Materials Science Forum Vols. 798-799 (2014) pp 407-412

doi:10.4028/www.scientific.net/MSF.798-799.407

Characterization of yttrium-Doped Barium Zirconate Nanocrystalline Powder Prepared by Spray Pyrolysis

E. N. S. Muccillo[1a], M. D. Gonçalves[1b], R. L. Grosso[1c], R. Muccillo[1d]

[1]Energy and Nuclear Research Institute - IPEN

PO Box 11049, S. Paulo, SP, 05422-970, Brazil

[a]enavarro@usp.br, [b]mayradg@usp.br, [c]roblopeg@usp.br, [d]muccillo@usp.br

Keywords: chemical synthesis; barium zirconate; microstructure

Abstract. Investigation on polycrystalline electroceramics involves the synthesis, the consolidation and the analysis of the electrical behavior, along with careful evaluation of the final microstructure. The synthesis of ceramic powders with controlled characteristics is crucial in the study of materials with optimized properties. Distinct properties may be found in ceramic materials prepared by the several existing methods, due to chemical and phase homogeneities, and to the particle size distribution or medium particle size. In this work, yttrium-doped barium zirconate proton conductor was synthesized by spray pyrolysis, and characterized by several techniques aiming identifying the influence of some parameters of this method of synthesis with particle characteristics. Nanocrystalline powders synthesized at 600-700ºC were found to be cubic and single phase. Moreover, depending on the gas flow and furnace temperature, spheroid and porous or cubic and solid particles may be obtained.

Introduction

Dense ceramics with optimized properties are required for a number of applications. This means that the physical and the chemical properties of the powder materials must be controlled envisaging their processing and sintering [1,2]. Among the diverse techniques for the synthesis of ceramic powders, the spray pyrolysis is a versatile solution method that allows for obtaining significant changes in the physical properties of powder particles by small changes in the synthesis parameters [3]. The spray pyrolysis is a powerful technique for the synthesis of complex oxides with submicrometer grain size and homogeneous shape [4]. In most of the cases, the materials synthesized by this technique do not give rise to amorphous phases, but instead exhibit chemical homogeneity and similar stoichiometry of the precursor solution [5,6]. This technique has been currently used to synthesize a number of ceramic compositions [6-9].

In the spray pyrolysis technique the precursor solution containing the desired cations is atomized inside a reactor where the small formed drops are subjected to steps of evaporation of the solvent, drying and thermal treatment giving rise to microporous and subsequently to dense particles. Diverse particle morphologies can be obtained with this technique [10]. Volume precipitation is essential to produce dense and solid particles. This requirement is accomplished by a suitable choice of the synthesis parameters. A disadvantage of this technique of synthesis is the difficult control on the particle morphology. In this context, the synthesis parameters should be determined and controlled.

Barium zirconate-based polycrystalline ceramics have been systematically investigated for applications in fuel cells, for hydrogen separation and generation [11], and for humidity sensors. Yttrium containing barium zirconate, BZY, with $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ composition is usually prepared by the conventional method of mixing of starting materials followed by solid state reaction at high temperatures, usually in excess of 1700ºC [12].

Bucko and Oblakowski [13] reported the preparation of pure BZY by spray pyrolysis by adjusting the cation solution concentration. Spherical-like particles with average sizes depending on the concentration of the cation solution were obtained. The particle size spanned from 90 to 500 nm

for a highly diluted solution (0.001 M) and 1200ºC as the temperature of precursor decomposition. Stuart et al. [14] synthesized the $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ composition starting from a 2.5 $mmol.L^{-1}$ nitrate solution and obtained agglomerated particles with approximately 250 nm of size. This material gave rise to compacts with 91% of relative density after sintering at 1500ºC for 1 h. Dahl et al. [15] prepared BZY by the ultrasonic spray pyrolysis starting with a precursor solution of 0.2 M. The produced powder was calcined at 1000ºC for 24 h in air and at 1100ºC for 6 h in nitrogen. After calcination the powder was milled and sieved. Dense pellets (~ 98% of relative density) were obtained after hot pressing at 1550ºC.

In this work, yttrium doped barium zirconate powder, $BaZr_{0.8}Y_{0.2}O_{3-\delta}$, was synthesized by the spray pyrolysis technique aiming identifying the influence of the gas flow and decomposition temperature on particle structure and morphology.

Experimental

The composition $BaZr_{0.8}Y_{0.2}O_{3-\delta}$, hereafter called BZY20, was synthesized by spray pyrolysis using a nitrate solution of the precursor cations with concentration of 10^{-2} $mol.L^{-1}$. The concentration of the cation solution was determined by gravimetry. The starting materials were barium nitrate, zirconium nitrate and yttrium nitrate of high purity (> 99.9%, Aldrich). The argon gas flow and the furnace temperature were varied from 2.0-5.0 $L.min^{-1}$ and 400-700ºC, respectively. Some experimental conditions used in the experiments are listed in Table 1.

Table 1: Parameters of synthesis used in some experiments.

Batch #	T_1 (ºC)	T_2=T_3 (ºC)	Gas Flow ($L.min^{-1}$)
2	500	600	~ 2
7	400	500	~ 2
13	600	700	3.5
14	400	500	3.5

Other parameter of synthesis varied during the experiments was the voltage of the current collector, which was set 1.5 kV (batches # 2 and 7) and 2.8 kV (batches # 13 and 14). The three-zone furnace was programmed such that the temperature of the first zone (T_1) was fixed at 100ºC below the temperature of the other zones (T_2 and T_3).

The characterization of the produced powders was carried out by X-ray fluorescence (Shimadzu, EDX600), X-ray diffraction (Bruker-AXS, D8 Advance), field-emission scanning electron microscopy (FEI, Inspect F50 and Jeol, JSM 6701F) and transmission electron microscopy (Jeol JEM2100).

Results and discussion

The X-ray fluorescence spectroscopy evidenced the true composition of the prepared particles as $Ba_{1.84}Zr_{0.76}Y_{0.14}O_{3-\delta}$. Then, the concentration of starting solution was adjusted to match the nominal composition.

After the initial tests with the gas flow and furnace temperature, the experimental conditions were fixed as 3.5 $L.min^{-1}$ and temperatures T_1= 600ºC and T_2=T_3=700ºC. Fig. 1 shows X-ray diffraction patterns of BZY20 synthesized by spray pyrolysis and conventional method, for comparison purpose.

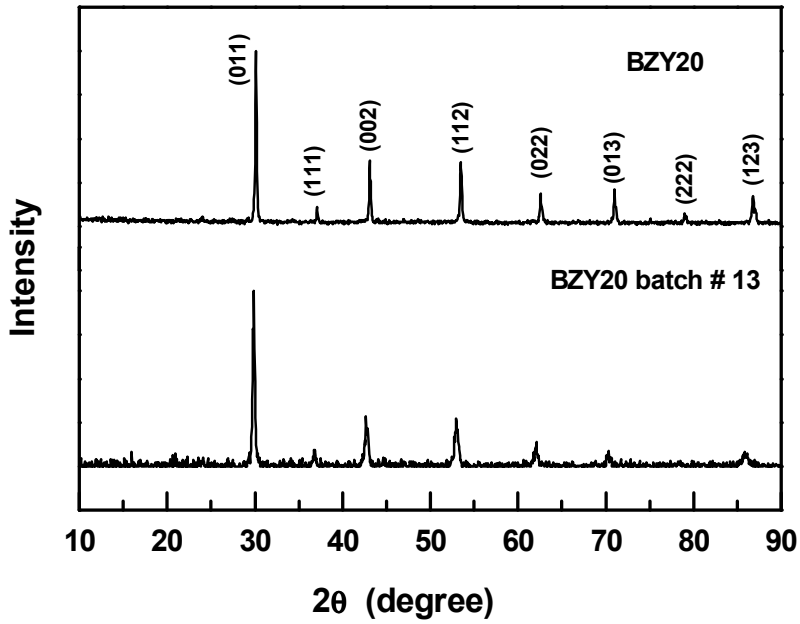

Fig. 1: X-ray diffraction patterns of BZY20 prepared by spray pyrolysis (BZY20 batch #13) and by the conventional method (BZY20).

It may be seen that both patterns are essentially cubic and single phase. Thus, the BZY20 was synthesized for the first time at a relatively low temperature. Increase of the gas flow allowed for increasing the voltage of the current collector, thereby increasing the yield of the reaction.

Fig. 2 shows FE-SEM micrographs evidencing different morphologies of the prepared BZY20 particles.

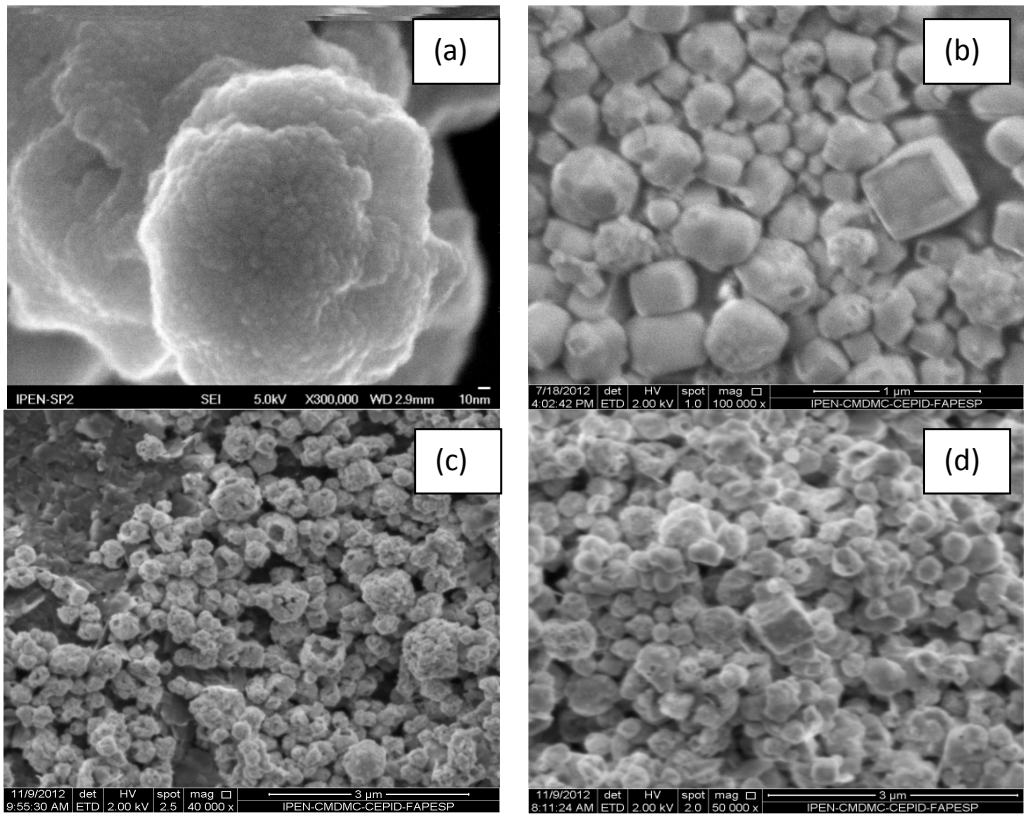

Fig. 2: FE-SEM micrographs of BZY20 powder particles synthesized by spray pyrolysis. Batches: a) 2, b) 7, c) 13 and d) 14.

It is worth noting that independent on the synthesis parameters the produced particles are in the submicronsize and nanosize ranges, although they clearly differ in shape. The most frequent particle shapes are spheroid (Fig. 2a) and cuboid (Fig. 2 b-d). For the specific conditions employed here the spheroid BZY20 particles (Fig. 2a) exhibit an average size of 5 nm and are highly agglomerated. In Fig. 2b the BZY20 particles are preferentially cuboids in shape with average size of 500 nm. Increase of the gas flow and decomposition temperature resulted in particles with sponge-like shape (Fig. 2c). In this case, it may be seen the well-known phenomenon of explosion, which is a consequence of crust formation at the drying step by precipitation of solute close to the surface of the droplet, due to rapid evaporation of solution, resulting in hollow particles [16]. This undesirable effect may be attributed to both increase of the gas flow and decomposition temperature. This phenomenon has been previously observed in BZY prepared at 800ºC [14]. Reduction of the decomposition temperature gave rise to predominance of cuboid and solid particles as shown in Fig. 2d.

Fig. 3 shows transmission electron microscopy micrographs of BZY20 particles from batch # 2.

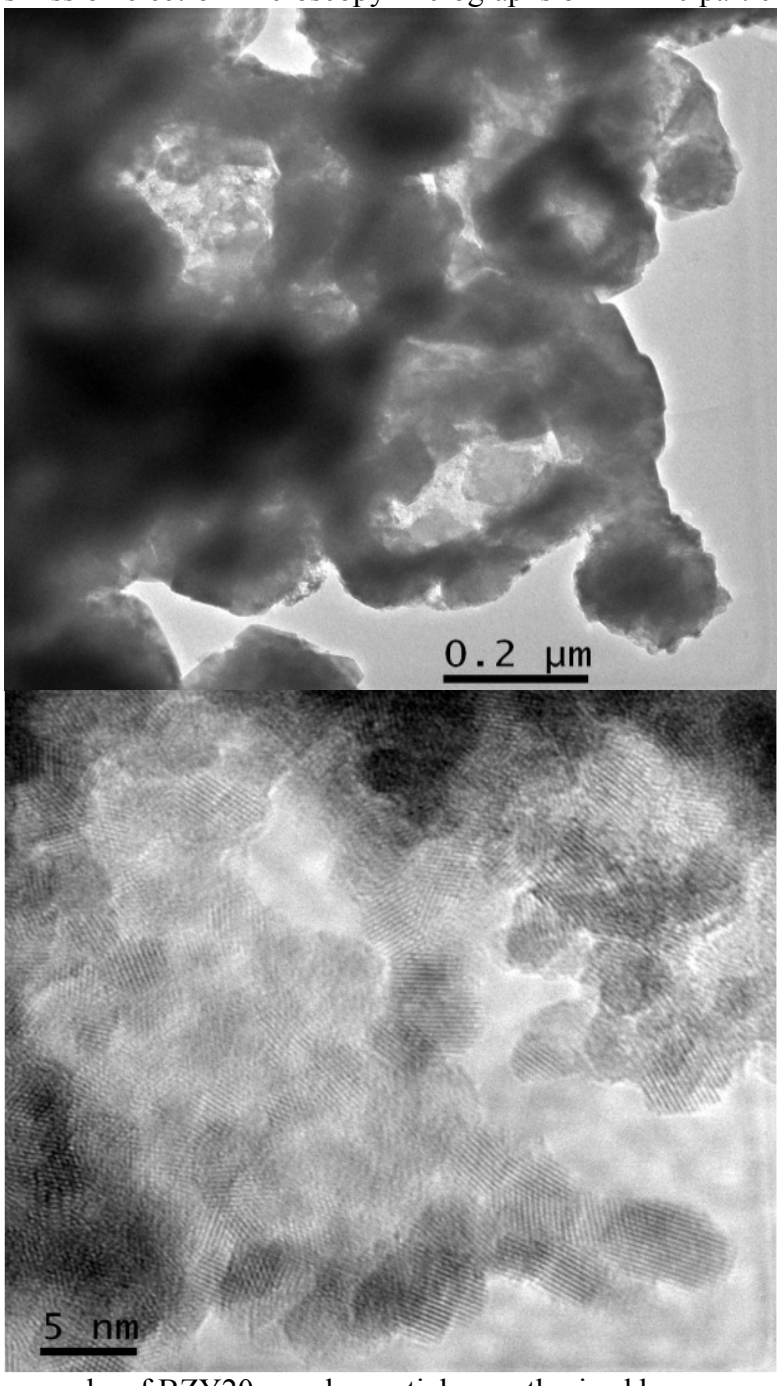

Fig. 3: TEM micrographs of BZY20 powder particles synthesized by spray pyrolysis (batch # 2).

The relatively low size and agglomeration state of the powder particles are clearly seen in this figure. The high resolution micrograph (Fig. 3 bottom) reveals that the particles prepared at low temperature (600ºC) are crystalline with homogeneous and regularly spaced crystalline planes.

Conclusions

Yttrium-doped barium zirconate powder with diverse morphology was synthesized by spray pyrolysis. The yield of the reaction was controlled by the decomposition temperature, the gas flow and the voltage of the current collector. By setting up the temperature of the hot zone in the furnace at 700ºC, a crystalline and cubic single phase powder was produced. High yield was obtained with a gas flow of 3.5 $L.min^{-1}$. FE-SEM micrographs evidenced the particle size in the submicrometer range.

Acknowledgements

The authors acknowledge FAPESP, CNPq and CNEN for financial supports, and to the Laboratory of Electron Microscopy of CCTM-IPEN for some SEM and TEM observations.

References

[1] H. Gleiter, Nanostructured materials: basic concepts and microstructure, Acta Mater. 48 (2000) 1-29.

[2] H.K. Bowen, Basic research needs on high-temperature ceramics for energy applications, Mater. Sci. Eng. 44 (1980) 1-56.

[3] R.C. Flagan, in Aerosol Science: Industry, Health and Environment vol. 1, S. Masuda, K. Takahashi (Eds.), Pergamon Press, 1990.

[4] F. Boulch, E. Djurado, Structural changes of rare-earth-doped, nanostructured zirconia solid solution, Solid State Ionics 157 (2003) 335-340.

[5] M. Gaudon, E. Djurado, N.H. Menzler, Morphology and sintering bevaviour of yttria stabilised zirconia (8-YSZ) powders synthesized by spray pyrolysis, Ceram. Int. 30 (2004) 2295-2303.

[6] H. Ishizawa, O. Sakurai, N. Mizutani, M. Kato, Homogeneous Y_2O_3-stabilized ZrO_2 powder by spray pyrolysis method, Am. Ceram. Soc. Bull. 65 (1986) 1399-1404.

[7] T.J. Gardner, G.L. Messing, Magnesium salt decomposition and morphological development during evaporative decomposition of solutions, Thermochim. Acta 78 (1984) 17-27.

[8] T. Rudin, K. Wegnaer, S.E. Pratsinis, Uniform nanoparticles by flame-assisted spray pyrolysis (FASP) of low cost precursors, J. Nanoparticle Res. 13 (2011) 2715-2725.

[9] T. Gonzalez-Carreno, M.P. Morales, C.J. Serna, Barium ferrite nanoparticles prepared directly by aerosol pyrolysis, Mater. Lett. 43 (2000) 97-101.

[10] G.L. Messing, S.C. Zhang, G.P. Jayanthi, Ceramic powder synthesis by spray-pyrolysis, J. Am. Ceram. Soc. 76 (1993) 2707-2726.

[11] B. C. H. Steel, A. Heinzel, Materials for fuel-cell technologies, Nature 414 (2001) 345-352.

[12] U. Anselmi-Tamburini, M.T. Buscaglia, M. Viviani, M. Bassoli, C. Bottino, V. Buscaglia, P. Nanni, Z.A. Munir, Solid-state synthesis and spark plasma sintering of submicron BaYxZr1-xO3-x/2 (x=0, 0.08 and 0.16) ceramics, J. Eur. Ceram. Soc. 26 (2006) 2313-2318.

[13] M. M. Bucko, J. Oblakowski, Preparation of BaZrO3 nanopowders by spray pyrolysis method, J. Eur. Ceram. Soc. 27 (2007) 3625-3628.

[14] P. A. Stuart, T. Unno, R. A. Rocha, E. Djurado, S. J. Skinner, The synthesis and sintering behaviour of BaZr0.9Y0.1O3-δ powders prepared by spray pyrolysis, J. Eur. Ceram. Soc. 29 (2009) 697-702.

[15] P. I. Dahl, H. L. Lein, Y. Yu, J. Tolchard, T. Grande, M.-A. Einarsrud, C. Kjolseth, T. Norby, R. Haugsrud, Microstructural characterization and electrical properties of spray pyrolyzed conventionally sintered or hot-pressed BaZrO3 and BaZr0.9Y0.1O3-δ, Solid State Ionics 182 (2011) 32-40.

[16] D. H. Charlesworth, W. R. Marshall, Jr., Evaporation from drops containing dissolved solids, AIChE J. 6 (1960) 9-23.