

# SYNTHESIS AND SINTERING BEHAVIOR OF THE LANTHANUM CHROMITE DOPED WITH STRONTIUM AND COBALT FOR SOFC INTERCONNECT APPLICATIONS

L.F.G. Setz, H.P.S. Correa, C. Yamagata, S.R.H. Mello-Castanho  
IPEN, Energy and Nuclear Research Institute, Av. Lineu Prestes, 2242  
05.508-900 São Paulo, SP, Brazil.

## ABSTRACT

Lanthanum Chromite has been the main candidate as interconnect material for high temperature fuel cell applications, SOFC. So all researches on the direction to clarify some aspects of this material continue to be an interesting contribution to understand and modify the behavior of the Lanthanum Chromite in use. The effort of this work is attaining doped Lanthanum Chromite by combustion synthesis, optimizing the parameters of the synthesis process and studying the influence of the conditioning powder process as milling, atmosphere and temperature of the sintering and also additives concentration on the final density, crystalline structures and expansion thermal behavior. The main characterization techniques used were BET determinations, Archimedes density method, dilatometry, scanning electronic microscopy, X ray diffraction and Rietveld method for refinements of the phases quantification. The homogeneous Lanthanum Chromite doped with Strontium and Cobalt with sintered densities around 97th% and thermal expansion coefficient compatible for SOFC applications ( $12 \times 10^{-6} \text{ } ^\circ\text{C}$ ) were attained with control of the adequate concentrations additives, synthesis conditions, the control of the atmosphere, time and temperature of the sintering process.

## INTRODUCTION

The rapid development of fuel cell technology in recent years, together with a global effort to reducing greenhouse gas emissions is focusing world opinion on options for future hydrogen economies. The solid oxide fuel cells (SOFC) are promising clean and efficient power sources, particularly for stationary applications [1,2]. Although many of the challenges in the development of high performance low-cost SOFCs can be solved with improving materials. Among one of the major challenges in the SOFC development is the interconnect materials whose the main attribute is to provide the conductive path for electrical current to pass between the electrodes and the external circuit [3, 4]. This material must have good electrical conductivity to minimize ohmic losses. The interconnect material is contacted to both cathode and the anode, that is required to be stable in both oxidizing and reducing conditions. SOFCs operate at high temperatures and the interconnect material must have a thermal expansion coefficient (TEC) close to those of other cell components to minimize thermal stresses. And also other requirements of the interconnect materials include adequate mechanical strength, low permeability to oxygen and hydrogen, reasonable thermal conductivity and easily to fabricate to contributing for the cost-effective manufacture of fuels cells.

Several types of  $\text{ABO}_3$  Chromites, including  $\text{La}(\text{M})\text{CrO}_3$ , where M is Mg, Ca, Sr or Co have been developed that meet these requirements. It is also required a high density to provide gas tightness in the interconnection. It is known that most Cr-containing oxides are difficult to sinter in air to high density because of vapor-phase transport, which cause grain growth without densification [1, 5, 6]. Sintering of Chromites in air is relied on the formation of liquid phases by introducing sintering aids, such as, Co, Ni or Ca with formation of second perovskite phase, although some problems were reported resulting from such additives in

SOFC applications [7,8,9]. Although Co additions promote the densification of  $\text{LaCrO}_3$  in air at low temperatures it also increase the expansion thermal coefficient (TEC) after sintering. The influence of the Sr- doping, is verified to contributing by the reduction on the TEC in the same conditions.

Besides of sintering processing, the precursor powder are primordial to obtain high density interconnects. The characteristics of the precursor powder depend on the method of the synthesis. There are a variety of methods of multi-cation oxide precursor powder synthesis. Conventional method for multi-cation oxide preparation is based on solid-state reaction technique. In this method, ball milling and grinding steps are time consuming and energy intensive. The calcinations and sintering with long holding times at high temperatures make the method expensive [2]. Citrate method (Pechini) [10,11] is another way for multi-cation oxide synthesis. Popa [12] synthesized  $\text{LaCoO}_3$  powders by a polymerizable complex technique based on the Pechini-type reaction route.

Synthesis by combustion reaction is been used to produce a lot of ceramic materials. This method's main advantage is the possibility of obtaining homogenous composition nanometric particles ceramic powder. It is considered a fast, simple and economic process [13]. 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, reaching high temperatures simultaneous with a fast and sustainable reaction [14]. The metallic oxide production by simple calcinations process, where the metallic nitrates are decomposed into oxides, needs a constant supply of energy. On the other hand, the combustion reaction, usually has its ignition at temperatures lower than the phase formation ones. The energy released during the exothermic reaction between the nitrates and the fuel in the combustion reaction can heat fast and intensely the system, maintaining the heat for a long period, even without an external heat source to guarantee the desired phase formation [14, 15]. That is the reason why the combustion synthesis is considered more worth-while than simple thermic calcinations. The heat releases gas species before the nitrate decomposition, when the water is released, the temperature increases starting the ignition of the fuel (oxidation). The reaction's outset is observed by flames that achieve high temperatures, around  $1000^\circ\text{C}$  [14], they guarantee ceramic formation and crystallization in a short period of time. This is a method that is considered simple because it does not need further treatment steps.

Oxi-reduction reactions as well combustion reactions are usually exothermic and if they are not properly controlled, an explosion can happen. Nevertheless, the reactions from nitrates and urea are self propagating they are exothermic but not explosive. Urea is commercially available, low price and produces higher temperatures what makes it interesting to the synthesis process [14, 15, 16](Segadães et al., 1998).

The base of combustion reaction for powder synthesis comes from explosives and propellants' thermodynamics concepts. Jain [17] proposed a simple calculation method of stoichiometric coefficient establishing a valence balance of elements on reducing and oxidant reactants form the mixture. Stoichiometric composition calculation of the nitrate/urea mixture is based on the total valences from the fuel and oxidant, and it is valid when the concerning valence values are:  $[(\sum \text{oxidant elements coefficients (O)} / n(-1)\sum \text{reducing element coefficient (F)}) = 1]$  and it corresponds to the maximum energy released to the reaction. The considered valences are the ones form the product elements of the combustion reactions that are:  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$ . In this calculation, the carbon and the hydrogen are considered reducing elements, presenting the valences +4 and +1 respectively. The oxygen is considered an oxidant element with a valence of -2, and the nitrogen is considered valence zero.

When extrapolate this concept to oxides that means metals like La and Cr (or other) can be considered reducing elements. Taking into account the structure Lanthanum Chromite ( $\text{LaCrO}_3$ ), it is considered the valences corresponding to the coordination of the desired components, that is +3 for both. In stoichiometric mixtures, there are a relation between oxidant and reducing total power and the reaction heat calculated from the formation heat of the reactants and products from the reaction [18]. The temperature of the flame produced by the combustion depends on the reducing power available and the quantity of gases that are formed. This conditions influence the characteristics of the produced powder, like particle size and agglomeration state.

In their studies, Manoharan and Patil [19], observed the urea influence in some characteristics of the produced powder. After the reaction its use provided a better porosity because this fuel produces less gas per mol of fuel (1 mol of urea = 1 mol of gas) [13, 19]. The metallic nitrate are the most used salts to the synthesis on combustion reactions since they are soluble in water and in general they have low decomposing temperatures what guarantees a good homogeneity in the solution.

Biamino and Badini [20] studied the behavior involving nitrates and the urea during the combustion reaction to obtain  $\text{LaCrO}_3$  and they observed that besides the apparent simplicity of the method, a series of intermediate complex compounds are formed and they are difficult to present in only one chemical reaction.

In the last years many studies are been made to obtain  $\text{LaCrO}_3$  from combustion reaction technique using several types of fuels. Morelli [11, 21, 22], as well as Biamino and Badini [20] used urea as fuel to the synthesis of  $\text{LaCrO}_3$ . Comparing this route of synthesis to the oxide mixture technique and Pechini, Morelli [11], they observed that the obtained powder from combustion presented better sinterability than ones obtained by other techniques.

The present work reports synthesis of Cobalt and Strontium doped Lanthanum Chromite by combustion reaction synthesis. This method was chosen because it is a relatively simple and fast method, and it uses for the reactions as start materials or reagents easily found in the market [13]. However this simple method is strongly influenced by the kind and the concentration of the fuel and the kind and content of the additive used. It will influence the structures and the morphology of the powder resultant.

## EXPERIMENTAL

The aqueous nitric solutions of the metals were prepared by dissolving their respective nitric salts,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (>99% Aldrich),  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (98% Aldrich) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98% Aldrich), Strontium Nitrate ( $\text{Sr}(\text{NO}_3)_2$  (99%), Urea ( $(\text{NH}_2)_2\text{CO}$ ) as fuel also were used as start materials. The prepared nitric salt solutions of metals were mixed in stoichiometric amounts. The prepared compositions as  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$ , with x varying from 0 to 0,2 and y from 0 to 0,10 and labeled as p.e. LS20CCo5 corresponding to  $\text{La}_{0,80}\text{Sr}_{0,20}\text{Cr}_{0,95}\text{Co}_{0,05}\text{O}_3$ . The nitrate salts were stoichiometrically mixed, (according to Eq. 1), in water media with simultaneous urea addition. The influence of the molar ratio of urea to Lanthanum nitrate was observed varying the molar ratio from 1:3 to 1:6 as previous studies[23, 24]. The solutions were warmed in a hot blanket, releasing the water steam and volatiles species until the temperature of the starting the reaction that occurs quickly following the flame. The powders resultants as foam were observed by SEM (Philips mod. XL30) analysis. Same samples were attrition milling in isopropilic media for 2 hours before specific surface determinations (Quanta Chrome, Nova-2000). X-ray diffractions using the diffractometer Rigaku - RINT2000 with Cu or Cr rotating anode and the Rietveld method refinements were used for identify the crystalline structures, phases presents and theoretic densities. For sintering studies pellets were conformed by pressing (90MPa) in cylindrical

shaped. 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 1600°C for steps varying from 2 to 10 hours. For all heating treatments a protect CoO powders bed or inert oxide 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. Thermal expansion coefficient (TEC) were determined by dilatometric experiments in air (Netzsch, mod. DIL402C).

## RESULTS AND DISCUSSION

The powders results after combustion synthesis show soft foam form consisting of aggregated powder for all composition studied. Calcinations treatments are not required for this process but the rate between the reactants and the fuel may influence on the final powders aspects.

According with stoichiometry for the combustion reaction the rate of La:urea to obtain pure  $\text{LaCrO}_3$  is 1:5. However in this studies the influence of the fuel concentration on the combustion reaction synthesis showed in Figure 1 that the highest surface specific area was observed on powders resultant when de 1:4 fuel/La were used. The X-ray diffraction diagrams resultants from these same samples are shown in the Figure 2.

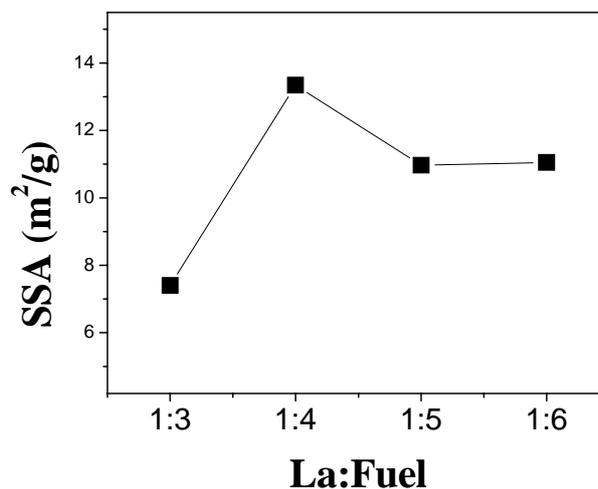


Figure 1: Specific surface area variations as the fuel concentration used for synthesis.

XRD patterns of  $\text{LaCrO}_3$  synthesized by combustion reaction process using different rate of La:fuel is given in Figure 2. The  $\text{LaCrO}_3$  phase was indexed for samples from the ratios of 1:6, 1:5 and 1:4. The XRD pattern from the 1:4 rate specimen show that it was slightly unpurified by a small amount of a second phase whose peaks were identifiable as belong to the  $\text{LaCrO}_4$ ,  $\text{SrCrO}_4$  compounds. X-ray diffraction analysis results from compositions the doped Lanthanum Chromite. XRD patterns from the sample obtained using 1:3 (La:fuel) rate almost  $\text{LaCrO}_3$  peaks is not observed. The influence of the additive on the  $\text{LaCrO}_3$  combustion synthesis was studied using the rate Lanthanum: urea constant as 1:4.

The sponge SEM micrographs are show in Figure 3 for (a) pure  $\text{LaCrO}_3$ , (b) Co doped  $\text{LaCrO}_3$ , (c) Sr doped  $\text{LaCrO}_3$ , and as labeled LC, LCCo10, LCSr10, respectively. SEM micrographs from Figure 3 (a) and (b) for LC and LCCo20 specimens reveled agglomerates formed by very fine size particles lightly linked. In the case of the sample Sr doped submicron particles are also founded with acicular or plate form as showed in the Figure 3(c).

This particular morphology may be related to  $\text{SrCrO}_4$  phase. Similar results were obtained for  $\text{LSrCCo}$  compositions Figure 3(d).

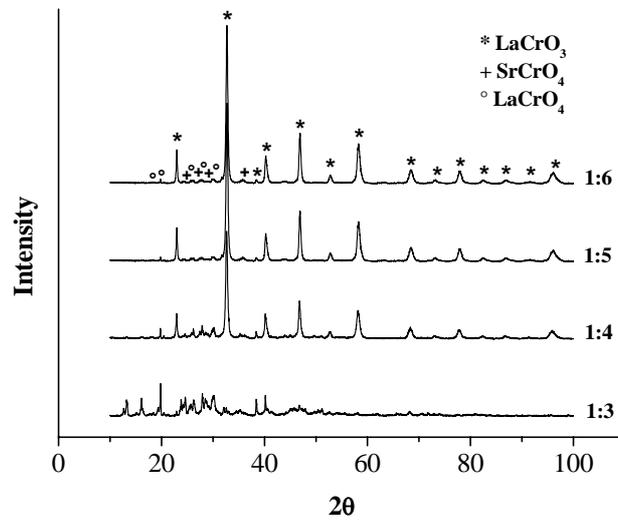
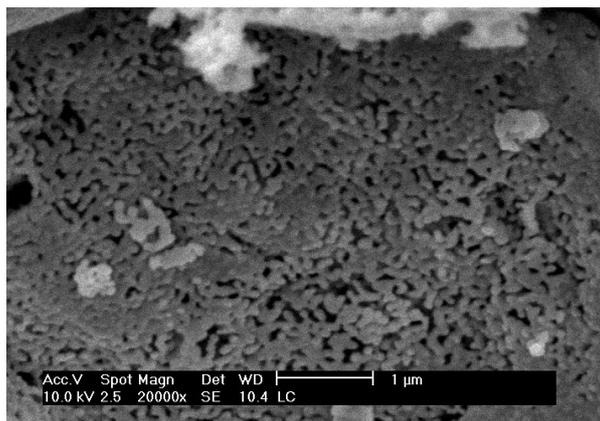
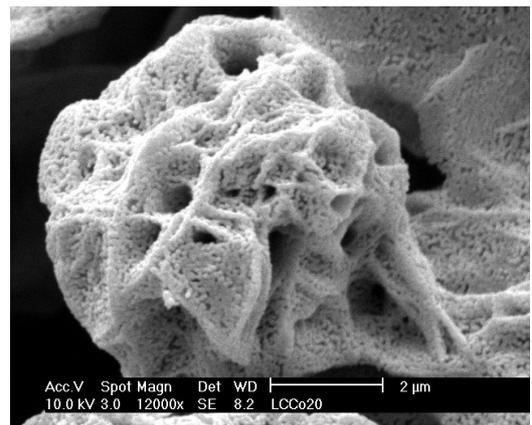


Figure 2. XRD patterns of powders from several ratios La: fuel used in combustion reaction.



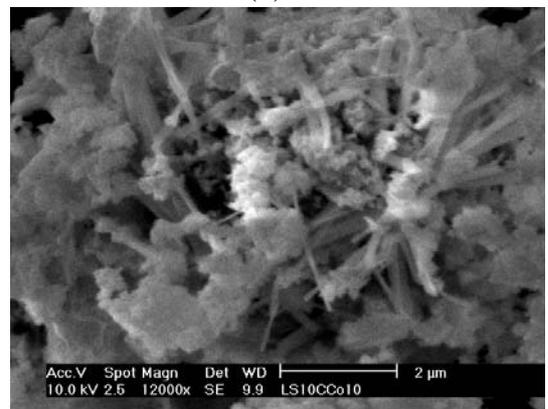
(a)



(b)



(c)



(d)

Figure 3. SEM micrographs from (a) LC, (b) LCC20, (c) LS15C e (d) LS10C10 samples as obtained.

The main objective of the Sr additions on  $\text{LaCrO}_3$  is to promote the increase on the electric conductivity [25, 26, 27]. DRX diffraction patterns of Sr doped  $\text{LaCrO}_3$  are given in Figure 4. The  $\text{LaCrO}_3$  patterns peaks (n.71-1231-ICDD) were observed in all compositions. The small peaks founded refer to  $\text{LaCrO}_4$  e  $\text{SrCrO}_4$  phases according to card pattern n. 49-1710 and n. 35-74 3 respectively.

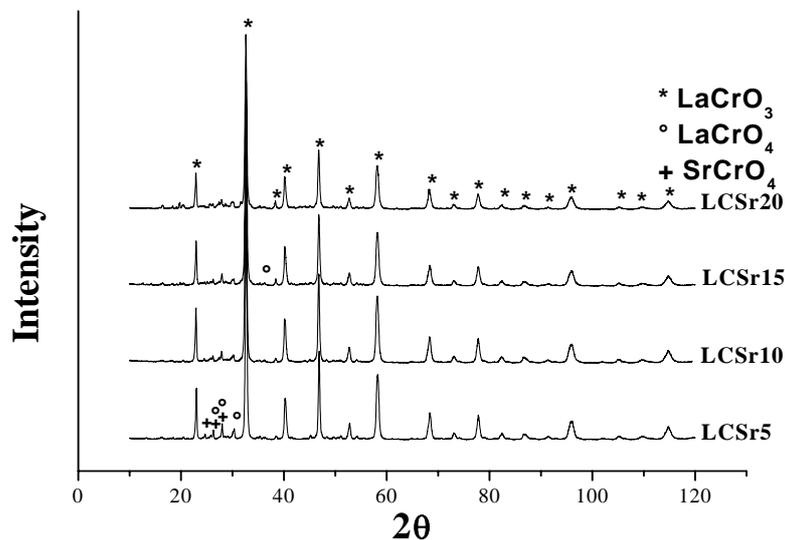


Figure 4 – Diffraction patterns from the powder samples of Sr- $\text{LaCrO}_3$ .

The quantitative analyses phases were made using the Rietveld method. The results presented on Figure 5 show that the quantity of  $\text{LaCrO}_3$  formed phase is higher than 90 wt % for all conditions studied. The concentration of  $\text{SrCrO}_4$  increases by increasing the amount of Sr added. It is possibly related to the solubility limits of Sr in the  $\text{LaCrO}_3$ .  $\text{LaCrO}_4$  is considered an intermediate phase in the lanthanum Chromite formation, because it becomes  $\text{LaCrO}_3$  at around  $600^\circ\text{C}$  losing one oxygen [28, 29].

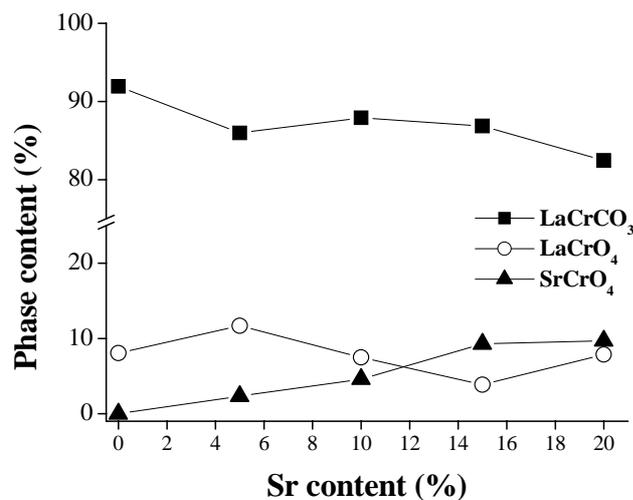


Figure 5. Quantified phases presents on Sr doped  $\text{LaCrO}_3$ .

The values of specific surface areas determined for the powder doped with Sr are given in Table I. It can be observed that the addition of Sr results in the increasing superficial area of the powder. The medium size of the particles calculated from the values of SSA (specific surface area), were 150 nm to pure Lanthanum Chromite and 110 nm to LaCrO<sub>3</sub> doped with Sr.

Table I. SSA (m<sup>2</sup>/g) Sr content on doped LaCrO<sub>3</sub> as synthesized.

Sample	SSA (m <sup>2</sup> /g)
LC	606 ± 0,05
LCSr5	8,05 ± 0,04
LCSr10	7,98 ± 0,05
LCSr15	8,37 ± 0,06
LCSr	8,44 ± 0,04

Addition of Co in LaCrO<sub>3</sub> has the main objective to improve the sintering process [22, 30]. X-ray analysis performed in powders from samples LCCo are presented on Figure 6. It can be observed that LaCrO<sub>3</sub> is formed in all the compositions. Therefore it is also observed a slight enlargement of the peaks while the Co concentration increases. It is related to the solid solution formation by Co Cr substitutions.

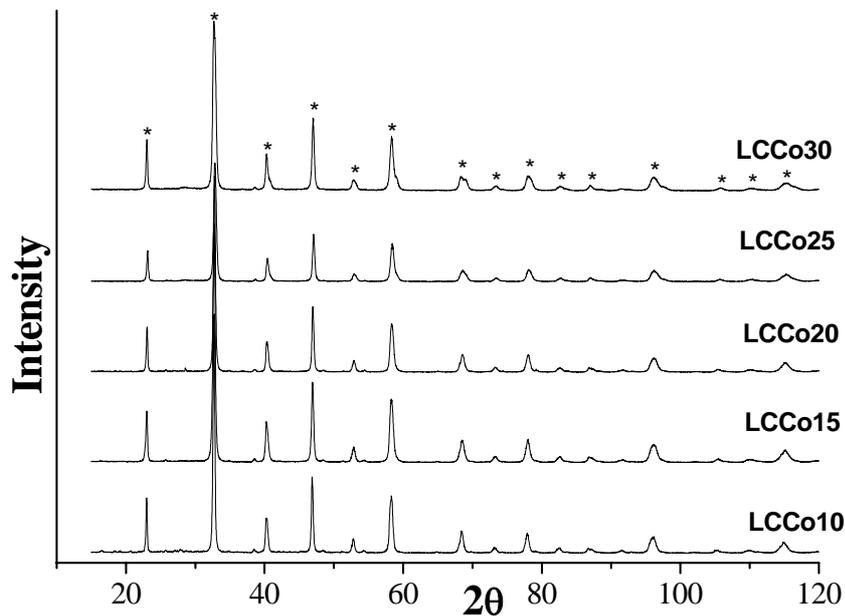


Figure 6. XRD diffractions patterns from Co doped LaCrO<sub>3</sub>.

The values of specific surface areas determined for the powder doped with Co are given in Table II. It can be observed that the additions of Co results in the increasing superficial area of the powder are lower than the Sr doped LaCrO<sub>3</sub>. The medium size of the particles calculated from the values of SSA (specific surface area), were 100nm for LCCo15 and LCCo25 compositions.

Table II. Specific Superficial Area (SSA) obtained from pure Lanthanum Chromite powder and cobalt doped powder

Sample	SSA (m <sup>2</sup> /g)
LC	6,06 ± 0,05
LCCo10	5,70 ± 0,03
LCCo15	9,18 ± 0,06
LCCo20	6,51 ± 0,05
LCCo25	8,59 ± 0,05
LCCo30	7,24 ± 0,04

The influence of strontium and cobalt simultaneous addition in the synthesis reaction of Lanthanum Chromite doped with both additives show the X-ray diffraction spectra similar to the obtained for previous compositions, LSrC and LCCo. Besides the LaCrO<sub>3</sub> characteristic picks, there are also observed the presence of LaCrO<sub>4</sub>, SrCrO<sub>4</sub> and Sr(NO<sub>3</sub>)<sub>2</sub> phase peaks formed in the Sr presence. All crystalline structures refined by Rietveld method had the pure Lanthanum Chromite (LC) structure as base, with Sr substituting La and Co in the position of Cr in a *Pnma* symmetry (orthorhombic) indexed from XRD pattern card 89098 – ICSD. The considered occupation sites were based on starting reactants stoichiometry during the refining, maintaining their nominal values. In all the refining the obtained residue were within the values typically accepted as goodness of fit (S) lower than 1.7.

The whole LSCCo samples presented LaCrO<sub>3</sub> besides the LaCrO<sub>4</sub> and SrCrO<sub>4</sub> phases. For the Rietveld method refinement, the presence of the 3 phases in the composition was considered. The quantitative analyses from Rietveld showed in Table III that while the Co concentration increases for the same Sr concentration, the density values also increase. And while the Sr quantity increases, maintaining the Co concentration as constant, the density values decrease. This behavior is probably due to the atomic mass difference from the basic structure components (La and Cr) and the doping elements and (Sr and Co) it is consistent when each additive was used.

Evidently the LaCrO<sub>3</sub> is the dominant phase identified in all synthesized compositions. Nevertheless, its concentration varies according to the doping concentration used. The same behavior was observed in the samples containing Sr (LCSr) only, indicating that the presence of this additive may to induce secondary phase formation.

Table III. Phases content in LSCCo compositions quantified by XRD using Rietveld methods refinements.

PHASES	LS10CCo5	LS10CCo8	LS10CCo10	LS20CCo5	LS20CCo8
LaCrO <sub>3</sub>	85,03	83,03	82,1	73,92	71,24
LaCrO <sub>4</sub>	7,74	6,82	5,63	11,64	15,69
SrCrO <sub>4</sub>	7,23	10,15	12,27	14,44	13,07

Specific surface area values determined for the Lanthanum Chromite powder simultaneously doped with strontium and cobalt are shown in Table IV. It is observed that increasing the doping concentration, the SSA value increases too. At the same time, the

average particles' size, calculated by the SSA values was 70 nm for all compositions, using the calculated density from the crystallographic data obtained by Rietveld method.

Table IV. Specific Superficial Area (SSA) for the compositions LSCCo as attained.

Composition	SSA(m <sup>2</sup> /g )	Composition	SSA(m <sup>2</sup> /g )
LS10CCo5	12,76 ± 0,06	LS20CCo5	13,25 ± 0,06
LS10CCo8	13,08 ± 0,05	LS20CCo8	13,34 ± 0,05
LS10CCo10	12,93 ± 0,04	LS20CCo10	13,98 ± 0,05

Before sintering process the powders were milled and press conformed. After conditioning by milling, a significant increase in the SSA as resulted due the sponges' desegregation (Table V). This fact also improves to the sintering powder activity by increasing the surface area.

Table V. SSA (m<sup>2</sup>/g) values for the samples of LSCCo, after milling.

Composition	SSA milling (m <sup>2</sup> /g )	Composition	SSA milling (m <sup>2</sup> /g )
LS10CCo5	17,66 ± 0,08	LS20CCo5	16,85 ± 0,08
LS10CCo8	18,35 ± 0,07	LS20CCo8	17,84 ± 0,07
LS10CCo10	18,53 ± 0,05	LS20CCo10	18,55 ± 0,07

The powder after milling were pellet shaped and to seek the mass reduction from losses by Co volatilization during sintering, it was used a protector powder bed of CoO in the sealed Al<sub>2</sub>O<sub>3</sub> crucible. The loss mass with the temperature is given in the Figure 7. Analyzing the mass variation with time and sintering temperature, maintaining Co concentration as constant (10% in mol) in all samples it is observed that even with the powder protect bed there are mass losses. This behavior in Figure 7 shows that this loss increases with sintering time until 4 hours of treatment and after this period of time, it becomes constant.

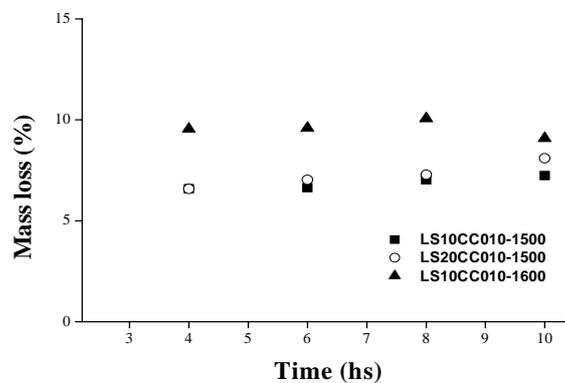


Figure 7. Mass loss variation from sintering samples at 1500 and 1600°C by sintering time.

As this results the mass loss increase as the Sr content in  $\text{LaCrO}_3$  when the temperatures used are 1500 or 1600°C. In sintering samples on same experimental conditions (1600°C/10 hours), it is verified a mass loss of 6.14% for LCSr10 composition and 9.77% for LCSr20 sample composition. These results show that the mass loss during Lanthanum Chromite sintering is influenced by the time and composition and not only by the temperature used because similar values were obtained for the same composition sintering at 1500 and 1600°C. The mass loss, probably happened due to the volatilization of compounds made of Sr, Cr and maybe Co, even using protector bed powder.

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 Figure 8. 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.

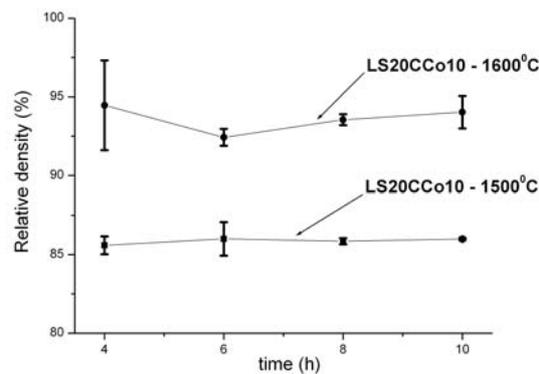


Figure 8. Influence of the time and the temperature on the sintered densities of the compositions containing 10%(mol) Co and 20%(mol) Sr after sintering at 1500 and 1600°C.

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. Figure 9 shows that, by increasing sintering temperature and Sr concentration, the values of density after sintering were increased [31]. It may attribute to the  $\text{SrCrO}_4$  liquid phase formed in the first stage in sintering, with low-melting point than  $\text{LaCrO}_3$  [32].

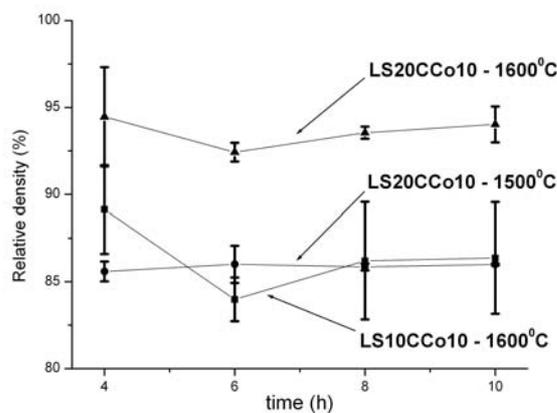


Figure 9. Influence of the time and the temperature on the sintered densities of the compositions containing 10%(mol) Co and 10-20%(mol) Sr after sintering at 1500 and 1600°C.

Despite the Co has proved to be a great assistant in the densification process a significant contribution of Sr in the same phenomenon is observed. The values of density attained at 1500°C for the composition with 20% of Sr (mol) are practically the same of that at 1600°C with 10% of Sr.

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 Figure 10. 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  $(78.68 \pm 0.17)\%$ .

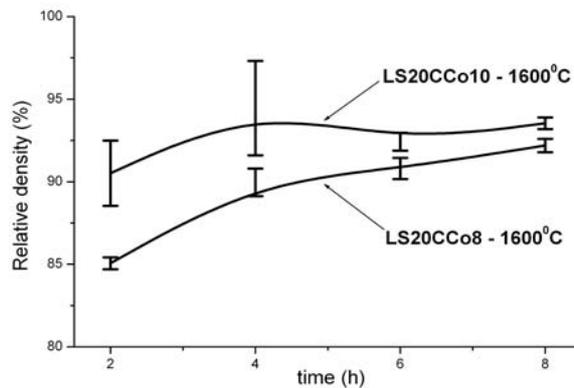


Figure 10. Sintered densities data for compositions LS20CCo8 and LS20CCo10 after sintering at 1600°C.

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  $\mu\text{m}$ , 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 Figure 11(a, b and c), respectively.

The Cobalt present in  $\text{LaCrO}_3$  helps the densification and also contributes to increase the thermal expansion coefficient (TEC) what consists one of the restrictions to its use in solid oxide fuel cell, SOFC. For this reason the Co concentration was reduced to achieve high densities and compatible thermal expansion coefficient (TEC) to the specification to application on SOFC.

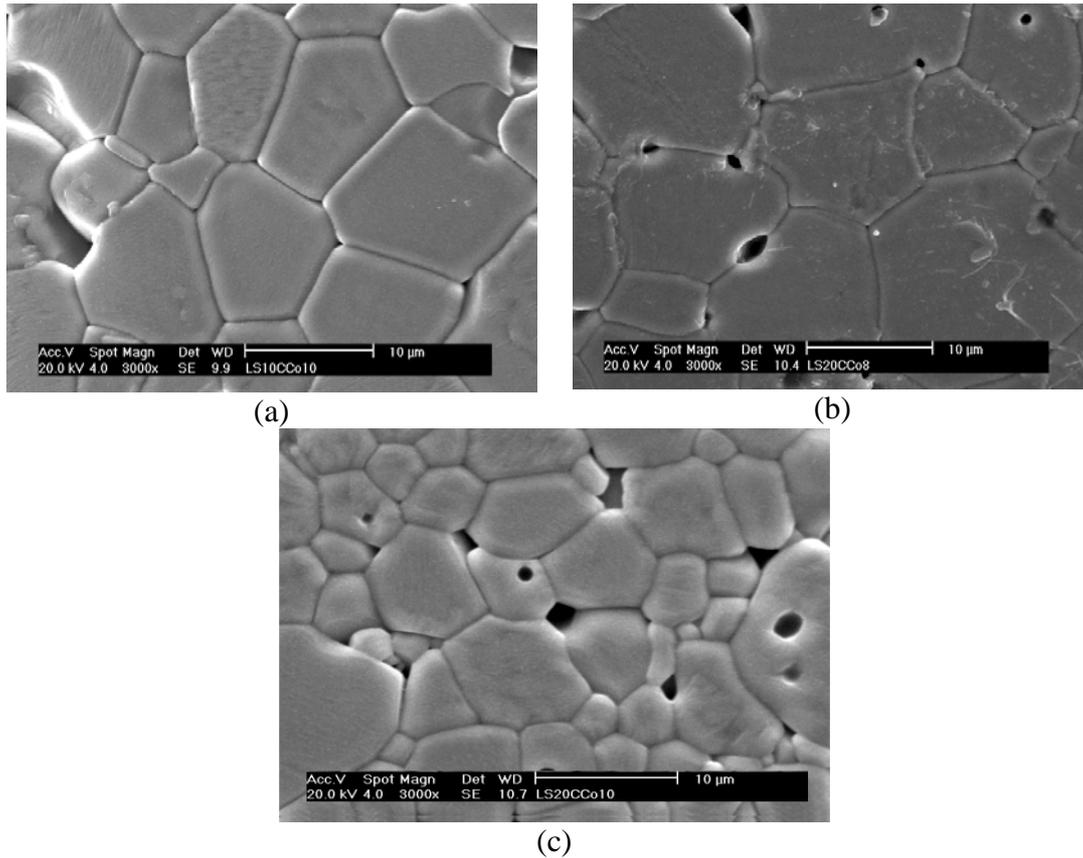


Figure 11. Micrographs (MEV) from the compositions (a) LS10CCo10, (b) LS20CCo8 and (c) LS20CCo10.

The thermal behavior of Lanthanum Chromite strontium and cobalt doped until the temperature used in a SOFC (1000°C) with normal air atmosphere is reported on Figure 12. This results show that all the tested compositions presented similar behavior of thermal expansion with the increase of temperature.

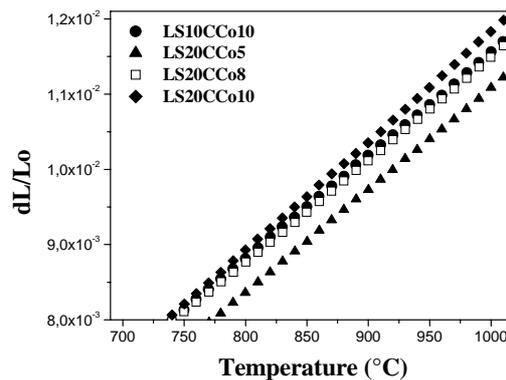


Figure 12. Sr, Co-doped  $LaCrO_3$  Linear thermal expansion in air.

Calculating the thermal expansion coefficient for each composition (Table VI), for the same range of temperature, it is observed that it increases when the Co concentration increases. However comparing these results with the specified for SOFC application (YSZ –  $10,5 \times 10^{-6}/^{\circ}C$ ), it is verified that there are still adjustment to be made in the additive concentration used.

Table VI. Thermal expansion coefficient values (TEC), within the temperatures 250 e 1000°C, in air.

Composition	Valores de TEC (*10 <sup>-6</sup> /°C) 250 - 1000°C
LS10CCo10	13,4
LS20CCo5	13,0
LS20CCo8	13,1
LS20CCo10	14,0

## CONCLUSIONS

Sr, Co-doped LaCrO<sub>3</sub> nanometric particles size, in order the 70nm, were attained by combustion synthesis reactions. The LaCrO<sub>4</sub> and SrCrO<sub>4</sub> secondary phases for all the compositions formulated with strontium doped were observed. The samples sinterized at 1600°C/4 hours, using CoO powder protection showed great values of relative densities. For the composition La<sub>0.80</sub>Sr<sub>0.20</sub>Cr<sub>0.90</sub>Co<sub>0.10</sub>O<sub>3</sub>, 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.

## ACKNOWLEDGES

The authors wish to thank the State of Sao Paulo Research Foundation (FAPESP/BR), proj.n. 2006/06357-4; National Council for Scientific and Technological Development (CNPq/BR) of Brazil; CAPES/Br ,

## REFERENCES

- [1] N.Q. Minh, Ceramic Fuel Cells, *J. Am. Ceram. Soc.*, **76**, p. 563-88 (1993).
- [2] S.P.S. Badwal, Stability of solid oxide fuel cell components, *Solid State Ion.*, **143**, p. 39-46 (2001).
- [3] D. Linden, *Handbook of Batteries and Fuel Cells*, McGraw-Hill Book Company (1984)
- [4] J.W. Fergus, Lanthanum chromite-based materials for solid oxide fuel cell interconnects, *Solid State Ion.*, **171**, p. 1-15 (2004).
- [5] S. Hayashi, K. Fukaya, H. Saito, Sintering of lanthanum chromite doped with zinc or copper, *J. Mater. Sci. Lett.*, **7**, p. 457-58 (1988).
- [6] L.Groupp, H.U. Anderson, Densification of La<sub>1-x</sub>Sr<sub>x</sub>CrO<sub>3</sub>, *J. Am. Ceram. Soc.*, **59**, p. 449-50 (1976).
- [7] L.W. Tai, P.A. Lessing, Tape casting and sintering of strontium-doped lanthanum chromite for a planar solid oxide fuel cell bipolar plate, *J. Am. Ceram. Soc.*, **74**, p. 155-60 (1991).
- [8] W.Z. Zhu, S.C. Deevi, Development of interconnect materials for solid oxide fuel cells. *Mater. Sci. Eng. A*, **348**, p. 227-43 (2003).
- [9] L.A. Chick, J. Liu, J.W.; Stevenson, T.R. Armstrong, D.E. McCreedy, G.D. Maupin, G.W. Coffey, C.A. Coyle, Phase transitions and transient liquid-phase sintering in calcium-substituted Lanthanum Chromite, *J. Am. Ceram. Soc.*, **80**, p. 2109-20 (1997).
- [10] N. Sakai, T. Kawada, H. Yokokawa, M. DOKIYA, I. KOJIMA, Liquid-phase-assisted sintering of calcium-doped lanthanum chromites, *J. Am. Ceram. Soc.*, **76**, p. 609-16

- (1993).
- [11] M.R. Morelli, B. Derby, R.J. Brook, Combustion synthesis of  $\text{LaCrO}_3$  powders. *Cerâmica*, **42**, p.435-38 (1996).
- [12] M. Popa, M. Kakihana, Synthesis of lanthanum cobaltite ( $\text{LaCoO}_3$ ) by the polymerizable complex route, *Solid State Ion.*, **151**, p. 251-57 (2002).
- [13] V.C. Sousa, *Síntese de pós por reação de combustão para a obtenção de varistores de ZnO*, Thesis (DSc), Universidade Federal de São Carlos, Brasil (2000).
- [14] A.M. Segadães, M.R. Morelli, R.G.A. Kiminami. Combustion synthesis of aluminium titanate, *J. Eur. Ceram. Soc.*, **18**, p. 771-81 (1998).
- [15] D.A. Fumo, M.R. Morelli, A.M. Segadães, Combustion synthesis of calcium aluminates, *Mater. Res. Bull.*, **3**, p.1243-55 (1996).
- [16] V. C. Sousa, A. M. Segadães, M. R. Morelli and R. H. G. A. Kiminami, Combustion synthesized ZnO powders for varistor ceramics, *Int. J. Inorg. Mater.*, **1**, p. 235-41 (1999).
- [17] S.R. Jain; K.C. Adiga, R.P. Verneher, A new approach to thermo chemical calculations of condensed fuel-oxidizer mixture, *Comb. Flame*, **40**, p. 71-79 (1981).
- [18] H.S. Ferreira, *Processamento de pós de  $\text{Al}_2\text{TiO}_5$  Obtidos por reação de combustão, com e sem aditivos*, Thesis(DSc) - Universidade Federal de São Carlos, Brasil (2002)..
- [19] S.S. Manoharan, K.C. Patil, Combustion synthesis of metal chromite powders, *J. Am. Ceram. Soc.*, **75**, p. 1012-15 (1992).
- [20] S. Biamino, C. Badini, Combustion synthesis of lanthanum chromite starting from water solutions: investigation of process mechanism by DTA–TGA–MS. *J. Eur. Ceram. Soc.*, **24**, p. 3021-34 (2004).
- [21] M.R. Morelli , B. Derby, B. Brook, Sintering of  $\text{LaCrO}_3$ , CBECIMAT, 12°, *Proceedings...*, **1**, p. 414-17 (1996).
- [22] M.R. Morelli , B. Derby, B. Brook, Sinterização de  $\text{LaCrO}_3$  com adição de  $\text{LaCoO}_3$ . CBECIMAT, 12°, *Proceedings...*, **1**, p. 418-21 (1996).
- [23] L.F.G. Setz, *Obtenção de  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$  Por Reação de Combustão*, Thesis (MSc), Instituto de Pesquisas Energéticas e Nucleares, Brasil (2005)
- [24] R.V. Fornari,. S. Silva, S.R.H. Mello Castanho, Contribuição ao estudo da síntese do cromito de lantânio CBC, 44°, *Proceedings...*, Ref., 130-03 (2000).
- [25] S.W. Paulik, S. Baskaran, T.R. Armstrong, Mechanical properties of calcium- and strontium- substituted lanthanum chromite, *J. Mater. Sci.*, **33**, p. 2397-04 (1998).
- [26] M. Mori, Y. Hiei, N.M. Sammes, Sintering behavior and mechanism of Sr-doped lanthanum chromites with A site excess composition in air, *Solid State Ion.*, **123**, p. 103-11 (1999).
- [27] Y.J. Yang, T.L. Wen, H. Tu, D.Q. Wang, J. Yang, Characteristics of lanthanum strontium chromite prepared by glycine nitrate process. *Solid State Ion.*, **135**, p. 475-79 (2000).
- [28] J.D. Carter, H.U. Anderson, M.G. Shunmsky, Structure and phase transformation of lanthanum chromate. *J. Mater. Sci.*, **31**, p. 551-57 (1996).
- [29] A.E. Gobichon, J.P. Auffrédic, D.Louër, A temperature-dependent powder diffraction study of chromium lanthanum nitrate,  $\text{LaCr}(\text{NO}_3)_6 \cdot 12\text{H}_2\text{O}$ . *Powder Diffr.*, **15**, p. 23-25 (2000).
- [30] R. Koc, H.U. Anderson, Effect of cation substitution on the thermal expansion coefficient of  $\text{LaCrO}_3$ . *J. Mater. Sci. Lett.*, **11**, p. 1191-92 (1992).
- [31] L.F.G. Setz, S.R.H Mello Castanho, Influência das Adições de Sr e Co nas características do  $\text{LaCrO}_3$  sinterizado. CBECIMAT, 15°, *Proceedings...*, Ref., 825 (2004).
- [32] S. Simner, J. Hardy, J. Stevenson, T. Armstrong, Sintering mechanisms in strontium doped lanthanum chromite. *J. Mater. Sci.*, **34**, p. 5721-32 (1999).