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A high temperature study on thermodynamic, thermal expansion and electrical properties of $BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ proton conductor

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HIGHLIGHTS

- BCZY was synthesized by solid state reaction and sintered at 1600 °C 12 h.
- Proton incorporation was studied under O_2 and H_2 atmospheres between RT and 950 °C.
- The bulk conductivity of BCZY was independent regardless wet atmosphere.
- Grain boundary conductivity strongly depends on atmosphere nature and thermal history.
- Conductivity change between H_2O and D_2O O_2 atmosphere reveals protonic conductivity.

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ABSTRACT

$BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ (BCZY) was synthesized by solid state reaction, calcined and sintered at 1600 °C for 12 h. Crystal structure was studied by X-ray diffraction (XRD). Morphology and porosity were determined by scanning electron microscopy (SEM). Crystalline structure, oxygen non-stoichiometry, linear expansion and electrical conductivity were characterized under oxidizing and reducing atmosphere by high temperature X-ray diffraction (HT-XRD), thermogravimetry (TG), dilatometry, and electrochemical impedance spectroscopy (EIS), respectively. Chemical stability under CO_2-rich atmosphere was evaluated by TG. BCZY electrical conductivity was studied by EIS under O_2-containing atmosphere with water vapor (2% H_2O) and heavy water vapor (2% D_2O) in order to evaluate protonic conductivity. Throughout these techniques, interstitial proton incorporation/loss was observed under oxidizing and reducing atmosphere, between 300 and 500 °C. The conductivity presents two contributions. The bulk conductivity at high frequencies takes the same value regardless wet oxidizing or reducing atmosphere, decreasing its value in presence of D_2O vapor supporting H-conductivity. On the other hand, the grain boundary conductivity was strongly dependent on the nature of wet atmosphere.

1. Introduction

Barium cerates and zirconates oxides are capable of transporting protons through their crystal lattice [1,2]. This feature makes them potential candidates as hydrogen sensors, membranes for hydrogen purification and isotopic exchange (hydrogen, deuterium, tritium -H/D/T-) [3], and electrolyte for proton conductor solid oxide fuel cell (PC-SOFC) and solid oxide electrolyzer cell (PC-SOEC) [4].

Recently, $BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ compound (BCZY) was proposed as material for these applications [5–9]. BCZY presents high intra-granular (bulk) protonic conductivity and excellent CO_2 tolerance. However, proton conducting perovskites exhibit in certain cases high sintering temperature (1500–1700 °C) and low inter-granular (grain boundary) protonic conductivity. High CO_2 tolerance and suitable transport properties make BCZY a good electrolyte for anode supported PC-SOFC [10] when using low purity H_2 as fuel. Regardless the potential applications of this compound, non-detailed characterization was performed to date with the aim to obtain fundamental understanding about the behavior of this material under different operating conditions. In this work, high temperature properties of BCZY, such as crystalline structure, non-stoichiometry, linear expansion and electrical resistance are presented under both H_2- and O_2- rich atmospheres.

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2. Experimental

$BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ (BCZY) perovskite was synthesized by solid state reaction (SSR) from stoichiometric amounts of $BaCO_3$, CeO_2, ZrO_2 and Y_2O_3. The precursors were ball milled, calcined at 1350 °C for 4 h and sintered at 1600 °C 12 h. In cases where powders were required, sinteredpellets were grinded in mortar. Phase purity was evaluated by X-ray diffraction (XRD), by using PANalytical Empyrean diffractometer with Cu Kα radiation, a graphite monochromator and a PIXcel^{3D} detector.

Structural and microstructural parameters were obtained from the diffraction pattern of BCZY powders by using the Rietveld method and the FullProf Suite software [11]. The instrumental line broadening was obtained from a pattern of Y_2O_3. All reflection peaks of BCZY were indexed according to the cubic symmetry, space group *Pm-3m*, N° 221 [5,6,12], previously reported. The microstructural parameters, such as crystallite size and microstrain effect, were calculated by using the Scherrer formula and isotropic microstructural model, respectively.

Microstructure of BCZY sintered pellets was observed by scanning electron microscopy (SEM) with a Philips 515 microscope. Elemental analysis was carried out by using energy dispersive spectroscopy (EDS). The porosity was analyzed from SEM images of polished cross sections of a sample by using ImageTool3 software [13–15]. In order to determine open and close porosity, the sample density was measured by hydrostatic weighing using a Cahn 1000 electrobalance [16] and diethyl phthalate as the immersion fluid, as described elsewhere [17].

Crystal structure as a function of temperature was studied by XRD, between room temperature and 900 °C under a mixture of ~80% N_2 and ~20% O_2 (synthetic air). Diffraction patterns of BCZY powders at high temperatures were collected by using an Anton Paar camera coupled to the PANalytical Empyrean diffractometer. Structural and experimental parameters at high temperatures were obtained by the Rietveld method, using sequential mode of the FullProf Suite software [11].

Thermodynamic stability of BCZY powder was studied by thermogravimetry (TG), making use of a Cahn 1000 electrobalance [16]. Mass variation (% Weight) was analyzed by thermal cycling the powder from room temperature to 1000 °C at heating/cooling rate of 1 °C min^{-1} under 20% O_2/Ar, followed by a second cycle under 10% H_2/Ar atmospheres. Also, CO_2 tolerance was evaluated by an ageing test under 10% CO_2/Ar, between room temperature and 1000 °C, at a heating/cooling rate of 5 °C min^{-1}.

Linear expansion coefficient of BCZY sintered pellet was determined by dilatometry, between room temperature and 900 °C, under atmospheric air and 5% H_2/Ar at a heating/cooling rate of 1 °C min^{-1}. The measurements were performed by using LINSEIS L75VS1000C vertical dilatometer.

Electrical conductivity of BCZY sintered pellets was determined by electrochemical impedance spectroscopy (EIS). The pellets were painted on both sides with Pt ink. Impedance spectra were collected between 100 and 600 °C, under 20% O_2/Ar and 10% H_2/Ar wet (2% H_2O vapor) atmospheres and under 20% O_2/Ar + 2% D_2O vapor. Measurements were performed by using an Autolab PGSTAT30 potentiostat/galvanostat, from 1 MHz to 0.1 Hz with 50 mV amplitude. EIS spectra were fitted with equivalent circuits (EEC), by using Zview2 software [18].

3. Results and discussion

Fig. 1 shows the diffraction pattern of BCZY powder under atmospheric air at room temperature, The X-ray data were indexed in the cubic symmetry and the *Pm-3m* space group. The lattice parameter (a), average crystallite size (d_c) and isotropic strains (IS)

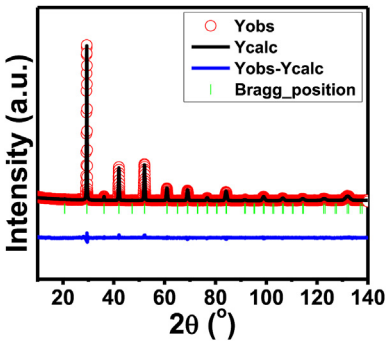

Fig. 1. X-ray diffraction pattern: experimental (○) calculated (−), difference between both (—) and Bragg positions (|) of BCZY powder under air at room temperature.

were a = 4.3022(1) Å, d_c = 357(1) nm and IS = 38.36(1) %%, respectively. This information was obtained from Rietveld refinement with a goodness of fits of R_p = 14.2, R_{wp} = 14.1 and χ^2 = 2.26. Nasani et al. [5] and Tu et al. [19] reported for this compound lattice parameters of 4.320 and 4.322 Å, respectively. These disagreements on lattice parameters could be due to different synthesis methods and/or degree of hydration (depending on storage conditions) for each sample. The incorporation of H_2O molecules into the BCZY structure can also explain the strain effects on the peak broadening due to lattice distortion.

Fig. 2a shows a SEM micrograph of a polished cross section of a

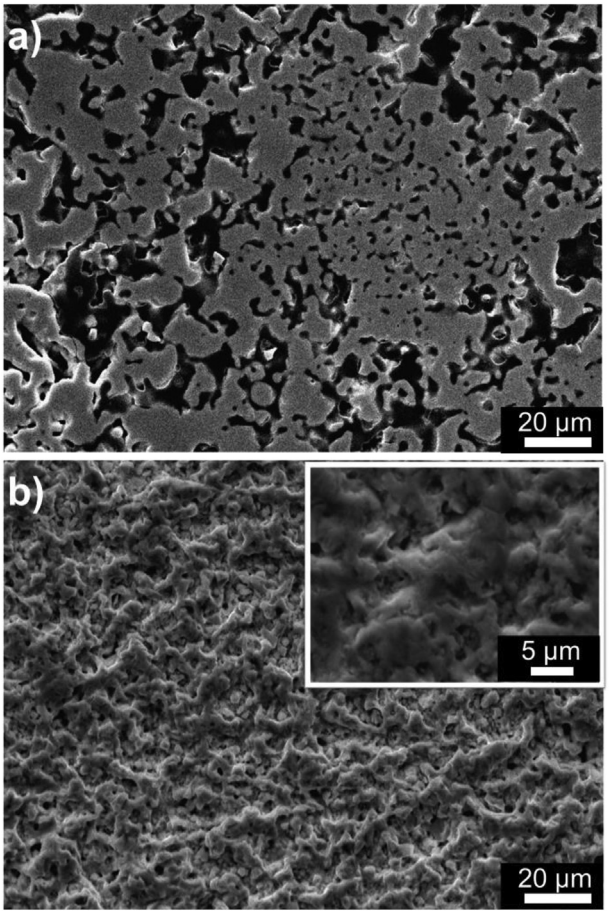

Fig. 2. SEM image of a BCZY sintered pellet, a) polished cross-section and b) front section.