

## Development of lanthanum chromites-based materials for solid oxide fuel cell interconnects

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### ABSTRACT

Lanthanum chromites ( $\text{LaCrO}_3$ ) are the main materials used as interconnect for solid oxide fuel cells. However, there are several difficulties involved in the processing of these materials. The objective of this work is to investigate and to characterize the relationships between microstructural development process and the electro-thermal-mechanical behavior of earth-alkaline metals doped lanthanum chromites-based ceramics. Calcium and strontium doped lanthanum chromites-based ceramic powders were produced by solution-based method from respective 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 corroborate the literature comments concerning the difficulty of lanthanum chromite-based ceramics with high densification level and evidence the great influence of the nature of the dopants on the sintering mechanism and the microstructural and electric characteristics of the produced ceramics. The best ones results, in terms of densification and homogeneity characteristics, had been gotten through multiple doping with calcium and strontium, and in sintering temperature conditions lower than the normally considered to pure or mono-doped lanthanum chromite-based ceramics.

**Keywords:** Lanthanum chromites, fuel cell, SOFC interconnects.

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### 1 INTRODUCTION

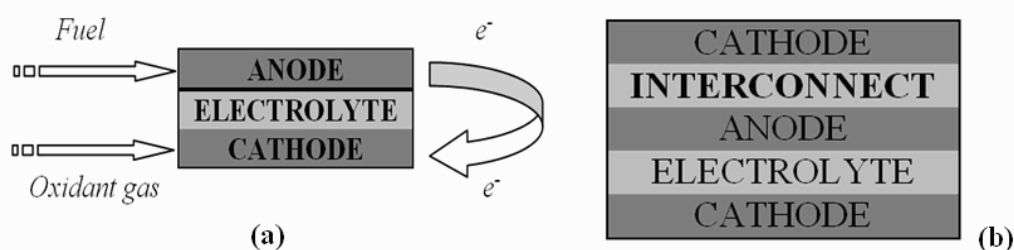
The perovskite ( $\text{ABO}_3$ -type) lanthanum chromite ( $\text{LaCrO}_3$ ) and especially doped  $\text{LaCrO}_3$ -based ceramics have recently received much interest as high-temperature electrode materials and solid oxide fuel cell interconnects, because it is a p-type electronic conductor in oxidizing 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), electrical interconnectors (completing the primary built electrical circuit) and an external electrical circuit for electrical current draining as schematically showed in the Figure 1.

SOFCs operate under high temperature (typically 800-1000°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 800-1000°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.



**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.

Only a few such oxide systems can satisfy the rigorous requirements for the interconnect materials in SOFC. Lanthanum chromite ( $\text{LaCrO}_3$ ) 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. The electronic conductivity of the stoichiometric  $\text{LaCrO}_3$  compound is increased by substituting divalent metal ions on either the A- or B-sites of the  $\text{ABO}_3$  perovskite lattice. However, the sintering ability of these chromite compounds is poor, mainly in oxygen-rich atmosphere, due to the vaporization of the chromium species during the sintering process [6, 8]. Many authors have indicated that both the sinterability and the electrical conductivity of  $\text{LaCrO}_3$  could be improved by the substitution of a lower-valent ion such as  $\text{Cu}^{2+}$  or  $\text{Mg}^{2+}$  at the  $\text{Cr}^{3+}$  site or of  $\text{Sr}^{2+}$  at the  $\text{La}^{3+}$  site [6, 8, 9]. Then, the most common dopants for  $\text{LaCrO}_{3-\delta}$  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 doped with earth-alkaline metals, correlating the microstructural parameters (mainly the densification level) and processing parameters with the electro-thermal-mechanic properties reached.

## 2 EXPERIMENTAL

### 2.1 Samples Preparation

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 were dried at 200<sup>o</sup>C and then calcined in air at 1000<sup>o</sup>C for 1 h and heated to 1200<sup>o</sup>C for 3 h. The ball-milled powders (Pulverisette 6 Fritsch, 24 h) were pressed into pellets and sintered at 1450<sup>o</sup>C for 3 h.

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

| System | Chemical composition (mol%)   |
|--------|---|
| LCC    | La <sub>0.90</sub> Ca <sub>0.10</sub> CrO <sub>3</sub>  |
| LSC    | La <sub>0.90</sub> Sr <sub>0.10</sub> CrO <sub>3</sub>  |
| LCCM   | La <sub>0.90</sub> Ca <sub>0.10</sub> Cr <sub>0.95</sub> Mg <sub>0.05</sub> O <sub>3</sub>                    |
| LSCM   | La <sub>0.90</sub> Sr <sub>0.10</sub> Cr <sub>0.95</sub> Mg <sub>0.05</sub> O <sub>3</sub>                    |
| LCSCM  | La <sub>0.90</sub> Ca <sub>0.05</sub> Sr <sub>0.05</sub> Cr <sub>0.95</sub> Mg <sub>0.05</sub> O <sub>3</sub> |

### 2.2 Characterization Methods

The phase composition was evaluated by X-ray diffraction (XRD, Diano XRD-8545,  $\lambda$ 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). The average grain sizes were determined by the intercept method [15].

## 3 RESULTS

The Table 2 presents 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, and the Table 3 presents the results concerning about electrical conductivity measurements (1000<sup>o</sup>C, air) and thermal expansion coefficient determination (between 25 and 1200<sup>o</sup>C) for the same systems.

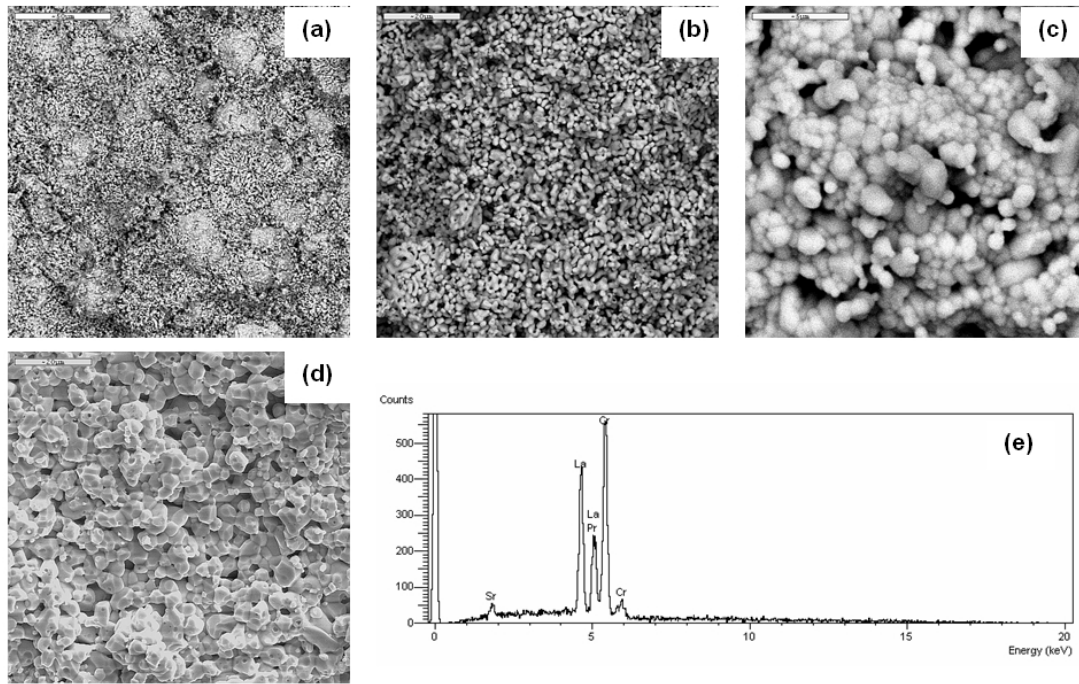
**Table 2:** Average grain size and densification degree of the studied lanthanum chromite-based ceramics.

| System | Average grain size ( $\mu$ m) | Densification degree (%) |
|--------|-------------------------------|--------------------------|
| LCC    | 10.20 $\pm$ 1.50              | 92.1 $\pm$ 0.3           |
| LSC    | 11.10 $\pm$ 1.30              | 94.2 $\pm$ 0.3           |
| LCCM   | 9.30 $\pm$ 1.60               | 94.8 $\pm$ 0.4           |
| LSCM   | 9.40 $\pm$ 1.10               | 95.4 $\pm$ 0.3           |
| LCSCM  | 8.90 $\pm$ 1.70               | 96.1 $\pm$ 0.3           |

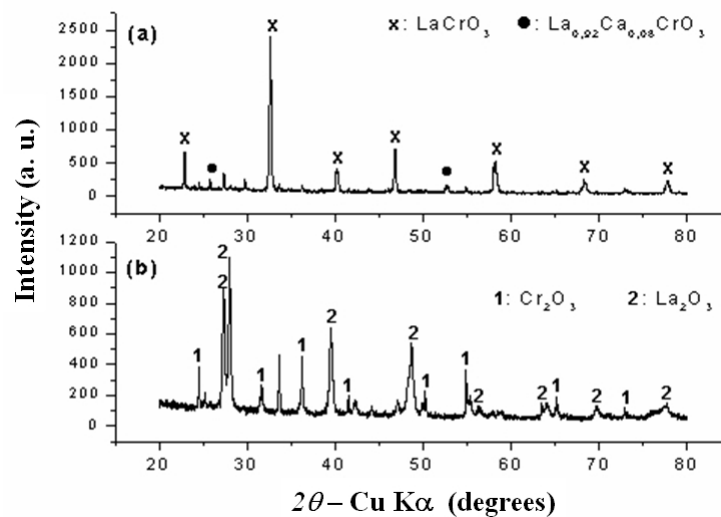
**Table 3:** Electrical conductivity and thermal expansion coefficient of the studied lanthanum chromite-based ceramics.

| System | Electrical conductivity (S/cm) | Thermal expansion coefficient ( $\times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ ) |
|--------|--------------------------------|---|
| LCC    | 16.4 $\pm$ 1.9                 | 9.1 $\pm$ 0.5   |
| LSC    | 18.5 $\pm$ 1.7                 | 8.8 $\pm$ 0.6   |
| LCCM   | 21.3 $\pm$ 1.9                 | 9.7 $\pm$ 0.4   |
| LSCM   | 22.1 $\pm$ 1.6                 | 9.8 $\pm$ 0.2   |
| LCSCM  | 21.8 $\pm$ 3.4                 | 9.9 $\pm$ 0.5   |

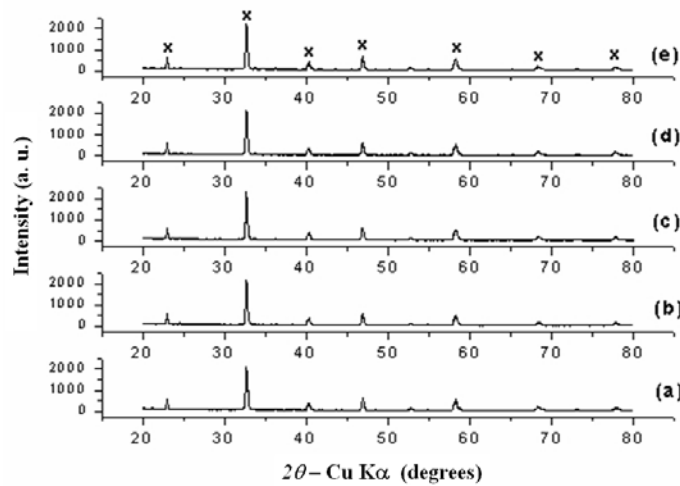
Figure 2 show photomicrographies (SEM) characteristics of the microstructures of the studied systems. Figure 3 shows the X-ray diffraction patterns of the original powder mixture after calcination and of the LCC system sintered for 4 h and Figure 4 shows the XRD analysis results of the studied lanthanum chromite-based ceramic systems (2 h sintered). Additionally, the Figure 5 shows the thermal analysis spectra of the LCSCM system.



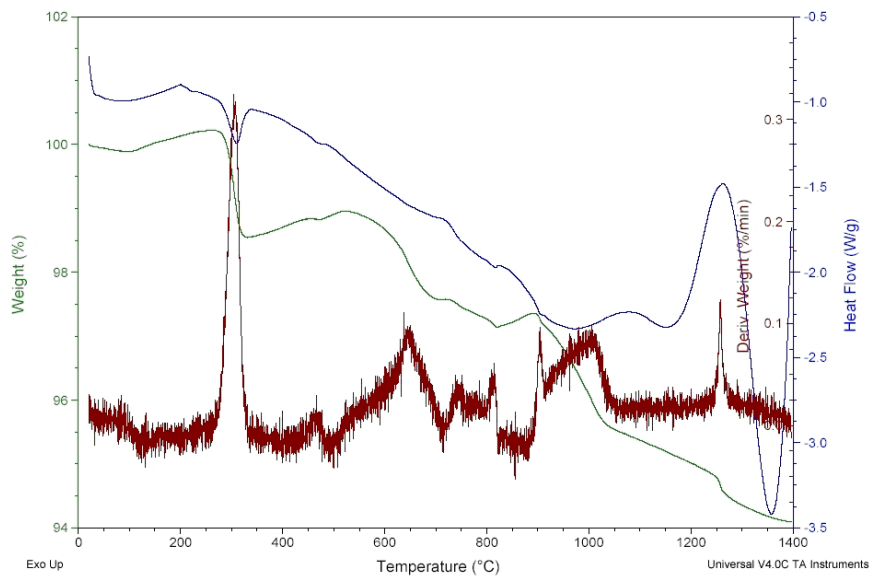
**Figure 2:** Microstructural characterization. Photomicrographies (SEM): (a) LCC 1200<sup>0</sup>C (bar = 50 μm), (b) LSC 1300<sup>0</sup>C (bar = 20 μm), (c) LSCM 1300<sup>0</sup>C (bar = 5 μm), (d) LCSCM 1400<sup>0</sup>C (bar = 20 μm), (e) EDS analysis result of the microstructure shown in Fig. 2(d).



**Figure 3:** XRD analysis result: (a) LCC system (sintered for 4 h); (b) original powder mixture after calcination.



**Figure 4:** XRD analysis results ( $x = \text{LaCrO}_3$  phase): (a) LCC, (b) LSC, (c) LCCM, (d) LSCM, (e) LCSCM.



**Figure 5:** Thermal behavior (TGA, TDA and heat flow) associated with the synthesis and evolution of the LCSCM system.

#### 4 DISCUSSION

The results presented in Tables 2 and 3 show that, mainly in the monodoped systems, there are high values of average grain size, as well as a significant variability of this parameter, indicating grain size bimodal distributions. Also, the Ca, Sr e Mg simultaneously doped system (LCSCM) 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. 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].

The lanthanum chromite-based ceramics doped with Sr (LSC and LSCM) had presented greater densification degree than those doped with Ca (LCC and LCCM). In fact, the densification mechanism depends on of the metal dopant, and with the Sr the transient liquid phase formed ( $\text{SrCrO}_4$ ), 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  $1000^\circ\text{C}$ , since that electric charge compensation between involved ions take place through oxygen vacancy formation and the transition between  $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$  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 (LCSCM system), although the synergetic action mechanism is not yet clear [17, 18]. In fact, in mono-doped systems, Ca-doped  $\text{LaCrO}_3$  expands more than Sr-doped  $\text{LaCrO}_3$  does, because of greater ionic size difference between Ca and La than between Sr and La, contributing, in the second case, to the stability and densification of the ceramic body [6]. Additionally, possibly the doping with Sr, which might increase the vacancy concentration or suppress the chromium volatilization is more effective in the improving of the bulk densification [16].

The photomicrographies (SEM) showed in Figure 2 are characteristics of the microstructures of the studied systems. The distributions of porosity are seen clearly, either in incipient sintering conditions or in the best densification microstructure (LCSCM), Figure 2(d), in which can be seen the intergranular porosity incidence. A SEM photomicrograph of the LCSCM sample for the selected sintering conditions is shown in Figure 2(d). According to these photos and the results of the Table 2, dense lanthanum chromite-based materials can be fabricated by sintering in air, suggesting that the present powders obtained by combustion method have good sintering capability, although the sintering conditions still need to be improved, since only some well-defined grain boundaries were observed (Figure 2(d)). This feature of the microstructure usually is present in a densely sintered ceramic compact.

In general, the results presented in Table 2 are reflected on the electrical and dimensional characteristics shown in Table 3. The electrical conductivity values are in the range characteristic of lanthanum chromites mono- and dual-doped, and especially for LCSCM system also presents great variability. The usually considered as acceptable TEC values are in the range of  $9.9 \times 10^{-6}$  to  $10.6 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  [6, 11, 12]. Particularly the LSCM and LCSCM systems had presented the more adequate TEC values.

Figure 3 shows the X-ray diffraction patterns of the original powder mixture after calcination and of the LCC system sintered for 4 h, evidencing the  $\text{LaCrO}_3$  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 4 shows the XRD analysis results of the studied lanthanum chromite-based ceramic systems (2 h sintered). For all compositions, X-ray diffraction analysis revealed no second phase.

The Figure 5 shows the thermal analysis spectra of the LCSCM system. There are two subsequent events in high temperatures, one exothermic peak at about  $1250^\circ\text{C}$ , and another endothermic peak at about  $1350^\circ\text{C}$ , with probable formation of liquid phase in the first event. In the  $1250\text{-}1400^\circ\text{C}$  interval occurs the gradual reduction (after transient wetting and subsequent densification) of  $\text{SrCrO}_4$ , which dissolves into  $\text{LaCrO}_3$  at increasing temperature.

The literature has considered the Sr-doped lanthanum chromite-based ceramics as main candidates for application in SOFC interconnects, in detriment of the  $\text{LaCrO}_3$  mono-doped with Ca or Mg. This emphasis is corroborated by the present work, since that the LSCM system presented good electrical conductivity and TEC values. Additionally, it was verified that the LCSCM system also presents potential for application in SOFC interconnects in function of possible synergetic effects associated with multiple doping. However, also the studied systems present the inherent difficulties associated to lanthanum chromite-based ceramics: nonlinear thermal expansion and poor sintering behavior [3, 5]. Future research certainly will be concerned with finding solutions to these problems.

## 5 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  $\text{LaCrO}_3$ -based systems, being that 96.4% 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. The Mg-doped  $\text{La}_{(1-x)}\text{Sr}_x\text{CrO}_3$  system provided increase in electrical conductivity and in the densification level, and the resultant thermal expansion coefficient was found to be close to ideal range. Additionally, it was verified that  $\text{La}_{0.90}\text{Sr}_{0.10}\text{Cr}_{0.95}\text{Mg}_{0.05}\text{O}_3$  and  $\text{La}_{0.90}\text{Ca}_{0.05}\text{Sr}_{0.05}\text{Cr}_{0.95}\text{Mg}_{0.05}\text{O}_3$  systems can be considered potential candidates for application in solid oxide fuel cell interconnects.

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