DEVELOPING AND EVALUATING CERAMIC MATERIALS FOR HIGH TEMPERATURE SOLID OXIDE FUEL CELL INTERCONNECTS [1]

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Abstract

High temperature solid oxide fuel cells (HTSOFC) are very attractive devices for cogeneration applications. However, due the severe operational conditions, there are several restrictions on the materials that can be used in this fuel cell type. The aim of this work is to evaluate the relationships between microstructural characteristics and electro-thermal-mechanical performance of multiple doped lanthanum chromites-based ceramics for HTSOFC interconnects. Multiple metal-doped lanthanum chromites-based ceramic powders were produced by auto-ignition combustion process from metallic nitrates. Samples were prepared by pressing and sintering procedures. The phase composition was evaluated by X-ray diffraction and densification level by Archimedes method. The microstructural characterization was made by scanning electron microscopy, energy dispersive X-ray spectroscopy and thermal analysis techniques. Electrical tests were used to evaluate the electrical conductivity of the samples, and thermal expansion coefficient was determined by dilatometric measurements. The obtained experimental results show that the chemical synthesized powders provided the production of electronically conducting lanthanum chromites-based ceramics, which present high electrical conductivity, high densification level and coefficient of thermal expansion around 11.5 x 10^{-6} K^{-1}, showing adequate compatibility with the other SOFC components and prepared in sintering temperature conditions lower that the normally considered to pure or monodoped lanthanum chromite-based ceramics.

Key words: Lanthanum chromites; SOFC interconnects; Densification.

DESENVOLVIMENTO E AVALIAÇÃO DE MATERIAIS CERÂMICOS PARA INTERCONECTORES DE PILHAS A COMBUSTÍVEL DE ÓXIDO SÓLIDO DE ALTA TEMPERATURA

Resumo

Pilhas a combustível de óxido sólido com altas temperaturas de operação (HTSOFC) são equipamentos bastante atrativos para sistemas de co-geração de energia. Contudo, devido às severas condições operacionais, existem muitas restrições acerca dos materiais que podem ser utilizados neste tipo de pilha a combustível. O objetivo deste trabalho é avaliar as relações entre características microestruturais e o desempenho eletrotérmico e dimensional de cerâmicas à base de cromita de lantânio com múltipla dopagem para uso em interconectores de HTSOFC. Cerâmicas de cromita de lantânio dopadas com metais alcalinos terrosos foram produzidas a partir dos respectivos nitratos metálicos mediante o processo de reações em estado sólido. A composição de fases foi avaliada por meio de difração de raios-X e o grau de densificação através do método de Arquimedes. A caracterização microestrutural foi efetuada por microscopia eletrônica de varredura e espectroscopia de raios-X por dispersão de energia. Ensaios elétricos permitiram a determinação da condutividade elétrica das cerâmicas estudadas. Os resultados experimentais obtidos mostram que os pós sintetizados proporcionaram a produção de cerâmicas relativamente densas e com condutividade elétrica adequada para a aplicação em questão, bem como coeficiente de expansão térmica médio por volta de 11,5 x 10^{-6} K^{-1}, mostrando adequada compatibilidade com outros componentes de uma HTSOFC e sinterizadas em condições de temperatura inferiores às normalmente consideradas para cromitas de lantânio pura ou monodopadas.

Palavras-chave: Cromitas de lantânio; Interconectores; Densificação.

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INTRODUCTION

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 it is a p-type electronic conductor in oxidizing conditions and is stable to low oxygen partial pressures.(1-3)

The solid oxide fuel cell (SOFC) is one of the most promising technologies for the production of electric energy, with potential to be a typical future distributed cogeneration system.(4) 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. In Figure 1(d) is showed an example of a SOFC ceramic interconnect.

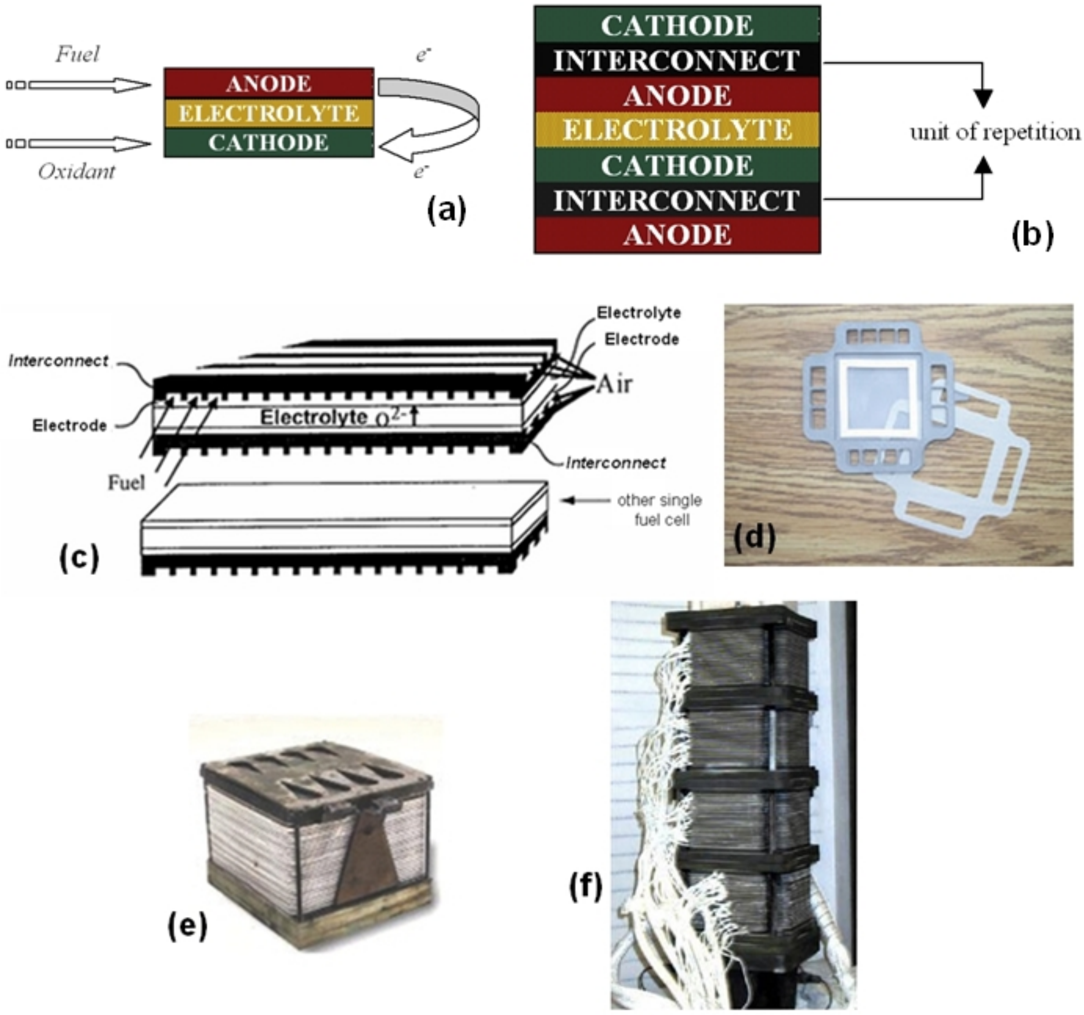

Figure 1. (a) Schematic diagram of a fuel cell; (b) scheme of the connection of the anode of a single fuel cell to the cathode of the subsequent single fuel cell, constituting a solid oxide fuel cell stack; (c) scheme of a planar SOFC; (d) ceramic interconnector; (e) a short SOFC stack; (f) complete SOFC stack module.

SOFCs operate under high temperature (typically 800°C -1000˚C) conditions compared with the other types of fuel cells. High efficiency and fuel impurity tolerance are the major advantages. However, there are severe restrictions on the materials and components that can be used in a SOFC.(5,6)

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.(6,7) Interconnect should have adequate stability in terms of dimension, microstructure, chemistry, and phase at operating temperature around 800°C -1000°C in both reducing and oxidizing atmospheres, since they are exposed to oxygen on one side and fuel on the other. Interconnect should display exceptionally low permeability for oxygen and hydrogen to minimize the crossover direct combination of oxidant and fuel during cell operation. Thermal expansion coefficient (TEC) of interconnect should be comparable to those of electrodes and electrolyte between ambient and operating temperatures, so that the thermal stress developed during stack startup and shutdown could be minimized. No reaction or inter diffusion between interconnect and its adjacent components, specifically, anode and cathode, is allowed to occur under operation conditions. Interconnect should possess fairly good thermal conductivity (5 W/m.K is considered to be the low limit).(5,7) Excellent oxidation, sulfidation and carburization resistances are required attributes for interconnect to qualify for application in SOFC-like environments. In addition, cost-effective manufacture of fuels cells requires that the interconnect materials be easy to fabricate. The costs of raw materials as well as manufacture processes for interconnect are also supposed to be as low as possible so that they will not present hurdles to commercialization. Cost reduction of interconnect is particularly attractive for anode-supported planar SOFC since it is the bulkiest part of all components,(7) and, finally, interconnect should also show adequate high temperature strength and creep resistance. This requirement is of special relevance to the planar SOFC where interconnect serves as a structural support.

Only a few such oxide systems can satisfy the rigorous requirements for the interconnect materials in SOFC. Lanthanum chromite ($LaCrO_3$) 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.(6) Nevertheless, the conductivity of pure lanthanum chromite is not sufficiently high for use as an interconnect material, but can be increased through doping and a major difficulty with such lanthanum chromite-based interconnects is the difficulty of sintering to full density. Lanthanum chromite powders do not sinter easily, especially in oxidising atmospheres. 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.(6,8,9) 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.(10,11) The large alkaline-earth ions, most commonly strontium and calcium,(11) although barium-doped lanthanum chromite has also been reported,(7,12) 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.$^{(12-14)}$

The objectives of this study are to investigate and to characterize the microstructural development of lanthanum chromite-based ceramics multiple-doped with earth-alkaline metals, correlating the microstructural parameters (mainly the densification level) and processing parameters with the electro-thermal-mechanic properties reached.

EXPERIMENTAL

Powders of different doped lanthanum chromite compositions, as shown in Table 1, were synthesized by solid-state reaction method (combustion method with urea as fuel) from the corresponding metallic nitrates. The desired compositions were prepared by dissolving known amounts of the selected metallic nitrates in water. The homogeneous powder mixtures, with urea/metal nitrates ratio equals 2, were heated on a hot plate at 150°C and it was converted to a viscous gel due to evaporation of water. The mixture was then heated in a muffle furnace at 600°C until self-ignition. The homogeneous powder mixtures were dried at 200°C and then calcined in air at 1000°C for 1 h, with air flow rate of 60 mL/min, and heated to 1200°C for 3 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 poor oxygen atmosphere at 1300°C - 1500°C (at a constant heating rate of 5°C/min) for three hours.

The phase composition was evaluated by X-ray diffraction (XRD, Diano XRD-8545, λCuKα 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 (STA 402/409 E Netzsch dilatometer). The average grain sizes were determined by the intercept method.$^{(15)}$

Table 1 – Designation and chemical composition (in molar percentage) of the studied multiple-doped lanthanum chromite-based ceramics.

System	Chemical composition (mol%)
CM	$La_{0.90}Ca_{0.10}Cr_{0.95}Mg_{0.05}O_3$
SM	$La_{0.90}Sr_{0.10}Cr_{0.95}Mg_{0.05}O_3$
SCM	$La_{0.90}\ Ca_{0.05}Sr_{0.05}Cr_{0.95}Mg_{0.05}O_3$

RESULTS AND DISCUSSION

The Figures 2 and 3 present, respectively, the results obtained from average grain size measurements and densification analysis (densification degree in percentage of the respective theoretical density) of the studied lanthanum chromite-based ceramics.

The results presented in Figures 2 and 3 show that there are high values of average grain size, as well as a significant variability of this parameter, indicating grain size bimodal distributions, mainly in the bi-doped systems (CM and SM), however, being smaller than those typical monodoped systems.$^{(3)}$ Also, the Ca, Sr e Mg simultaneously doped system (SCM) shows considerable variability of the microstructural parameters, but even so, it has presented the best densification level. These results indicate that probably the characteristics of this system still can be optimized by changes in the processing conditions and/or doping studies, mainly by sintering in reducing atmospheres.(3,10,11) 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%.(7)

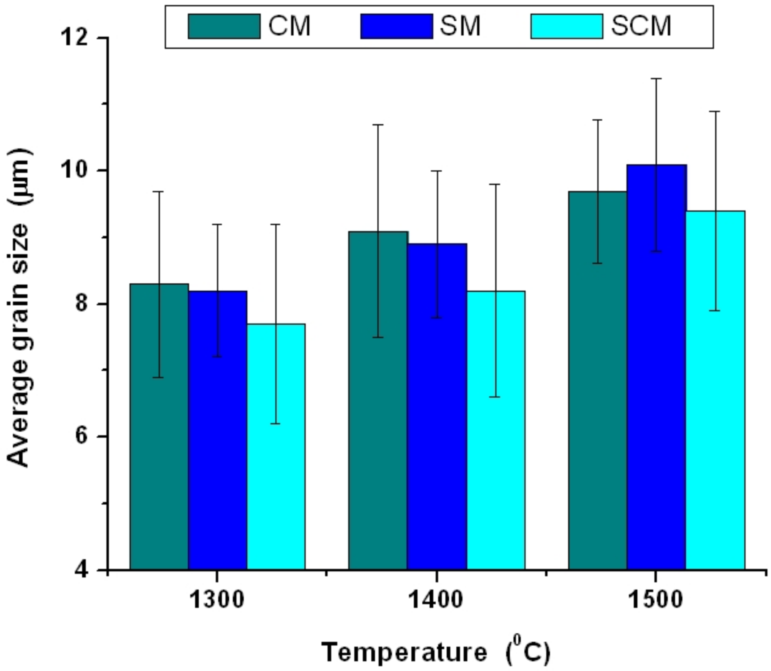

Figure 2. Average grain size of the studied lanthanum chromite-based ceramics.

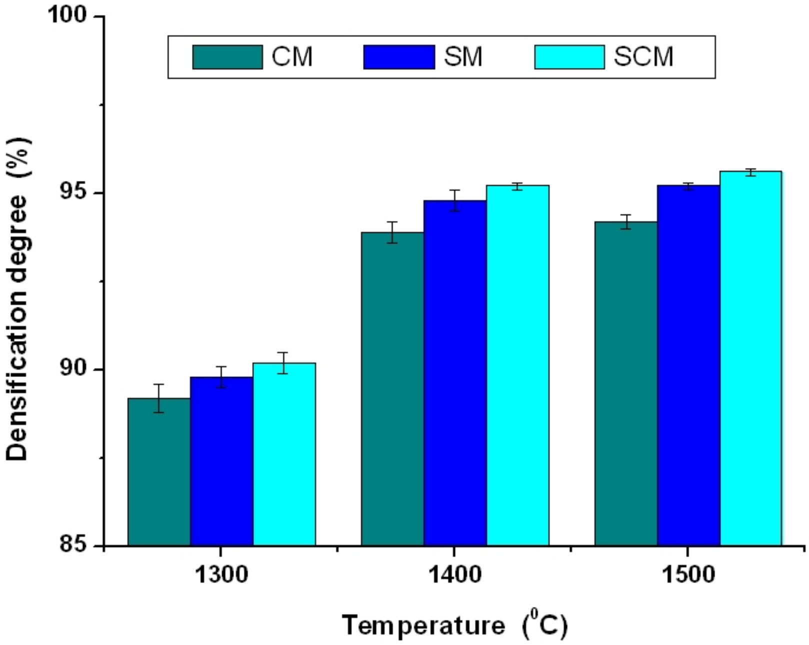

Figure 3. Densification degree of the studied lanthanum chromite-based ceramics.

In all sintering temperatures studied the triple doping (SCM) resulted in decrease of the average grain size (this formulation provided a grain growth inhibition) and the densification degrees obtained in 1400°C and 1500°C are comparable. The lanthanum chromite-based ceramics doped with Sr (SC and CM) had presented greater densification degree than those doped with Ca/Mg (CM). In fact, the densification mechanism depends on of the metal dopant, and with the Sr the transient liquid phase formed ($SrCrO_4$), beyond it exists in bigger proportion, it results in better wetting condition, intensifying the densification process. However, as reported in literature(6,16) the increase in acceptor concentration can result in material dilatation, when under reducing conditions, nearby 1000°C, since that electric charge compensation between involved ions take place through oxygen vacancy formation and the transition between Cr^{3+} and Cr^{4+} is reversible, resulting in electrical conductivity decrease and TEC increase, due to increase of the chromium ionic radius. Thus, the Sr concentration must be optimized and, moreover, the multiple doping studies can contribute for the stabilization of the properties of these lanthanum chromite-based ceramics. The additional doping with Mg resulted in the best densification condition (SCM system). Figures 4 and 5 show photomicrographies (SEM) characteristics of the microstructures of the studied systems. The distributions of porosity are seen clearly, either in incipient sintering conditions (Figure 4(d)) or in the best densification microstructure (SCM) – Figure 4(c).

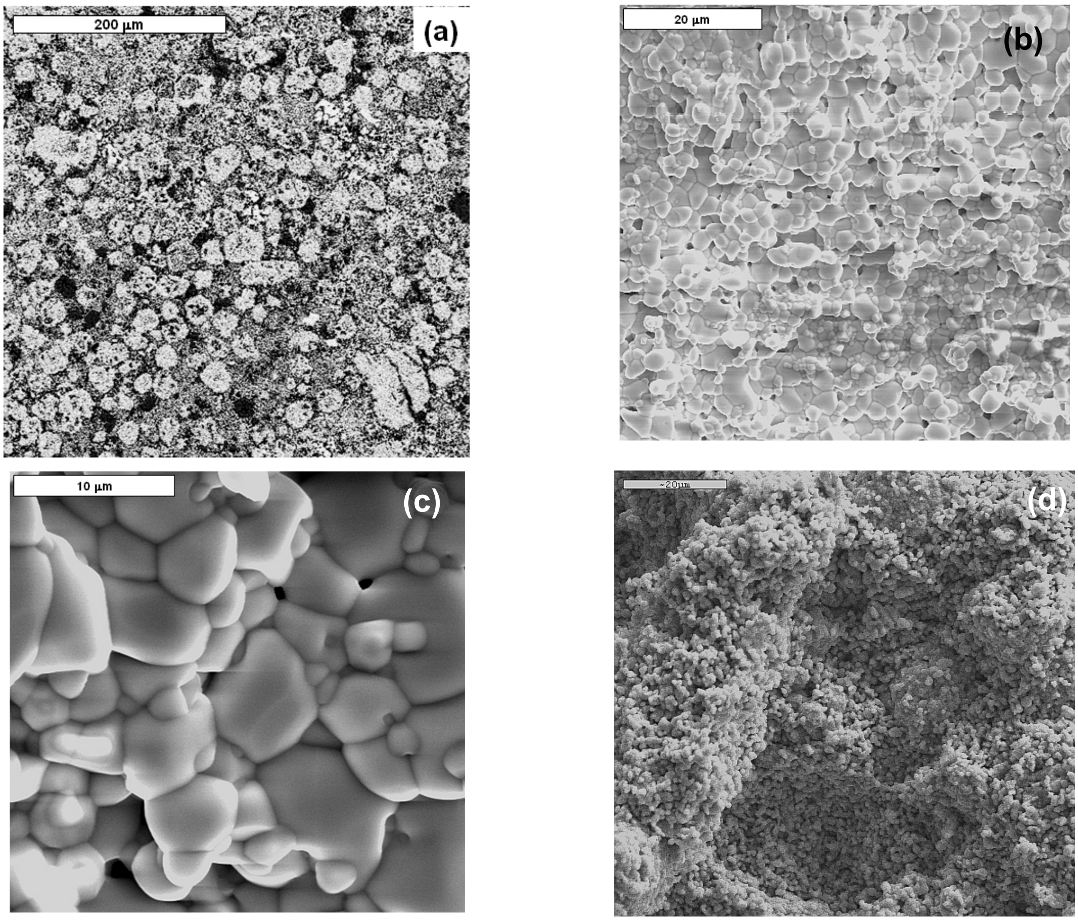

Figure 4. SEM photomicrographs of SCM ceramics: (a) calcined powder; (b) and (c) sintered at 1450°C/4h; (d) sintered (1300°C/1h).

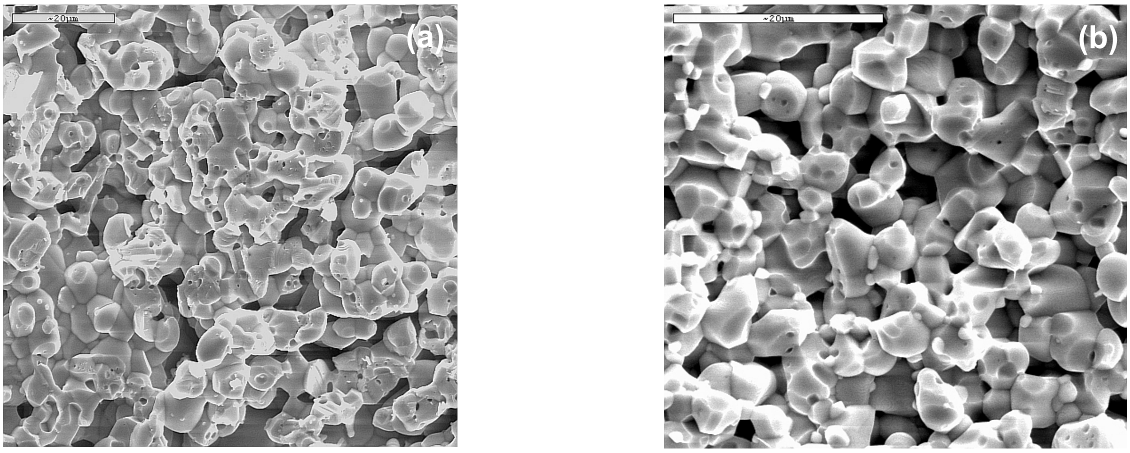

Figure 5. SEM photomicrographs of $LaCrO_3$-based ceramics sintered at 1400°C: (a) CM; (b) SM.

Based on images showed in the Figures 4 and 5 it is possible to note that the SCM sample is more densified than SM and CM samples. In fact, in the Figure 4(b) and 4(c) 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 Figs. 5(a) and 5(b) there is a significant presence of intergranular porosity, although in both cases there is not verify the presence of secondary phases.

Also in function of the SEM analysis (Figures 4 and 5) it is found that, in general, the microstructure of the 1500°C sintered sample of SCM consisted of equiaxial grains with and average grain size in the range 7.9 - 10.9 μm (Figure 2). On the other hand, all the systems sintered at 1300°C 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 (1500°C) ceramic compact (95.6%). Additionally, no abnormal grain growth was observed in the studied specimens.

Figure 6 shows SEM-EDS analysis of a full-densified microstructure region of a SCM sample also showing clear grain boundaries and characteristic bulk elemental analysis. In all studied cases there is not verify the presence of secondary phases and, in fact, the DRX results show in the Figure 7 presents only the peaks characteristics of the $LaCrO_3$-based ceramics, or well, evidencing the $LaCrO_3$ characteristic peaks and the its solid solution calcium doped peaks, in function of the small calcium ionic radius (0.099 nm), when compared with lanthanum ionic radius (0.115 nm).

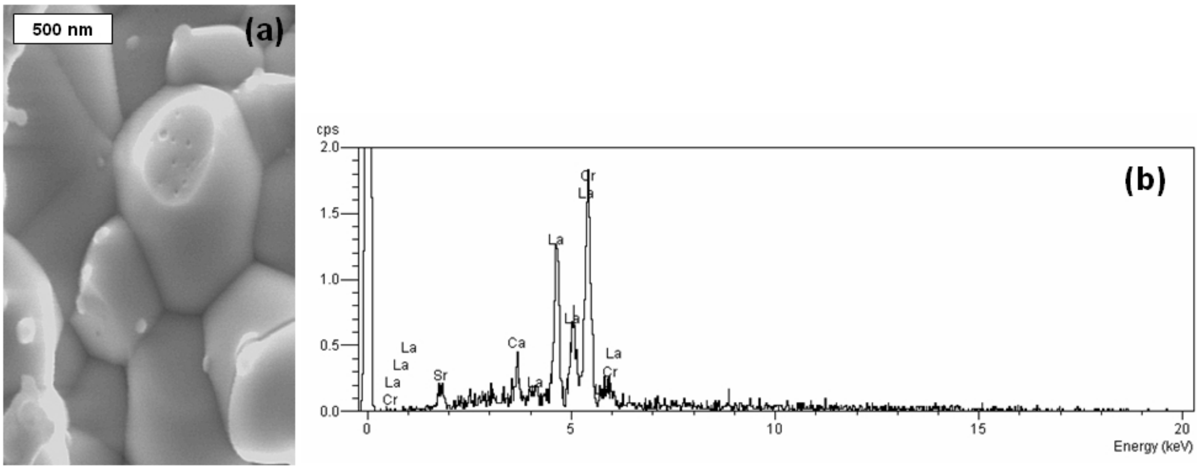

Figure 6. SEM-EDS analysis of a full-densified microstructure region (a) of SCM ceramic (sintered at 1450°C) showing a EDS scanning analysis (b) characteristic of this bulk region.

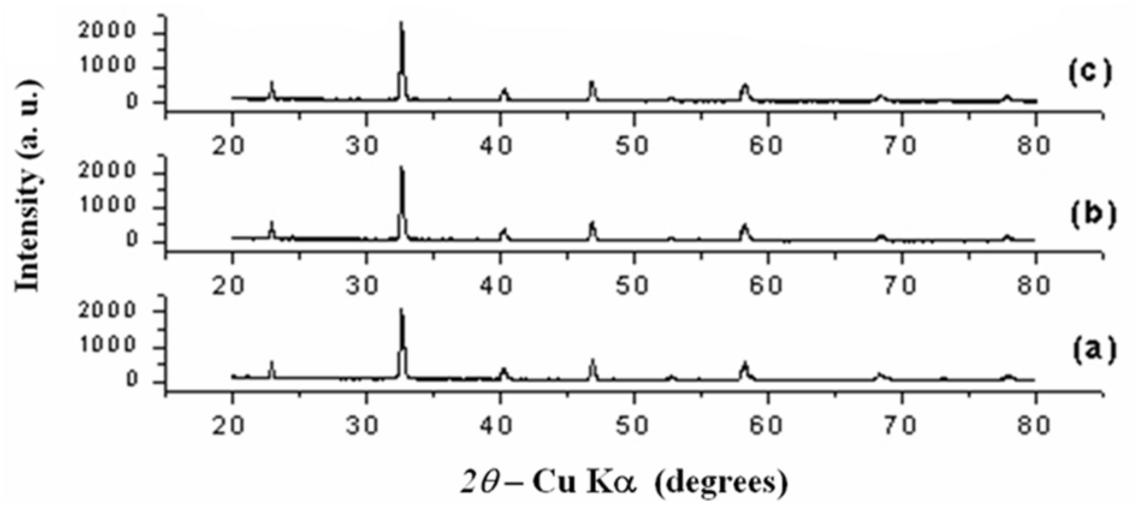

Figure 7. XRD analysis results (x = $LaCrO_3$ phase): (a) CM, (b) SM, (c) SCM.

The Figures 8 and 9 present, respectively, results concerning about electrical conductivity measurements (1000°C, air) and thermal expansion coefficient determination (between 25°C and 1200°C) for the studied systems.

In general, the results presented in Figures 2 and 3 are reflected on the electrical and dimensional characteristics shown in Figures 8 and 9. The electrical conductivity values are in the range characteristic of multiple-doped lanthanum chromites, but with presents great variability. As was expected there is a direct relationship between densification degree and electrical conductivity, which present the same behavior in relation to sintering temperature, but a small increment in density result in significative increment in electrical conductivity. Also there is a linear relationship between temperature and electrical conductivity, which, in turn, obeys the small polaron conductivity mechanism, because the electrical conductivity is a thermally activated process.(16) The good value of electrical conductivity of SCM ceramic is related to its microstructure (Figuress 4(b) and 4(c)), which is typical of a full-densified ceramic with well-defined grain boundaries. The usually considered as acceptable TEC values are in the range of 9.9 x 10^{-6} to 10.6 x 10^{-6} $^{0}C^{-1}$.(6,11,12) Particularly the SM and mainly SCM systems had presented the more adequate TEC range values.

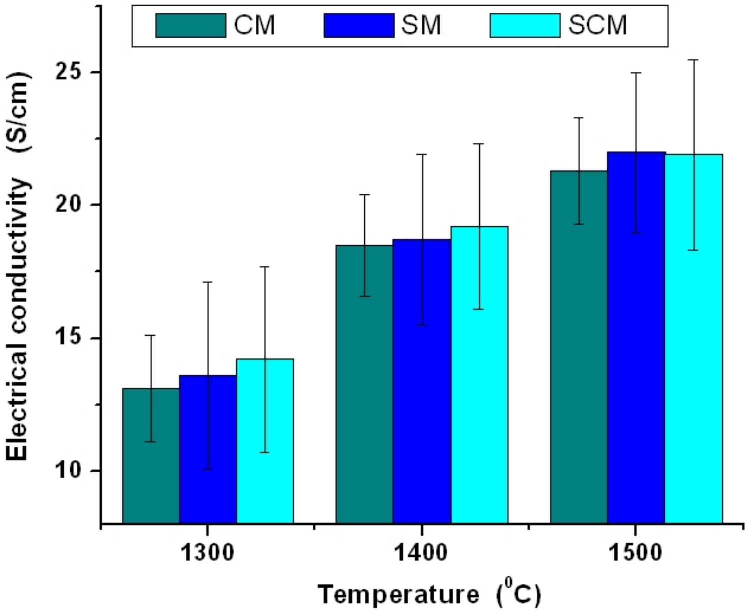

Figure 8. Electrical conductivity of the studied lanthanum chromite-based ceramics.

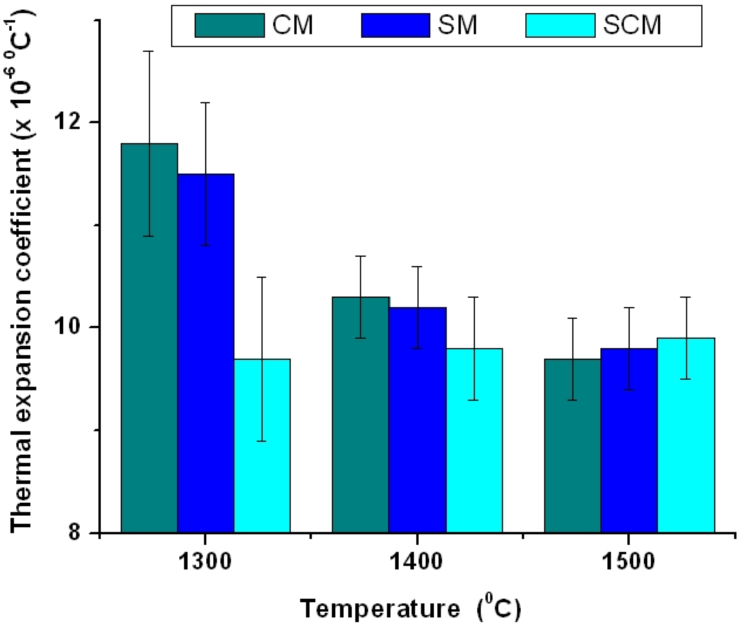

Figure 9. Thermal expansion coefficient of the studied lanthanum chromite-based ceramics.

CONCLUSIONS

It was verified that the solid-state reaction method from metallic nitrates was efficient for the production of multiple doped lanthanum chromite-based ceramics. In general, obtained results corroborate the literature on the difficulty of densification of $LaCrO_3$-based systems, being that 95.6% 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. Additionally, it was verified that $La_{0.90}Ca_{0.05}Sr_{0.05}Cr_{0.95}Mg_{0.05}O_3$ ceramics presenting average coefficient of thermal expansion compatible with the other SOFC components and relatively high electrical conductivity can be considered potential candidates for application in solid oxide fuel cell interconnects.

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