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A SEM Study on the Sintering and Densification of Doped Lanthanum Chromites

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Abstract – Lanthanum chromite-based ceramics are the main materials used as solid oxide fuel cell interconnects. However, there are several difficulties involved in the processing of these materials. In this work, we report the results on the densification and microstructural characterization of (Sr, Ca)-doped lanthanum chromites synthesized by auto-ignition process. The results indicate that $La_{0.80}Ca_{0.10}Sr_{0.10}CrO_{3-\delta}$ ceramic is suitable to be used in interconnects of solid oxide fuel cells.

Lanthanum chromites (LaCrO₃) are mixed-oxides with perovskite-type structure and have been investigated as ceramic interconnect materials to be used in solid oxide fuel cells (SOFC). For this purpose the lanthanum chromites have been shown as a versatile material, being used as bulk device to high-temperature SOFC or as thin films coatings of metallic materials to intermediate temperature SOFC (IT-SOFC), because to their thermal-mechanical and chemical stability and high electrical conductivity at both reducing and oxidizing atmospheres [1]. Nevertheless, the conductivity and the sinterability of pure lanthanum chromite are not sufficiently high for use as an interconnect material, but can be increased through doping. The electronic conductivity of the stoichiometric LaCrO₃ compound is increased by substituting divalent metal ions on either the A- or B-sites of the ABO₃ perovskite lattice [2]. Similarly, the doping and the ceramic synthesis with Cr deficiency (Cr_{1-z}O_{3- δ}) provide a sinterability increasing effect in lanthanum chromites, reaching highest densities [3].

Nano-fine powders of $(La_{1-x-y}Ca_xSr_y)(Cr_{1-z}O_{3-\delta})$ lanthanum chromite compositions were synthesized by auto-ignition process (combustion method with urea as fuel) from P. A. grade reagents. The final ball-milled powders were dry cold isostatic pressed at 200 MPa into pellets and sintering was carried out in controlled atmosphere at 1250-1350°C (at a constant heating rate of 5°C/min) for 5 hours. Doped mixed-oxide samples were microstructurally characterized by scanning electronic microscopy (SEM) and energy-dispersive X-ray analysis (EDS), as well as by electrical measurements and thermal-dilatometric analysis. In this work we report the results on the densification and microstructural characterization of (Sr, Ca)-doped lanthanum chromites.

Figure 1 shows SEM micrographs of the fracture surface of sintered lanthanum chromite ceramics, revealing partial-densified microstructures, although in both cases it is note the tendency to formation of clusters, which the grain boundaries of the samples became more clear, resulting in non-uniform sintering of the powder particles, but showing that these regions were densely sintered. Figure 2 shows a SEM-EDS analysis of a full-densified microstructure region of a (Sr, Ca)-doped lanthanum chromite sample also showing clear grain boundaries and characteristic bulk elemental analysis. The results indicate that Cr deficiency can be effective to increase the densification of lanthanum chromites corroborating the results recently obtained by Wang *et al.* [4]. It was verified that $La_{0.80}Ca_{0.10}Sr_{0.10}CrO_{3-\delta}$ ceramic synthesized by auto-ignition process showed better sinterability that of other compositions studied, achieving high densification and good electronic conductivity (about 3.1 S/cm), with thermal expansion coefficient compatible with other fuel cell components, make it appropriate for use in SOFC interconnects.



Figure 1: SEM photomicrographs of the (Sr, Ca)-doped lanthanum chromite ceramics sintered at: (a) 1350° C; (b) 1250° C.



Figure 2: SEM-EDS analysis of a full-densified microstructure region (a) (Sr, Ca)-doped lanthanum chromite ceramic; (b) EDS scanning analysis characteristic of this bulk region.

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