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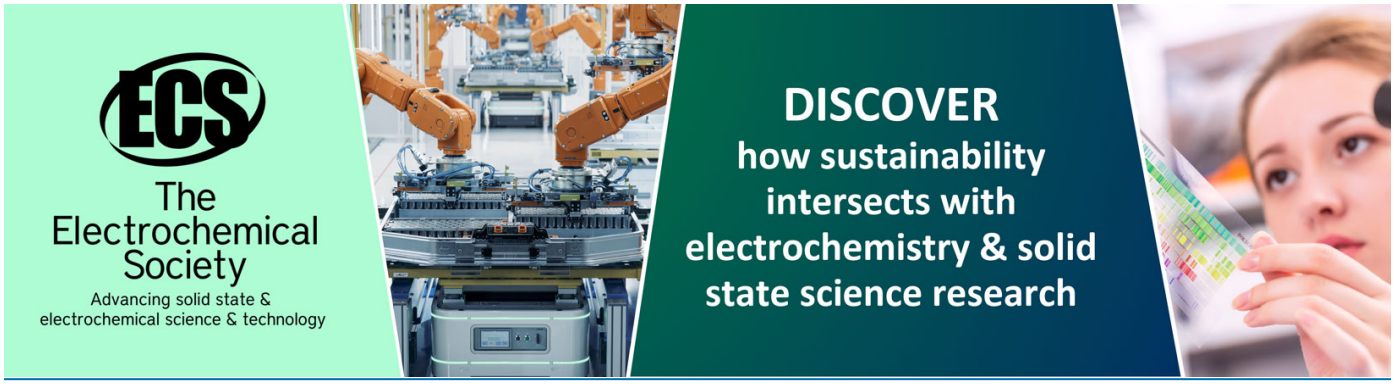

Structural and electrical study of $LaCrO_3$ modified with Fe and Co

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Abstract: The present work shows the effect of a modification on $LaCrO_3$ oxide using Fe and Co cations over the structural and electrical properties in order to evaluate its response to applications as electrode in solid oxide fuel cells (SOFC). The $LaCr_{0.8}Fe_{0.2}O_3$ and $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$ oxides were synthetized by polymerization-combustion method using citric acid as complexing agent. The characterizations by means of X-ray diffraction (XRD), energy dispersive X-ray (EDX), and Raman spectroscopy revealed the conformation of a $LaCrO_3$ single phase with an orthorhombic structure (Pnma 62) in both ceramics and average crystal size of 131nm. The images of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed the conformation of materials with relevant morphological characteristics obtained because of synthesis method used. Analysis by Impedance spectroscopy (IS) from room temperature to 800°C, indicated that both oxides were semiconductor type in accordance to thermal activation process.

1. Introduction

Solid oxide fuel cells (SOFC) are an important technological alternative for the optimal use of hydrogen as fuel on the production of sustainable energy. These devices are a key factor in power generation with low greenhouse emissions and a high efficiency [1]. The current study on these systems confirm that the use of modified perovskites as electrode components, mainly focused on development on anodic components based on $LaCrO_3$ systems, could resolve the problems related with the low catalytic efficiency and the stability of solid at high temperatures when the oxidation fuel process take place [2]. However, some drawbacks related with the obtainment of impure phases and the necessity of diminish the calcination periods in the synthesis by the conventional solid state reaction that affect the structure and the electrical response, have allowed the development and adaptation of new synthesis methods that provide a major control on aspects related with particle size, chemical and structural stability, electrical behaviour, sinterability and reduction of chromium volatilization [3-4]. In this context, this investigation is focused in the synthesis by the polymerization-combustion method and corresponding characterization of two oxides based on $LaCr_{0.8}Fe_{0.2}O_3$ and $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$ systems, in order to identify the effect of doping in the B site of perovskite over the structural and electrical properties.

2. Experimental

For the synthesis of materials, stoichiometric amounts of $La(NO_3)_3.6H_2O$, $Fe(NO_3)_3.9H_2O$, $Cr(NO_3)_3.9H_2O$ and $Co(NO_3)_3.9H_2O$ (99.99%) were dissolved and dossed in glass reactors with temperature control, magnetic stirring and reflux. Each solution was heated to 80°C during 120min.

Then a quantity of citric acid 2.00M was added in a 0.5:1 molar ratio. The solutions were heated at 350°C for 24 hours obtaining the solvent evaporation and the consolidation of dense gels. The gels were calcinated at 850°C during 12 hours to obtain the corresponding powders.

The X-ray diffraction measurements were performed in a Panalytical X´pert PRO-MPD equipment, with a Bragg-Brentano configuration using Cu radiation (Kα=1.54056Å), between 10 and 80° (2Θ). The Debye-Scherrer equation permitted to evaluate the crystal size of samples, using a constant of 0.89 in all cases. The surface morphology was observed using scanning electron microscopy and transmission electron microscopy using a Leica-Zeiss LEO 440 microscope and a JEOL 2100 equipment using a LaB_6 thermionic gun operated with an acceleration voltage of 200kV, equipped with a CCD imaging system, respectively. The elementary chemical composition was confirmed by energy dispersive X-ray analysis. Raman spectroscopy measurements were carried out in a HR-UV 800 infinity microprobe (Jobin-Yvon) spectrometer equipped with a CCD detector (–70◦ C) and a laser power of 10.7mW. The Raman spectrums of the solids were collected between 100 and 800cm^{-1}, projecting a continuous wave laser of He-Ne. The electrical characterization was performed using a Agilent 4294A spectrometer from 25°C to 800°C, with solid pellets compacted in an uniaxial form at 5Mpa. The electrical results were collected and corrected using a solid state reference cell in each determination.

3. Results and discussion

The XRD results are shown in Figure 1, and reveal the formation of a single perovskite phase in both oxides. No secondary phases were detected. The detailed analysis of the samples allows to establish that $LaCr_{0.8}Fe_{0.2}O_3$ and $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$ oxides have a high similarity with the reference pattern of $LaCrO_3$ (JCPDS=01-089-0478), an orthorhombic structure Pnma (62), cell parameters a=5.4790Å, b=7.7562Å, c=5.5161Å and a cell volume of 234.41$Å^3$, in accordance with similar compositions [5,6]. In all cases the crystal size was calculated using the highest diffraction signals along (1 1 2) facet, confirming the obtainment of crystals around 131nm.

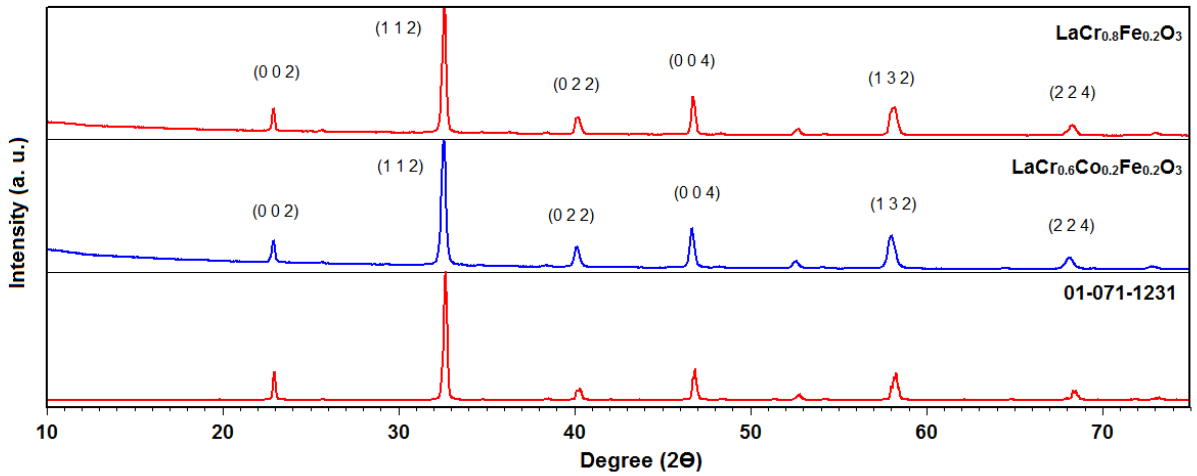

Figure 1. XRD patterns of $LaCr_{0.8}Fe_{0.2}O_3$ and $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$ oxides.

The Figure 2 show the SEM images of $LaCr_{0.8}Fe_{0.2}O_3$ and $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$ oxides. In both materials, particles present semispherical and regular morphology with a distribution according to synthesis process. Additionally, it is observed interconnect irregular porosity originated by decomposition of volatile compounds in the combustion and calcination of samples [7,8]. The EDX analysis of the Figure 3 reveal the presence of Cr, Fe, Co and O, validating the proposed stoichiometry in terms of a high purity and chemical stability of oxides.

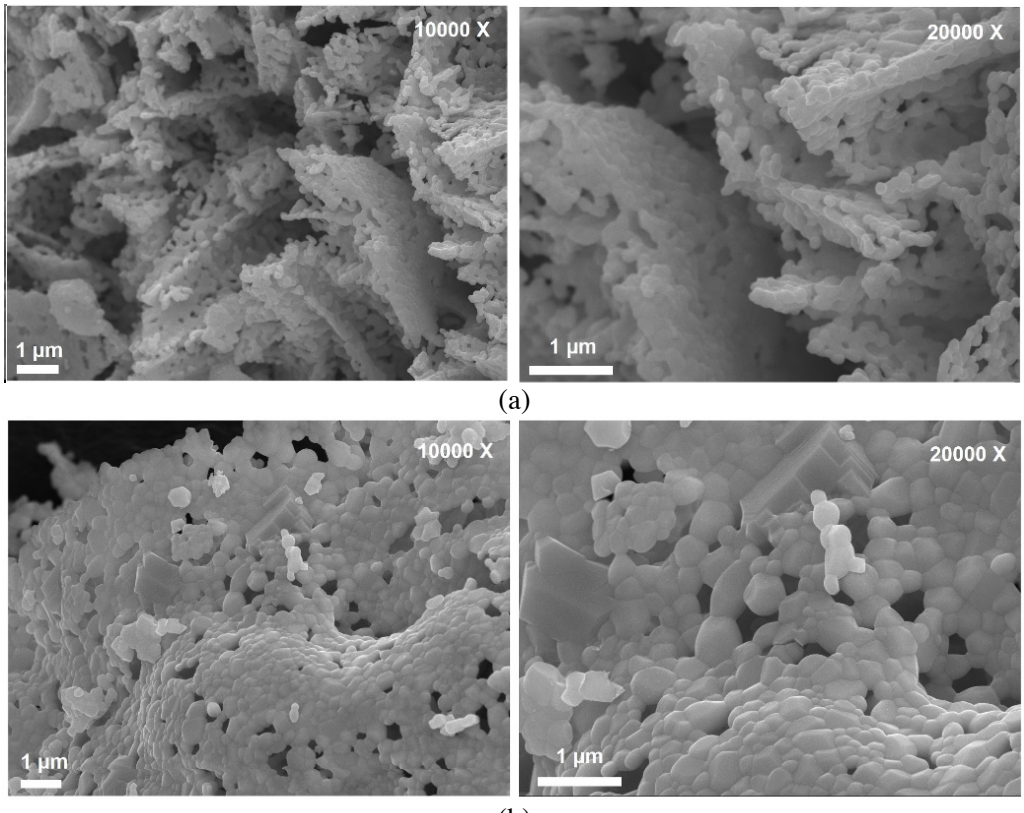

Figure 2. SEM images of (a) $LaCr_{0.8}Fe_{0.2}O_3$ and (b) $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$ to different magnifications.

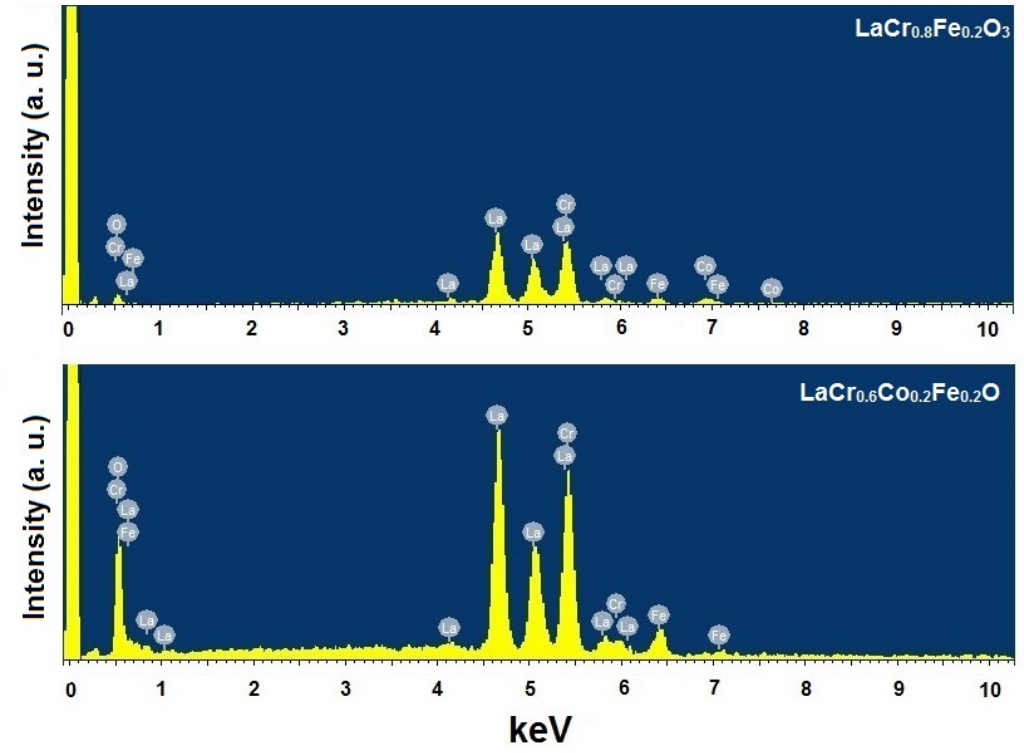

Figure 3. EDX analysis of $LaCr_{0.8}Fe_{0.2}O_3$ and $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$.

Figure 4 with the TEM images allows to observe the crystalline nature of the particles, showing a homogeneous distribution of particles with an average size around 168nm, and interplanar distances of 0.86nm corresponding to the (1 1 2) facets in accordance with XRD results [9].

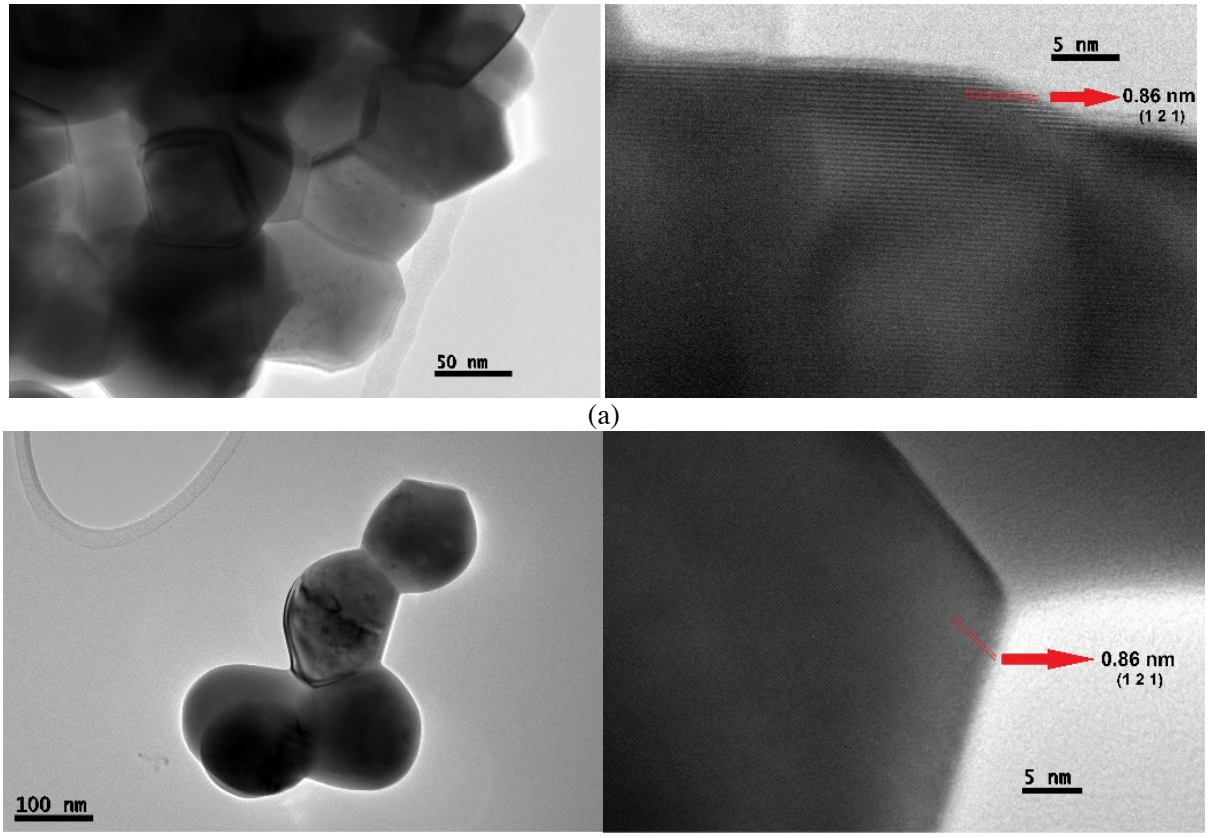

Figure 4. TEM images of interplanar distance and average particle size of (a) $LaCr_{0.8}Fe_{0.2}O_3$ and (b) $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$.

The Raman results of the Figure 5 confirm the presence of vibrational active modes $\Gamma=A_g+7B_{1g}+5B_{2g}+5B_{3g}+8A_u+10B_{1u}+8B_{2u}+10B_{3u}$, with 24 Raman actives to $\Gamma=7A_g+7B_{1g}+5B_{2g}+5B_{3g}$ According to above, the signals located at 432 and 467cm^{-1} are related with A_g modes, and the signals at 524 and 701cm^{-1} corresponding with B_{2g} modes [10]. The absence of another additional peaks suggests the consolidation of a pure and single structures related with $LaCr_{0.8}Fe_{0.2}O_3$ and $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$ oxides.

Finally, the electrical characterization shown in Figure 6, confirm that conductivity of $LaCr_{0.8}Fe_{0.2}O_3$ and $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$ samples increases with temperature in a thermal activation process, which provoke a major mobility of the charge carriers through B-O-B bonds [11]. The modification of oxides with a high concentration of Co promotes an increase in the conductivity, allowing to calculate the activation energy from corresponding Arrhenius plots. The low values of activation energy indicate that conductivity is presented by means of electronic mechanisms more than ionics [8,12]. Furthermore, the incorporation of Co in perovskite oxides produce an increasing in density of charge carriers which are stimulated by thermal activation process related with the conductivity.

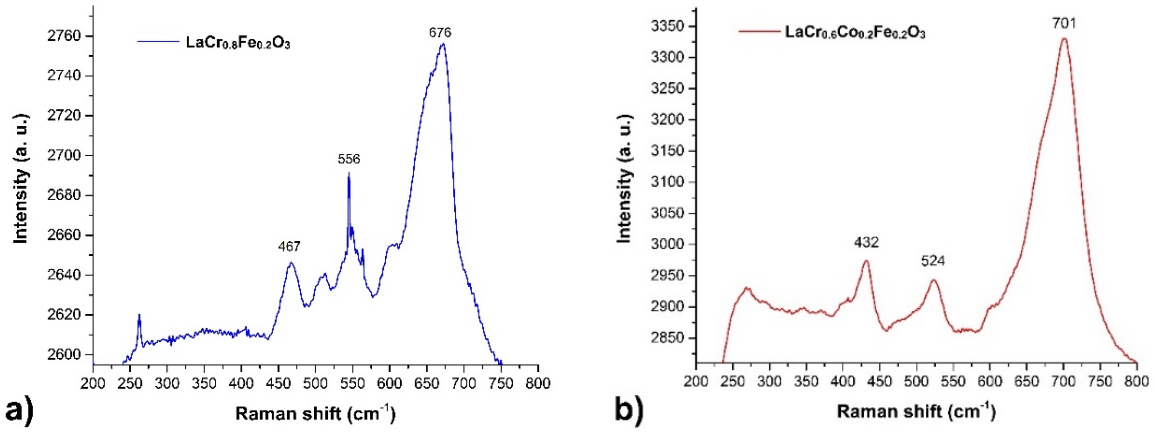

Figure 5. Raman shift of (a) $LaCr_{0.8}Fe_{0.2}O_3$ and (b) $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$.

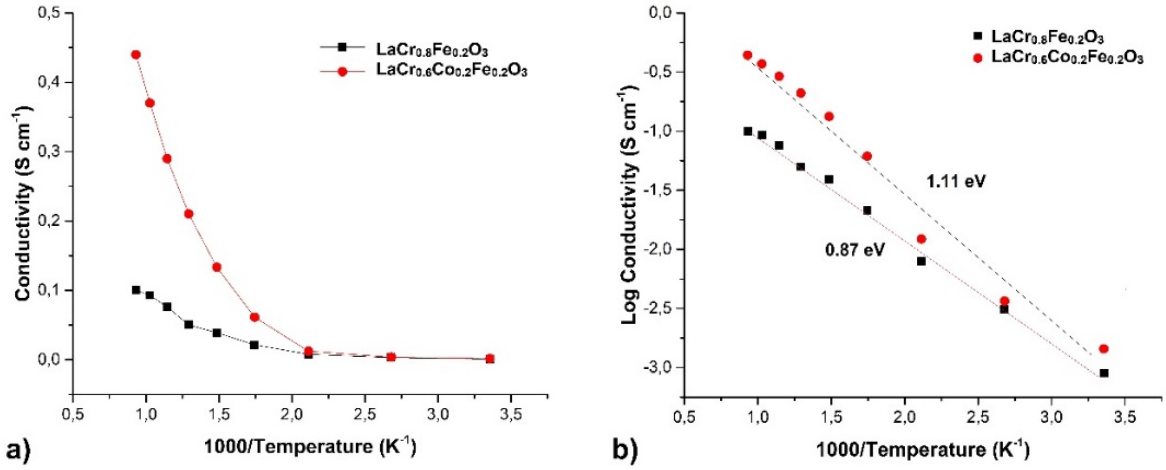

Figure 6. (a) Plot of conductivity and (b) Arrhenius plot from 25 °C to 800 °C of $LaCr_{0.8}Fe_{0.2}O_3$ and $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$.

4. Conclusions

The $LaCr_{0.8}Fe_{0.2}O_3$ and $LaCr_{0.6}Co_{0.2}Fe_{0.2}O_3$ oxides were obtained by means of polymerization-combustion method with crystal sizes of nanometric scale and morphological properties of relevance. The XRD analysis allowed to verify the formation of a pure phase with an orthorhombic structure, Pnma (62) space group and crystal sizes around 131nm in both perovskites. SEM and TEM characterization techniques confirmed that the synthesis method facilitates the obtaining of materials with homogeneous surfaces, high porosity, and regular morphology. Impedance spectroscopy analysis showed as the addition of Co reduced the resistivity to high temperatures of both semiconductor type ceramics for potential applications in design of advanced electrodes for solid oxide fuel cells.

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