



Strontium and cobalt doped-lanthanum chromite: Characterisation of synthesised powders and sintered materials

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Abstract

Perovskite powders prepared by combustion synthesis with a nominal composition of $\text{La}_{0.800}\text{Sr}_{0.200}\text{Cr}_{0.920}\text{Co}_{0.080}\text{O}_{3.000-\delta}$ were obtained from the corresponding metal nitrates, and characterised in terms of in-situ phase development (crystalline structure and thermal behaviour). Synchrotron X-ray powder diffraction (SXRPD) and Rietveld analyses demonstrated that the as-prepared powder showed an orthorhombic perovskite structure with an estimated composition of $\text{La}_{0.803}\text{Sr}_{0.197}\text{Cr}_{0.966}\text{Co}_{0.034}\text{O}_{3.000-\delta}$. Second phases present in the as-prepared powder were $m\text{-LaCrO}_4$, $\text{CoLa}_{1.250}\text{Sr}_{0.750}\text{O}_{4.000}$, $c\text{-CoCr}_{2.000}\text{O}_{4.000}$ and $m\text{-SrCrO}_{4.000}$. Sintering processes, including phase transition (from orthorhombic to rhombohedral) of the main phase and, melting/evaporation of second phases have been studied by DTA/TGA and dilatometric studies; the results were in full agreement with those detected by High-Temperature Synchrotron X-ray powder diffraction (HT-SXRPD). The transition temperature was determined to be ~ 1380 °C by dilatometric studies, and between 1240 and 1405 °C by HT-SXRPD.

Dye-pressed samples sintered at 1600 °C/4 h showed a density of $\sim 98.9 d_{th}\%$. The phase transition is an irreversible process since the sintered perovskite, measured at room temperature after cooling, only showed the rhombohedral phase as main phase. The evaluation of the linearity of the conductivity versus the inverse of temperature and the activation energy values of the sintered material indicated that the electrical conduction occurs via the non-adiabatic small-polaron mechanism in either air or hydrogen atmosphere. In the reducing environment, the perovskite shows significantly reduced electrical conductivity compared with that in air, as it is expected for a p-type conductor.

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1. Introduction

Doped-lanthanum chromites have interesting properties, such as high melting points (~ 2500 °C), good mechanical properties and electrical conductivity at high temperatures as well as chemical stability at 1000 °C in oxidising and reducing atmospheres. These properties make M-LaCrO_3 ($\text{M}=\text{Ca}, \text{Sr}, \text{Co}, \text{etc.}$) perovskites attractive for high temperature solid oxide fuel cells (SOFCs) as

ceramic supports or coatings for interconnector materials [1–3] at operating temperatures of 1000 °C. As electrically conducting refractory materials they are also of interest for electrode applications in magnetohydrodynamic (MHD) generator channels [4] and as heating elements in high temperature furnaces [5]. Since the synthesis of doped-lanthanum chromite is complex, new routes, such as sol–gel and Pechini's method, have been explored [6]. In this sense, the combustion synthesis using aqueous solutions is in focus because it is a relatively simple, fast and economically viable method [7], in which the starting materials or reagents are easily found in the market. Furthermore, LaCrO_3 -based

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perovskites are difficult to sinter in air due to vapour-phase transport of higher-valence oxides of Cr [8–11]. According to Tai and Lessing [12] and Anderson et al. [13] this behaviour is similar to that for Cr_2O_3 and MgCr_2O_4 in which densification is maximised in a gaseous atmosphere which oxygen activity is near that in equilibrium with Cr(s) and $\text{Cr}_2\text{O}_3(\text{s})$ ($p\text{O}_2 < 10\text{--}11$ atm in the temperature range $1600\text{--}1700$ °C). The occurrence of a liquid phase beyond 1600 °C in the $\text{Cr}_2\text{O}_3\text{--Cr}$ system could explain this result [14]. However, other works [15,16] show significant improvements in sinterability in air through both the use of nanosized powders and the substitution of some elements, i.e. Ca or Sr for La and Co, Cu, Zn or Ca for Cr. The use of dopants in these materials is extremely useful, and they can also improve their electrical properties, i.e. Sr., and enhance the thermal expansion coefficient [1,17–21], i.e. Co, which can also improve the densification of the samples.

Pure LaCrO_3 is a p-type conductor [22] with quite low conductivity in either oxidising or reducing environment, e.g. 0.33 S/cm at 800 °C in air and 0.09 S/cm at 800 °C in reducing atmosphere. In general, doping alkaline earth (AE) elements such as Mg, Ca, Sr and Ba at the A-site in LaCrO_3 do improve the conductivity value of perovskites. In addition, doping bivalent AE elements may introduce a Cr^{3+} to Cr^{4+} transition [23] and hence more electronic holes in the valence band maximum primarily composed by O^{-2} p level, which is a common process for a charge-transfer type insulator with redox transition metals like Cr and Mn. The high-electrical conductivity of the perovskite in air makes that composition promising as interconnector in SOFCs, however with a decrease in $p\text{O}_2$, the electrical conductivity of the perovskite decreases. As it is well-known, the Sr^{2+} on the La^{3+} sites is compensated by oxygen vacancies giving rise to ionic conductivity [24,25]. The values of ionic radii for Co^{2+} (VI) and Co^{3+} (VI) are 0.065 nm and 0.055 nm, respectively [26], and fall slightly above and below of that for Cr^{3+} (VI) (0.062 nm), respectively [26]. Thus, it should allow Co to enter, either state, to the perovskite lattice.

Due to the high operating temperature, 1000 °C, it is essential to control the effect of the temperature on different parameters involved in the process, such as the formation of new crystalline phases, phase transitions, thermal expansion coefficient, and density and electrical properties of the formed material. The combustion synthesis of strontium and cobalt doped lanthanum chromite powder [27], $\text{La}_{0.800}\text{Sr}_{0.200}\text{Cr}_{0.920}\text{Co}_{0.080}\text{O}_{3.000-\delta}$, and its colloidal processing [28,29], have been reported elsewhere; however, thermo-diffraction studies and electrical properties of that sintered material, prepared by combustion synthesis, have not been reported yet to the best of our knowledge.

There is a double objective in this work. First, to study the effect of the temperature on the structural parameters, phase transition and chemical reactions during heating of our lab-prepared strontium and cobalt doped lanthanum chromite powder. For that purpose, the powder was characterised through HT-SXRPD, DTA–TGA and dilatometric studies. Second, to study the doped lanthanum chromite material after sintering, since it may be used as ceramic support or coating for interconnector materials for HT-SOFCs [1,2]. The sintered material was characterised in terms of laboratory X-ray powder

diffraction (LXRPD), electron microscopy, thermal expansion coefficient, and electrical properties.

2. Experimental

2.1. Synthesis and characterisation of strontium and cobalt doped lanthanum chromite powder

A powder with the nominal composition of $\text{La}_{0.800}\text{Sr}_{0.200}\text{Cr}_{0.920}\text{Co}_{0.080}\text{O}_{3-\delta}$ was prepared by combustion synthesis as described elsewhere [27]. The precursors used were the following: (1) chromium (III) nitrate nonahydrated, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%, Aldrich, Germany); (2) lanthanum (III) nitrate hexahydrated, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Aldrich, Germany); (3) strontium nitrate, $\text{Sr}(\text{NO}_3)_2$ (99%, Aldrich, Germany); and (4) cobalt (II) nitrate hexahydrated, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Vetec, Brazil). Urea ($\text{CO}(\text{NH}_2)_2$, for synthesis, Nuclear, Brazil) was used as a fuel. The synthesized powder was attrition milled in ethanol media (ethanol absolute, Casa Americana, Brazil) using silicon nitride balls for 2 h, and further dried in a muffle at 60 °C.

The nitrogen content of the as-prepared powder was determined with a LECO TC-436 (Michigan, USA) nitrogen analyser, employing the gas fusion method. The chemical analysis of the carbon content of the as-prepared powder was performed using a LECO analyser, CS-200 model (Michigan, USA). Three measurements were performed in both analyses in order to obtain an average value.

The as-prepared powder was characterised through High Temperature Synchrotron X-Ray Powder Diffraction (HT-SXRPD). High resolution synchrotron powder patterns were collected, as a function of the temperature, from room temperature (RT) up to 1400 °C, on ID31 powder diffractometer of European Synchrotron Radiation Facility (ESRF) (Grenoble, France) using a short wavelength $\lambda = 0.29980(3)$ Å (41.34 keV) selected with a double-crystal Si (1 1 1) monochromator and calibrated with Si NIST ($a = 5.431195$ Å). The Debye–Scherrer (transmission) configuration was used with the sample loaded in a rotating borosilicate glass capillary of diameter of 1.0 mm at RT and in Platinum capillary with an inner diameter of 0.6 mm and a wall size of 40 µm at high temperature. The capillaries were rotated at ~ 200 r.p.m. during data collection to improve particle statistics. The data acquisition time was ~ 45 min at each temperature to assure good counting statistics over the angular range $4\text{--}25^\circ$ (in 2θ). The multi-analyser Si (1 1 1) stage coupled with nine point detectors was used. However, only seven of them were used to normalise data owing to problems with the side detectors at such high energy. Data were summed up to 0.003° step size with local software to produce the final raw data. A parabolic mirror furnace composed of three halogen lamps [30] was used to heat the samples up to ~ 1400 °C. The real temperature of the powder was calculated from the platinum unit cell variation [31].

SXRPD patterns were analysed by using the Rietveld method as implemented in the General Structure Analysis System (GSAS) software package [32] using the EXPGUI graphic interface [33], in order to perform a structural study of the RT-SXRPD pattern [34,35] and Rietveld Quantitative Phase Analysis (RQPA) of the HT-SXRPD patterns to

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