Effect pH variation of powder materials of the composite oxide $Ba_{(x)}Sr_{(1-x)}Co_{(y)}Fe_{(1-y)}O_{3-d}$ obtained by Citrate-EDTA Method

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Abstract. The $Ba_{(x)}Sr_{(1-x)}Co_{(y)}Fe_{(1-y)}O_{3-d}$ (BSCF) powder, used with cathode in intermediated temperature solid oxide fuel cells (ITSOFCs), has been prepared by Citrate-EDTA method and calcined at 900°C for 5h. Among the parameters to be checked in a liquid phase reaction, the pH of precursor solution is very important to control the disposal of organic, crystal structure and powders morphology. In this work, precursor solution pH has been variegated 2, 4, 6 and 8. The thermal decomposition has been observed in infrared, two absorption peaks are observed at 1436 and 860 cm^{-1}, after calcination, corresponding to the presence of CO_3^{2-}, in the samples with pH 2, 6 and 8. The single phase of Perovskite crystalline structure is seen only in the synthesis at pH 4 and 6, verified by X-ray diffraction (XRD). Morphological analysis, by scanning electron microscope (SEM), shows the powder is agglomerated and has similar trend independent of precursor solution pH.

Introduction

The mixed-conducting oxides are of great importance in studies of cathode components for Fuel Cell Solid Oxide. These type Perovskites oxide (e.g. $LaCoO_3$, $LaSrCoFeO_3$, $LaMnO_3$, $BaSrCoFeO_3$, etc.) described by stoichiometric formula ABO_3, have been considered importants due to their potential application as solid oxide fuel cell electrode materials, gas sensors, oxygen permeable membranes and catalyst for steam and hydrocarbon reforming[1]. Several perovskite type oxides, such as cobalt based mixed conducting oxides have been studied as oxygen permeable membrane due to their high oxygen ion permeability[1,2,3]. The compositions with Sr-doped has been shown interest, because of their high electrical conductivity. The substitution of a divalent cation (Sr^{2+}) for (Ba^{2+}) can be responsable by formation of oxygen vacancies, result mostly in a higher ionic conductivity in traditional cathode materials such as $BaCoO_3$. However, the development of alternative cathode materials with high electrochemical performance is indispensable to make intermediate temperature (600-800ºC) solid oxide fuel cells (SOFCs)[4,5].

The $Ba_{(x)}Sr_{(1-x)}Co_{(y)}Fe_{(1-y)}O_{3-d}$ (BSCF) presents the physical, chemical and microstructural appropriate to electrode materials cathode of a ITSOFC (Intermediate Temperature Fuel Cell Solid Oxide)[5,6,7]. The challenge of SOFCs is to investigate how to lower its operating temperature, thus enabling the use of materials more accessible in its construction[8,9], in this case, the BSCF powder, obtained by combined EDTA-citrate method, have been studied and characterized in detail. The study for synthesis of BSCF powder has shown that some parameters may affect the characteristics such as morphology, crystallite size, conductivity and surface microstructure the powder. Accordingly, the relationship between the powder synthesis route and the cathode properties is important for optimizing the cathode performance.[1]

The EDTA-citrate synthesis method was study by Shao and Haile[7], this method is based in complexing agents with mixture of salts of cation of interest. This synthesis method allow than the most characteristics of final product can be controlled, e.g., composition with pure phase, grain size, morphology, stoichiometry, among others. In order to study the effects caused by variation of pH of precursor solution, this paper shows the main features of BSCF powder obtained at different pH values.

Experimental

The BSCF powder with stoichiometry $Ba_{0,50}Sr_{0,50}Co_{0,80}Fe_{0,20}O_{3-\delta}$ has been prepared by EDTA-Citrate synthesis method (Fig. 1), consisting of nitrate salts mixed in buffer solution of EDTA (ethylenediaminetetraacetic acid) and NH_4OH, with subsequent addition of citric acid. The precursor solution contains NH_3-EDTA: citric acid: metal ions with molar ratio 1:1.5:1 and control of pH was varied at 2.0, 4.0, 6.0 and 8.0, with NH_3-H_2O. The solution was stirred and heated until the formation of viscous gel and subsequently taken to heat treatment at 200°C for 5h. The product formed has the appearance of sponge "puff" and then is calcinated at 900°C for 5h.
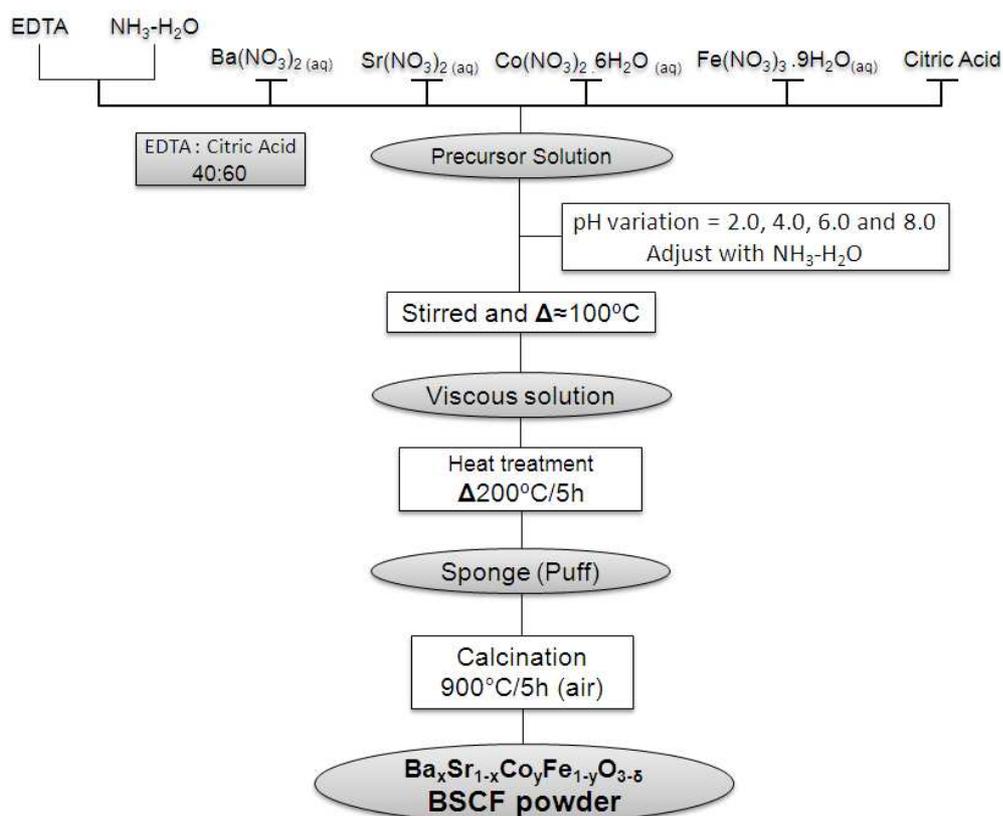

Fig. 1 – Synthesis method EDTA-Citrate to obtain BSCF powders.

The identification of the crystal structure and evaluation of crystallinity of BSCF with different pH values was made by X-ray diffraction using the Rigaku Diffractometer (XRD), model Multiflex, with graphite monochromator, using Cu-Kα radiation (wave length λ =1.5418 Å). The samples were scanned in the 2θ range 10-90º at a scan rate of 0.02°/min.
The characterization of organic compounds present in material, sponge and powder calcinated has been checked by Fourier Transformed IR spectra using a FTIR Spectrophotometer in the wave number range of 4000 cm^{-1} to 400 cm^{-1}, in transmittance mode. The morphology of calcined powder was observed by scanning electron microscopy (SEM).

Results and discussion

X-ray diffraction patterns of BSCF powders calcined at 900°C for 5 hours in air, obtained with pH variation at 2.0, 4.0, 6.0 and 8.0, are shown in Fig. 2. The sample obtained with pH 8.0 show the main peaks of the perovskite structure with secondary phases not determinate. The samples obtained with pH 2.0, 4.0 and 6.0 show single phase crystalline perovskite structure, showing the importance of control pH value during the sol-gel synthesis by complexation method.
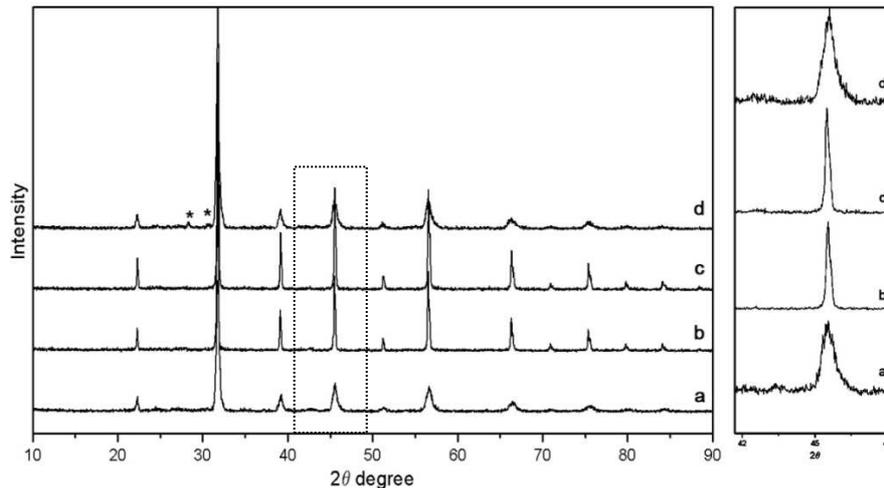

Fig. 2 – X-ray patterns of BSCF powders: a) obtained with pH 2.0; b) obtained with pH 4.0; c) obtained with pH 6.0; d) obtained with pH 8.0.

Powders synthesized with pH 4.0 and 6.0, show better crystalline patterns, without secondary phase. The observation of peaks allows the evaluation of crystallinity and, the crystallite size was calculated by Scherrer equation, following Eq. 1.

$$t = 0.9\lambda/(\beta_{obs.} - \beta_{resol.}).\cos\theta \tag{1}$$

The Fig. 3 shows the relation between crystalline sizes of powder calcinated with pH value of precursor solution. In this case, the samples present sizes at 240, 778, 778 and 259 Å, for the pH value 2.0, 4.0, 6.0 and 8.0, respectively.
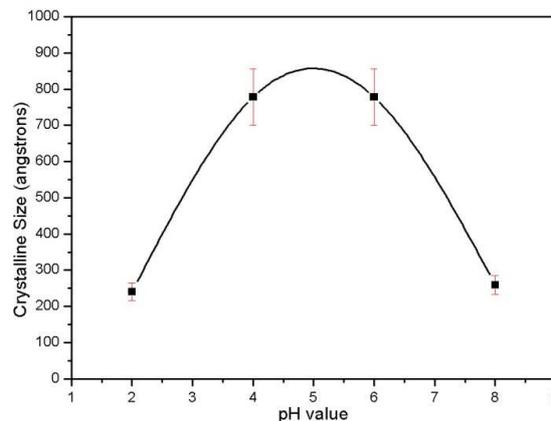

Fig. 3 - Crystallite size as a function of pH of precursor solution synthesis of BSCF.

The results of crystalline size show dependence of crystalline properties with synthesis parameter, such as controlling the pH value of precursor solution. Obtain particles with lower Gibbs free energy requires pH values around 4.0 and 6.0 during synthesis.
The morphology of agglomerate (Fig. 4) present characteristics of pre-sintered with different aspect texture.
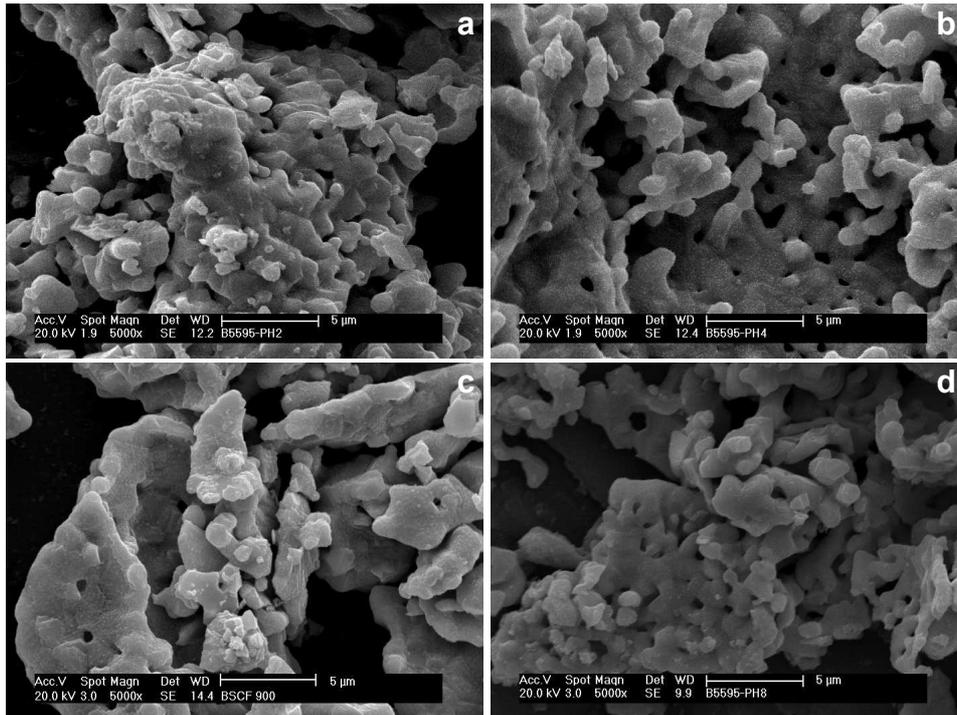
Fig. 4 – Micrographs obtained by SEM of BSCF powders synthesized at a) pH 2.0, b) pH 4.0, c) pH 6.0, d) pH 8.0, by EDTA-Citrate Method and calcinated at 900°C for 5h.

Samples obtained about pH 2.0 and 8.0 (a, d) show smooth surface whereas the samples obtained about pH 4.0 and 6.0 (b, c) show rough surface with the appearance of flakes in surface, as seen in Fig. 5.
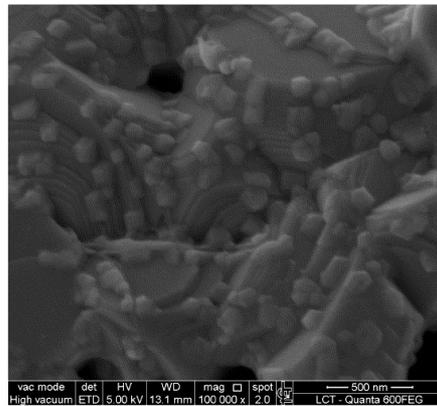

Fig. 5 – Micrograph obtained by SEM-FEG of BSCF powder, synthesized at pH 6.0 and calcinated at 900°C for 5h.

In the infrared absorption spectra, the position of the absorption peak is determined by the energy of molecule vibration[10]. FT-IR analysis shows the organic compound present before and after of calcination step, as seen in Fig. 6.
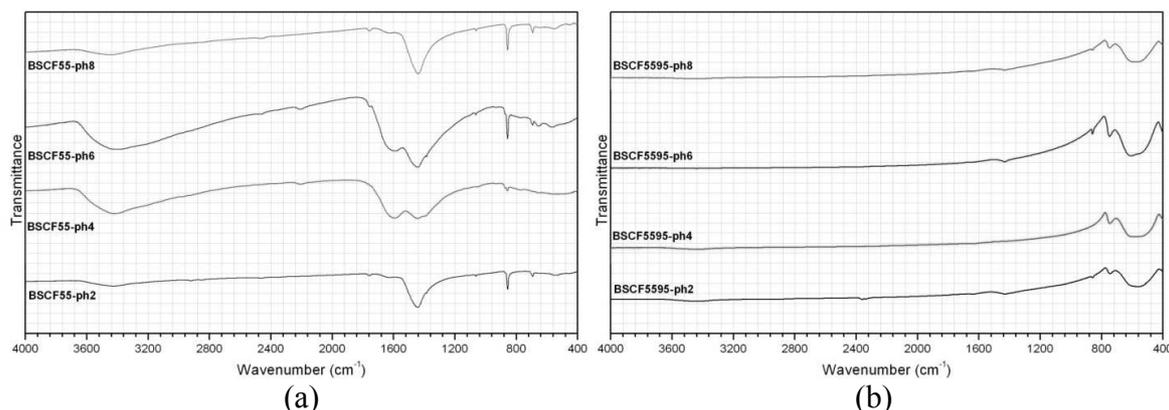
(a)	(b)

Fig. 5 – FTIR spectra of BSCF powder a) before calcination step, b) after calcination step at 900ºC for 5h.

The thermal decomposition phenomenon, in this case, can be observed by decrease intensity bands corresponding stretching vibrations of organic molecules. Bands absorption at approximately 1700 cm^{-1} are due to symmetric and asymmetric stretching vibrations of the carboxylate functional group in the samples with pH 4.0 and 6.0 (Fig. 5.a)[10]. Two absorption bands were observed at 1436 and 860 cm^{-1}, after calcination (Fig. 5.b), corresponding to the presence of twisting and stretching vibration of CO_3^{2-}[1], in the samples with pH 2.0, 6.0 and 8.0, indicating the presence of carbonate due to decomposition of the Ba-EDTA complex in the samples[11].

Conclusion

The sol-gel synthesis by EDTA-Citrate complexation method showed viable for obtaining $Ba_{(0.5)}Sr_{(0.5)}Co_{(0.8)}Fe_{(0.2)}O_{3-\delta}$ powder. The synthesis parameters for control pH value are most important for pure phase formation, crystalline structure and crystallinity of BSCF. Morphology of calcinated powder showed the formation of texture in the samples at pH 4.0 and 6.0 where the measurement of crystalline size was larger. The samples calcinated showed presence of carbonate, except for composition synthesized at pH 4.0.

Acknowledgement

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