

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 $\sim 1380^\circ\text{C}$ by dilatometric studies, and between 1240 and 1405°C by HT-SXRPD.

Dye-pressed samples sintered at $1600^\circ\text{C}/4\text{ h}$ showed a density of $\sim 98.9 d_{\text{th}}\%$. 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 ($\sim 2500^\circ\text{C}$), 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 ($\text{M}=\text{Ca}, \text{Sr}, \text{Co}$, 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

determine the phase transition. Peak shapes were fitted by using the pseudo-Voigt function [36] with the axial divergence correction implemented [37]. Pt peaks gave very significant contribution hence were excluded from the fits [38]. The evolution, with temperature of all the samples, including the powder from the sintered pellet (1600 °C) after crushing and those measured at RT, was studied using X'Pert Highscore Plus software from PANalytical B.V., version 3.0e in order to identify the diminishing and/or disappearance of phases. The as-prepared powder was analysed by means of field-emission scanning electron microscopy-energy dispersive X-ray (FE-SEM-EDX) (Hitachi S-4700 type I, Tokyo, Japan) and by means of transmission electron microscopy-energy dispersive X-ray (TEM-EDX) (Jeol JEM1400, Tokyo, Japan).

Differential thermal (DTA) and thermogravimetric (TGA) analyses were performed in a NETZSCH STA-409 Thermoanalyzer (Germany) in air, using alumina as the reference material, in the temperature range of 20–1500 °C at a heating rate of 10 °C/min.

Dynamic sintering studies were performed with discs with 10 mm in diameter prepared by dye pressing at 90 MPa. These experiments were performed in air up to 1600 °C in a differential dilatometer with alumina rod (Model 402E/7, Netzsch, Germany) with constant heating and cooling rates of 10 °C/min. The thermal expansion coefficient (TEC) was calculated from the data obtained from the dilatometer equipment in the temperature range from 50 to 1000 °C. The TECs of our perovskite was calculated from the following equation:

$$\alpha = (1/L_1)(L_2 - L_1)(T_2 - T_1) \quad (1)$$

where α is the TEC, T_1 is the starting temperature, T_2 is the final temperature, and L_1 and L_2 are the initial and final lengths, respectively.

2.2. Sintering and characterisation of strontium and cobalt doped lanthanum chromite materials

Sintering studies were conducted using the green discs prepared by dye-pressing at 90 MPa and further sintering at 1600 °C/4 h in air. The average density value of the sintered samples was obtained by Archimedes' method in water.

Laboratory X-Ray Powder Diffraction (LXRPD) studies were performed on ground powder obtained from a sintered dye-pressed sample. Patterns were recorded on an X'Pert MPD PRO diffractometer (PANalytical) using strictly monochromatic $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54059 \text{ \AA}$) [Ge (1 1 1) primary monochromator] and working in reflection geometry ($\theta/2\theta$). The X-ray tube worked at 45 kV and 40 mA. The optics configuration was a fixed divergence slit ($1/2^\circ$), a fixed incident antiscatter slit (1°), a fixed diffracted anti-scatter slit ($1/2^\circ$) and X'Celerator Real Time Multiple Strip (RTMS) detector, working in scanning mode with maximum active length. Data were collected from 10° to 140° (2θ) during ~ 2 h. The samples were rotated during data collection at 16 r.p.m. in order to enhance particle statistics.

LXRPD pattern was analysed following the same methodology explained for SXRPD patterns.

The microstructure of the sintered sample (bulk) was observed on polished (down to $1 \mu\text{m}$) and thermally etched surfaces (1590 °C for 6 min, heating and cooling rates of 10 °C/min) by means of field-emission scanning electron microscopy-energy dispersive X-ray (FE-SEM-EDX) analyses (Hitachi S-4700 type I, Tokyo, Japan). The polished material was gold sputtered prior to FE-SEM observations.

The powder obtained by grinding the sintered bulk was dispersed in ethanol; once the solvent was evaporated, the

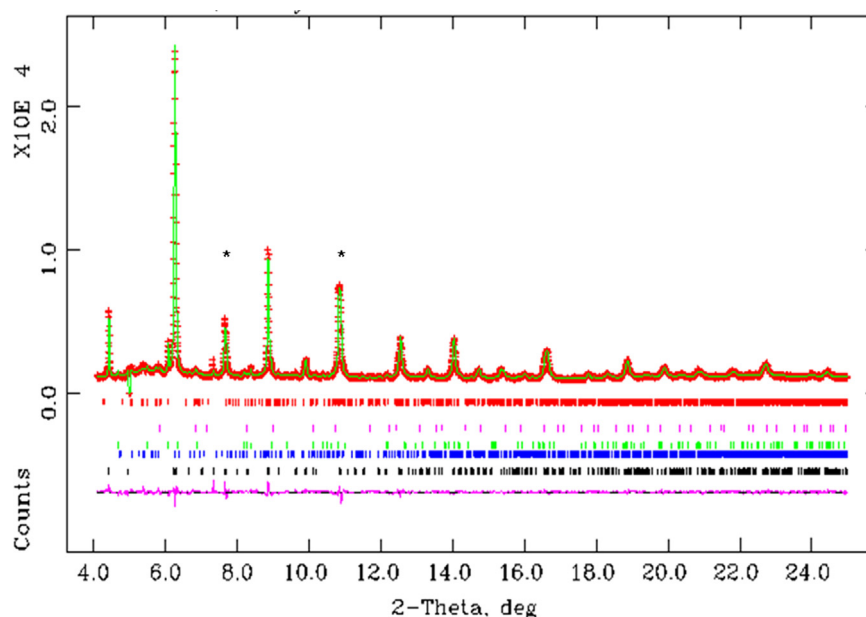


Fig. 1. Rietveld refinement of SXRPD data of the as-prepared powder measured at room temperature. Crosses correspond to the experimental scan, solid line is the calculated pattern and the bottom line is the difference curve, respectively. Selected areas (2θ ranges from 7.55° to 7.75° and from 10.6° to 11.0° , $\lambda = 0.23 \text{ \AA}$) further analysed by HT-SXRPD (in Fig. 2) are marked with an asterisk.

powder was analysed by transmission electron microscopy, TEM (Jeol JEM1400, Tokyo, Japan) combined with energy dispersive spectroscopy (EDX).

Sintered samples were electrically measured by a dc four-terminal method using Pt as electrode and a Lake Shore 370 AC resistance bridge (USA), and a digital multimeter (Keithley, mod. 2000, USA) monitored the temperature measured by a type K thermocouple positioned close to the sample. Bar samples ($8 \times 2 \times 1$ mm) cut from cylindrical pellets (sintered at $1600^\circ\text{C}/4$ h) were measured in air and H_2 (4 wt%) from RT up to 800°C during heating and cooling ($3^\circ\text{C}/\text{min}$), excited by 2 mA DC.

Table 1

Direct RQPA results (wt%) for the as-prepared powder measured at room temperature.

Phase	wt%	ICSD
Orthorhombic- $\text{La}_{0.803}\text{Sr}_{0.197}\text{Cr}_{0.966}\text{Co}_{0.034}\text{O}_{3.000-\delta}$	68.3(1)	9938 (<i>o</i> - LaCrO_3)
<i>m</i>-$\text{LaCrO}_{4.000}$	23.3(6)	81938
<i>CoLa</i>$_{1.250}\text{Sr}_{0.750}\text{O}_{4.000}$	5.9(1)	415895
<i>c</i>-$\text{CoCr}_2\text{O}_{4.000}$	0.8(1)	69503
<i>m</i>-$\text{SrCrO}_{4.000}$	1.6(1)	40922

Table 2

Selected structural parameters for the as-prepared perovskite measured under SXRPD (at room temperature).

	RT
La/Sr(1) , 4, (<i>x</i> , <i>y</i> , 1/4)	
<i>x</i>	0.993(1)
<i>y</i>	0.015(1)
Iso-ADP $\times 100$ ($\text{\AA}^2$)	0.1(1)
Cr/Co (1) , 4, (0, 1/2, 0)	–
Iso-ADP $\times 100$ ($\text{\AA}^2$)	0.4(1)
O(1) , 4, (<i>x</i> , <i>y</i> , 1/4)	
<i>x</i>	0.069(2)
<i>y</i>	0.494(2)
Iso-ADP $\times 100$ ($\text{\AA}^2$)	–2.1(3)
O(2) , 8, (<i>x</i> , <i>y</i> , <i>z</i>)	
<i>x</i>	0.733(3)
<i>y</i>	0.288(2)
<i>z</i>	0.033(2)
Iso-ADP $\times 100$ ($\text{\AA}^2$)	0.2(2)

Table 3

Cell parameters for the as-prepared perovskite measured at different temperatures under SXRPD.

Space group	RT <i>Pbnm</i>	1071 °C <i>Pbnm</i>	1198 °C <i>Pbnm</i>	1240 °C <i>Pbnm</i>	1405 °C <i>R-3c</i>	RT-after sintering 1600 °C <i>R-3c</i>
<i>a</i> ($\text{\AA}$)	5.5140(2)	5.5642(4)	5.5675(3)	5.5648(9)	5.5608(2)	5.4952(1)
<i>b</i> ($\text{\AA}$)	5.4726(2)	5.5293(4)	5.5456(3)	5.5602(4)	5.5608(–)	5.4952(1)
<i>c</i> ($\text{\AA}$)	7.7611(2)	7.8522(4)	7.8559(5)	7.8576(4)	13.613(1)	13.2990(1)
<i>V</i> ($\text{\AA}^3$)	234.20(1)	241.58(4)	242.55(3)	243.13(3)	364.56(5)*	347.79(1)**

*In order to compare the volumes, the volume of the hexagonal unit cell should be divided by 1.5, yielding $243.04 \text{ \AA}^3$.

**In order to compare the volumes, the volume of the hexagonal unit cell should be divided by 1.5, yielding $231.86 \text{ \AA}^3$.

3. Results and discussion

3.1. Laboratory-prepared strontium and cobalt doped lanthanum chromite powder

As reported in a previous work [28], the average particle size of the milled powders measured by laser diffraction is $2.1 \pm 0.1 \mu\text{m}$, but according to scanning electron microscopy observations these are agglomerates consisting of nanosized particles that behave as unitary particles. In addition, the powder shows a specific surface area (S_s) of $10 \pm 2 \text{ m}^2/\text{g}$ [29]. The as-prepared powder showed average contents of nitrogen and carbon of 0.80 and 0.30 wt%, respectively. This may well be related with the presence of some unreacted nitrate precursors, intermediate products from the fuel, and/or N_2 and CO_2 byproducts of the combustion reaction occluded in the nanopowders.

Fig. 1 shows the Rietveld plot for the RT-SXRPD pattern (SXRPD pattern measured at room temperature) of the as-prepared powder. Crosses correspond to the experimental scan, solid line is the calculated pattern and the bottom line is the difference curve, respectively. The two peaks marked with asterisk will be further discussed in the temperature-dependent study. The Rietveld fit is very good as evidenced by the flatness of the difference curve and the low disagreement factors. RQPA is shown in Table 1. The as-prepared powder is mainly formed by orthorhombic- $\text{La}_{0.803}\text{Sr}_{0.197}\text{Cr}_{0.966}\text{Co}_{0.034}\text{O}_{3.000-\delta}$, (68.3(1) wt%), a slightly different composition than the nominal formulation. Since there is not a published structure of lanthanum chromite doped with Sr and Co, an orthorhombic- LaCrO_3 (*o*- LaCrO_3) (ICSD-9938) was used as starting point for the Rietveld analysis and Sr and Co atoms were added to the structure manually according to the expected stoichiometry and finally, the atomic occupation factors were refined. The proposed structure provides an improvement in the values of disagreement factors, R_{wp} and R_F , from 4.6% to 4.5% and from 2.6% to 2.5% respectively, when compared with the nominal structure. It is known that Cr and Co have nearly identical scattering factors, and La and Sr are correlated, hence the real stoichiometry might be slightly different. However, the evolution of the fit for the refined stoichiometry yields to non-arbitrary and consistent results. Due to the presence of high amounts of second phases, 31.6 wt%, in the as-prepared powder, spectroscopic methods such as FE-SEM and TEM combined with EDX did not provide useful information about

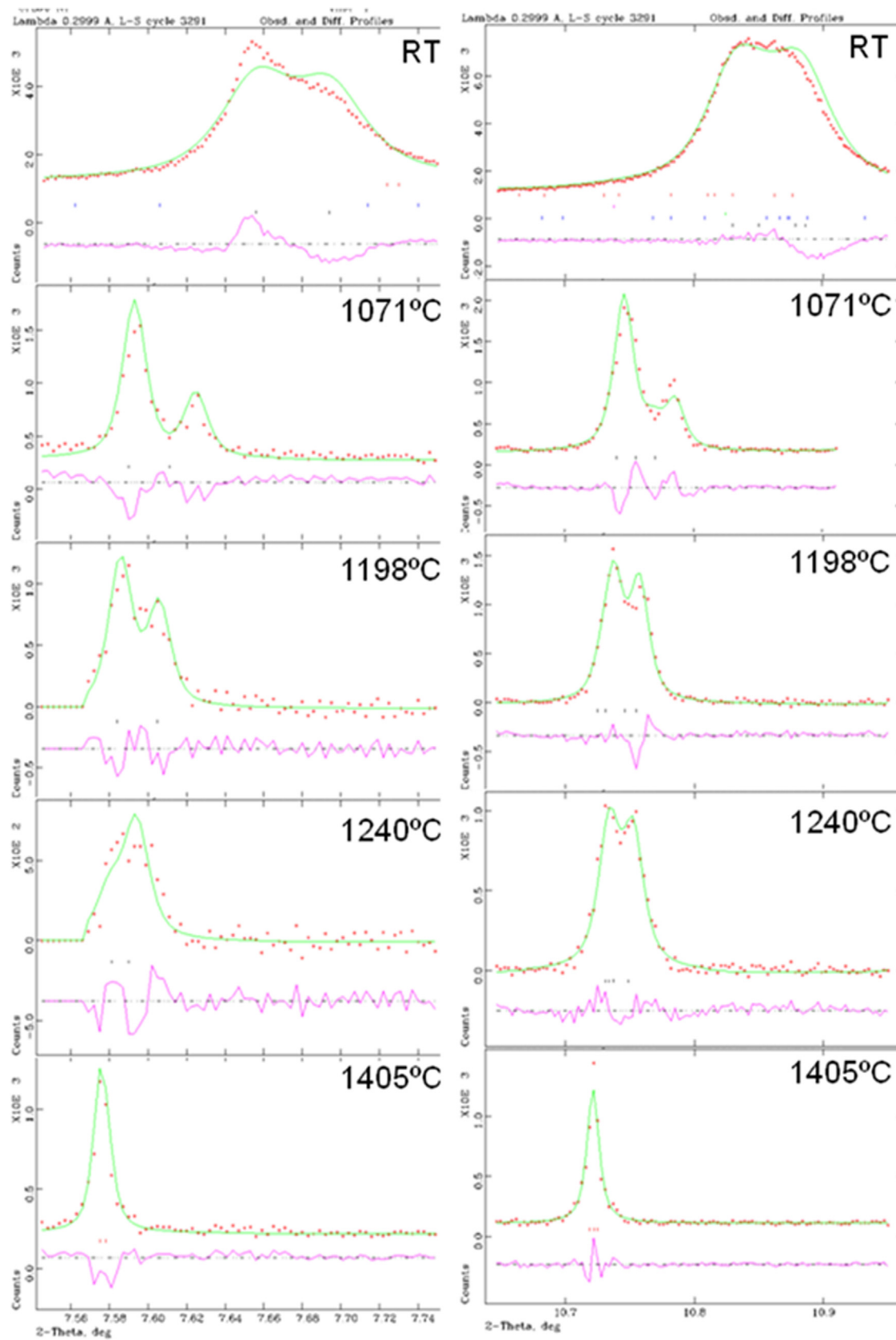


Fig. 2. Selected areas (2θ ranges from 7.55° to 7.75° and from 10.6° to 11.0° , $\lambda=0.23 \text{ \AA}$) of SXRPD Rietveld plots at different temperatures (RT, 1071, 1198, 1240 and 1405 °C) of the as-prepared powder, which are marked with an asterisk in Fig. 1 (sample measured at RT).

the stoichiometry of the cations. The second phases are $m\text{-LaCrO}_{4.000}$, $\text{CoLa}_{1.250}\text{Sr}_{0.750}\text{O}_{4.000}$, $c\text{-CoCr}_{2.000}\text{O}_{4.000}$ and $m\text{-SrCrO}_{4.000}$. The percentages and corresponding ICSD codes of the crystallographic descriptions used for the fit are shown in Table 1. The presence of $m\text{-SrCrO}_{4.000}$ implies that the temperature reached during the combustion synthesis was, at least, 800 °C [39,40] due to the limited alkaline earth solubilisation at intermediate temperatures. According to Colomer et al. [41], temperatures of 857 °C were reached in the combustion synthesis of lanthanum-based perovskites prepared from nitrates and using urea as fuel, following the same conditions of synthesis employed in this study.

The refined structural parameters for the as-synthesized orthorhombic- $\text{La}_{0.803}\text{Sr}_{0.197}\text{Cr}_{0.966}\text{Co}_{0.034}\text{O}_{3.000-\delta}$, major phase

obtained from RT-SXRPD, are shown in Tables 2 and 3. We used several constraints in order to fit the same atomic positions (x,y,z) and isotropic atomic displacement parameters (Iso-ADPs) values for those atoms occupying the same position. The rest of the values were refined freely. The presence of Sr and Co in the crystal structure does not produce significant changes in the structural parameters; only the lattice parameters and volume are affected by the dopants. There is disorder in the structure (due to the atomic non-stoichiometry) which results in the strain-induced peak broadening in the powder patterns (diffraction peaks in the high angle regions are quite broad). A very small and negative thermal displacement factor, Iso-ADP, given in Table 2 for O(1) has unphysical meaning, being mainly caused by the inherent disorder of the structure.

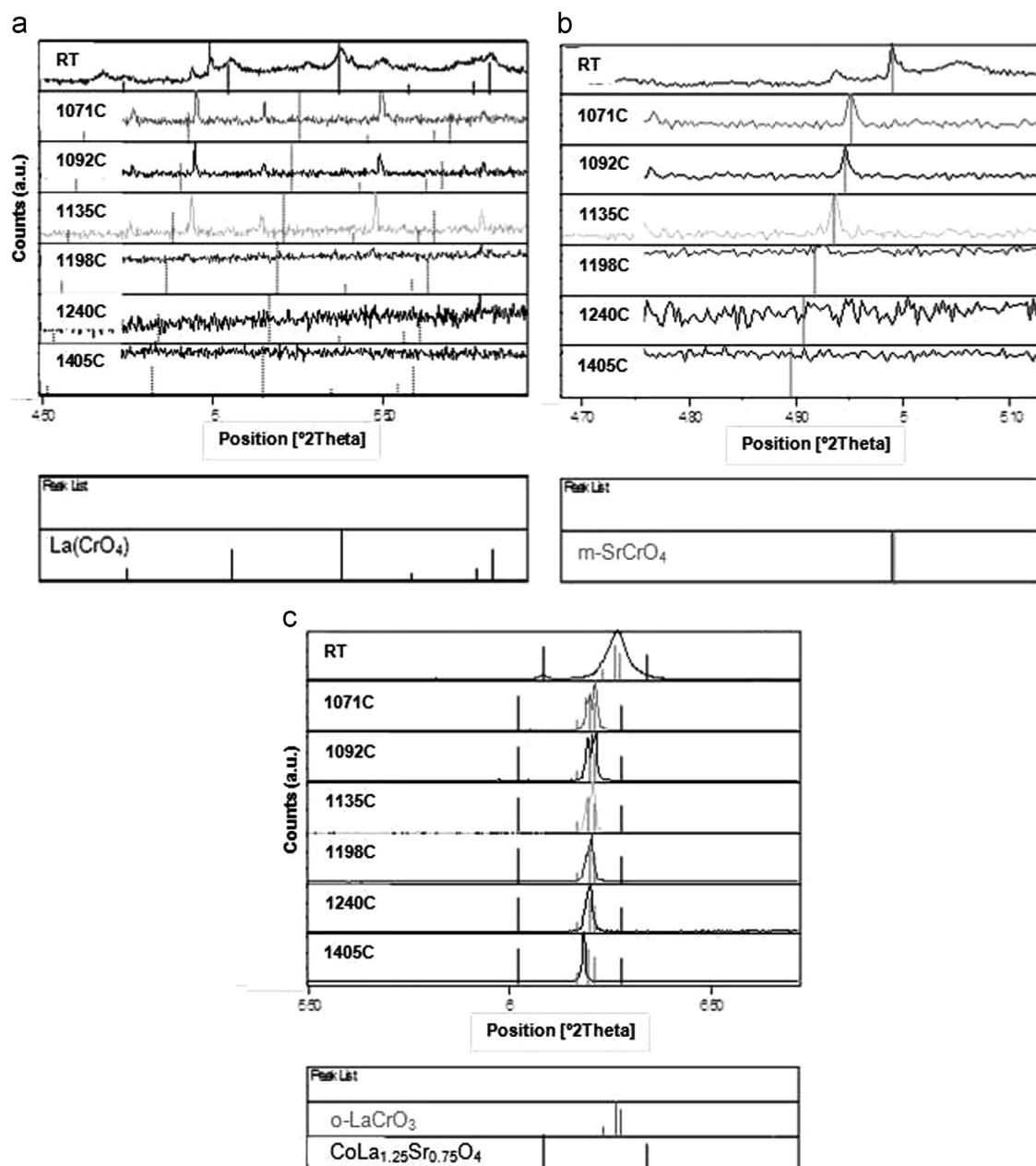


Fig. 3. Selected areas of all the SXRPD raw patterns measured at different temperatures. The diffraction peaks position and its evolution with temperature of the different phases is also shown: (a) $\text{LaCrO}_{4.000}$, (b) $\text{SrCrO}_{4.000}$, (c) $\text{CoLa}_{1.25}\text{Sr}_{0.75}\text{O}_{4.000}$ and $o\text{-LaCrO}_{3.000}$.

Fig. 2 shows selected areas (2θ ranges of 7.55° – 7.75° and 10.6° – 11.0° , $\lambda=0.23 \text{ \AA}$) of the HT-SXRPD patterns for the as-synthesised powder when heating (RT, 1071, 1198, 1240, and 1405°C), which are marked with an asterisk in Fig. 1 (sample measured at RT). These areas were chosen to check the phase transition of the main component of the powder. The orthorhombic (9938-ICSD) to rhombohedral (167590-ICSD) structural phase transition of LaCrO_3 was observed above 1240°C . A coexistence of both orthorhombic and rhombohedral phases at 1240°C was revealed by the Rietveld refinement. This temperature is very high compared with that obtained in the literature for pure o - LaCrO_3 [42], which could be related with the presence of Sr and Co. Table 3 shows the cell parameters for the as-synthesised doped perovskite measured at different temperatures. The volume of the

unit cell increases by increasing the temperature for the same space group (from RT to 1240°C), as it is expected.

The evolution of the second phases during heating was also studied. Fig. 3 shows selected areas of the patterns measured at RT, 1071, 1092, 1135, 1198, 1240 and 1405°C by synchrotron radiation. Fig. 3a shows that $\text{LaCrO}_{4.000}$ is only present in the pattern measured at RT; Fig. 3b shows that m - $\text{SrCrO}_{4.000}$ is present in the material at RT, 1071°C , and 1092°C , with less proportion in the later. However, that phase is not present at temperatures $\geq 1198^\circ\text{C}$. Fig. 3c shows that $\text{CoLa}_{1.25}\text{Sr}_{0.75}\text{O}_{4.000}$ is not present at temperatures $\geq 1071^\circ\text{C}$, and orthorhombic- $\text{LaCrO}_{3.000}$ is not in the powder at 1405°C . To understand the reactions that occur during heating, both thermo-gravimetric and dilatometric analyses were performed.

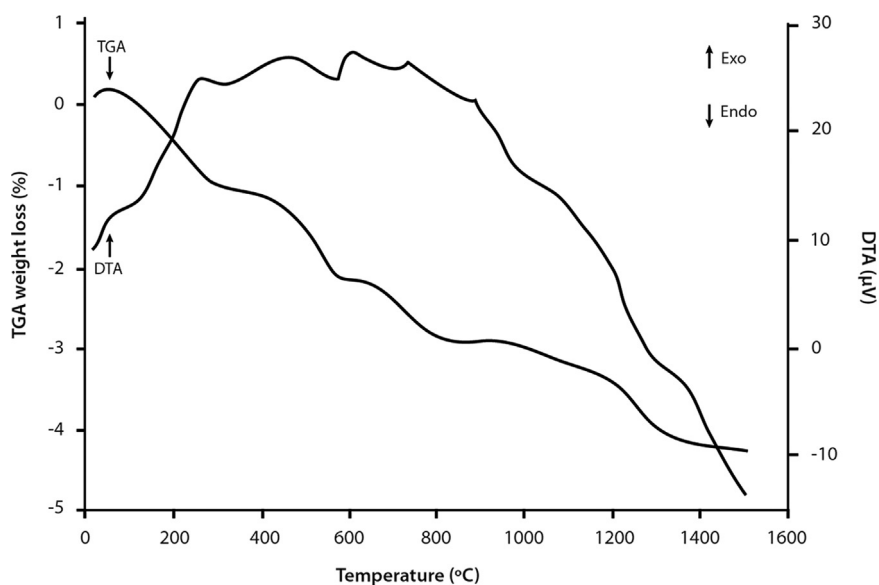


Fig. 4. DTA–TGA in air (25 – 1500°C) for the as-prepared powder.

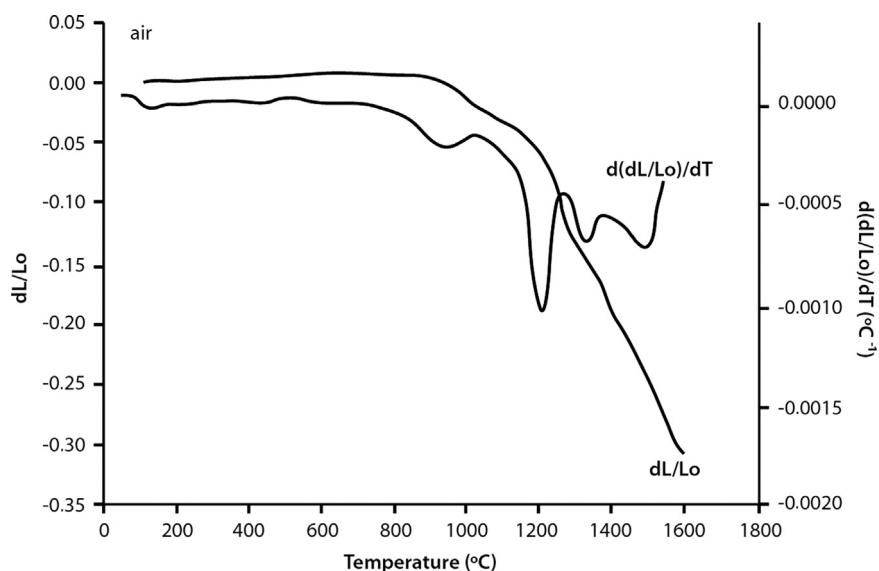


Fig. 5. Dilatometric studies in air (25 – 1600°C) for the as-prepared powder.

Fig. 4 shows the thermal evolution of the as-prepared Sr and Co doped-LaCrO_{3,000} powder measured by DTA/TGA in air, and Fig. 5 depicts the linear shrinkage curve and derivative plot with temperature of the as-prepared powder obtained by dilatometric studies. On the one hand, thermogravimetric (TG) results, from 25 to 1500 °C, Fig. 4, indicate an overall weight loss of ~4.25 wt%. The first weight loss, 0.5 wt%, is observed below ~200 °C, and is complemented by an endothermic event in the DTA curve, which can be due to the elimination of the physisorbed water. Another weight loss of ~0.5 wt%, with a different slope, is observed up to ~280 °C and is also complemented by an endothermic peak centred at ~210 °C that can be associated to the residual urea decomposition [43] and chemisorbed water elimination. An endothermic event at ~350 °C, coupled to a weight loss, can be due to the release of N₂ gas. The oxidation of the residual organics can be associated to an exothermic event (from 400 to 500 °C) also accompanied by a weight loss. Results obtained from 500 to 1500 °C by this technique will be explained jointly with those obtained by dilatometric studies.

On the other hand, the linear shrinkage curve, Fig. 5, shows a total shrinkage of ~32% by increasing the temperature from 500 to 1600 °C, where four peaks are appreciated in the derivative plot. Reactions occurring from 500 to 1500 °C are discussed later. The decomposition of *m*-LaCrO_{4,000} (LaCrO_{4,000} → LaCrO_{3,000} + 1/2O₂) [40,44,45] gives rise to an endothermic peak (Fig. 4) together with a weight loss at ~700 °C. This explains why this compound is only observed in the pattern measured at RT (Fig. 3.a). In addition, it is believed that a sufficient amount of *m*-SrCrO_{4,000} exsolves after calcination, ~700 °C, to facilitate the densification through a liquid phase formation [39,40], and it re-dissolves at around 1200 °C [39,40]. There is an endothermic event (Fig. 4) centred at ~1275 °C which may well correspond to the melting point of *m*-SrCrO_{4,000} [46]. This peak is accompanied by a weight loss and is related to the incongruent

melting in air of *m*-SrCrO_{4,000} to a liquid phase and Cr₂O₃, as depicted in the SrO–Cr₂O₃ phase diagram [47]. Oxygen is believed to be lost due to the reduction of Cr⁶⁺ in *m*-SrCrO_{4,000} to Cr³⁺ in the resulting Cr₂O₃. An additional weight loss (Fig. 4) is observed and can be ascribed to the oxidation of Cr₂O₃ to CrO₃ and volatilisation of the later [48], known to occur above 1000 °C [49,50]. This is in agreement with the first peak found in the dilatometric study, Fig. 5, at ~950 °C. The second peak of the derivative shrinkage plot (Fig. 5) is detected at ~1200 °C and can be related to the incongruent fusion of *m*-SrCrO_{4,000} forming Cr₂O₃ phase according to the binary phase diagram SrO–Cr₂O₃ [47]. Since the melting point of *m*-SrCrO_{4,000} was observed at ~1275 °C by DTA–TGA, it could enhance the sintering process by a transient liquid. All these results are in agreement with HT-SXRPD (Fig. 3), where *m*-SrCrO_{4,000} is present in the powder at RT, 1071 °C, and 1092 °C, with less proportion in the later. The third peak (Fig. 5) is centred at ~1380 °C and can be associated with the phase transition from the orthorhombic to

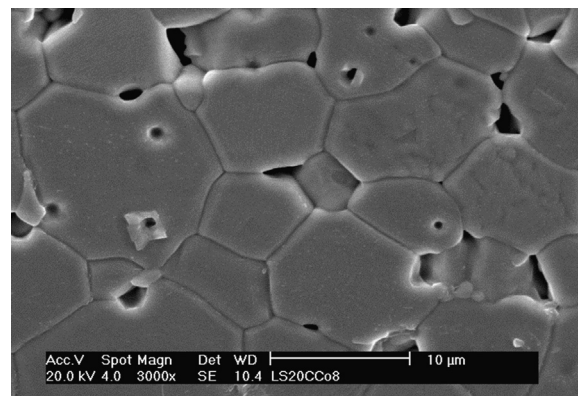


Fig. 7. FE-SEM micrograph of a sintered sample at 1600 °C/4 h after polishing and thermal etching.

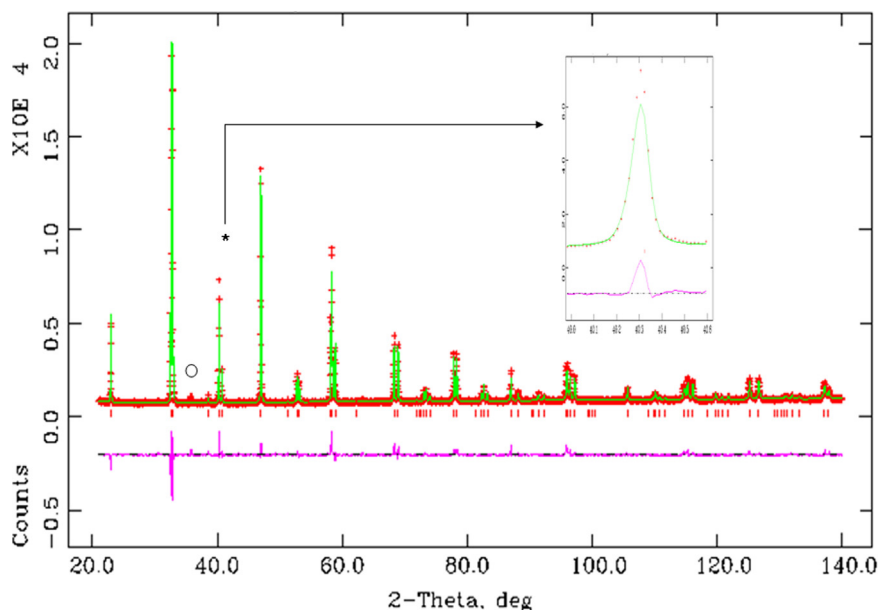


Fig. 6. Rietveld refinement of LXRPD data of the powder from the sintered pellet (1600 °C) after crushing, and measured at room temperature.

rhombohedral symmetries. The starting onset of the third peak at $\sim 1240^\circ\text{C}$ is in agreement with the coexistence of orthorhombic and rhombohedral phases found by HT-SXRPD (Fig. 2). The last peak (Fig. 5), $\sim 1500^\circ\text{C}$, is related to sintering and densification processes. Although our proposed La, Sr-chromite main phase shows slightly higher Cr content than the nominal one, the initial powder only contains 68.3(1) wt% of this phase. In addition, $\text{CoLa}_{1.25}\text{Sr}_{0.75}\text{O}_{4.000}$ can lose cobalt by evaporation during heating [51].

3.2. Sintered strontium and cobalt doped lanthanum chromite material

Sintered samples show an average density value of 98.9% theoretical density. Fig. 6 shows the LXPDP Rietveld plot for the ground powder of the sintered bulk measured at RT. Crosses correspond to the experimental scan, solid line is the calculated pattern and the bottom line is the difference curve. We can confirm that this powder is formed by the rhombohedral- Sr- and Co-doped $\text{LaCrO}_{3.000-\delta}$. This can be observed in detail in the inset which shows a selected area of the refined pattern at higher magnification (marked with an asterisk). Its lattice parameters and volume are shown in Table 3. Hence, this phase transformation from orthorhombic to rhombohedral by heating is irreversible when cooling. In addition, the pattern (Fig. 6) shows a minor second phase (marked with a circle) which does not correspond to any reported structure.

The ideal interconnector material for a SOFC device should show, among other features, a well-matched thermal expansion coefficient with those of the other cell components. The defect chemistry, and thus doping, also affects thermal expansion, which is important because thermal stresses can be generated when heating or cooling from the high operating temperature of SOFCs. For example, Hilpert et al. [51] showed that there is a direct

relationship between thermal expansion coefficient (TEC) and oxygen stoichiometry. Strontium is more effective than calcium in increasing the TEC, thus less strontium is needed to obtain a TEC that matches with that of YSZ ($10.7\text{--}10.8 \times 10^{-6}^\circ\text{C}^{-1}$) [52,53]. In this study, the calculation of the thermal expansion coefficient was obtained from the cooling curve of the dilatometric analysis shown in Fig. 5 using a range of temperature from 1000 to 250°C , which includes the operating temperature for HT-SOFCs. The calculated value was $14.8 \times 10^{-6}^\circ\text{C}^{-1}$, higher than that for YSZ [52,53]. However, a possible solution for minimising that difference is to modify the stoichiometry decreasing the amount of Co, according to Koc and Anderson [20]. In addition, the sample was kept in the dilatometer at 1600°C for 2 h in air and after this time no longer further shrinkage was observed.

FE-SEM combined with EDX analyses of a polished sintered sample (Fig. 7) indicate an average composition for the grains of $\text{La}_{0.800}\text{Sr}_{0.200}(\text{Cr}+\text{Co})_{0.800}\text{O}_{3.000-\delta}$.

Fig. 8 shows the total conductivity of sintered samples as a function of the inverse of the temperature in both air and hydrogen atmospheres. The substitution of La for Sr in the perovskite should result in the formation of Cr^{4+} and Co^{4+} in order to preserve the electrical neutrality. In the reducing environment, the perovskite shows significantly reduced electrical conductivity compared with that in air, as it is expected. A decrease in conductivity is commonly observed in p-type conductors when the oxygen partial pressure is reduced [54]. Strontium doped lanthanum cobaltites are effectively p-type conducting materials as the oxidation of Co^{3+} to Co^{4+} introduces acceptor levels in the charge carrying Co-arrays [22]. Under hydrogen atmosphere, oxygen vacancies are formed and the electrical conductivity decreases as a result of ionic compensation.

Linear regression was applied to calculate the activation energies and to evaluate the linearity. Calculated values of the activation energies are given in Table 4. In air, the first interval

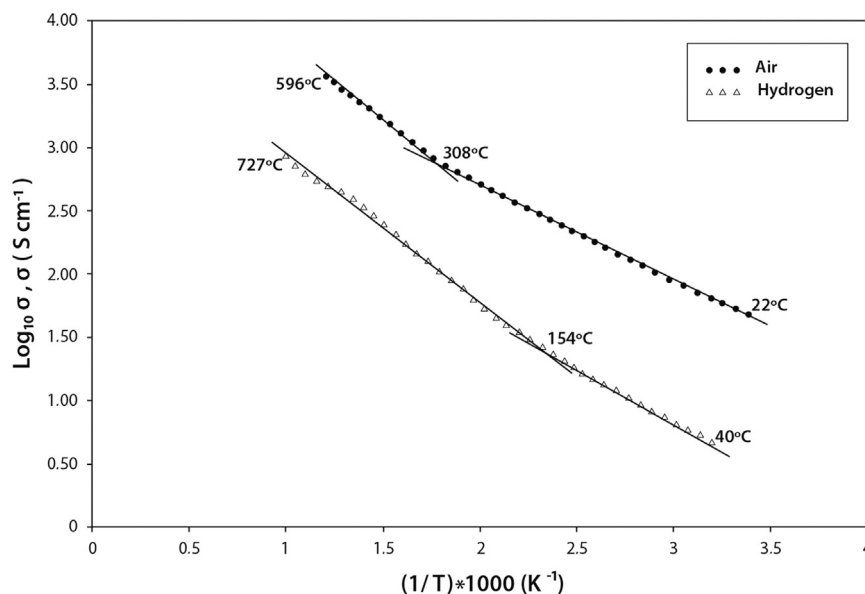


Fig. 8. Arrhenius plot of the total conductivity of the sintered perovskite in air and in H_2 atmospheres. The temperatures indicated in the graph correspond to the intervals with different characteristics for the electrical measurements and their fit (straight line).

Table 4

Activation energies for the non-adiabatic small-polaron mechanism under air and hydrogen in the sintered perovskite.

E_a (eV) air (1)	E_a (eV) air (2)	E_a (eV) hydrogen (1)	E_a (eV) hydrogen (2)
0.14	0.23	0.16	0.22

of electrical measurements and their fit (straight line) goes from 22 to 308 °C (1); meanwhile, the second interval of electrical measurements and their fit (straight line) goes from 309 °C to 596 °C (2). In hydrogen, the first interval of electrical measurements and their fit (straight line) goes from 40 to 154 °C (1). The second interval of electrical measurements and their fit (straight line) goes from 154 °C to 727 °C (2).

It is observed that σ increases with increasing temperature, showing temperature-dependent activation energy. The plot shows linearity and two different regions with different activation energy values for each range. R^2 values indicated good fits of data to the linear function. The evaluation of the linearity of the plots and the activation energy indicated that the electrical conduction occurs via the non-adiabatic small-polaron mechanism in both atmospheres [55,56]. In that mechanism, the substitution of Sr for La in the La(Cr,Co)O₃ lattice results in the formation of Cr⁴⁺ and Co⁴⁺ in order to preserve the electrical neutrality, as it is mentioned above [57]. Formation of both Cr⁴⁺ and Co⁴⁺ increases the small-polaron concentration and decreases the activation energy for conduction. A similar behaviour was observed in (La,Ca)(Cr,Co)O₃ perovskites by Hjalmarsen et al. [57]

4. Conclusions

This work reports the in-situ phase development and behaviour during heating of an orthorhombic-perovskite obtained by combustion synthesis with an estimated composition by Rietveld refinement of La_{0.803}Sr_{0.197}Cr_{0.966}Co_{0.034}O_{3.000-δ}. An orthorhombic to rhombohedral structural phase transition of that perovskite was observed at ~1380 °C. HT-SXRPD revealed the coexistence of orthorhombic and rhombohedral phases at 1240 °C.

The ground powder of the sintered sample measured by LXRPD (measured at RT) demonstrated that the main phase is 100% rhombohedral. Then, the phase transition is an irreversible process. The evaluation of the linearity of the conductivity versus the inverse of the temperature and the activation energy values indicated that the electrical conduction occurs via the non-adiabatic small-polaron mechanism, in either air or hydrogen atmosphere, in which the substitution of Sr for La in the La(Cr,Co)O₃ lattice results in the formation of Cr⁴⁺ and Co⁴⁺ in order to preserve the electrical neutrality. Under hydrogen atmosphere, oxygen vacancies are formed and the electrical conductivity decreases as a result of ionic compensation.

Acknowledgments

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