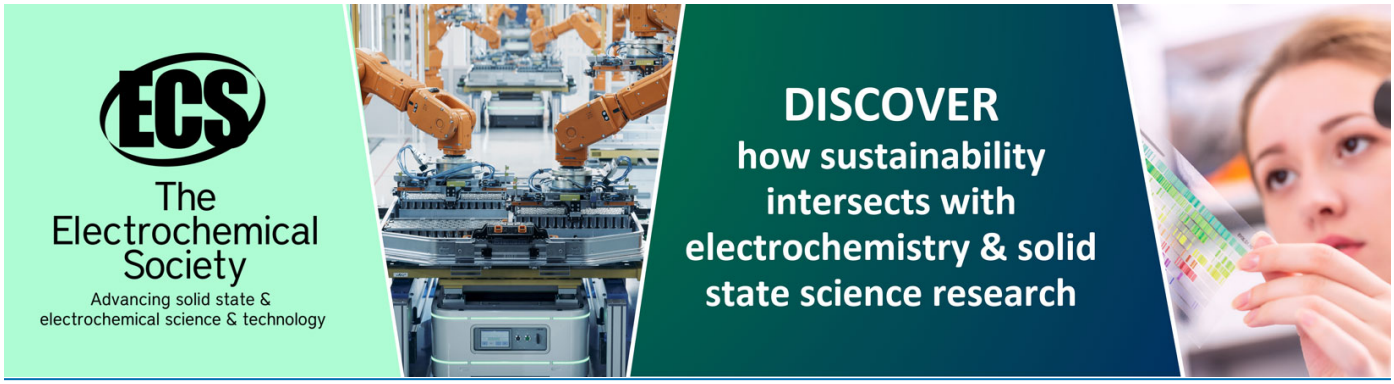
Electrical and structural behaviour of the perovskite $LaCr_{0.4}Co_{0.4}Fe_{0.2}O_3$



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Electrical and structural behaviour of the perovskite $LaCr_{0.4}Co_{0.4}Fe_{0.2}O_3$

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Abstract: The electrical and structural properties of the $LaCr_{0.4}Co_{0.4}Fe_{0.2}O_3$ perovskite are investigated. The oxide is synthetized by polymerization-combustion method, using citric acid as a chelating agent and low calcination temperature. The X-ray diffraction, Raman spectroscopy and transmission electron microscopy analysis show conformation of a pure phase with rhombohedral *(R-3c)* structure and confirmed high structural crystallinity facilitated by synthesis method. The characterization by means of impedance spectroscopy is performed at room temperature. It is observed that the oxides behave as materials of the semiconductor type and that the conductivity increase in accordance to a thermal excitation phenomenon.

1. Introduction

The perovskite $LaCrO_3$ had been extensively studied as electrode material in solid oxide fuel cells because it has shown good stability in both oxidizing and reducing atmospheres. It has been found that this oxide presents an orthorhombic lattice at room temperature, rhombohedral lattice at 260°C, and cubic lattice at 1600°C, which gives it diverse properties [1]. Furthermore, it has been observed that modified $LaCrO_3$ materials show a high resistivity towards carbon deposition and an excellent electrochemical activity to hydrocarbon reforming reactions, which can be significantly enhanced by introduction of transition cations in the structure as Fe and Co. Several methods have been employed as solid state reaction [2], hydrothermal [3], sol-gel [4] and co-precipitation [5] to try controlling Cr volatilization, which is one of the main drawbacks of these oxides, but the polymerization-combustion has shown the best results for their control, due to the use of citric acid in the formation of metal-citrate compounds and the low calcination temperatures [6-8]. In this paper the perovskite $LaCr_{0.4}Co_{0.4}Fe_{0.2}O_3$ is synthesized by the polymerization-combustion method and it is study with the aim of evaluating doping effect on the electrical and structural properties.

2. Experimental

The starting materials were $La(NO_3)_3.6H_2O$, $Fe(NO_3)_3.9H_2O$, $Cr(NO_3)_3.9H_2O$ and $Co(NO_3)_3.9H_2O$ (99.99%) (1.00M). Citric acid (2.00M) was used as chelating agent in a 0.5:1 molar ratio with respect to total metal cation content. The dissolution was drying to 90°C by 120min with continuous stirring and reflux. It was continued with heating at 350°C for 2 hours until the consolidation of a gel, which was calcinated for 12 hours at 850°C. The structural characterization was carried out in a Panalytical X´pert PRO-MPD diffractometer from 10 to 80° (2Θ) using Cu radiation and Bragg-Brentano configuration. The transmission electron microscopy observations were performed with a JEOL 2100

microscope employing an acceleration voltage of 200kV and a LaB_6 thermionic gun. An HR-UV 800 infinity microprobe (Jobin-Yvon) spectrometer with a laser of 785nm was employed to collect the Raman shift. The electrical characterization was performed in an Agilent 4294A spectrometer using pellets of solids compacted and coated with platinum on the surface.

3. Results and discussion

Figure 1 reveals the formation of a rhombohedral *R-3c (167)* single phase perovskite with cell parameters *a*=5.4619Å, *c*=13.5284Å, volume of cell=349.511Å^3, unlike what happens with the un-doped lanthanum chromite that tends to be orthorhombic [1]. The Fe and Co doping generated a reduction on the BO_6 octahedron and smaller B-O bond distances than $LaCrO_3$, for which a rhombohedral crystalline structure was formed, according to previous reports in where the doping at the site B of the lattice generated a lower distortion of the BO_6 octahedron [9]. No additional peaks were found, suggesting that all metal elements were integrated within the perovskite structure. The crystalline size was calculated with Debye-Scherrer equation [10], using a constant of 0.89 and the strongest peak (1 2 1). The estimated crystallite size was 31nm.

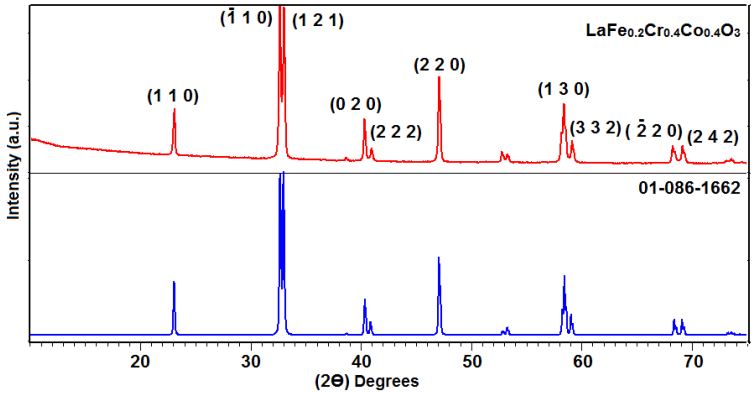

Figure 1. XRD pattern of $LaCr_{0.4}Co_{0.4}Fe_{0.2}O_3$.

TEM images reveal the crystalline that the materials reached. Figure 2(a) shows an interplanar spacing of 3.15Å corresponding to the (1 2 1) plane, ratifying the results obtained by means of X-ray diffraction about the nanometric size of the sample. Figure 2(b) confirms high crystallinity obtained by polymerization-combustion method without the formation of planar defects, moreover ratifying the existence of a rhombohedral crystalline structure.

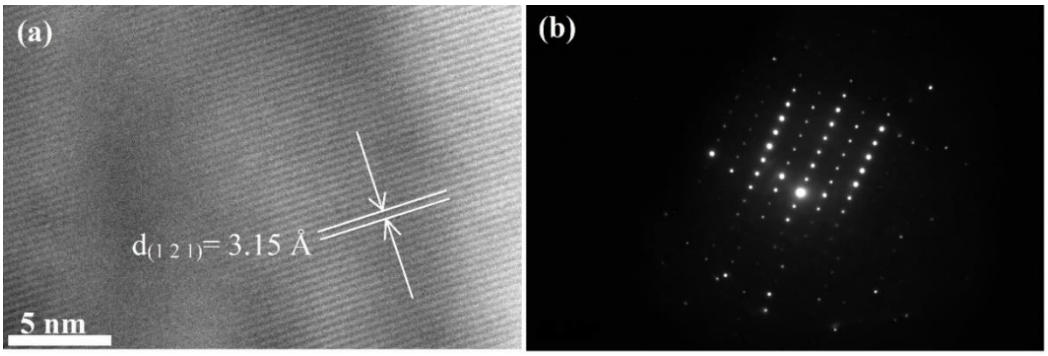

Figure 2. TEM images of $LaCr_{0.4}Co_{0.4}Fe_{0.2}O_3$.

Figure 3 shows the existence of signals at 553 and 647cm^{-1}, which are associated to B_{1g} stretch modes of a rhombohedral structure [8]. The Co and Fe doping generated a displacement of the peaks of the $LaCrO_3$ original perovskite toward a lower Raman shift and doing the peaks located below

300cm^{-1} more diffuse [11], since in other reports $LaCrO_3$ have been seen that the same vibrational modes appear in 590 and 719cm^{-1} [12].

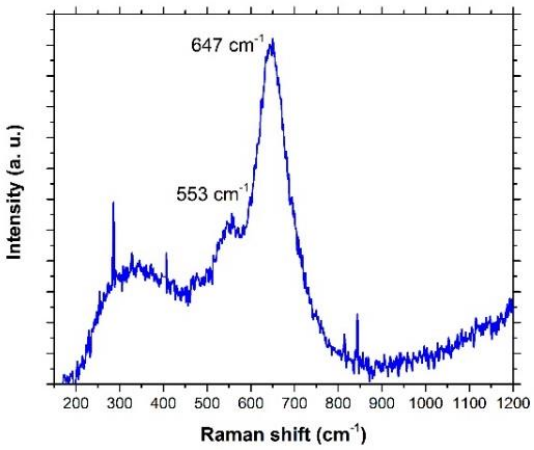

Figure 3. Raman shift of $LaCr_{0.4}Co_{0.4}Fe_{0.2}O_3$.

The electrical properties were measured as a function of the temperature. Figure 4(a) exhibits the impedance spectra in where an only semi-arc is observed without the appearance of a charge transfer resistance, where resistivity decreases with increasing of the temperature, besides at high temperatures an ohmic resistance is observed, indicating that the oxide has a semiconductor type behaviour [13]. Figure 4(b) confirms that the perovskite is formed by resistance inside (bulk) and at the grain boundary, since the peaks appear at both low and high frequencies [8].

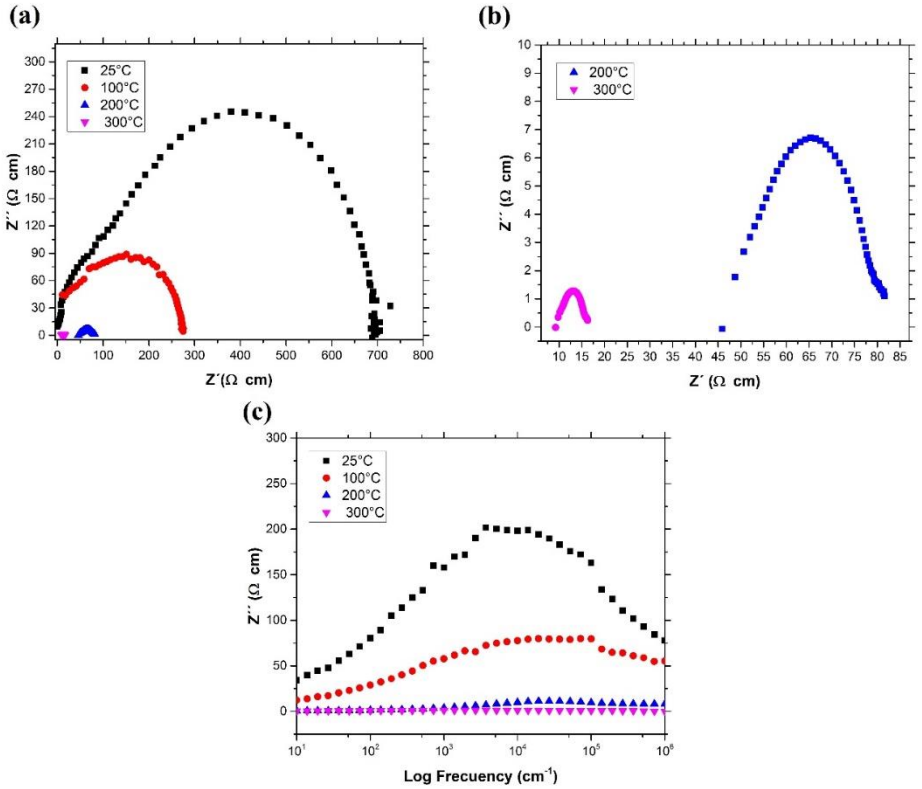

Figure 4. (a) (b) Nyquist and (c) Imaginary part of impedance (Z´´) vs Frequency logarithm plots of $LaCr_{0.4}Co_{0.4}Fe_{0.2}O_3$.

Figure 5 shows that conductivity increase with an increment of the temperature, which indicate that oxide present a thermal excitation phenomenon that enhances the mobility of the charge carries between B-O-B bonds. This behaviour allows linear slope of the Arrhenius plot to be the activation energy value. The value of the activation energy was 1.05 eV. Both the linear tendency and low value of the slope of the Arrhenius plot indicate that the conductivity mechanisms are mainly caused by electronic species, according to the Nyquist plots [14,15].

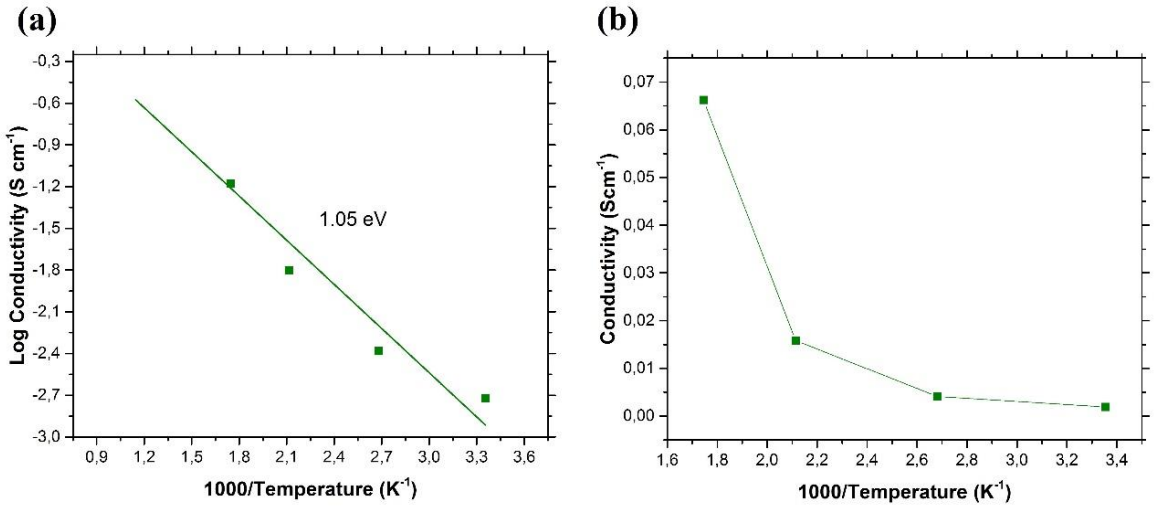

Figure 5. (a) Conductivity and (b) Arrhenius plots of $LaCr_{0.4}Co_{0.4}Fe_{0.2}O_3$.

4. Conclusions

The perovskite $LaCr_{0.4}Co_{0.4}Fe_{0.2}O_3$ synthesized through polymerization-combustion method reached outstanding structural and electrical properties to be applied as electrode in solid oxide fuel cells. The oxide showed a rhombohedral *(R-3c)* single phase with the deformation of the BO_6 octahedron caused by incorporation of Co and Fe, which also induced a displacement of the Raman peaks toward lower Raman shift with respect to un-doped $LaCrO_3$. The material presented a semiconductor type electrical behaviour with a thermal excitation phenomenon and an activation energy of 1.05eV.

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