



# Conductivity study of dense BaZr<sub>0.9</sub>Y<sub>0.1</sub>O<sub>(3-δ)</sub> obtained by spark plasma sintering

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## ABSTRACT

10% yttrium doped barium zirconate (BZY10) was synthesized by solid state reaction and a 99.8% dense and transparent sample was prepared by spark plasma sintering (SPS) at 1700 °C for 5 minutes. A single phase compound was obtained, with no evaporation of barium. High-Resolution Transmission Electron Microscopy (HRTEM) images revealed a distinct grain boundary across two grains, confirming no secondary phase formation along grain boundaries. The conductivity was determined as a function of temperature, at two different water vapor pressures, as well as in the D<sub>2</sub>O vapor exchanged state. The activation energy corresponding to protonic conduction has been determined, and compared to values from literature. The decrease in activation energy with increasing lattice parameters is confirmed. Furthermore, the effective space charge layer width has been estimated at 1.2–1.3 nm.

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## 1. Introduction

Yttrium doped barium zirconate has been widely studied as proton conductor at intermediate temperatures (about 600 °C) [1–10], with yttrium doping content between 5% and 20% of the B-site (referred to as BZY5 and BZY20 respectively). Its chemical and mechanical stability makes it attractive as an electrolyte for protonic ceramic fuel cells (PCFCs). Unfortunately, these compounds require very high sintering temperature to achieve densities of over 90%: for example, Duval et al. [9] obtained 91% dense BZY10 after 24 h at 1720 °C, Iguchi et al. [11] reported a densification between 96 and 98% while sintering BZY5 at 1700 to 1800 °C and Katahira et al. [2] obtained BZY10 with density exceeding 95% after 5 h at 1800 °C. One should also be aware that barium evaporation can occur during sintering at high temperature, with a detrimental effect on the conductivity [12]. To avoid this phenomenon, the pellets should be embedded in powder with an excess of barium during sintering [8].

One possibility for improving the densification is the use of sintering aids such as Zn [13–15], Co [16,17] or other transition metals (Cu, Ni, Fe...) [17–19]. These, however, may contaminate the grain boundaries and have an impact on the conductivity. Other ways are:

- to increase the sintering temperature further: 99.7% density was reached by sintering at 1850 °C for 1 h in a vacuum furnace [7],

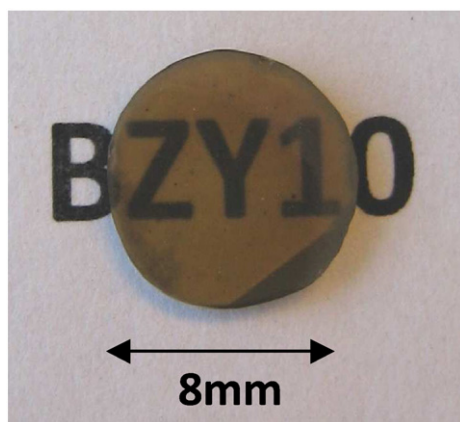
- to anneal the sample at extremely high temperature: Duval et al. [9] annealed at 2200 °C in oxidizing atmosphere a sample sintered 24 h at 1720 °C, and obtained a 98.5% dense sample,
- to use other methods for sintering than the conventional method. Kjølseth et al. [20] used hot pressing and Spark Plasma Sintering (SPS) and achieved a densification of BZY10 of over 95% for two different sintering conditions: 1 hour at 1650 °C under 50 MPa or 5 min at 1600 °C under 100 MPa. Anselmi-Tamburini et al. [21] made BZY8 and BZY16 pellets by SPS with densities between 94.4 and 97.9% at 1600 °C. 98% dense nano-sized BZY8 was also prepared by SPS by Park et al. [22]. In a previous work [23], a 99.8% dense BZY10 sample was prepared using SPS with a 5 min dwell at 1700 °C.

Discrepancies in the conductivity of barium zirconate are present in literature and have been carefully summarized by Babilo et al. [8]. These can be explained by differences in the synthesis and sintering processes (shape, size of the grains and grain boundaries), the evaporation of barium while sintering (leading to secondary phases or distortions of the cell) and/or the electrodes used for conductivity measurements: at high temperature, Pt electrodes exhibit electrode resistance effects which can be mistakenly ascribed to the electrolyte. Moreover, Azad et al. [4] have suggested the presence of two phases in yttrium doped barium zirconate, with one of these displaying a higher protonic conductivity. According to these authors, the proportion of the phases depends on the synthesis and sintering conditions.

Barium zirconates exhibit lower conductivity than cerates do, although the bulk conductivity of barium zirconate is higher than the one of cerate [8,13,24,25]. It follows that the difference is due to the

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**Fig. 1.** Picture of the BZY10 pellet obtained by SPS, after annealing at 800 °C in air and polishing.

grain boundary conductivity which is lower for zirconate than for cerate. Many explanations have been proposed for this effect:

- inevitable lattice distortion at intergranular boundaries which affects the mobility of protonic defects as well as structures arising at the boundaries with small point contact between grains [7],
- evaporation of barium [8,11],
- incorporation of yttrium in the A-site of the perovskite [8],
- nonstoichiometry [8],
- core-space charge layer effects [20,26],
- second phases [27].

The substitution of zirconium by yttrium makes the compounds more difficult to sinter [21]. However this substitution is necessary to create oxygen vacancies, essential for the incorporation of protons, as shown in equation (1) [28–34]:



This study deals with  $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{(3-\delta)}$  prepared by solid state reaction and sintered by SPS. The main goals were:

- to determine the conductivity of an extremely dense BZY10 sample and compare it to values from literature,
- to study the grain boundaries of the specimen obtained by SPS.

## 2. Experimental

The  $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{(3-\delta)}$  powder was prepared by solid state reaction.  $\text{BaCO}_3$  (Aldrich, 99+%),  $\text{CeO}_2$  (Aldrich, 99.9%, <5 μm),  $\text{Y}_2\text{O}_3$  (Sigma-Aldrich, 99.99%), YSZ (Aldrich, submicron powder; 99.5%, 5.3 wt.% of yttria) were mixed in stoichiometric proportions for 20 h in a ball mill. The dried mixture was calcined in air at 1400 °C during 24 h ( $150\text{ °C}\cdot\text{h}^{-1}$ ).

SPS was carried out in the equipment *Sumitomo SPS 2080* provided by Plateforme PNF2, Université Paul Sabatier, CIRIMAT, Toulouse, France. The  $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{(3-\delta)}$  powder, without binding material, was set in a graphite die with an inner diameter of 8 or 20 mm and sintered under vacuum (roughly 1 Pa). The experiments were done at 1700 °C for 5 min. The uni-axial pressure was maintained at 100 MPa during the process. The heating rate for all SPS experiments was maintained at around  $150\text{ °C}\cdot\text{min}^{-1}$ , and the natural cooling rate down from 800 °C was  $100\text{ °C}\cdot\text{min}^{-1}$ . The temperature was controlled by an optical pyrometer focused on a small hole (1.8 mm diameter, 3 mm depth) at the surface of the die. One should be aware that the temperature of the sample is slightly higher than the one measured at the outside of the die, and the difference depends of the

thermal conductivity of the sintered material. Shrinkage was recorded from the dilatometer provided with the SPS machine.

Crystallographic phases and lattice parameters were determined at room temperature with a *Bruker D-8* X-ray diffractometer, using  $\text{CuK}_{\alpha 1}$  radiation. The data were fitted using the cell refinement of *WinXPOW* software, with the space group Pm3m of the cubic symmetry.

Scanning Electron Microscope (*Zeiss, SUPRA 35*) experiments were performed to assess the morphology of the sintered products. The samples were fully polished after sintering, hence the microstructure could only be observed after revealing the grain boundaries with a thermal etch. The samples were etched at 1400 °C in air for 30 min ( $200\text{ °C}\cdot\text{h}^{-1}$ ). Deposition of a thin carbon layer was necessary because of the insulating properties of the samples.

The TEM thin foils were prepared by ion milling technique utilizing a *Fischione* desk-top precision ion milling and polishing system. All TEM work was done on JEOL 3000 F, a field-emission analytical 300 KV TEM equipped with a Gatan Imaging Filter (GIF) and a scanning TEM (STEM) unit. Elemental analysis was performed with STEM-EDS method utilizing 1 nm probe size (INCA X-ray microanalysis system).

For AC electrical measurements, the pellet was coated with platinum paste (Ferro 308a) and heated two hours at 1000 °C and two hours at 1200 °C. Impedance spectroscopy was performed from 120 to 800 °C in wet reducing atmosphere ( $\text{N}_2/\text{H}_2$  (9%),  $\text{P}(\text{H}_2\text{O}) = 0.015\text{ atm}$  or 0.030 atm) in the frequency range of 42 Hz to 1 MHz, using a *Hioki 3225–50* LCR analyser. The spectra were corrected for the inductance of the cell and analyzed with *EqCwin* software, written by André Wisse and Bernard Boukamp. The activation energies were estimated by linear regression. The isotope exchange was studied using  $\text{D}_2/\text{D}_2\text{O}$  instead of  $\text{H}_2/\text{H}_2\text{O}$ . The bottles of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  were kept at the same temperature (13 °C), giving vapour pressures of 0.015 atm for light water and 0.013 atm for heavy water [35].

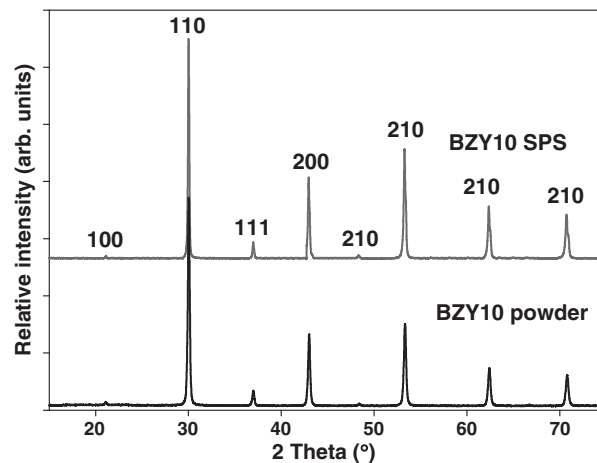
## 3. Results and discussions

### 3.1. Synthesis

The diffractogram recorded on the BZY10 powder after synthesis shows a cubic single phased compound with a lattice parameter of  $4.199 \pm 0.001\text{ Å}$  [23].

### 3.2. Sintering

The sintered pellet was covered by a carbon layer, coming from the graphite die, giving it a black color. The sample was then heated 2 h at 800 °C in air and polished to a 1 micron finish, leading to a transparent



**Fig. 2.** XRD patterns of the BZY10 powder synthesized at 1400 °C in air (24 h), and BZY10 pellet sintered by SPS at 1700 °C. XRD patterns are shifted vertically for clarity.

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