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Oxygen stoichiometry of $Ba_{0.50}Sr_{0.50}Co_{0.80}Fe_{0.20}O_{3-\delta}$ obtained by EDTA–citrate method and measured by X-ray and neutron diffraction

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Abstract The compound $Ba_{0.50}Sr_{0.50}Co_{0.80}Fe_{0.20}O_{3-\delta}$ (BSCF) has been used as a good candidate for air electrodes in Intermediate Temperature Solid Oxide Fuel Cells. Present work deals with the oxygen vacancy of this compound synthesized by using the EDTA–Citrate method. To obtain a single-phase sample, three portions of the compound were calcined at 700, 800 and 900 °C. Only the sample calcined at 900 °C showed a single phase. The stoichiometry of the single-phase sample, in particular of the oxygen atom, was determined by applying the combined X-ray and neutron Rietveld refinement to X-ray and neutron powder diffraction patterns measured with the sample.

Keywords Fuel cell · X-ray diffraction · Neutron diffraction · Oxygen vacancies · BSCF

Introduction

Perovskite-type oxides, described by stoichiometric formula ABO_3, have been considered important materials due to their potential application as solid oxide fuel cell (SOFC) electrodes, gas sensors, oxygen permeable membranes and catalysts for steam and hydrocarbon reforming [1]. Several perovskite-type oxides, such as cobalt based mixed conducting oxides, have been studied as oxygen permeable membranes for fuel cells due to their high oxygen ion permeability [1–3].

The fuel cell system can be defined as an electrochemical converter device that produces electrical energy by electrochemical reactions between a fuel (e.g. hydrogen) and an oxidant substance (e.g. oxygen, usually from air). A SOFC, a fuel cell that belongs to a class of high-temperature cells, is composed totally by ceramic components. Such components are good ionic conductors, specially the cathode and the electrolyte as the ionic oxygen conductor. All porous electrodes and the dense electrolyte are responsible by the basic structure of the unit cell circuit (Fig. 1).

Compounds of general formula $Ba_{(x)}Sr_{(1-x)}Co_{(y)}Fe_{(1-y)}O_{3-\delta}$ have attracted interest due to their high oxygen permeability and favorable structural stability [1, 4]. Moreover, these compounds present physical, chemical and microstructural properties that make them appropriate to be used as cathode of an Intermediate temperature solid oxide fuel cell (ITSOFC) [5–7]. Recently, ITSOFCs have attracted much attention because they operate in the range of temperature 600 to 800 °C, allowing the use of more accessible materials in their constructions [8, 9].

According to Patra et al. [1] compound $Ba_{0.50}Sr_{0.50}Co_{0.80}Fe_{0.20}O_{3-\delta}$ (BSCF) is a cubic perovskite oxide and its functional properties are generally influenced by the synthesis methods, calcination conditions (temperature, time and atmosphere) and A and/or B site substitution in the structure.

Theory

Amongst the synthesis methods used in the preparation of cathode materials the most used are solid-state reactions and wet chemical reactions as sol–gel, co-precipitation,

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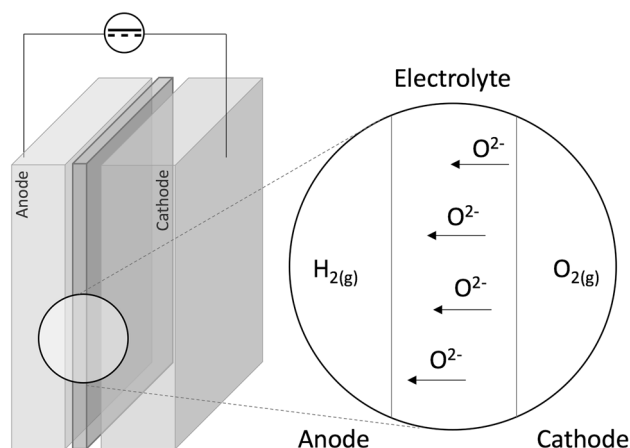
Fig. 1 Scheme showing the basic components of a SOFC unit cell

hydrothermal synthesis, etc. The glycine-nitrate (GN) method was studied by Liu and Zhang [10], the sol–gel thermolysis (SGT) method by Subramania et al. [11] and the EDTA–citrate (EC) method, for synthesis of nanocrystalline BSCF powders, by Shao and Haile [12]. The EC method has shown to be more stable than the others to control process parameters as pH, homogeneous ionic distribution, etc. [13].

Many studies have shown that the different methods may modify the powder characteristics such as: morphology, crystalline size and surface microstructure. Transport properties and catalytic activity of BSCF are directly associated to its perovskite structure (ABO$_3$), substitution of A and/or B site and presence of oxygen vacancies in the structure. The formation of oxygen vacancies in p-type conductors can be general described (using Kröger–Vink notation) by Eq. (1):

$$O_0^x \rightarrow \tfrac{1}{2}O_2 + 2e^- + V_0^{\bullet\bullet} \tag{1}$$

corresponding (O_0^x) to the oxygen atom at a lattice position and $(V_0^{\bullet\bullet})$ to the oxygen vacancies in the O site lattice.

Zhou et al. [5] mentioned that the substitution of Sr^{2+} by Ba^{2+} may increase the oxygen vacancy concentration, thus optimizing the composition of BSCF as it increases the oxygen ion conductivity. Investigation of these parameters is usually made by X-ray diffraction obtaining important information such as crystal structure, lattice parameter and atomic substitution amongst other characteristics of the studied material. Concerning the oxygen atoms, number and positions are better determined by neutron diffraction owing to the small atomic number Z of these atoms when compared with those of the metal atoms in the compound [14].

Ion conduction in perovskite oxides occurs due to the existence of oxygen vacancies in the crystalline structure of the material. Itoh et al. studied the relationship between

oxygen vacancy and ion conductivity showing the importance of the oxygen stoichiometry in these oxides [15].

Main purpose of present work is to obtain BSCF, via the EC method, and determine the stoichiometry of the synthesized oxide.

Experimental

The BSCF powder with stoichiometry Ba$_{0.50}$Sr$_{0.50}$Co$_{0.80}$Fe$_{0.20}$O$_{3-\delta}$, has been synthesized by the EC method. A Flow Chart of the experimental procedure used in the synthesis is shown in Fig. 2.

Barium, strontium, cobalt and ferrite nitrate salts, in solution, are mixed with a buffer solution of ethylenediaminetetraacetic acid (EDTA) and NH$_3$.H$_2$O. Citric acid is then added to the solution. The precursor solution contains EDTA, citric acid and metal ions, with the molar ratio (1:1.5:1). The pH is maintained around 6.0 by adding NH$_3$.H$_2$O to the solution. The solution is stirred and heated until a viscous gel is formed. The gel is heat treated at 200 °C for 5 h. The product formed had the appearance of a "puff" sponge.

In order to obtain a single-phase sample with a perovskite structure, portions of the product were successively calcined in air for 5 h at different temperatures. Calcinations started in 700 °C and the temperature step adopted
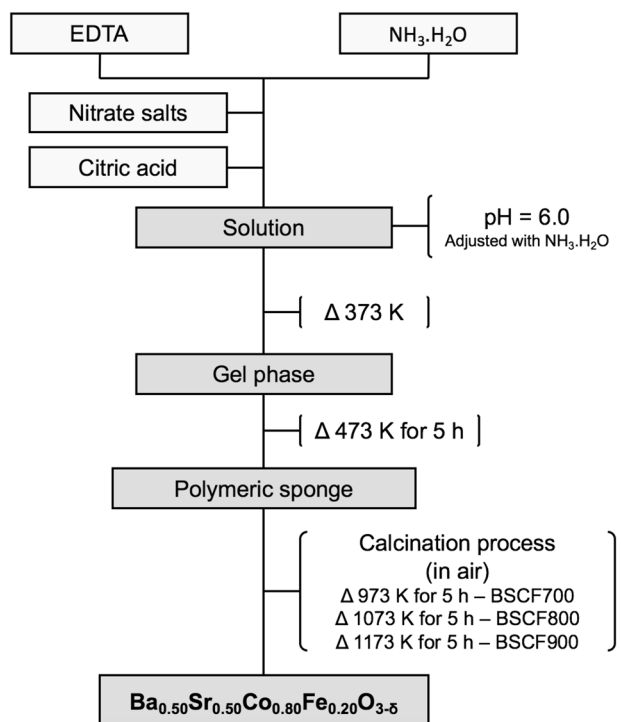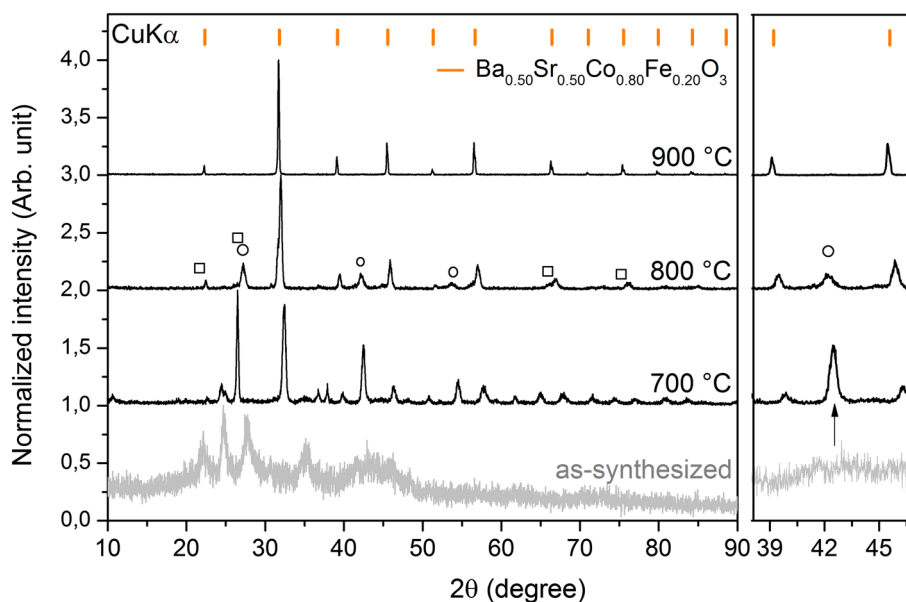

Fig. 2 Flow chart of the experimental procedure by the EDTA–citrate method to obtain the BSCF powder

was 100 °C. After each calcination process, an X-ray pattern of the sample was measured. The measurements were carried out in a Rigaku X-ray Diffractometer, model Multiflex, employing Cu-Kα₁ radiation (wavelength λ = 1.5418 Å) monochromatized by a graphite monochromator. The scan was continuous at a rate of 0.02° min⁻¹ in the 2θ range 10–90°. The pattern obtained with the sample at 900 °C (BSCF900) showed a single perovskite phase without contamination of minor phases (see next section for details about the phase analysis). With sample BSCF900 a new X-ray pattern was measured with enough quality to be used for a Rietveld refinement. For this pattern, the measurement was carried out in steps of 0.02°, 2θ range 10–90° and counting time 6 s per point. A neutron diffraction pattern of sample BSCF900 was also measured using the High-Resolution Powder Diffractometer (HRPD) Aurora, constructed at IPEN/CNEN-SP and installed on the IEA-R1 nuclear reactor of the institute [16]. A vanadium cylindrical sample holder, with an inner diameter of 3.17 and 67 mm height, was used in the measurement. The monochromatic neutron beam wavelength used to carry out the neutron diffraction measurements was 1.4119 Å.

Results and discussion

The X-ray patterns obtained for the three calcined samples are shown in Fig. 3. In this figure, patterns of the first two calcined samples (700 and 800 °C) show peaks of a main phase identified as BSCF and peaks of secondary phases identified as $BaCoO_2$ and $BaFeO_2$. In the pattern of sample BSCF900 only peaks of the expected perovskite structure

of BSCF appeared. These results show the importance of calcination to obtain secondary phase elimination. It is worth noting that the crystallinity of the samples increased with the increasing calcination temperature. This can be inferred from observing the diminution in the peak widths following the patterns from 700 to 900 °C.

Figures 4 and 5 show, respectively, the results obtained from application of a combined X-ray and neutron Rietveld refinement [17] to the X-ray and neutron diffraction powder patterns of BSCF900. In these figures, circles indicate the experimental points and full lines the theoretical patterns. Difference patterns are also shown in the figures. The refinement was carried out using the program GSAS [18], taking into account the effect of magnetic scattering in the
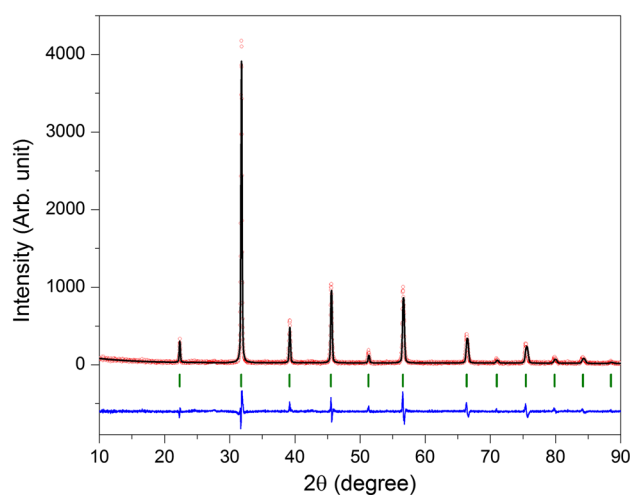

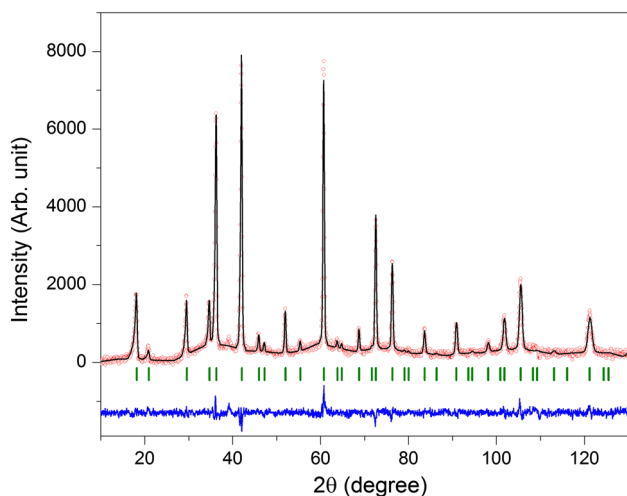**Fig. 4** X-ray diffraction pattern of BSCF900 refined by the combined Rietveld method

Fig. 3 X-ray diffraction patterns of BSCF obtained by EDTA–citrate method as-synthesized (200 °C) and calcined at 700, 800 and 900 °C for 5 h in air. Secondary phases are represented by *open circle* for $BaCoO_2$ and *open square* for $BaFeO_2$

Fig. 5 High-resolution neutron diffraction pattern of BSCF900 refined by the combined Rietveld method (magnetic and nuclear peaks)

Table 1 Positional, occupancy and isotropic thermal parameters obtained from the combined X-ray and neutron Rietveld refinement of BSCF900; space group Pm3m and $a = 7.9594(2)$ Å

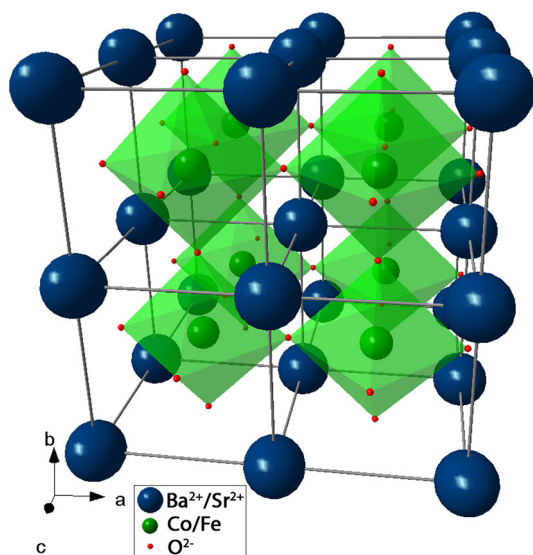| Parameters	Atoms				
	Ba	Sr	Co	Fe	O
Site	1a	1a	1b	1b	3c
Occupancy	0.46(1)	0.54(1)	0.800(1)	0.200(1)	0.809(4)
U_{iso}	2.66(5)	2.66(5)	2.64(6)	2.64(6)	0.32(4)
R_{wp} (R-X)	0.184				
R_{wp} (X-ray)	0.046				
Reduced χ^2	1.88				

Fig. 6 Representation of the perovskite crystalline structure of BSCF

neutron pattern. Table 1 lists positional, occupancy and isotropic thermal parameters obtained from the combined X-ray and neutron Rietveld refinement of BSCF900. Two of the often-used numerical criteria of fit are also listed in the table.

The Fig. 6 is a representation of the perovskite crystalline structure of BSCF. In the figure, large spheres represent Ba or Sr atoms, medium ones Co or Fe and small ones O.

With the oxygen occupancy equal to 0.809(4), the stoichiometry of this atom in the formula results 2.427 ($\delta = 0.573$). The loss of lattice oxygen occurs by β-desorption of oxygen in the perovskite structure which is responsible for the ionic conductivity of the material [19].

Conclusions

By EDTA–citrate method is possible to obtain BSCF with a perovskite-type cubic crystal structure. The first X-ray analyses are important to confirm that the process of calcination at 900 °C, for 5 h in air, is sufficient to avoid the possible formation of secondary phases and confirm that the main phase has the correct perovskite structure. A combined Rietveld refinement of both step-scanned X-ray and high-resolution neutron patterns permitted to determine the oxygen occupancy in the structure with a quite good precision. Finally, the compound synthesized and heat treated, according to the processes here described, can be represented by the formula $Ba_{0.45}Sr_{0.55}Co_{0.80}Fe_{0.20}O_{2.427}$.

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