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# Electrical conductivity of the proton conductor $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ obtained by high temperature annealing

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**Abstract**

The influence of a high temperature annealing (~2200 °C) on the microstructure and the electrical properties of $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ has been examined. The high temperature annealing was achieved using an optical floating zone furnace. The obtained sample is homogeneous with an average grain size of about 5 μm. No additional phases were found in the XRD pattern and the structure was identified to be cubic. After the high temperature annealing, the grain boundary conductivity is increased by approximately two orders of magnitude, while the bulk conductivity remains the same.


*Keywords:* BZY; Proton conductor; Perovskite; Grain boundary; Optical floating zone

## 1. Introduction

Many acceptor doped perovskites exhibit proton conductivity in an intermediate temperature range between 300 and 700 °C. This class of materials has attracted attention for potential applications in sensors and in fuel cells. A key point for applications is to find a material which combines fast proton conductivity and thermodynamic stability. The state-of-the-art over the past 20 years [1,2] is that $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY10) is a very stable material but shows a low overall proton conductivity. Based on data on the formation and the mobility of protonic charge carriers combined with structural information, it has been recently demonstrated [3] that BZY10 should in contrast be a fast proton conductor that competes even with $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (BCY10). In this recent study, the low overall conductivity is attributed to blocking grain boundaries limiting the overall proton transport [3]. But the underlying causes for this are not clear yet.

Microstructural properties such as grain size and grain boundary density depend to a large extent on the preparation conditions. The highly refractory nature of BZY10 (melting point ~2600 °C) results in small grain sizes and a large total grain boundary area, when prepared by the standard solid-state reaction method and sintered at 1720 °C [4]. As a consequence, conventional preparation methods are not expected to produce a material with high proton conductivity. In order to increase the grain size and decrease the grain boundary density, higher sintering temperatures would be advantageous but have not been investigated so far. The present work used the optical floating zone technique, which is commonly applied to grow single crystals in order to study the annealing influence up to ~2200 °C of a sintered sample. The effect of such high annealing temperature on the BZY10 phase, microstructure and conductivity will be discussed.

## 2. Experimental

### *2.1. Sample preparation*

$BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY10) powder was prepared by the solid-state reaction method. Stoichiometric amounts of barium carbonate (Fluka, purity: 99%), zirconium dioxide (Tosoh,

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purity: 99.9%) and yttrium oxide (Stanford Materials, purity: 99.9%) were ball milled in isopropanol with $ZrO_2$ balls of 3 mm diameter. The powder was then dried at 70 °C and calcined at 1200 °C for 10 h. After dry ball milling for 48 h, the powder was calcined at 1400 °C for 10 h. The as calcined powder was milled in a planetary mill (200 rpm) in a $ZrO_2$ container for 3 h, isostatically pressed into a rod and sintered at 1720 °C for 24 h using a powder bed of pre-sintered BZY10 powder. The sintered sample will be henceforth known as the SB (sintered body)-sample.

The as sintered rod was finally annealed in an optical floating zone furnace (FZ-T-10000-H-IV-VP-PC, Crystal System Corp., Japan) using four 1000 W halogen lamps as a heat source. The focused light was moved along the rod (back-and-forth) with a rate of 5 mm/h. The maximum temperature in the hot zone was ~2200 °C. The annealing was performed in oxidizing atmosphere (5% $O_2$ in Ar) at a pressure of 2 bars and a gas flow of 250 ml/min. The sample after annealing in the optical floating zone furnace will be henceforth known as the ZA (zone annealing)-sample.

### 2.2. Sample characterisation

The phase analysis was performed using X-ray powder diffraction (XRD) with a Ni-filtered Cu Kα ($\lambda=0.15405$ nm) radiation (PANanalytical, X'Pert PRO) on ground SB- and ZA-samples. The lattice parameters were determined using X'Pert-software applying pseudo-Voigt as fitting functions.

The microstructure was examined with a scanning electron microscope (SEM) (Zeiss Leo 1530).

The apparent density of the SB- and ZA-samples was determined and compared to the theoretical value for BZY10 (~6.2 g/cm$^3$) [5].

Electrical measurements were performed on the SB-sample (a disk-shaped pellet of 15.91 mm diameter and 2.32 mm thickness) and on the ZA-sample (a disk of 4.55 mm diameter and 1.23 mm thickness, cut from the middle of the rod). Both sides of the disks were painted with Pt-paste (Metalor A4338A). The paste was dried at 150 °C for 15 min. This procedure was repeated 3 times and the samples were finally fired at 1000 °C for 1 h. The conductivity measurements were performed in a ProboStat™ (NorECs AS) cell. The conductivity was measured by impedance spectroscopy (Solartron 1260 FRA) with a frequency sweep from 0.5 Hz to 3 MHz and an oscillation amplitude of 1 V. The temperature was varied from 1000 °C to room temperature in steps of 50 °C. The experiments were performed in humid oxygen ($pH_2O=2200$ Pa, so-called wet conditions) obtained by passing the gas first through a gas diffuser filled with water and second through a KBr saturated solution at room temperature. Additional measurements were carried out in dry oxygen ($pH_2O=10$ Pa, so-called dry conditions) by passing the gas through a $P_2O_5$ powder [6]. Prior to the conductivity tests under dry conditions, the samples were conditioned under dry oxygen at 900 °C for 14 h.

The impedance data are analysed in terms of an equivalent circuit by using the ZView software (Scribner Associates, Inc.). Parallel arrangements of a resistor and a capacitive constant phase element were used to describe the bulk, grain boundary and electrode responses [7,8]. The conductivity results are corrected for the sample geometry.

## 3. Results and discussion

### 3.1. Phase and microstructural analysis

The X-ray diffraction patterns of the SB- and ZA-samples are presented in Fig. 1. For both samples, the XRD patterns are consistent with a single cubic phase corresponding to BZY10. The cubic lattice parameters of the SB- and ZA-samples are 0.4206 and 0.4212 nm, respectively. These values are in agreement with data published by Schober and Bohn [9].

The microstructures of BZY10 SB- and ZA-samples, displayed in Fig. 2, are relatively homogeneous with grain sizes of about 2 and 5 μm, respectively. The density increases from 91% of the theoretical density for the SB-sample to 98% for the ZA-sample.

The maximal temperature (~2200 °C) allowed by the optical floating zone furnace was far below the melting temperature of BZY10 (~2600 °C). Therefore, the optical furnace was not used for its standard purpose (i.e. growing single crystal) but, in the present work, it served just for a high temperature annealing. The obtained ZA-sample unless still polycrystalline, certainly, displays a more homogeneous microstructure, an increased density and as twice as larger grains, without any visible change in the XRD pattern.

### 3.2. Electrochemical results

Nyquist plots for both the SB- and ZA-samples in wet oxygen are shown in Fig. 3 as a function of the temperature. A first arc at the high frequency end is resolved for temperatures below 300 °C and can be described by using a resistor in parallel to a constant phase element ($R_1Q_1$). An additional second (low frequency) arc ($R_2Q_2$) is resolved between 100 and 500 °C. Based on previous studies [4,5,7,8,10,11], the high frequency semicircle is attributed to the bulk transport,

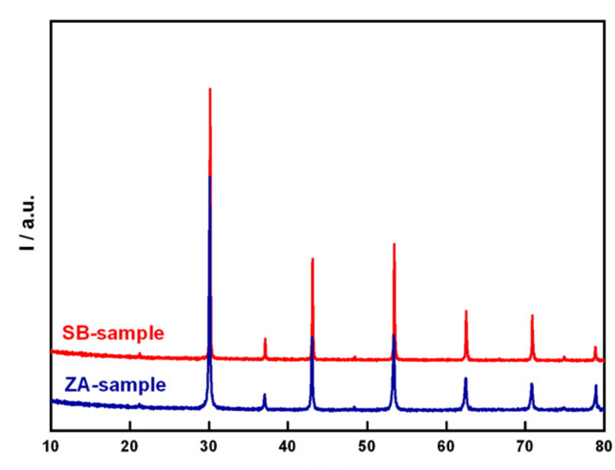


Fig. 1. X-ray diffraction patterns of BZY10 SB- and ZA-samples.