Sintering of cobalt and strontium doped lanthanum chromite obtained by combustion synthesis

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Abstract: Lanthanum chromite ($LaCrO_3$) is one of the most adequate material for use as interconnector in solid oxide fuel cell (SOFC) applications, due to its intrinsic properties, namely its good electrical conductivity and resistance to environment conditions in fuel cell operations. Due to difficulties in sintering, additives are usually added to help in the densification process. In this work, the influence of added cobalt and strontium, in the sintering of $LaCrO_3$ obtained by combustion synthesis was studied. The starting materials were respectively nitrates of chromium, lanthanum, cobalt and strontium, and urea was used as fuel. The results show that by increasing the strontium and cobalt concentrations it is possible to reduce the temperature of sintering. Using both additives, the sintering processes took place in lesser times than normally used for this material, as well as greater values of density were attained.

Introduction

The lanthanum chromite ($LaCrO_3$) is one of the materials that have received particular attention for applications in SOFC. It is due this present unique properties, such as good chemical compatibility with other components, good electric conductivity (p-type) and stability during the fuel cell operation, that are: to resist both the reducing conditions at the anode side and the oxidant conditions of the cathode [1, 2, 3]. These characteristics make it especially indicated to be used as membranes between the electrodes [4].

The $LaCrO_3$ is suitable for use as interconnector, however, due its high stability, is difficult to sintering until high density. In order to modify this characteristic and to improve its electrical properties, generally additives and/or dopants are employed [5].

The influence of the Sr- and Co-doping, on the lanthanum chromites obtained by combustion reaction synthesis, and in the sintering behavior were investigated.

Experimental

Amongst the many routes of synthesis for $LaCrO_3$ powders, the combustion reaction synthesis was chosen because it consists of a relatively simple and fast method, and uses start materials or the reagents forthe reactions are easily found in the market [6]. The process begins with a mixture of oxidant reagents (nitrates, sulfates, carbonates, among others) and an organic fuel (urea, carboidrazina, maleica hydrazine, etc.), which acts as a reducing reagent. The solution with the mixture is warmed up until auto-ignition, occurring a fast and auto-

sustainable reaction, reaching high temperatures, of the order of 1000°C [7], For the synthesis studies the - Chromium (III) Nitrate ($Cr(NO_3)_3.9H_2O$), Aldrich (99%); - Lanthanum(III) Nitrate ($La(NO_3)_3.6H_2O$), Aldrich (99.99%); - Strontium Nitrate ($Sr(NO_3)_2$ (99%); - Cobalt(II) Nitrate ($Co(NO_3)_2.6H_2O$), Vetec (98%); - Urea ($(NH_2)_2CO$), Nuclear were used as start materials. The prepared compositions were $La_{1-x}Sr_xCr_{1-y}Co_yO_3$, with x = 0.1; 0.2 and y = 0.05; 0.08; 0.10.

The nitrates were stoichiometrically mixed, (according to Eq. 1), in water media. The molar ratio of urea to lanthanum nitrate used in all compositions was 4:1, in accordance with previous works [5].

$$La(NO_3)_3 + Cr(NO_3)_3 + 5CO(NH_2)_2 \rightarrow LaCrO_3 + 5CO_2 \uparrow + 8N_2 \uparrow + 10H_2O \qquad (1)$$

The solutions were warmed in a hot blanket, releasing the water steam and volatiles species until the temperature of the starting of the reaction that occurs to quickly following the intense flame. The compositions studied with their respective symbols are presented in Table1.

Table 1. Studied compositions and respective symbols.

Symbol	Composition	Symbol	Composition
LS10CCo5	$La_{0.90}Sr_{0.10}Cr_{0.95}Co_{0.05}O_3$	LS20CCo5	$La_{0.80}Sr_{0.20}Cr_{0.95}Co_{0.05}O_3$
LS10CCo8	$La_{0.90}Sr_{0.10}Cr_{0.92}Co_{0.08}O_3$	LS20CCo8	$La_{0.80}Sr_{0.20}Cr_{0.92}Co_{0.08}O_3$
LS10CCo10	$La_{0.90}Sr_{0.10}Cr_{0.90}Co_{0.10}O_3$	LS20CCo10	$La_{0.80}Sr_{0.20}Cr_{0.90}Co_{0.10}O_3$

The powders resultant after reactions were characterized using the diffractometer Rigaku - RINT2000 with Cu rotating anode for identifications of the crystalline phases formed. The phases of all compositions were identified. The BET method for specific surface determinations was used. (isto vai em RESULTADOS!)The pellets were conformed by pressing at the 90MPa in cylindrical forms in a mold of the 10 mm diameter. The apparent densities of the green compacts by the geometrical method were determined. The sintering studies were conducted in a vertical furnace (LindbergBlue) and held at 1500 and 1600ºC for steps of the 2 to the 10 hours. For all heating treatment a protect powders bed of CoO based were used. The densities of the sintered samples were determined by using Archimedes methods. The homogeneity of the grain size was observed on the polished and thermal attached surface for all of the sintered samples. For this analysis, the scanning microscopy apparatus was used.

Results and Discussion

Fig. 1 shows that the lanthanum chromite was synthesized by combustion reaction process for all prepared compositions. However, for some the particular Sr and Co contents, same different peaks from other crystalline phases were observed. These peaks are related from to the other phases such as $LaCrO_4$, $SrCrO_4$ and $Sr(NO_3)_2$, present in less quantities.

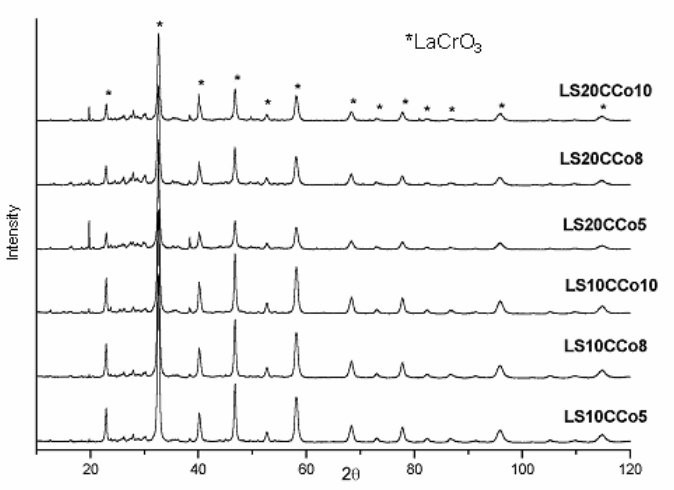


Figure 1 – Sr- and Co-doped lanthanum chromite histograms.

Table 2 presents the values of relative density determinations from the green compacts specimens of the each prepared composition. These values are around 35%th (theoretical density) and increase when the dopant concentrations increase.

Table 2- Relative density determined from the green compact. specimens with different aid content.

Sample	Green compact (%)	Sample	Green compact (%)
LS10CCo5	33.9 ± 0.1	LS20CCo5	35.5 ± 0.2
LS10CCo8	34.1 ± 0.1	LS20CCo8	35.6 ± 0.3
LS10CCo10	34.7 ± 0.1	LS20CCo10	36.6 ± 0.1

The influence of the time and the temperature on the sintering behavior of the samples performed at 1500 and 1600°C on the densification tendency is shown in the Fig. 2. For the same compositions (LS20CCo10), stable values after 4 hours of heat treatment were reached. It observed that sintering densities is strongly dependent of the additives concentrations.

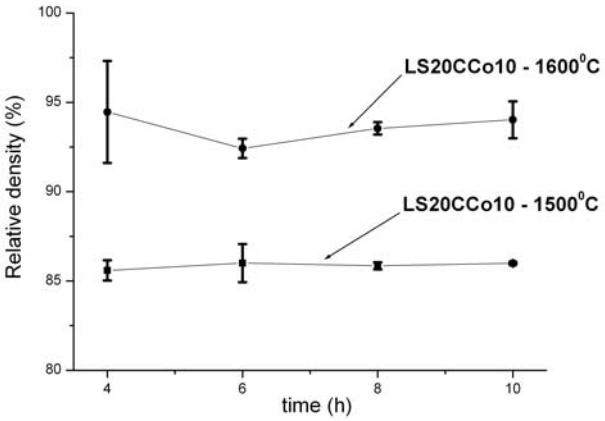


Figure 2 – Influence of the time and the temperature on the sintered densities of the compositions containing 10%(mol) Co and 20%(mol) Sr after sintering at 1500 and 1600°C.

High density values were obtained for the lanthanum chromite samples sinterized at 1600°C for 4 hours.

The influence of the strontium aid in the densification behavior for LS10CCo10 LS20CCo10 samples were studied. Fig. 3 shows that, by increasing sintering temperature and Sr concentration, the values of density after sintering were increased [8]. The increase of densities values were attributed by the $SrCrO_4$ liquid phase formed in the first stage in sintering, with low-melting point than $LaCrO_3$ [9].

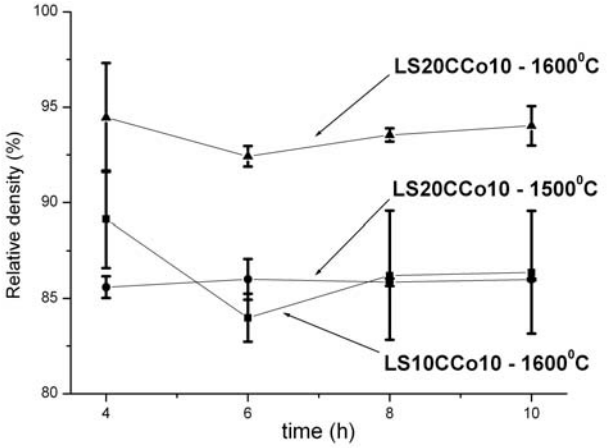


Figure 3 – Influence of the time and the temperature on the sintered densities of the compositions containing 10%(mol) Co and 10-20%(mol) Sr after sintering at 1500 and 1600°C.

Still in this figure it is interesting despite the Co has proved to be a great assistant in the densification process, that a significant contribution of Sr in the same phenomenon. Were also observed the values of density gotten at 1500°C for the composition with 20% of Sr (mol) are practically the same of that at 1600°C with 10% of Sr. These fact are attributed the phase liquid assisted sintering ($SrCrO_4$) present in increase amount.

The Influence of the cobalt doping in the densification behavior for compositions containing Co concentration in the range 5 - 10%(mol), while fixing the concentrations of Sr at 20%(mol). After sintering, the results of density with time and temperature of treatment are presented in Fig. 4. From all the studied sintering conditions, the LS20CCo10 sample presented the high values of density using a step of 2 hours of sintering. The sinterized samples using 5%(mol) of Co presented a low value for the relative density, namely, of (78.68 ± 0.17)%.

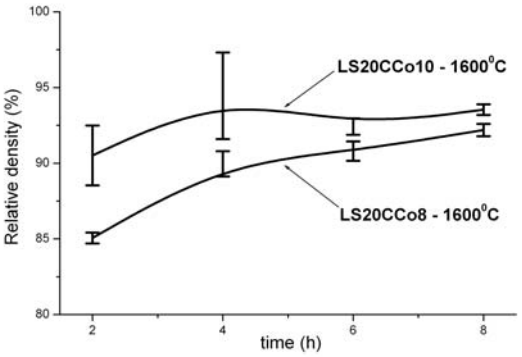
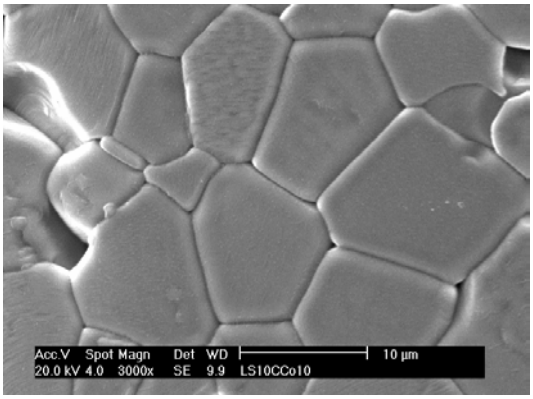
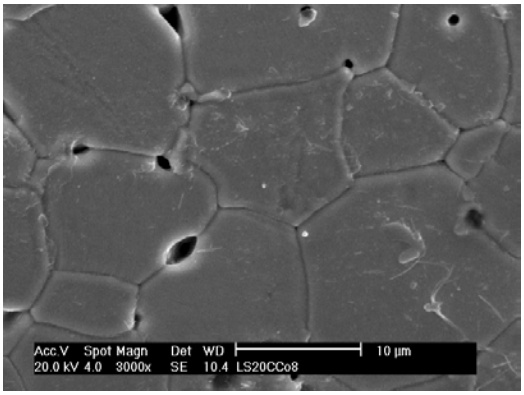


Figure 4 - Sintered densities data for compositions LS20CCo8 and LS20CCo10 after sintering at 1600°C.

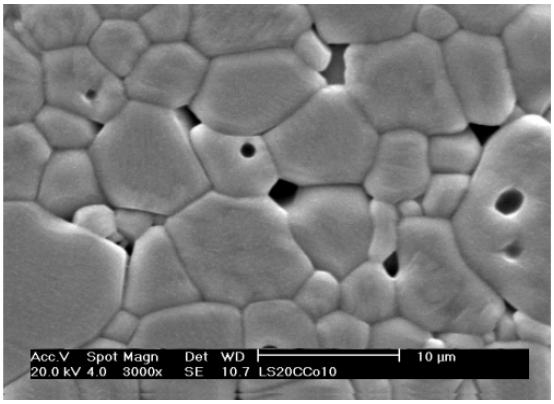
The microstructural analysis of the sinterized lanthanum chromite from the samples after sintering at 1600°C in some studied compositions showed microstructural aspects, such as homogeneity, grains with sizes of approximately 5 - 10 μm, porosity located mainly in the grain boundaries, compatible with the respective values of density. The microstructures observed for LS10CCo10, LS20CCo8 and LS20CCo10 samples are presented in Fig. 5 (a, b and c), respectively.



(a)



(b)



(c)

Figure 5 – Micrographs (MEV) from the compositions (a) LS10CCo10, (b) LS20CCo8 and (c) LS20CCo10.

Conclusions

The studies of synthesis of doped lanthanum chromite powders, the secondary phases formation for all the compositions formulated with strontium doping were observed.

The size particles for all compositions synthesized by combustion reaction synthesis were 70nm.

The samples sinterized at 1600°C/4 hours, using CoO powder protection showed great values of relative densities. For the composition $La_{0.80}Sr_{0.20}Cr_{0.90}Co_{0.10}O_3$, for instance, a value of 94.86% of theoretical density was obtained. This magnitude of density demonstrates that it is possible to sinterize lanthanum chromite at shorter times than those reported in literature, namely, at least 10 hours.

The adequate use of the dopants and the optimized conditions of sintering allowed the increase in the density of the compact material, in average, above 90% of the theoretical density for each studied composition.

The density values of sinterized material are adequate for applications as SOFC interconnector (~90% theoretical density).

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