Synthesis of Bi0.4Sr0.6FeO3-δ (BSF) powders and ceramics

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Abstract. By mean of mechanical alloying the synthesis of \( Bi_{0.4}Sr_{0.6}FeO_{3-\delta} \) ceramic powders were achieved according to the stoichiometric relations of \( Bi_2O_3, Fe_2O_3 \) and \( SrCO_3 \) initial powders. Then thermal treatments in air both 800 °C as 825 °C as a function on time was carried out on the processed ceramic powders, which were posteriorly characterized via X-ray diffraction and thermogravimetric. Finally, uniaxial compaction of the chosen processed powders to 800 °C was performed adding polyvinyl alcohol (PVA) or butyral alcohol (PVB) to find a higher porosity. The milled ceramic compound presented a single cubic phase with lattice parameters of 3.95 Å when it was thermally treated at 800 °C and only 30 min of thermal treatment. No change on lattice parameter was found with higher treatment time. Thermogravimetric analysis showed processed powder are stable to work at the operation temperature of the solid oxide fuel cell chosen. In regard to porosity, the results showed that an adequate porosity 27 % with addition of PVB was achieved.

Keywords Cathode, porosity in ceramics, solid oxide combustion cell.

1. Introduction
The solid oxide fuel cells (SOFCs) are electrochemical devices that generate electricity, namely convert the chemical energy of a fuel and an oxidizing medium directly into electricity without producing pollution emissions [1]. Furthermore, these fuel cells work conveniently at high temperatures in a range of 600°C to 1000 °C with an efficiency between 50 % and 60 % [2]. Therefore, there are raised considerable interest in development and characterization of electrochemical devices in the new materials area.
Currently, the advances in SOFC cells depend mainly on the type and the structure of materials that make up the anode (fuel oxidation), the electrolytes (ionic conducting), the cathodes (oxygen reduction) and interconnectors and stamps [3]. Regarding the cathodic electrode, must be fulfilled some requirements such as high ionic and electric conductivity, stability in oxidizing means and porosity between 20 % and 40 %, that allow a constant flow of oxygen [4]. At the present-day, the most used material is the lanthanum-strontium manganite (LSM) because it presents a high electric conductivity and great thermal compatibility with the other components of the cell, however, its low catalytic activity prevent a higher electric conductivity. To overcome this last disadvantage, researchers have been studying perovskite-like materials based on Bi, Fe and Sr, to speed up the kinetic of the oxygen reduction reaction (ORR) and; also to optimize the level of usable energy due high density of oxygen flow, fast kinetic of surface exchange and low specific resistance [5]. To accomplish these features, a cubic structure of high symmetry is required in this perovskites which generates a high density of oxygen vacancies, high coefficients of chemical diffusion and a high surface exchange [6]. \( Bi_{1-x}Sr_xFeO_{3-\delta} \) powder have been synthesized by solid state reaction from metal oxides, sol-gel and other chemical methods, as for example a combined EDTA-citrate complexing process, which is based on steps of reaction, evaporation, pre firing, the synthesis of cubic BSFO is achieved after a calcination step at 950 °C for 5 h [7, 8, 9]. Worth noting that irrespective of the method, a calcination

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step is needed at temperatures from 650 °C to 1500 °C and times between 5 h and 100 h, which influences the Bi/Sr substitution and thus the structural, magnetic and electronic conducting properties of perovskites \([3, 6–10]\). Several reports are based on solid state reaction with a subsequent calcination step \([7, 9]\). According to the phase diagram of the bismuth ferrite (BFO) to obtain a highly pure material with cubic perovskite structure with an alpha-solid phase is due to a temperature between 800 °C - 825 °C \([11]\).

The purpose of this work is to synthesize porous ceramics of \(Bi_{0.4}Sr_{0.6}FeO_{3-\delta}\) by mechanic alloying, compaction and thermal treatment in order to optimize the structure, study the thermical stability of the compound and to determine its porosity; looking convert the bismuth ferrite in a promissory material like cathode to possible applications in a solid oxide fuel cell.

2. Experimental process

The synthesis of \(Bi_{0.4}Sr_{0.6}FeO_{3-\delta}\) powder was performed for mechanical alloying in vibratory mill MM 400 RETSCH, using stoichiometric amounts of 3.87 g of \(Bi_2O_3\) (99.999%), 1.66 of \(Fe_2O_3\) (99.5%) and 0.61 g of \(SrCO_3\) (99.5%) with 7 drops of acetone, with a powder-mass to ball-mass ratio of 1:1 during 2 h. This work was based on the results of synthesis of powders found in a previous work, in which were obtained, after the powder a thermal treatment with oxygen, the pure cubic phase of the compound \([6]\). After the milling, the process was divided in two phases: a) thermal treatment of milled powders in air within tubular furnace using temperatures of 800 °C and 825°C and calcination times of 30, 900 and 1800 min; with the purpose of determined the optimal parameters of thermal treatment in air, in which the pure cubic phase is obtained. The structures of the previous samples were analyzed by X-ray diffraction (XRD) using a Rigaku diffractometer with the line Cu-\(K_\alpha\). The identification of phases was performed with the High X’pert software and the GSAS software was used for the refinement of the structural parameters. b) The pore size, the morphology and porosity of the cathode regulate the transport of gases through the electrodes, affecting or improving its performance \([12]\). To obtain the porosity of the ceramic probe within the established range, tests were carried out with different additives and solvents. Therefore, the porosity of the ceramic probe was studied starting from milled powders and three types of samples were fabricated: without using additive, with addition of 2 wt % polyvinyl alcohol (PVA) and with butyral polyvinyl (PVB).

The PVB was previously prepared with solvent (Isoamyl or Isopropanol Alcohol) or without solvent, as is detailed in table 1. Later, the powders were uniaxially compacted to different pressures during 10 min, as in indicated in table 2, getting ceramics probes with a diameter of 1.014 cm and then were thermally treated to 800 °C during 30 min. The porosity percentage of the ceramic probes was found applying the ASTM 373-88 norm (Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products). Also, thermogravimetric analysis was performed to the calcined powders to 800 °C during 30 min, to determine the thermal stability of the compound during the operating temperature of the solid oxide combustion cell, in the range of 600 °C to 1000 °C a speed of 5 °C / min.
Table 1. Previous preparation of the PVB

| Type of Solvent | Quantity of Solvent (g) | PVB wt% | Dissolved (Solvent +PVB) wt % |
|-----------------|-------------------------|---------|-----------------------------|
| Neither         | 0.0                     | 16.0    | 0.0                         |
| Neither         | 0.0                     | 26.0    | 0.0                         |
| Isoamyl Alcohol | 2.0                     | 4.0     | 3.0                         |
| Isoamyl Alcohol | 2.0                     | 16.0    | 2.0                         |
| Isopropanol Alcohol | 2.0                   | 4.0     | 3.0                         |
| Isopropanol Alcohol | 2.0                   | 16.0    | 2.0                         |

Table 2. Pressures to which the ceramic probes were submitted according to additives added to the powders.

| Additive         | Compaction Pressure (MPa) |
|------------------|---------------------------|
| Neither          | 3.4, 6.9 and 10.3         |
| PVA (2 %)        | 3.4, 6.9 and 10.3         |
| PVB (2% y 3%)    | 2.47                      |

3. Results and analysis

3.1. X-Ray Diffraction

In figure 1 are presented the diffractograms of the milled powders after being treated thermally at different temperatures and times. It is observed that by having calcined the powders in air during times of 900 min and 1800 min, a cubic pure perovskite phase \( Bi_{0.4}Sr_{0.6}FeO_3 \) as well as a spurious phase of \( Bi_{1.33}Sr_{0.67}O_{2.67} \) was developed. However, to calcination time of 30 min at 800 °C and 825 °C only the formation of the cubic pure structure \( Bi_{0.4}Sr_{0.6}FeO_3 \) was found with a lattice parameter of 3.95 Å, angles \( \alpha = \beta = \gamma = 90^\circ \) and a volume of 61.6 \((Å)^3\); with more intense peaks in the planes \((1 0 0)\) in 22.49° and \((1 1 0)\) in 32.02° corresponding to the positions of the peaks, in accordance with expected phase. It was found that at extended times of calcination the lattice parameter remains unchangeable. In addition, based on the results of a previous work [6] in which the desired phase \( Bi_{0.4}Sr_{0.6}FeO_3 \) was obtained submitting the powders to thermal treatment in oxygen atmosphere during 30 min at 800 °C and 825 °C (figure 1), we could to establish that is not necessary to perform the process in oxygen, since the same crystal structure, lattice parameter, angle and volume of the cell, were achieved. Therefore, to decrease the costs and manufacturing time of the ceramic probe; it was determined by the authors to work with fixed parameters of temperature and calcination time of 800 °C and 30 min, respectively, in air.
Figure 1. X-rays diffraction patterns of $\text{Bi}_{0.4}\text{Sr}_{0.6}\text{FeO}_3$ powders treated in air at different temperatures and times, after being alloyed mechanically during 2 hours.

3.2. Thermogravimetric analysis

With the purpose of determining that powders with cubic phase of $\text{Bi}_{0.4}\text{Sr}_{0.6}\text{FeO}_3$ have thermal stability in the temperature range from 600 °C to 1000 °C in which a solid oxide fuel cell usually operates, a thermogravimetric curve (TGA) was taken. Figure 2 shows the variation of weight percentage in function of the temperature for the powders previously treated at 800 °C and 30 min. It is observed that the weight remains approximately constant up to about 900 °C and then, a not significant loss of weight of 1.2 % is produced, but that can be attributed to a possible start of a decomposition reaction from this temperature. Consequently, we could find that the $\text{Bi}_{0.4}\text{Sr}_{0.6}\text{FeO}_3$ compound obtained is stable and will not present losses in the area and/or volume of the cell that could affect its functionality.

Figure 2. TGA curve into the range of SOFC operation of treated powders at 800 °C during 30 min.
3.3. Porosity of the ceramic probe

Regarding ceramic probes without additive and with 2.0 wt % PVA were obtained porosities of 10.0% and 12.0% respectively, when a pressed of 9.3 MPa was employed, so not significant variations of porosity in both cases were noted. Some reports suggest that porosity of the cathode is controlled by means of pore formers [12]; nevertheless, with the method applied using PVA in the present work it’s difficult to control the pores distribution. From previous results, with a constant pressure of 2.47 MPa and PVB pore former was improved a residual porosity in the electrode [4]. Therefore, PVB was added in our experimental route in two ways: powder and liquid, like was indicated previously in table 1. Our results show that the ceramic probe with presence of 4.0 wt% or 16.0 wt% dissolved PVB either in isoamyl alcohol or isopropanol alcohol, had porosity within a range of 12.0% - 16.0%. However, the ceramic sample with an addition of 16.0 wt% PVB not dissolved in solvent (powder) showed porosity of 27.1% and, also, it was evidenced that during calcination this particular sample was not deformed nor did it show visible loss of material (These results are summarized in table 3). In the figure 3a we can see an image of the last mentioned sample. This result of 27.1% of porosity is acceptable because a percentage below 20 % affects the oxygen flow and a higher porosity than 40 % although facilitates the diffusion of oxygen, minimizes the limitation of oxygen transportation to the interface of electrode-electrode and/or electrode-electrolyte [4]. In addition, high porosity causes the reduction of electronic and ionic conductivity because reduce fraction of the solid available for the electrons or ions transportation and it could affect the mechanical properties of the cathode [4]; that is, the device loses efficiency outside this range of porosity.

In the figure 3b we have an image of the sample with 26.0 wt% PVB where a porosity of 28.9 % was calculated. Clearly after thermal treatment, was noted that when there is a high porosity elevated loss of mass together with a distorted form were obtained.

| Table 3. Porosity of the ceramics probes depending on the type and amount of solvent |
|----------------------------------------|--------|--------|
| Type of Solvent | PVB (wt %) | Porosity (%) |
| Neither | 16.0 | 27.1 ± 0.1 |
| Neither | 26.0 | 28.9 ± 0.3 |
| Isoamyl Alcohol | 4.0 | 12.8 ± 0.8 |
| Isopropanol Alcohol | 4.0 | 12.8 ± 0.2 |
| Isoamyl Alcohol | 16.0 | 12.4 ± 0.4 |
| Isopropanol Alcohol | 16.0 | 15.6 ± 0.6 |
4. Conclusions
The ceramic powders of the system $Bi_{0.4}Sr_{0.6}FeO_3$ showed a cubic perovskite structure with lattice parameters $a = b = c = 3.95 \text{ Å}$ obtained from thermal treatment in air atmosphere at 800 °C during the short time of calcination of 30 min. Thus, reducing on this way manufacture costs of the ceramic probes and later, those of the cathode. It was found from the thermogravimetric analysis that this ceramic powder with such structure is thermal stable at operating temperature (600 °C – 1000 °C) of the solid oxide fuel cell (SOFC) with a high porosity of 27.1 % when 16.0 wt% PVB at 2.47 MPa is added to the milled powder. In order to finish the characterization, it’s important to take measurements of impedance which proposes to be done as a continuation of the work.

Acknowledgments
The authors we thank Dr. Juan Muñoz Saldaña from CINVESTAV-Querétaro (Mexico) for your great collaboration with experimental aspects in this work.

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