Synthesis and characterization of $BaCe_{1-x}Y_xO_{3-\delta}$ protonic conductor

A. Santucci [1, 2], **V. Esposito** [2], **S. Licoccia** [2] **and E. Traversa** [2]
[1]*ENEA, Dip. FPN, C.R. ENEA Frascati, Via E. Fermi 45, Frascati (RM) I-00044, Italy.*
[2]*Dept. of Chemical Science and Technology, Via della Ricerca Scientifica, 00133 Roma, Italy.*

E-mail: alessia.santucci@enea.it

Abstract. In recent years, doped perovskites such as barium cerates ($BaCeO_3$), strontium cerates ($SrCeO_3$) and barium zirconates ($BaZrO_3$) have been studied as ceramic proton conductors for several technological applications: protonic membranes, hydrogen separation, catalytic support and solid oxides fuel cell components. Among those compounds, yttrium doped barium cerates have the best performances in terms of protonic conductivity at lowest temperature.
In this activity, doped BCY oxide powders was synthesized via novel soft chemical route. The method is based on the formation of a metallorganic xero-gel at room temperature. The structural phase of powders and dense pellets were analyzed using X-ray diffraction (XRD), while the morphology was investigated by field emission scanning electron microscope (FE-SEM). Electrochemical impedance spectroscopy (EIS) measures were performed on dense pellet under synthetic air flux and hydrogen atmosphere in a temperature range between 200-750 °C with a frequency range of 10mHz-10MHz.

1. Introduction

Several oxide with the ABO_3 perovskite structure have shown protonic conductivity between 500-1000 °C [1-4]. These oxides are doped on the B-site by lower valence elements, typically a trivalent rare-earth metal (M), to introduce oxygen defects. The exposure of the doped material to humid atmospheres results in the formation and incorporation of hydroxyl groups to oxygen vacancies followed by the migration of the lone protons by hopping between oxide ions via a Grotthus-like mechanism. The formation of the hydroxyl defects may be written using Kröger-Vink notation (1).

$$H_2O(g) + V_O^{\bullet\bullet} + O_O \leftrightarrow 2(OH)^{\bullet} \quad (1)$$

According to Irvine et al. [5] the most technologically promising moderate-temperature proton conductors are those perovskites based upon the cerates or zirconates of barium doped with yttria or lanthanide oxides. Barium cerates generally exhibit the highest proton conductivities; but these materials are unstable at high temperature in the presence of CO_2 and steam, while the zirconates are much more resistant to degradation. The zirconates do not sinter easily, and the highest conductivities are only obtained when sintering occurs at or approaching 1700 °C, in fact the highest conductivities are influenced by some form of phase transformation or segregation or, as suggested by Snijkers et al. by a slow kinetic process of water absorption. The stability of doped $BaCeO_3$ is improved by the introduction of Zr at the B site, but the typical sintering temperature of Zr-replaced $BaCeO_3$ is still above 1550 °C. However, very significant differences exist in reported values of conductivities, which seem to be related to the synthesis procedure.

In general, the $BaCeO_3$ powders were synthesized by the conventional solid state reaction, in which oxide precursors are repetitively milled and calcined at high temperature. However, these conventional ceramic powder processes can have several drawbacks such as relatively large and varied grain sizes, inhomogeneities in the chemical composition [6,7], and of course high cost related to the high sintering temperature.

In this view, one possible approach to overcome these difficulties is to employ a soft chemical process which has the following advantages: lower sintering temperature, shorter processing time, and the possibility of obtaining high purity and ultrafine powders. Essentially, these methods can produce nanocrystalline materials, which appear to be a promising approach to combine the superior characteristics of these nanoscaled ceramics with the proton conducting properties of doped perovskite [8].

In this activity a new synthesis route for the $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (BCY20) called sol gel combustion, has been investigated. The method is based on the autocombustion reaction of the gel resulting from a novel sol gel process. The technique involves three different steps: the preparation of a stable and homogenous sol, the formation of a gel, and the

combustion of the so-formed gel. This synthesis procedure allows us to obtain the requisite phase for BCY20 at lower temperature and dense pellet with high conductivity.

2. Experimental

The novel synthesis method consists of the formation of a gel of the nitrate solution using agar powder. The metal nitrates were dissolved in water in the correct stoichiometric ratio, and then the solution was heated to 80 °C. At that temperature the agar powder (20% of weight) was added. Agar is a polysaccharide and it works as a gelling agent. The dissolution process of the agar in the solution was completed by several minutes of stirring at 80 °C. The agar induced the complete gelation at 4 °C in a few minutes. During cooling the viscosity increased rapidly and there was the formation of a self-sustaining gel, then the gel was burned in a reactor. The reactor had two different holes that allowed the continuous flux of air that was essential to ensure the complete combustion of the gel inside. The precursor powders were ground into an agate mortar and calcined at the appropriate temperature in order to have a pure perovskite phase. Then the powders were uniaxially pressed at 4 tons in order to form a 3 mm diameter pellet. The discs were sintered in air in a tubular furnace. The sintering temperature required for the agar method was 1450 °C. After sintering the surface of the pellet were polished and stripped off with a thermal etching.

The precursor powder obtained with the agar method was characterized by simultaneous thermogravimetric-differential thermal analysis (TG/DTA) performed on a NETZSCH STA 409. The sample was held in a platinum holder under air atmosphere. The phase composition was analyzed by X-ray diffraction (XRD). X-ray diffraction data were acquired using a Philips X'PertMPD using CuKα radiation. The phases present in the BCY20 sample at different stage of calcination were analyzed in the Bragg angle range $20° < 2\theta < 85°$. The microstructure of the sample was then characterized by field emission scanning electron microscopy (FE-SEM LEO 1530) after polishing and thermal etching. The densification rate has been determined with samples of 10,40 mm length and a diameter of 8,02 mm, it was sintered in a dilatometric up to 1600 °C using a constant heating rate of 5 K min^{-1} and cooled down to a room temperature with a rate of 10 K min^{-1}. The shrinkage was recorded during heating and cooling. Finally conductivity measurements on the BCY20 agar sample were performed in order to investigate the electrical property of the material. The BCY20 pellet was assembled in a cell (Fig. 1): the cell apparatus was connected with a frequency response analyzer to measure the conductivity across the electrolyte. The measurements have been performed in a frequency range between 10mHz-10MHz, and in a temperature range between 200-750 °C.

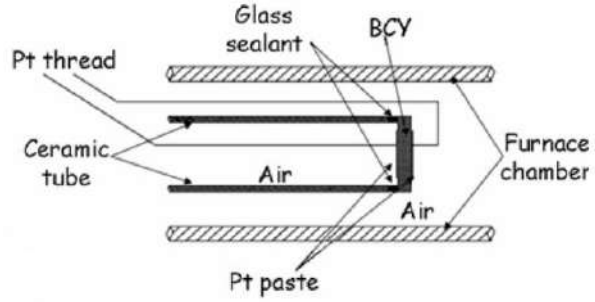

Fig. 1. – Scheme of the cell apparatus.

3. Results and discussion

3.1 TG/DTA

The powders obtained after burning the gels at 200 °C were characterized by Thermogravimetric/Differential Thermal Analysis (TG/DTA), in order to study the crystallisation process and choose the suitable temperature range for calcination. The TG (Fig. 2) revealed that the weigh loss, for a heating rate of 5 °C/min, was completed at 1150 °C with a total weigh loss less than 10%. The results showed two plateaux: between 700-800 °C and over 1200 °C. According to the DTA, from 600-700 °C, the reaction is exothermic, associated with the initial decomposition stage of the organic species involved in the gel.

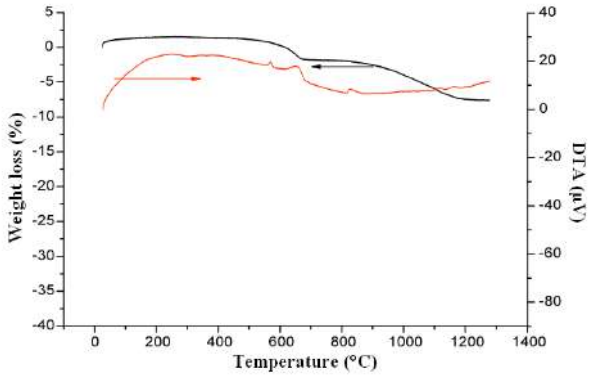

Fig. 2. – TG/DTA of the BCY 20 precursor synthesized with the agar method.

3.2 XRD Measurements

The X-ray diffraction patterns of BCY20, powder and pellet, obtained with the Agar synthesis are shown in figure 3.

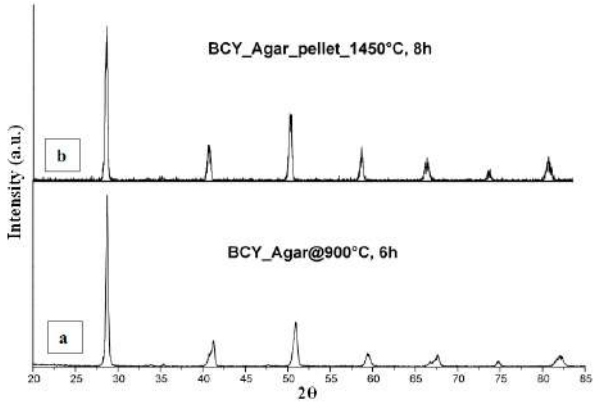

Fig. 3. - XRD patterns of the BCY20 obtained with the agar synthesis method, a) powder calcined at 900 °C for 6 h, and b) pellet sintered at 1450°C for 8 h.

The XRD reveals that, with this method, a pure perovskite phase is reached at 900 °C while, with the standard synthesis procedure, the phase was pure only when temperature approached 1100 °C.

Another relevant aspect is related to the sintered pellet: in fact, the BCY20 pellet (90% of the theoretical density) was obtained with a sintering treatment carried out at 1450 °C for 6 hours. The decrease of the sintering temperature (usually around 1600 °C) avoids the presence of secondary phases related to aggregation processes caused to barium evaporation.

3.3 Dilatometric measurements

To better understand the sintering behaviour of the BCY20 obtained with the described synthesis procedure, dilatometric measures have been performed on two BCY20 samples: one sample was prepared with the Agar synthesis method, and one sample was realized using a traditional ethylene glycol method.

Figure 4 reports the dilatometric behaviour of the two BCY20 samples. From the results it is possible to observe that in the sample prepared with the agar method the shrinkage starts between 900-1000 °C, while in the sample prepared with the EG method the shrinkage starts at 1200 °C. Another important difference in the sintering behaviour of the two samples is recorded in the temperature range between 1100-1200 °C. At that point, in fact, the sample prepared with the EG method expands and then the shrinkage starts. The different dilatometric behaviour between the two BCY20 samples has a macroscopic effect as reported in figure 5 which shows the samples after the dilatometric measurements. From that picture it is clear that both samples are cracked, but in the EG sample the cracks are more.

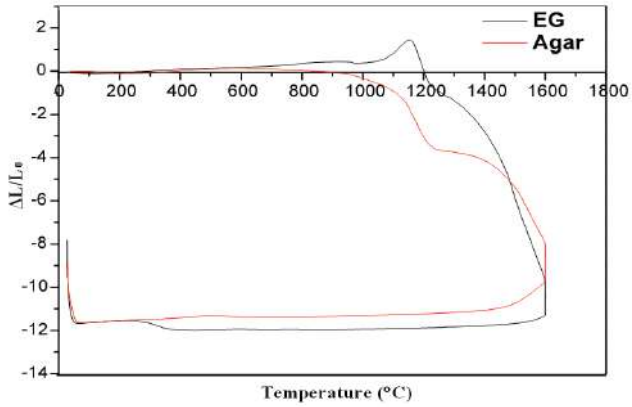

Fig. 4. - Dilatometric shrinkage of the two BCY20 samples obtained with the Agar synthesis (red line) and with the EG synthesis (black line).

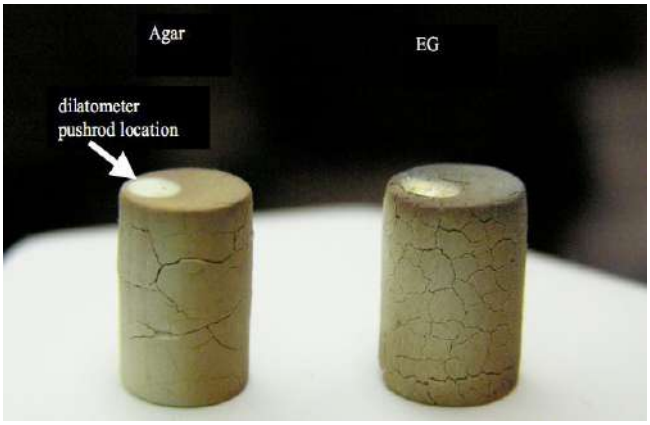

Fig. 5. - Picture of the two BCY20 samples after the dilatometric measurement.

3.4 SEM micrographs

The SEM micrographs reveal what the dilatometric measures have already shown. In fact, as figures 6 and 7 report, the BCY20 powders and pellets have a different microstructures according to the used synthesis procedures.

In particular figure 6 shows the SEM micrograph of the calcined BCY20 powder obtained with the agar method (a) and with the EG method (b), respectively. The main differences between the two BCY 20 powders are related to the dimension of the particles and to the different phases of the two powders. In fact,: the particles obtained with the agar synthesis route are smaller than the other while the different shapes of the powders reveal different phases. In figure 7 the surface micrographs of the two BCY20 sintered pellet are reported. Even in this case, a difference in the particles size is observed. In fact, in the agar sample, the average grain size is around 100 nm, while in the EG sample, the average grain size is about 1-2 μm. Also the density of the two samples is different, in particular the BCY20 pellet obtained with the agar method, sintered at 1450 °C, is more dense than the EG sample, sintered at 1600 °C.

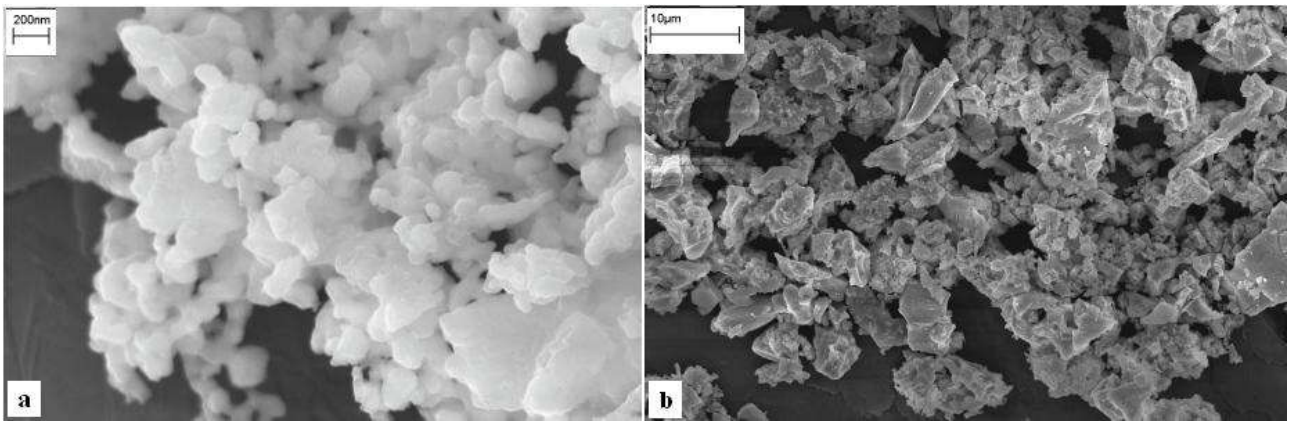

Fig. 6. - FE-SEM micrographs of the BCY20 powder, a) Agar method, b) EG method.

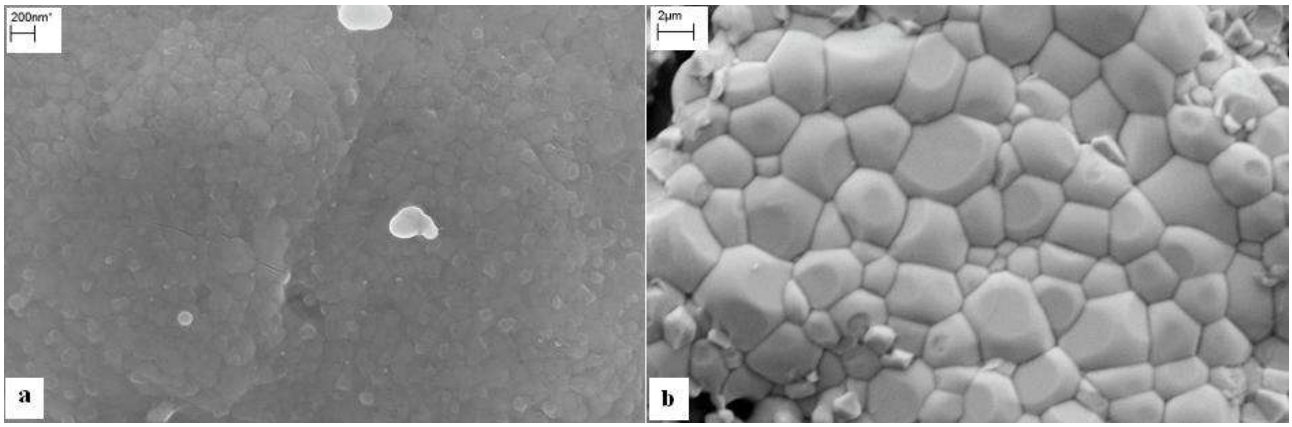

Fig. 7. - FE-SEM micrographs of the BCY20 pellet, a) Agar method, b) EG method.

3.5 Conductivity measurements

The electrolyte BCY20 pellet made with the agar method was placed into a single chamber reactor. The reactor was installed into a horizontal tube furnace and the cell was connected with a frequency response analyzer to measure the AC impedance spectra across the electrolyte. The conductivity of the perovskite sample with increasing temperature was measured and recorded in the range between 200-750 °C with steps of 25 °C intervals in air and wet hydrogen atmosphere. The activation energy of the proton conduction mechanism can be determined from an appropriate Arrhenius plot. In this way, the slope is equal to –E/k, where E is the activation energy and k is the Boltzmann constant. The Arrhenius plot for BCY20 is shown in figure 8. The activation energy for BCY20 is 0.40 eV, in agreement with the values reported in literature.

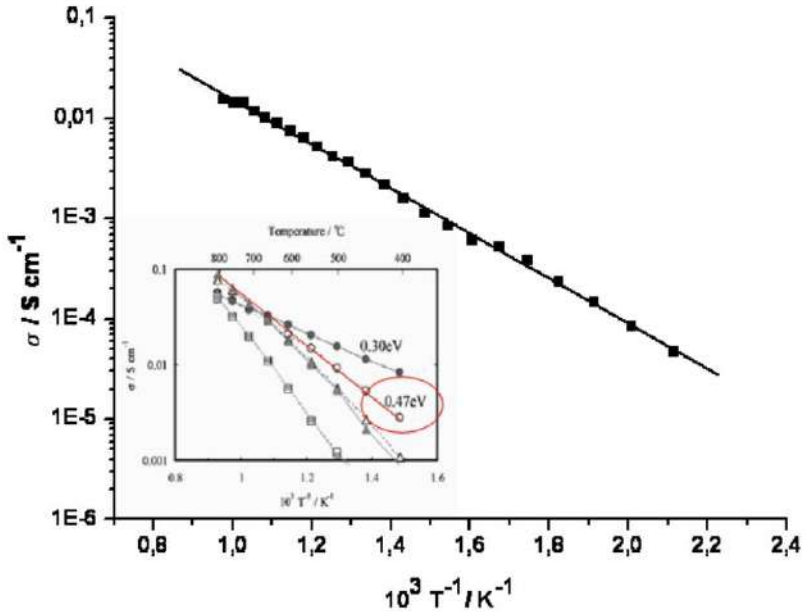

Fig. 8. - Arrhenius plot for BCY20 compared with literature data [9].

Acknowledgments

This work was supported by the Ministry of University and Research (MIUR) as part of a PRIN project. We gratefully thank Dr. Sean Bishop for the dilatometric measures.

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