

Figure 1 shows X-ray diffraction patterns of the lanthanum chromite powders doped with calcium obtained under hydrothermal conditions. The diffraction peaks of these powders (Fig. 1), $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$, were indexed to the orthorhombic $LaCrO_3$ structure (JCPDS 33-701); furthermore, a slight shift of the diffraction peaks to toward a higher angle was determined by increasing the dopant content. This behavior might be associated with the difference between the ionic radii of Ca^{2+} (0.99Å) and La^{+3} (1.15 Å). In fact, the lattice parameters of the doped powder, summarized in Table I, agree with the inference proposed above.

Typical aspects of the morphology of the $La_{0.9}Ca_{0.1}CrO_3$

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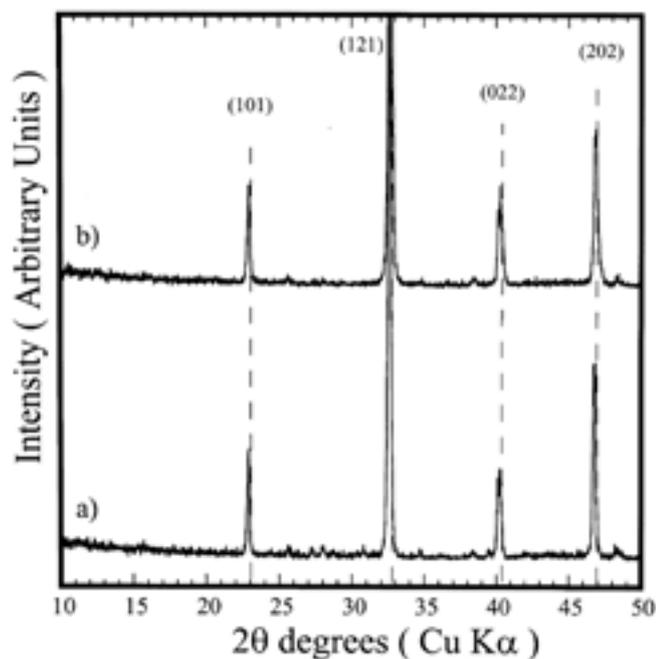**Bol. Soc. Esp. Ceram. V., 45 [4] 271-277 (2006)**

Fig. 1- X-Ray diffraction patterns of various doped lanthanum chromite powders obtained under hydrothermal conditions for 1 h at several temperatures: a) $La_{0.9}Ca_{0.1}CrO_3$ at 400°C and b) $La_{0.8}Ca_{0.2}CrO_3$ at 425°C.

and $La_{0.8}Ca_{0.2}CrO_3$ powders determined by SEM, revealed that raspberry-like particles, irregular in shape with an average particle size of 400 nm, were preferentially crystallized under hydrothermal conditions. These preliminary results were further studied by TEM observations (Figure 2), which revealed that the particles of $La_{0.9}Ca_{0.1}CrO_3$ had very irregular shapes (Fig. 2a), and in some cases the shape of the
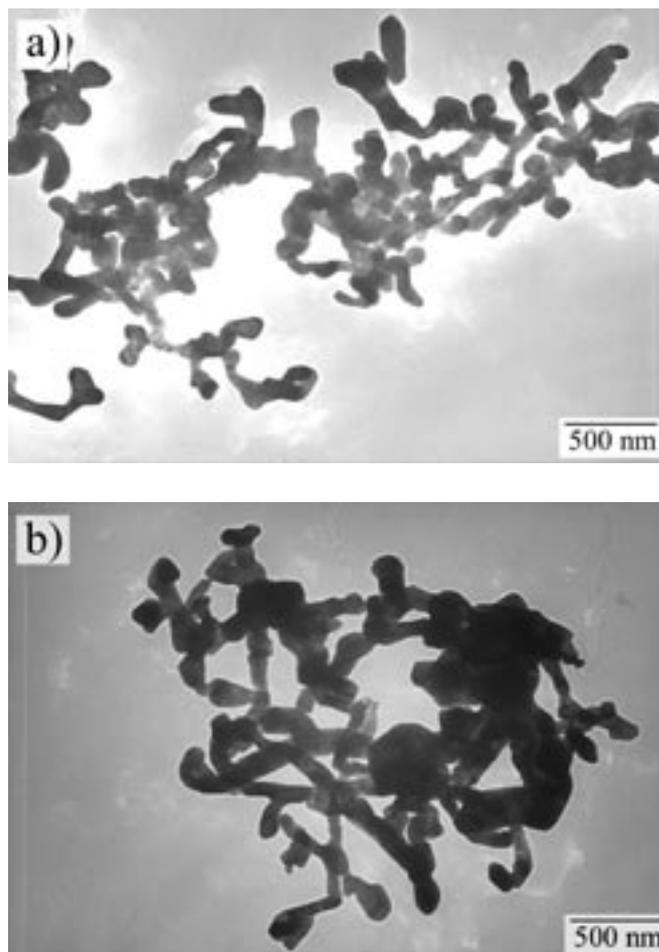
Fig. 2- Transmission electron micrographs of Ca-doped lanthanum chromite powders obtained under hydrothermal conditions for 1 h at several temperatures: a) at 400°C, $La_{0.9}Ca_{0.1}CrO_3$; and b) at 425°C, $La_{0.8}Ca_{0.2}CrO_3$.

TABLE I. LATTICE PARAMETERS (a, b, c) AND ORTHORHOMBIC CELL VOLUME OF $La_{1-x}Ca_xCrO_3$ (X=0, 0.1 AND 0.2) POWDERS.

Composition	Lattice parameters			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)	234.68	6.7605
$La_{0.9}Ca_{0.1}CrO_3$	5.4615(9)	5.4956(9)	7.7559(9)	232.79	6.5336
$La_{0.8}Ca_{0.2}CrO_3$	5.4529(9)	5.4845(9)	7.7394(9)	231.46	6.2875

particles suggested that these had been further dissolved and subsequently bonded together during the hydrothermal treatment. Similar results to those described above regarding the shape and size of the powders were determined for the hydrothermal crystallizated of $La_{0.8}Ca_{0.2}CrO_3$ particles (Fig. 2b). The high solubility of the LC ceramic powders, even in water under hydrothermal conditions, was determined by Yoshimura et al. (13), who observed that $LaCrO_3$ particles were further dissolved by hydrothermal treatments conducted at temperatures above 400°C. Hence, the irregular morphology must be the result of a subsequent dissolution of the particles crystallized during intermediate stages of the hydrothermal reaction. The transference of species dissolved into the solvent

by convection did not take place, because the autoclave was kept at a uniform temperature. Therefore, the ionic species in the solvent were then recrystallized at the surface of the particles allowing some of them to bond together. Although the powders prepared under hydrothermal conditions do not have a controlled morphology (Fig. 2), we expect that these finer particles should exhibit superior sinterability even in air.

3.2. Sintering of $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$ powders by SPS and Conventional Firing

The conditions for the sintering treatments conducted by

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TABLE II. SUMMARY OF DENSITY AND GRAIN SIZE OF SINTERED CA-DOPED LANTHANUM CHROMITE POWDERS. La, Ca and Cr CONTENTS (ATM %) WERE ESTIMATED FROM THE EDX SPECTRA AND THE NOMINAL La:Ca:Cr RATIOS OF THE SAMPLES. THE SAMPLES $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$ WERE PREPARED UNDER HYDROTHERMAL CONDITIONS FOR 1 H AT 400 AND 425°C, RESPECTIVELY.

| Sample	Sintering Process	Composition	Sintering Conditions		Apparent Density (g/cm³)	Relative Density (%)	Grain Size (µm)	EDX analyses			La:Ca:Cr
			Temperature (°C)	Time (min)				La	Ca	Cr	
LCC-1	-	$La_{0.9}Ca_{0.1}CrO_3$	-	-	-	-	-	45.1(2)	4.9(2)	50.0(2)	0.9:0.1:1.0
LCC-2	-	$La_{0.8}Ca_{0.2}CrO_3$	-	-	-	-	-	39.9(5)	10.2(5)	49.9(5)	0.8:0.2:1.0
SPS1	Spark Plasma	$La_{0.9}Ca_{0.1}CrO_3$	1400	1	6.5786	97.30	1.36	44.8(7)	5.3 (7)	49.9(7)	0.9:0.1:1.0
SPS2	Spark Plasma	$La_{0.9}Ca_{0.1}CrO_3$	1500	1	6.5909	97.49	2.81	-	-	-	-
SPS3	Spark Plasma	$La_{0.8}Ca_{0.2}CrO_3$	1300	1	6.6204	97.92	<1	-	-	-	-
SPS4	Spark Plasma	$La_{0.8}Ca_{0.2}CrO_3$	1500	1	6.6639	98.57	1.35	40.2(5)	9.9(5)	49.9(5)	0.8:0.2:1.0
SPS5	Spark Plasma	$La_{0.8}Ca_{0.2}CrO_3$	1550	1	6.6739	98.71	2.29	40.1(8)	10.2(8)	49.7(8)	0.8:0.2:1.0
CS1	Conventional	$La_{0.9}Ca_{0.1}CrO_3$	1400	300	6.5439	96.79	11	44.5(5)	5.5(5)	50.0(5)	0.9:0.1:1.0
CS2	Conventional	$La_{0.9}Ca_{0.1}CrO_3$	1500	60	6.2871	92.99	8	-	-	-	-
CS3	Conventional	$La_{0.9}Ca_{0.1}CrO_3$	1500	300	6.4528	95.44	20	45.8(9)	5.3(9)	48.9(9)	0.9:0.1:1.0
CS4	Conventional	$La_{0.8}Ca_{0.2}CrO_3$	1400	300	6.6058	97.71	6	40.1(3)	9.8(3)	50.1(3)	0.8:0.2:1.0
CS5	Conventional	$La_{0.8}Ca_{0.2}CrO_3$	1500	60	6.4557	95.49	5	-	-	-	---
CS6	Conventional	$La_{0.8}Ca_{0.2}CrO_3$	1500	300	6.5194	96.43	13	40.6(5)	10.6(5)	48.8(5)	0.8:0.2:1.0
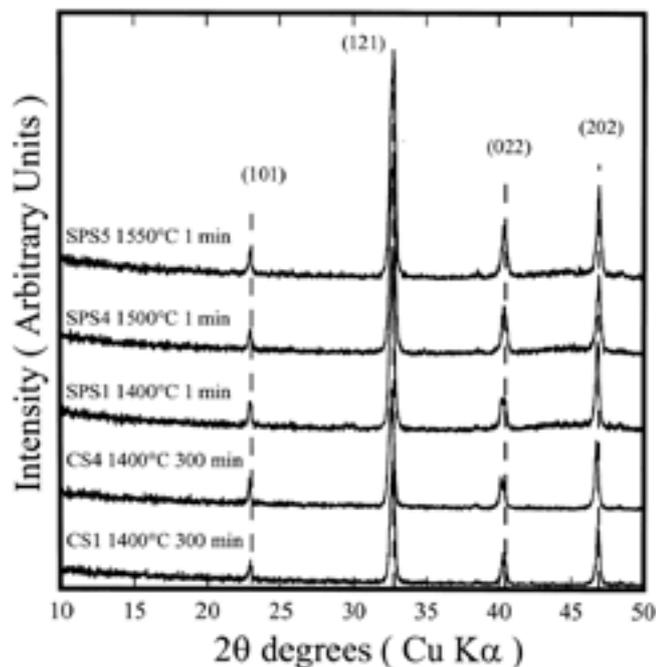
Fig. 3- X-ray diffraction patterns of calcium doped lanthanum chromite pellets sintered by SPS (samples SPS1, SPS4 and SPS5) and conventional firing (samples CS1 and CS4) methods.

Fig. 4- Variation of the normalized shrinkage of hydrothermally prepared fine $La_{0.9}Ca_{0.1}CrO_3$ (□) and $La_{0.8}Ca_{0.2}CrO_3$ (■) powders during the Spark Plasma Sintering conducted at 1500°C for 1 min.

the SPS technique and conventional firing are summarized in Table 2, together with properties of the sintered bodies. The compositions determined in SPS and conventionally fired specimens agree well with those of the hydrothermally prepared powder and their nominal atomic ratios agree within the experimental error (Table 2). These results indicate that any compositional variation of the cation content occurred during the SPS and the firing processes. In fact, the X-ray diffraction patterns obtained for some sintered specimens showed that no further structural or chemical compositional changes took place either during SPS or conventional firing (Fig. 3). The diffr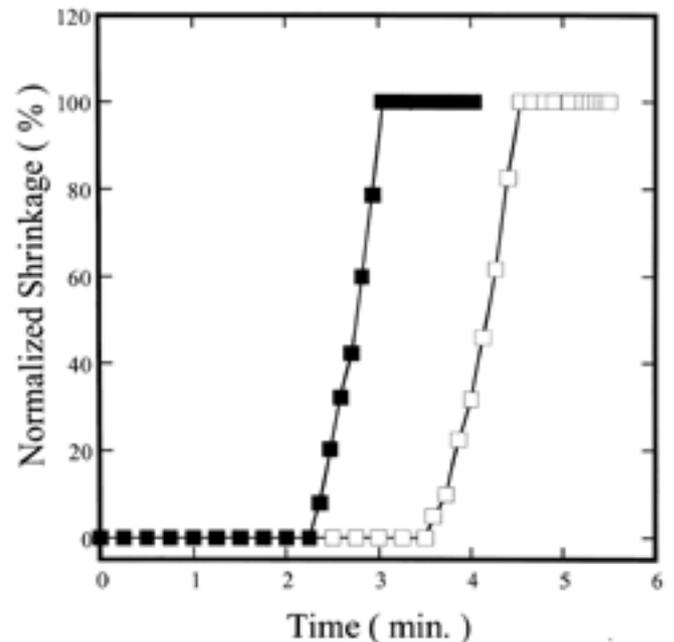action patterns corresponding to samples SPS1 and CS1 were well matched with that of $La_{0.9}Ca_{0.1}CrO_3$ with an orthorhombic structure (JCPDS Card 86-1133), whilst those of the samples SPS4, SPS5 and CS4 were indexed with the crystalline phase of the inorganic compound $La_{0.8}Ca_{0.2}CrO_3$ (JCPDS Card 89-480) (Fig. 3).

Figure 4 shows the sintering behavior of $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$ powders sintered by SPS, which is represented by the change on the normalized shrinkage of the powder bed against the sintering interval. In general, it was found that the sintering of $La_{0.8}Ca_{0.2}CrO_3$ powders proceeded faster at the heating stage, above 800°C, in comparison with the pellet of the $La_{0.9}Ca_{0.1}CrO_3$ compound. In both cases, the densification of the powders occurred within a very short time, 0.5 min,

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before reaching the sintering temperature of 1500°C. At the sintering temperature no further changes occurred on the specimen densification, because the shrinkage of the powder bed was nearly constant. The differences showed by our results might depend on the decomposition of the LC solid solution and the amount of the transient liquid that was formed under SPS conditions. This inference is supported by the fact that the hydrothermal derived $La_{0.8}Ca_{0.2}CrO_3$ exhibited the formation of a transient liquid at a lower temperature (990°C) than that of the $CaCrO_4$ liquid phase (1076°C)(1), this result was determined from the DTA curve showed in Figure 5. In addition, the peak in $La_{0.8}Ca_{0.2}CrO_3$ powder curve that indicates the formation of liquid is slightly bigger than that observed for the $La_{0.9}Ca_{0.1}CrO_3$ powder. Thus, this difference may accelerate the densification process under SPS conditions
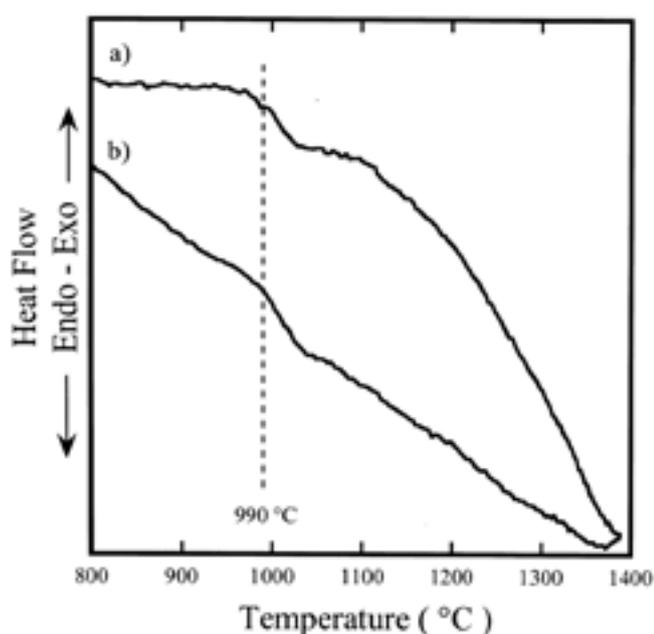
Fig. 5- DTA curves of raw powders $La_{0.9}Ca_{0.1}CrO_3$ (a) and $La_{0.8}Ca_{0.2}CrO_3$ (b) prepared under hydrothermal conditions at 400 and 425°C for 1 h, respectively.

for the highly Ca doped lanthanum chromate powders.

The densities of the SPS specimens reported in Table 2 showed that the powders $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$ prepared under hydrothermal conditions were highly densified (> 97%, Table 1) at temperatures in the range of 1300 – 1550°C in vacuum. Thus, relatively highly densified $La_{0.8}Ca_{0.2}CrO_3$ samples (> 98%, SPS4) were preferentially obtained by the SPS technique, in comparison with the maximum relative density achieved using powders doped with lesser amounts of calcium (10% mol). These differences observed in the degree of densification of the SPS samples may be associated with the amount of dopant (Ca), because the content of Ca can lead to a larger amount of transient liquid formed above 1050°C, which enhances the sintering process of Ca doped lanthanum chromite powders (2,7). In general, it might be expected that a partial decomposition of the $La_{1-x}Ca_xCrO_3$ solid solutions is likely to proceed faster during the SPS process because of the high voltage discharges between the particle gaps (15). This accelerates the formation of a transient liquid ($CaCrO_4$) which
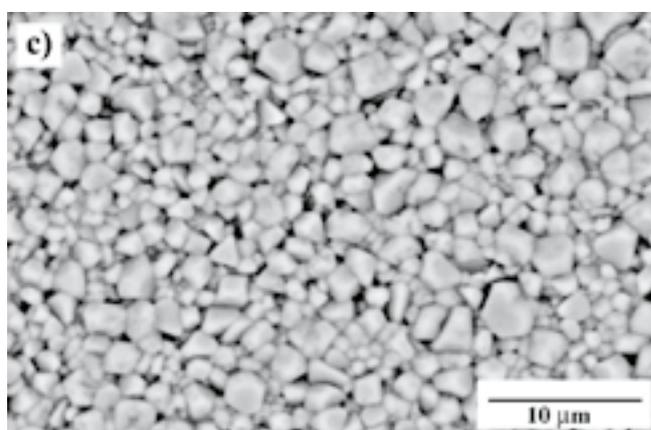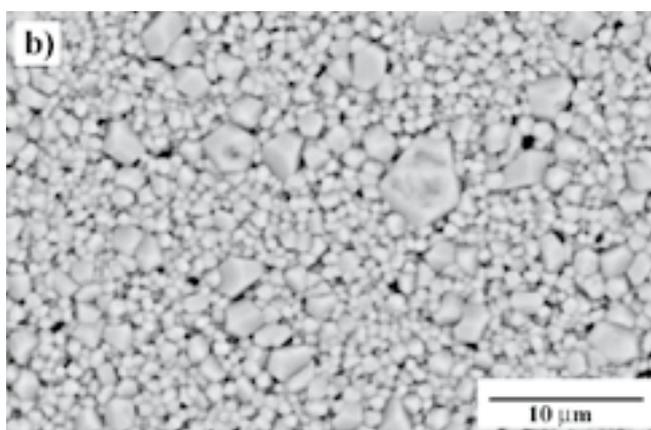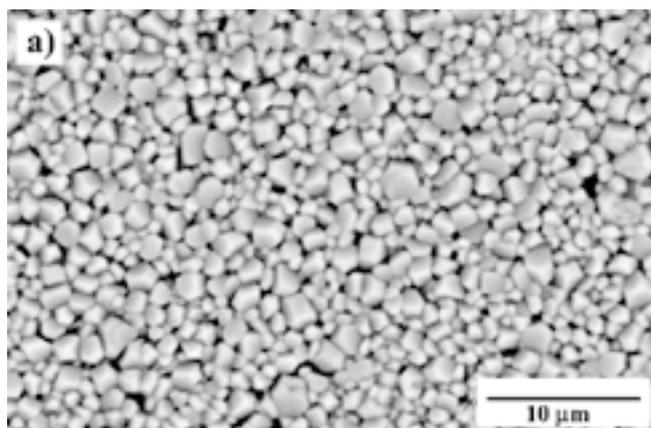

Fig. 6- SEM micrographs of calcium doped lanthanum chromite powders sintered by Spark Plasma Sintering for 1 min at several temperatures: of a) $La_{0.9}Ca_{0.1}CrO_3$ at 1400°C; b) $La_{0.8}Ca_{0.2}CrO_3$ at 1500°C and c) $La_{0.8}Ca_{0.2}CrO_3$ at 1550°C .

may be then simultaneously distribute between the grains by the uniaxial loading confined during the SPS process. These phenomena could accelerate the sintering process to full density for fine Ca-doped lanthanum chromite powder.

Figure 6 shows typical microstructures of SPS specimens revealed by thermal etching at 1190 and 1275°C for 90 min. SEM observations conducted on sintered specimens of $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$ showed that these samples generally had a microstructure of fine equiaxial grains less than 3 μm in size. These results agree with the relative density

measured on the pellets after sintering, because a very low amount of residual porosity was detected in each specimen (Fig. 6). These results are similar to those found for fine Sr-doped lanthanum chromite powders, in which excessive grain growth was further limited by the SPS process (9). However, the present results showed that a marked growth of a few grains occurred in the sample of $La_{0.8}Ca_{0.2}CrO_3$ sintered at 1500°C (Fig. 6b). In contrast, the increase in SPS temperature up to 1550°C resulted in a more homogeneous microstructure with an average grain size of 2.29 μm. We suggest that the abnormal grain growth must depend on the powder morphology and amount of dopant, because the marked agglomeration of irregular $La_{0.8}Ca_{0.2}CrO_3$ particles might produce various localized areas where the formation of very large grains can proceed rapidly. Thus, it is expected that under SPS conditions, an increase in the sintering temperature might produce a more homogeneous distribution of the transient liquid between the grain boundaries, resulting in a more controlled equiaxial grain size microstructure (Fig. 6c).

The specimens obtained using conventional firing conditions had high relative densities similar to that determined in SPS specimens, but the grain size was larger when compared with that for all the SPS specimens. The maximum densification obtained by conventional sintering was of 97.71% of the theoretical density for the specimen CS4 in Table 2, and the average grain size measured on this sample was 6 μm. Figure 7 shows typical microstructural aspects of
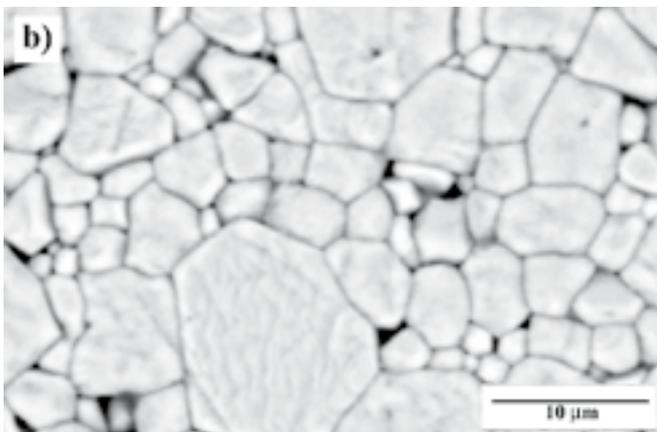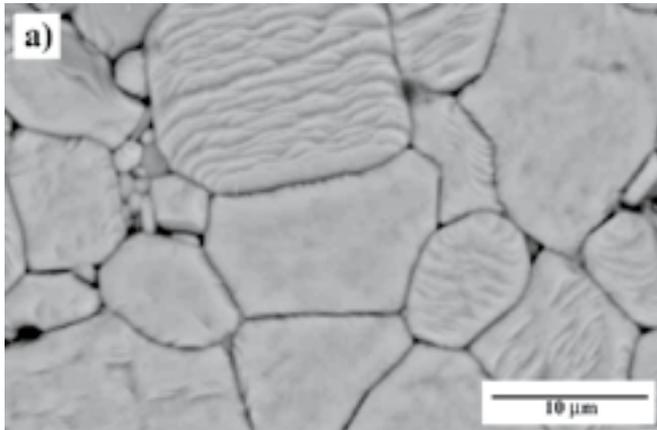

Fig. 7- Microstructural aspects revealed on dense samples of: a) $La_{0.9}Ca_{0.1}CrO_3$ and b) $La_{0.8}Ca_{0.2}CrO_3$ sintered at 1400°C for 5 h.
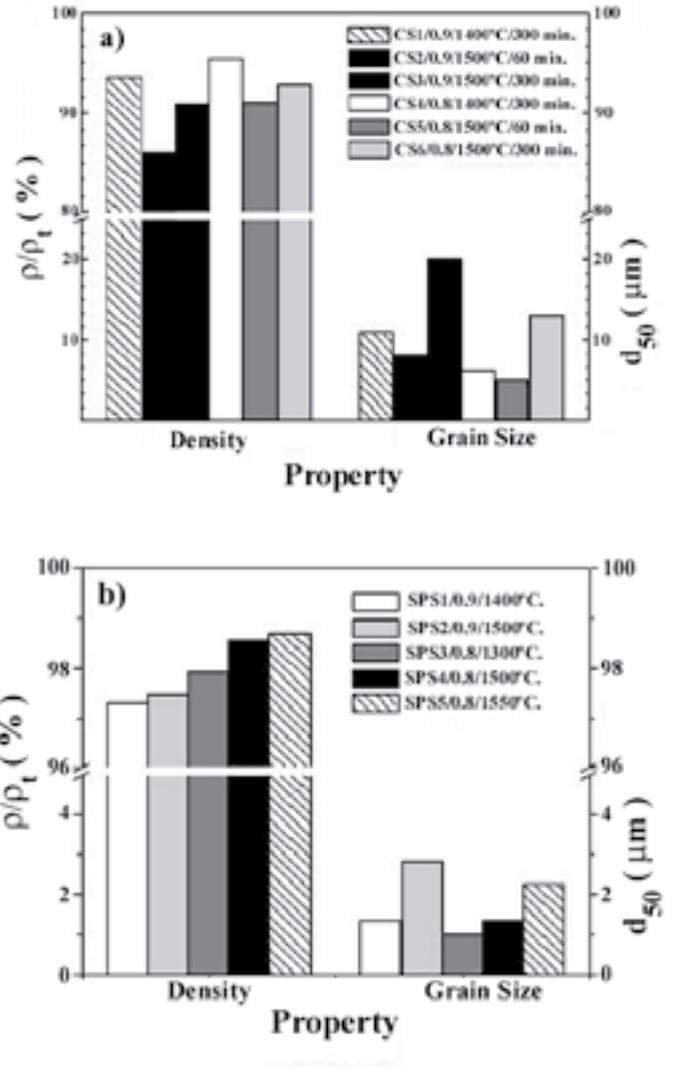

Fig. 8- Variation on the relative density and grain size of Ca doped lanthanum chromite densified pellets, $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$; sintered by processes such as: a) convencional firing and b) spark plasma sintering.

$La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$ samples fired in air at 1400°C for 5 h. The results showed that even under conventional firing conditions, the LCC powders exhibited good sinterability in air atmosphere at lower temperatures (1400°C) when compared with that reported for the sintering of Sr-doped lanthanum chromite powders (1600°C) (9). The differences in the grain size observed in the SPS and the conventionally fired specimens are mainly associated with the use of a relatively lower sintering temperature and shorter sintering time, mainly in the case of the SPS process (9,14). In addition to the above mentioned results, in Figure 8 are included the properties, relative density and grain size; for Ca doped lanthanum chromite pellets obtained by two different sintering processes. Thought, the SPS method is faster in achieving high densified bodies, we surmise that hydrothermally derived nanosized lanthanum chromite powders can be sintered at a relatively high density nearly 95 % using conventional firing, being the best conditions for this a temperature of 1500°C and a time of 60 min, which allow also to achieve a relatively small grain size (8 μm) in the sintered pellet. In fact, the pellets corresponding

to the samples of $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.9}Ca_{0.1}CrO_3$ prepared at the optimum conventional firing conditions, had electrical conductivity values of 15 and 18 Sm^{-1}, respectively (19), these values fit the electrical conductivity values required for the interconector material used in SOFC's. In general, it is clear that the Ca-doped lanthanum chromite powders, $La_{1-x}Ca_xCrO_3$, prepared under hydrothermal conditions exhibit good sinterability even in an air atmosphere, therefore, these powders can be used for preparing highly densified AE doped lanthanum chromite ceramics with potential use as SOFC's separators, because the leakage of fuel and oxidant gases through the interconnect might be further restricted at the SOFC's operational conditions (1000°C).

4. CONCLUSIONS

Ca-doped lanthanum chromite fine powders (< 400 nm) prepared at relative low temperature (400°C) under hydrothermal conditions, having an irregular shape and marked agglomeration without any contaminants, exhibited good sinterability by both SPS and conventional firing methods. Highly densified $La_{0.9}Ca_{0.1}CrO_3$ and $La_{0.8}Ca_{0.2}CrO_3$ pellets with relative densities above 97% and an average grain size of 3 μm, were obtained by SPS in a short sintering period (1 min). In contrast, only the $La_{0.8}Ca_{0.2}CrO_3$ powder was highly densified during conventional sintering, the relative density obtained in this specimen (97%) was similar to that determined for the SPS specimens. Under conventional firing, an excessive grain growth was found in the pellets of Ca-doped lanthanum chromite powders by increasing the sintering time and temperature.

ACKNOWLEDGEMENTS

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