

## Yttrium-Doped Barium Cerate Ceramic Powders for Protonic Solid Electrolytes

F.S. Fontes and R. Muccillo

Energy and Nuclear Research Institute, Pinheiros, C.P. 11049 São Paulo 05422-970, Brazil

**Keywords:** Citrate Technique, Protonic Conductors, Reactive Powders, Solid Electrolyte

**ABSTRACT:** Reactive yttrium-doped BaCeO<sub>3</sub> ceramic powders have been prepared by a chemical route based on the citrate technique. Barium carbonate, cerium nitrate, yttrium nitrate, polyethylene glycol and citric acid have been mixed and heated to produce polymeric resins, that upon heating, yielded BaCe<sub>1-x</sub>Y<sub>x</sub>O<sub>n</sub> fine ceramic powders. Pressing and sintering produced high density pellets. X-ray diffraction and electrochemical impedance spectroscopy analyses have shown that these pellets are perovskite single phase and protonic solid electrolytes, respectively. The main applications of these pellets are as solid electrolytes in many electrochemical devices such as methane-based solid oxide fuel cells and hydrogen or steam sensors.

### INTRODUCTION

Cerates of alkaline earth metals are known to present proton conductivity in water vapor environments [1-3]. They are then potential candidates as electrochemical transducers to be used as solid electrolytes in devices like fuel cells [4] and sensors for gaseous species (humidity and hydrogen). The interaction of oxygen vacancies in the oxides, with water molecules in the environment, produces the charge carriers (protons) required for the electric conduction in the bulk of the specimens. For the detection of hydrogen gas, the charge carriers are also protons produced by the interaction of the hydrogen molecule with electron holes. The solid electrolytes having high protonic conductivity are the rare-earth doped cerate oxides. The rare-earth dopants increase the density of crystalline defects in these cerium-based oxides, enhancing then their protonic conductivity.

The degree of homogeneity of a ceramic specimen is important for the electrical behavior. Highly homogeneous ceramic specimens might be prepared depending on the synthesis process. Solid phase conventional routes, mainly based on sieving, mixing and heat treating for sintering, are known to produce usually not only non-homogeneous ceramic pieces but also lead to incomplete chemical reactions. The liquid phase chemical routes, on the other hand, have as main advantages the production

of homogeneous ceramic powders, the easy stoichiometric control and lower sintering temperatures [5]. Several techniques have been developed: co-precipitation, sol-gel, hydrothermal synthesis, polymeric precursor and others. The polymeric precursor technique, also known as technique of polymerization in organic media or citrate technique or else Pechini's method [6] is a very promising technique, competing with other techniques due to a fairly easy experimental sequence and low cost of the main chemical reagents [7]. The technique consists basically in the formation of complex of the metallic cations in the solution of a citrate. Sterification occurs in a solution of a polyalcohol and polyesterification under heating leading to a homogeneous distribution of the metallic cations over the organic chain. Further heating of the polymeric chain leads to oxidation, elimination of organic residuals producing then the desired reactive ceramic powder [8].

In this paper the powder processing by the citrate technique of barium cerate-based protonic conductors with different yttrium oxide doping levels is reported. The evaluation of the ceramic powders is done by determining the electrical properties of sintered specimens. The Impedance Spectroscopy technique was used to the study of the electrical properties allowing for the determination of grain and grain boundary electrical resistivity of all specimens.

## EXPERIMENTAL

Reagent grade barium nitrate, 96% pure cerium hydroxide and 99% pure yttrium oxide were used as starting materials. The following compositions were prepared by the citrate technique:  $\text{BaCeO}_3$ , (hereafter 0Y);  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ , (01Y);  $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_3$ , (02Y);  $\text{BaCe}_{0.7}\text{Y}_{0.3}\text{O}_3$ , (03Y);  $\text{BaCe}_{0.6}\text{Y}_{0.4}\text{O}_3$ , (04Y).

The experimental sequence is shown in Fig. 1. Stoichiometric quantities of the starting materials were dissolved; barium nitrate in water, yttrium oxide in a nitric acid solution, and cerium hydroxide in a nitric acid plus hydrogen peroxide solution. Nitric acid is added after mixing all solutions. Then, a solution of citric acid and ethylene glycol is added, and the final solution is slowly heated up to polymerization, yielding a viscous blackish resin.

Thermogravimetric analysis has been performed in the resins to determine the optimum temperature for calcination in air. The resins were then pre-calcined at 350 °C during 1 hour and further at that temperature determined by thermogravimetric analysis, 600 °C during 1 hour. Even though some contamination might occur, all calcinations have been done in air using alumina crucibles. For electrical measurements the calcined powders were uniaxially cold-pressed to pellets of 10 mm diameter under a load of 780 kg, sealed in plastic bags under vacuum, and isostatically cold-pressed under 207 MPa. Sintering in air has been carried out inside a Lindberg super-khantal furnace according to the following temperature schedule: 10 degrees/min heating rate up to 1500 °C, dwelling at that temperature for three hours, and 15 degrees/min cooling rate to room temperature.

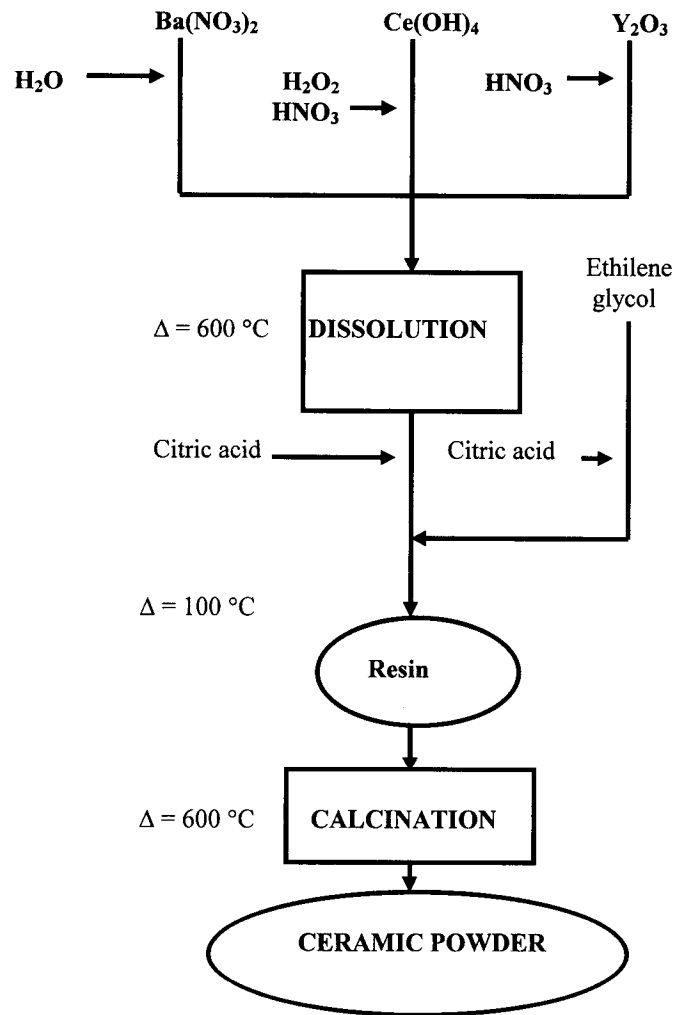


Figure 1. Experimental sequence for preparing yttrium-doped barium cerate ceramic powders by the citrate technique.

The ceramic powders and the sintered pellets have been analyzed by X-ray diffraction using a Bruker AXS D8 Advance diffractometer. For electrical measurements, a solution of colloidal graphite in isopropanol was used to apply electrodes in the parallel surfaces of the pellets. A sample chamber for three specimens, placed inside a tubular furnace was used for impedance spectroscopy measurements in air. The temperature of the specimen is monitored with a type S (Pt–Pt10%Rh) thermocouple.

Impedance spectroscopy measurements were performed from room temperature to 230 °C in the 5 Hz - 13 MHz frequency range with a Hewlett Packard model 4192A Low Frequency Impedance Analyzer connected to a HP Controller. Analysis of the impedance diagrams was done with a software supplied by Dr. M. Kleitz, LEPMI, Grenoble, France.

## RESULTS AND DISCUSSION

In Fig. 2 a typical thermogravimetric analysis of the resin obtained by the citrate technique is shown. The major part of the mass loss occurs in the 150 °C to 600 °C range as a result of loss of organic compounds. That temperature was chosen as the calcination temperature of the resins.

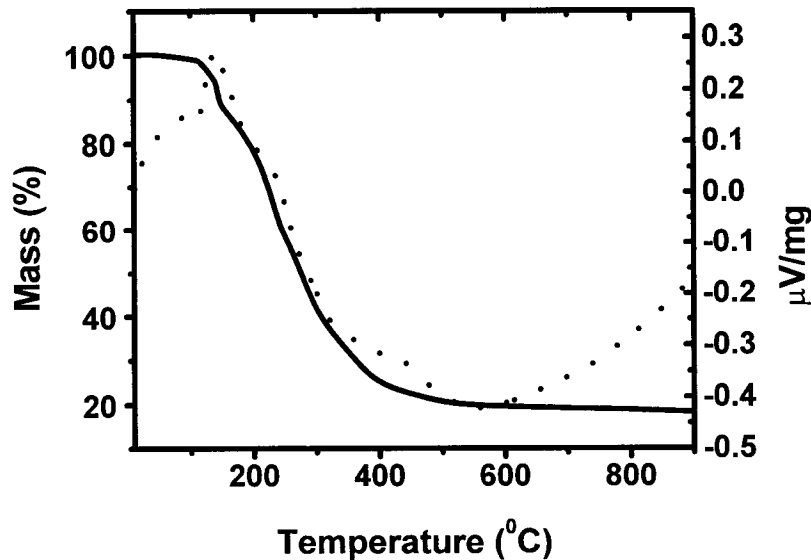


Figure 2. Thermogravimetric and thermal differential analyses of  $BaCe_{0.9}Y_{0.1}O_8$  compound.

The X-ray diffraction patterns of barium cerate and yttrium-doped barium cerates are shown in Fig. 3. No second phases are detected. As far as X-ray analysis is concerned, solid solution has been attained in the doped samples. Further evidence could be gathered by electrical measurements in a sense that the higher is the doping level, the higher should be the density of oxygen-compensating vacancies and consequently the intragranular conductivity of the samples.

The impedance diagrams of typical ceramic materials can be represented simply by an electric circuit composed of two parallel resistor/capacitor circuits in series, one representing the dielectric response of the grains and the other the dielectric response of the grain boundaries. The impedance diagram, represented by a  $Im(Z)$  versus  $Re(Z)$  is, in this case, composed of two semicircles (see, for example, the diagram of specimen 03Y in Fig. 4). In the impedance diagrams the resistance of the specimens is determined by the intercept of the semicircle with the X-axis. The results of Fig. 4 show the decrease of the electrical resistivity of specimens with different doping levels, as expected.

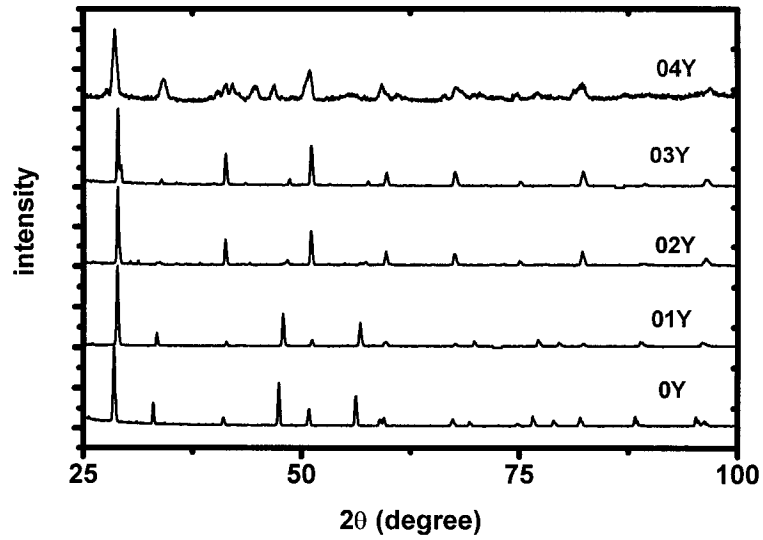


Figure 3. X-ray diffraction patterns of  $\text{BaCe}_{1-x}\text{Y}_x\text{O}_8$  compounds;  $x = 0.1/0.2/0.3/0.4$

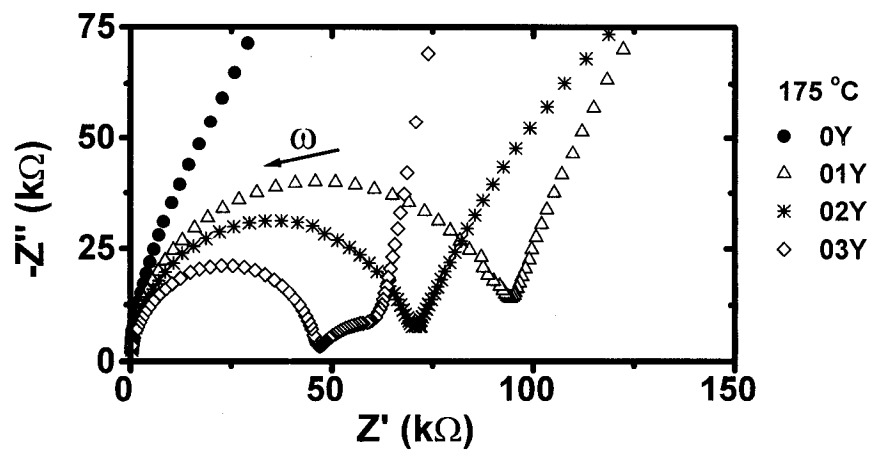


Figure 4. Impedance diagrams of  $\text{BaCe}_{1-x}\text{Y}_x\text{O}_8$  ( $x = 0, 0.1, 0.2, 0.3$ ) ceramic compounds at  $175\text{ }^\circ\text{C}$ .

Yttrium substituting for cerium is responsible for providing oxygen vacancies that, by their turn, increase the proton density in the specimens and, consequently, the density of charge carriers. This leads to an improvement of the electrical conductivity.

## CONCLUSIONS

Yttrium-doped barium cerate solid electrolyte ceramic powders can be prepared by the citrate technique. Reactive ceramic powders have been obtained after calcination at temperatures lower than those used in traditional methods. The powder has high chemical and structural homogeneity as determined by impedance spectroscopy and X-ray diffraction, respectively. The citrate technique can then be used for the fabrication of barium cerate powders for manufacturing solid electrolyte devices for humidity sensors and solid oxide fuel cells.

## ACKNOWLEDGEMENTS

To CNEN, FAPESP and PRONEX for financial support, and to CNPq for the scholarships. To M. V. Jardini and S. A. Jardino F. for preparing some of the powders used in this work.

## REFERENCES

- [1] K. Iwahara, T. Esaka, H. Uchida, N. Maeda, *Solid State Ionics* 3/4 (1981) 359
- [2] H. Iwahara, Proc. Int. Conf. Adv. Mat. (ICAM 91), Symposium A2: Solid State Ionics, Strasbourg, 27-31 May 1991, Ed. M. Balkanski, T. Takahashi, H. L. Tuller, Int. Union Mat. Res. Soc., Amsterdam, 1992, 575.
- [3] H. Iwahara, Advanced Ceramics for Protonics, in High Temperature Electrochemistry, Ceramics and Metals, Proc. 17<sup>th</sup> Riso Int. Symp. Mat. Sci., Ed. F. W. Poulsen, N. Bonanos, S. Linderoth, M. Mogenson, B. Zachau-Christiansen, Riso Nat. Lab., Roskilde, Denmark, 1996, Sept. 2-6.
- [4] K. Asano, T. Hibino, H. Iwahara, *A Novel Solid Oxide Fuel Cell System Using The Partial Oxidation of Methane*, *J. Electrochem. Soc.* 142, 10, (1995) 3241
- [5] L. M. Gan, L. H. Zhang, H. S. O. Chan, C. H. Chew, B. H. Loo, *J. Mat. Sci.* 31 (1996) 1071.
- [6] M. Pechini, U.S. Patent No. 3.330.697, (July 1967)
- [7] R. Muccillo, E. N. S. Muccillo, I. C. Cosentino, Y. V. França, F. C. Fonseca, N. H. Saito, *Mat. Sci. Forum* 299-300 (1999) 80-90.
- [8] P. A. Lessing, *Am. Ceram. Soc. Bull.* 68 (1989) 1002-7.

## **Advanced Powder Technology II**

doi:10.4028/www.scientific.net/KEM.189-191

## **Yttrium-Doped Barium Cerate Ceramic Powders for Protonic Solid Electrolytes**

doi:10.4028/www.scientific.net/KEM.189-191.166