

# A MICROSTRUCTURAL STUDY ON LANTHANUM CHROMITE-BASED CERAMICS<sup>1</sup>

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## **Abstract**

Lanthanum chromite-based ceramics are the main materials used as solid oxide fuel cell interconnects. The objective of this work is to investigate and to characterize the relationships between powder preparation methods and microstructural development process of metals doped lanthanum chromites-based ceramic systems. Calcium, strontium and magnesium-doped lanthanum chromites-based ceramic powders were produced by auto-ignition combustion process from respective metallic nitrates and by the traditional (solid state) ceramic method. The microstructural characterization was made by scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction and thermal analysis techniques. The results show that the chemical synthesized powders provided the production of well crystallized and sub-micrometric size powder for lanthanum chromites-based ceramics with more dense and more homogeneous grain size distribution than that produced by traditional ceramic method.

**Keywords:** lanthanum chromites; SOFC interconnects; Powder synthesis.

## UM ESTUDO MICROESTRUTURAL SOBRE CERÂMICAS À BASE DE CROMITAS DE LANTÂNIO

### **Resumo**

Cerâmicas à base de cromitas de lantânio são os principais materiais usados em interconectores de células a combustível de óxido sólido. O objetivo deste trabalho é investigar e caracterizar as relações entre métodos de preparação de pós e o desenvolvimento microestrutural destes materiais. Cromitas de lantânio dopadas com cálcio, estrôncio e magnésio foram produzidas pelos processos de combustão e do estado sólido. A caracterização microestrutural foi feita por microscopia eletrônica (MEV-EDS), difração de raios-X e análise térmica. Os resultados mostram que os pós quimicamente sintetizados proporcionaram a produção de cerâmicas mais densas e homogêneas que aqueles produzidos pelo método convencional.

**Palavras-chave:** Cromitas de lantânio; Interconectores; Síntese de pós cerâmicos.

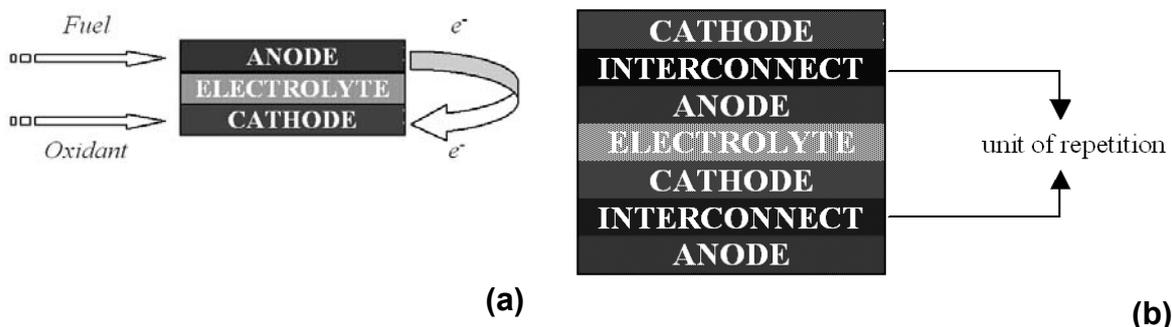
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# 1 INTRODUCTION

The solid oxide fuel cell (SOFC) is one of the most promising technologies for the production of energy, with potential to be a typical future distributed cogeneration system.<sup>(1)</sup> Typically, a SOFC system is constituted of at least seven distinct components: fuel feed, anode, electrolyte media (separating the two electrodes), cathode, oxidant agent feed (normally air), and electrical interconnectors (completing the electrical circuit) as schematically showed in the Figure 1. The perovskite ( $ABO_3$ -type) lanthanum chromite ( $LaCrO_3$ ) and especially doped  $LaCrO_3$ -based ceramics have recently received much interest as high-temperature electrode materials and solid oxide fuel cell interconnects, because they are p-type electronic conductor in oxidizing conditions and is stable to low oxygen partial pressures.<sup>(1-3)</sup>



**Figure 1.** (a) Schematic diagram of a fuel cell; (b) scheme of the connection of the anode of a single fuel cell to the cathode of the subsequent single fuel cell, constituting a solid oxide fuel cell stack.

In fact, lanthanum chromite is currently the most common candidate material since it exhibits relatively high electronic conductivity in both fuel and oxidant atmospheres, moderate stability in the fuel cell environments as well as fairly good compatibility with other cell components in terms of phase, microstructure and thermal expansion.<sup>(4)</sup> Nevertheless, the conductivity of pure lanthanum chromite is not sufficiently high for use as an interconnect material, but can be increased through doping. The electronic conductivity of the stoichiometric  $LaCrO_3$  compound is increased by substituting divalent metal ions on either the A- or B-sites of the  $ABO_3$  perovskite lattice. Many authors have indicated that both the sinterability and the electrical conductivity of  $LaCrO_3$  could be improved by the substitution of a lower-valent ion such as  $Cu^{2+}$  or  $Mg^{2+}$  at the  $Cr^{3+}$  site or of  $Sr^{2+}$  at the  $La^{3+}$  site.<sup>(4-7)</sup> Then, the most common dopants for  $LaCrO_{3-\delta}$  are alkaline-earth elements, which act as electron acceptors on the trivalent lanthanum or chromium sites, and thus increase p-type conduction by a small polaron mechanism.<sup>(8,9)</sup> The large alkaline-earth ions, most commonly strontium and calcium,<sup>(10)</sup> although barium-doped lanthanum chromite has also been reported,<sup>(2,11)</sup> occupy the lanthanum site. Magnesium, however, is much smaller and thus occupies the chromium site. Acceptor dopants (e.g. nickel, copper, cobalt) are more commonly used, although donor-doped (e.g. niobium) lanthanum chromite has been reported.<sup>(12-14)</sup> Although the lanthanum chromite phase has high electronic conductivity and good stability in both oxidizing and reducing atmospheres, it is difficult to synthesize the chromite-based perovskite

due to appreciable volatilization loss of chromium oxide at high sintering temperatures in an oxidizing atmosphere.<sup>(6)</sup>

In previous works<sup>(15,16)</sup> we investigated the microstructural development of lanthanum chromite-based ceramics doped with earth-alkaline metals and we selected some systems (ceramic formulations) more promising for further studies. In this present paper, we report a study on the microstructural characterization of the  $\text{La}_{0.90}\text{Ca}_{0.05}\text{Sr}_{0.05}\text{Cr}_{0.95}\text{Mg}_{0.05}\text{O}_3$  (LCSCM) ceramic system (mol%) obtained by auto-ignition urea-based combustion process (UCP) and traditional ceramic method (CM, mixture of oxides), both are solid-state powder synthesis methods.

## 2 EXPERIMENTAL

Powders of LCSCM lanthanum chromite composition were synthesized by solid-state reaction (auto-ignition) method (combustion method with urea as fuel) from the corresponding metallic nitrates and by traditional ceramic method from respective oxides, in both the cases using P. A. grade reagents. In the first case (UCP) the desired compositions were prepared by dissolving stoichiometric amounts of the metal nitrates in deionized water. Calculated amount of urea was also dissolved in deionized water, and the resultant solution was slowly added to the metal nitrate aqueous solution under constant stirring. The resulting complex solution was heated on a hot plate to concentrate to about 2 mol/litre on metal nitrate basis. The water in the solution quickly evaporated, the residual mixture autoignited and initiated a highly exothermic self-contained combustion process, forming a powder aggregate system. In the second case (CM) the powders were thoroughly mixed with distilled water for 8 h, using zirconia ( $\text{ZrO}_2$ ) milling media in a planetary ball mill (PM-4, Retsch). In both the cases the as-synthesized powders were milled again with distilled water for 6 h, and the homogeneous powder mixtures were dried at 200°C and then calcined at 1000°C in air for 2 h. The final ball-milled powders (Pulverisette 6 Fritsch, 24 h) were dry cold isostatic pressed at 180 MPa into pellets and sinterings were carried out in air at 1450°C (at a constant heating rate of 5°C/min) for sintering times between 2 and 6 hours.

The phase composition was evaluated by X-ray diffraction (XRD, Diano XRD-8545,  $\lambda\text{CuK}\alpha$  radiation) analysis and the densification level by Archimedes method (Mettler AE-200 analytical balance). The microstructural characterization was effected by scanning electronic microscopy (SEM, ZEISS DSM 960), X-ray energy dispersive spectroscopy (EDS, Oxford ISIS), and thermal-dilatometric analysis (SDT Q600 Thermogravimetric Analyzer and STA 402/409 E Netzsch dilatometer) used in the determination of the thermal expansion coefficient (TEC) and mass loss behavior. The average grain sizes were determined by the intercept method.<sup>(17,18)</sup> All the results that follow were obtained from three samples of each system under study.

## 3 RESULTS AND DISCUSSION

Table 1 presents the results obtained from average grain size measurements and densification analysis (densification degree in percentage of the respective theoretical density) of the studied LCSCM ceramics with respect to sintering time at sintering temperature of 1450°C, and the Table 2 presents the results concerning about electrical conductivity measurements (at 1000°C in air) and determination of the average thermal expansion coefficient (determined between 25 and 1200°C) for the LCSCM ceramics.

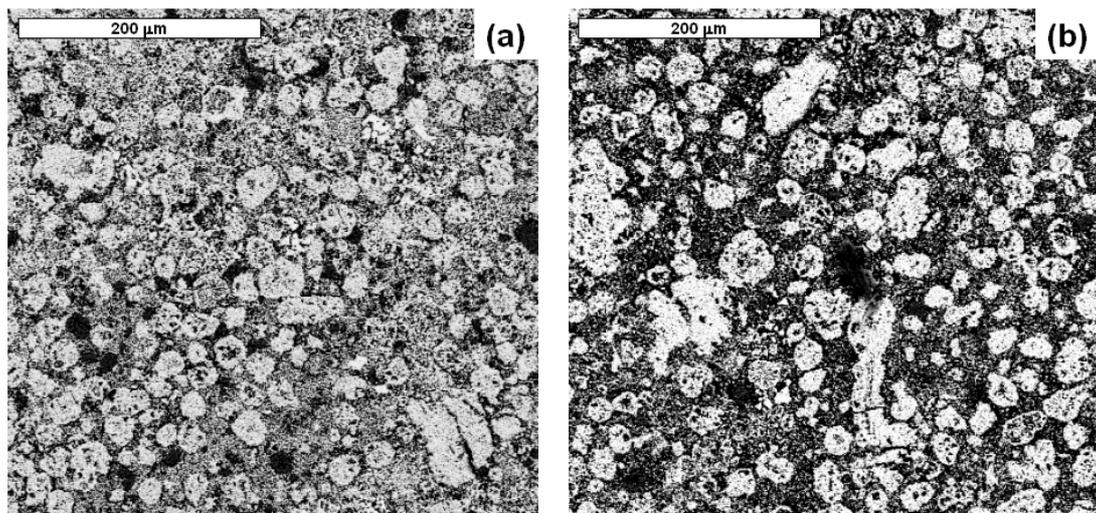
**Table 1** - Average grain size and densification degree of the LCSCM ceramics.

Sintering time (h)	Average grain size ( $\mu\text{m}$ )		Densification degree (%)	
	<u>UCP</u>	<u>CM</u>	<u>UCP</u>	<u>CM</u>
2	$8.20 \pm 1.40$	$9.70 \pm 1.80$	$92.0 \pm 0.3$	$89.8 \pm 0.3$
3	$8.90 \pm 1.70$	$10.20 \pm 1.80$	$96.1 \pm 0.3$	$91.3 \pm 0.3$
4	$9.10 \pm 1.60$	$10.60 \pm 1.70$	$97.1 \pm 0.4$	$92.4 \pm 0.3$
5	$9.40 \pm 1.10$	$11.30 \pm 1.70$	$96.3 \pm 0.4$	$93.8 \pm 0.3$
6	$9.90 \pm 2.10$	$12.20 \pm 2.50$	$95.4 \pm 0.3$	$92.3 \pm 0.4$

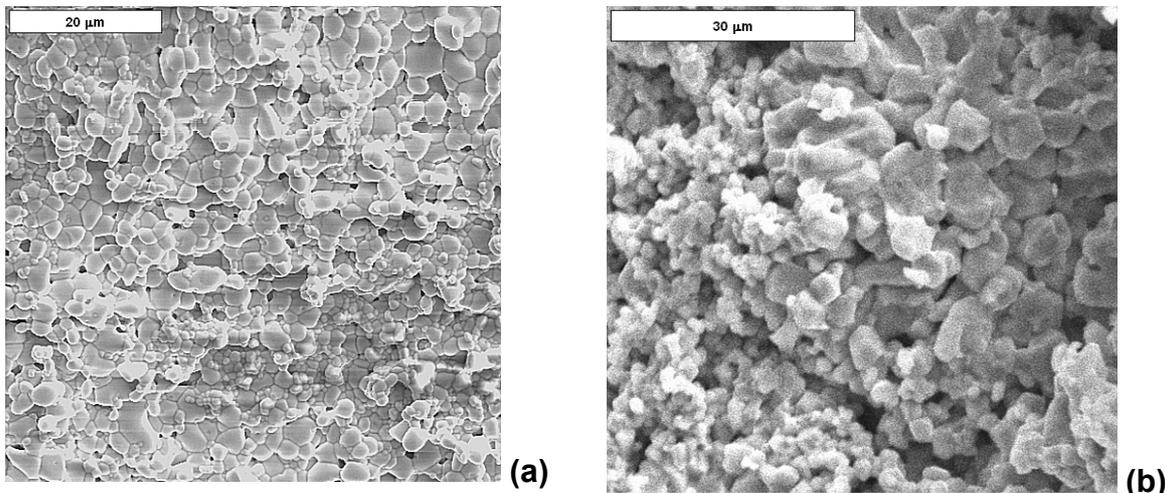
**Table 2** - Electrical conductivity and thermal expansion coefficient of the LCSCM ceramics.

Sintering time (h)	Electrical conductivity (S/cm)		Thermal expansion coefficient ( $\times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ )	
	<u>UCP</u>	<u>CM</u>	<u>UCP</u>	<u>CM</u>
2	$16.1 \pm 1.9$	$12.3 \pm 1.9$	$9.1 \pm 0.5$	$8.8 \pm 0.4$
3	$21.8 \pm 1.6$	$15.6 \pm 1.9$	$9.9 \pm 0.5$	$9.0 \pm 0.5$
4	$22.9 \pm 1.5$	$17.1 \pm 1.9$	$9.9 \pm 0.3$	$9.0 \pm 0.5$
5	$21.7 \pm 1.6$	$19.4 \pm 1.8$	$9.8 \pm 0.2$	$9.3 \pm 0.5$
6	$21.2 \pm 1.8$	$17.3 \pm 1.9$	$9.8 \pm 0.5$	$9.2 \pm 0.6$

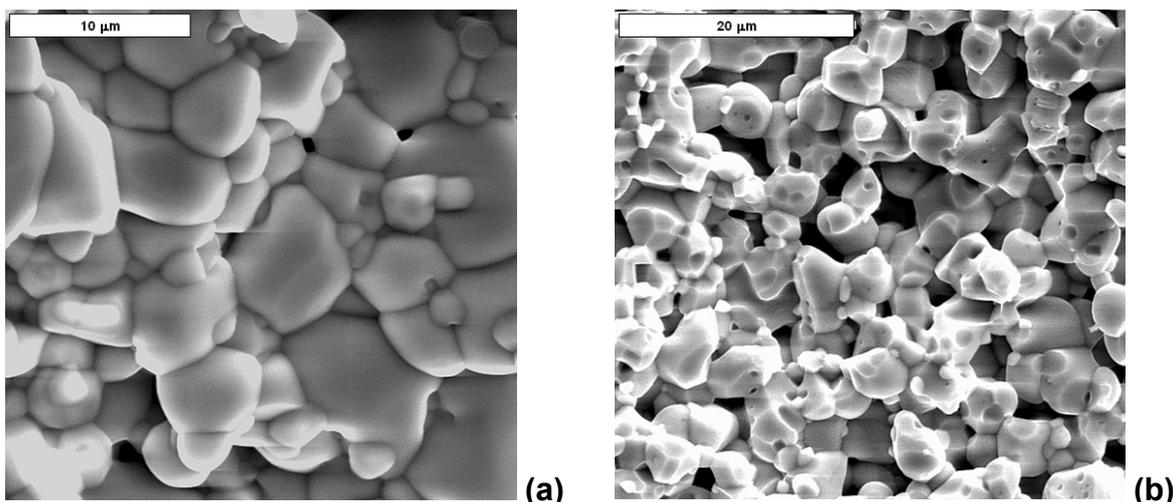
The results presented in Table 1 show that, in general, the average grain sizes (for each sintering time) are higher for MC powders than those synthesized by UCP, as well as the variability of the average grain size is greater in the first case, but in both cases there is no indication of the existence of significant grain size bimodal distributions. These observations are in agreement with the SEM powder images shown in Figure 2, which show that the CM synthesized powder is slightly larger than the UCP prepared powder, although in both cases it is note the tendency to formation of clusters or aggregated powder particles.

**Figure 2.** SEM photomicrographs of the calcined LCSCM powders obtained by: (a) combustion method (UCP); (b) mixture of oxides (CM).

These above-considered results indicate that probably the characteristics of this system still can be optimized by changes in the processing conditions and/or doping studies. This comment also finds endorsement in the fact of that the obtained density values are only acceptable, since that, in general, the SOFC interconnects must be had at least densification of 94%,<sup>(7)</sup> and the maximum apparent density of 97.1% was achieved on UCP specimens sintered at 1.450<sup>0</sup>C for 4 h. The average grain size measured on these sintered specimens was 9.10  $\mu\text{m}$ . An interesting point is that the maximum apparent density (93.8%) achieved for the CM samples was obtained for the 5 hours of sintering, for a respective average grain size (11.30  $\mu\text{m}$ ) 24% greater than that of the UCP powder prepared ceramic, probably because the CM powder is less fine than UCP powder as shown in the Figure 2 and indicated in the Table 1. The Figures 3 and 4 show SEM photomicrographs of fractured surfaces of the sintered LCSCM studied ceramics.



**Figure 3.** SEM photomicrographs of the sintered (1450<sup>0</sup>C/4h) LCSCM ceramics which powder was obtained by: (a) combustion method (UCP); (b) mixture of oxides (CM).

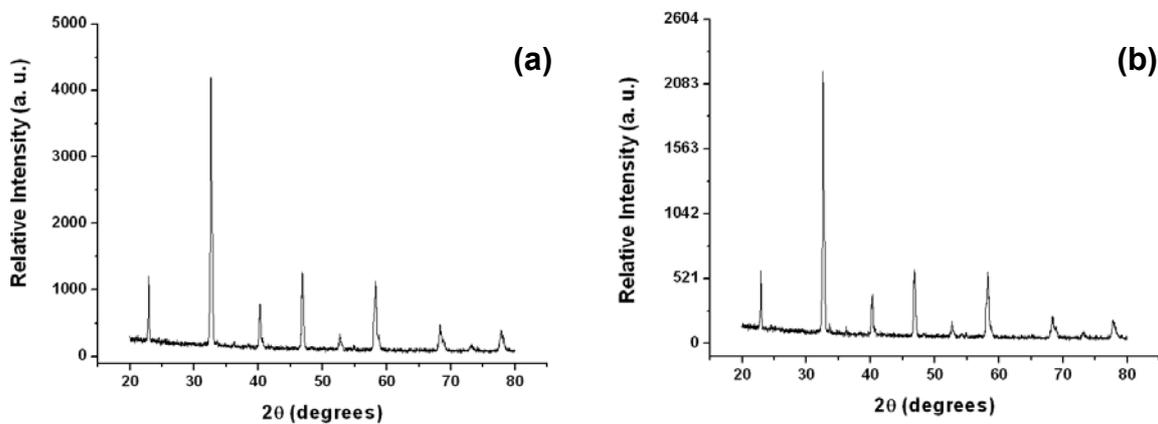


**Figure 4.** SEM photomicrographs of the best densified LCSCM ceramic systems which powder was obtained by: (a) combustion method (UCP), sintered (1.450<sup>0</sup>C/4h); (b) mixture of oxides (CM), sintered (1.450<sup>0</sup>C/5h).

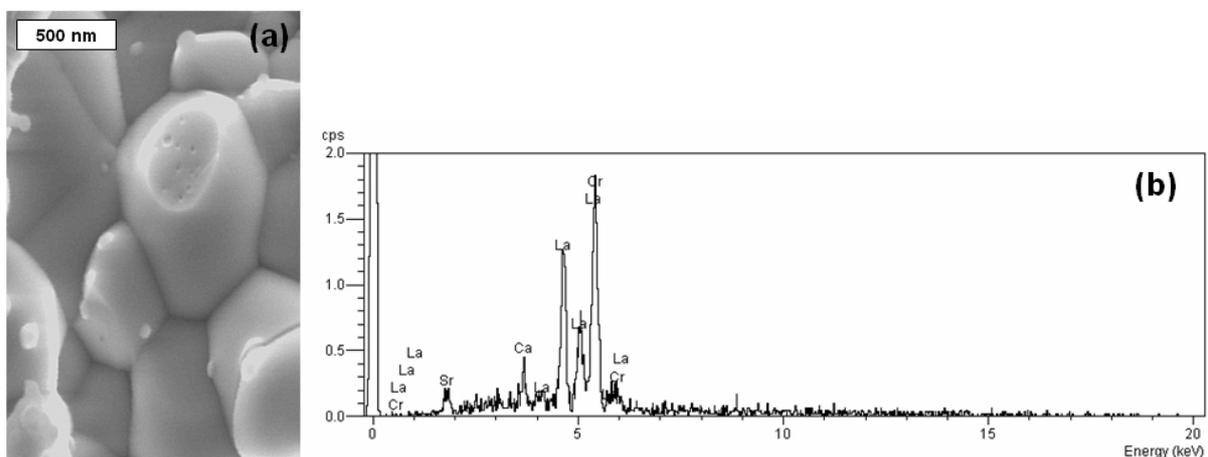
Based on images showed in the Figures 3 and 4 it is possible to note that the LCSCM/UCP sample is more densified than LCSCM/CM sample. In fact, in the Figures 3(a) and 4(a) it appears that the grain growth appeared perfectly straight along the boundary, and clear grain boundary was observed. This feature of the microstructure usually appears in the dense sintered body. On the other hand, in the

Figures 3(b) and 4(b) there is a significant presence of intergranular porosity, although in both cases there is not verify the presence of secondary phases and, in fact, the DRX results show in the Figure 5 presents only the peaks characteristics of the LCSCM ceramics.

Also in function of the SEM analysis (Figures 3 and 4) it is found that, in general, the microstructure of the sintered sample of LCSCM/UCP consisted of equiaxial grains with an average grain size in the range 8.20 - 9.90  $\mu\text{m}$  (Table 1). On the other hand, the LCSCM/CM powder showed relative 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 ceramic compact (93.8%). Additionally, no abnormal grain growth was observed in the LCSCM specimens. Figure 6 show SEM-EDS analysis of a full-densified microstructure region of a LCSCM/UCP sample also showing clear grain boundaries and characteristic bulk elemental analysis.



**Figure 5.** XRD analysis results of sintered ( $1.450^{\circ}\text{C}/4\text{h}$ ) LCSCM ceramics which powder was obtained by: (a) combustion method (UCP); (b) mixture of oxides (CM).



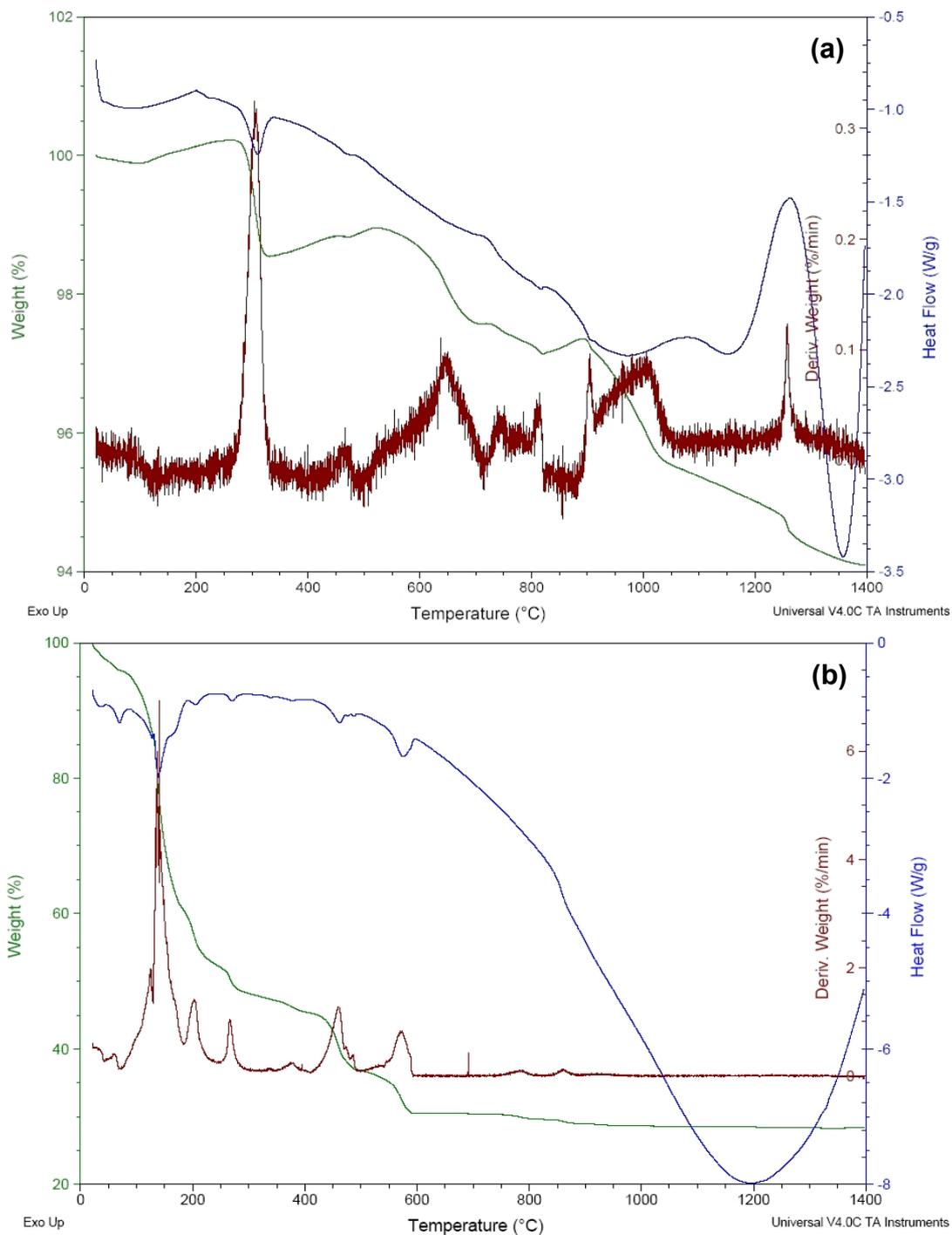
**Figure 6.** SEM-EDS analysis of a full-densified microstructure region (a) of LCSCM ceramic (UCP, sintered at  $1.450^{\circ}\text{C}/4\text{h}$ ) showing a EDS scanning analysis (b) characteristic of this bulk region.

In general, the results presented in Table 1 are reflected on the electrical and dimensional characteristics shown in Table 2. The electrical conductivity values are in the range characteristic of lanthanum chromites mono- and dual-doped and also presents great variability. In fact, under the SOFC operating environments, interconnect must exhibit excellent electrical conductivity (to minimize ohmic losses) with preferably nearly 100% electronic conduction. Since the interconnect provides

the conductive path for electrical current to pass between the electrodes and to the external circuit. A value of 1 S/cm is a well-accepted minimum electrical conductivity for the usefulness of interconnects in SOFC.<sup>(6,7)</sup> The usually considered as acceptable TEC values are in the range of  $9.9 \times 10^{-6}$  to  $10.6 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ .<sup>(6,11,12)</sup> Particularly the LCSCM/UCP samples sintered at 1450°C during 3 and 4 hours have presented the more adequate TEC values.

The Figure 7 shows the thermal analysis results for the LCSCM studied systems, in terms of TGA (Thermal Gravimetric Analysis), TDA (Thermal Differential Analysis) and heat flow profile. In Figure 7(a) for LCSCM/MC sample, with only 6% of total mass loss, there are two subsequent events in high temperatures, one exothermic peak at about 1.250°C, and another endothermic peak at about 1.350°C, with probable formation of liquid phase in the second event, although remaining secondary phases have not been observed in SEM analysis. In fact, the secondary liquid phase formation depends on doping level and in the studied cases were used low doping. In the 1.250°C-1.400°C interval occurs the gradual reduction (after transient wetting and subsequent densification) of SrCrO<sub>4</sub>, which dissolves into LaCrO<sub>3</sub> at increasing temperature.<sup>(11,19)</sup> In Figure 7(b) for LCSCM/UCP sample the total mass loss is significantly higher (about 70%), being characteristic of metallic nitrate based powder synthesis which presents large mass reduction starting around of 100°C due to loss of water hydratation of the nitrate precursors and small mass loss in temperatures above 600°C. The strong and subsequent peak is characteristic of the liquid phase formation and occurs at lower temperature than that of the first case probably in function of its smallest particle size.

The literature has considered the Sr-doped lanthanum chromite-based ceramics as main candidates for application in SOFC interconnects, in detriment of the LaCrO<sub>3</sub> mono-doped with Ca or Mg. This work show that the multiple doped lanthanum chromite-based ceramics LCSCM system presented good electrical conductivity, appropriate TEC values and adequate densification level during sintering, which can be optimized by thermal treatments or doping. Additionally, it was verified that the LCSCM/UCP system also presents potential for application in SOFC interconnects in function of possible synergetic effects associated with multiple doping and smaller particle size than LCSCM/CM. However, also the studied systems present the inherent difficulties associated to lanthanum chromite-based ceramics: nonlinear thermal expansion and poor sintering behavior due to high volatilization loss of chromium oxide at high sintering temperatures in an oxidizing atmosphere which is an obstacle to obtaining of full-densified lanthanum chromite-based ceramics. Future researches certainly will be concerned with finding solutions to these problems.



**Figure 7.** Thermal behavior (TGA, TDA and heat flow) associated with the synthesis and evolution of the LCSCM systems which powders was obtained by: (a) mixture of oxides (CM); (b) combustion method (UCP).

#### 4 CONCLUSIONS

It was verified that the urea-based combustion process from metallic nitrates was more efficient for the production of multiple doped lanthanum chromite-based ceramics than the traditional ceramic method, resulting in a microstructure characterized by more homogeneous grain size distribution. In general, obtained results corroborate the literature on the difficulty of densification of  $\text{LaCrO}_3$ -based systems, being that 97.1% was the biggest value reached for the densification

degree, and in lower temperature conditions than those normally considered for pure or mono-doped lanthanum chromites. Thus, it was verified that  $\text{La}_{0.90}\text{Ca}_{0.05}\text{Sr}_{0.05}\text{Cr}_{0.95}\text{Mg}_{0.05}\text{O}_3$  ceramics can be considered potential candidates for application in solid oxide fuel cell interconnects.

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