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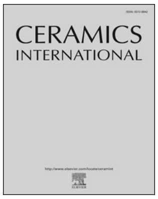

Effect of Zn addition on the structure and electrochemical properties of co-doped $BaCe_{0.6}Zr_{0.2}Ln_{0.2}O_{3-\delta}$ (Ln = Y, Gd, Yb) proton conductors

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ABSTRACT

In this work, $BaCe_{0.6}Zr_{0.2}Y_{0.2\text{-}x}Yb_xO_{3\text{-}\delta}$ and $BaCe_{0.6}Zr_{0.2}Gd_{0.2\text{-}x}Yb_xO_{3\text{-}\delta}$ (x = 0–0.20), proton conducting materials are prepared by the freeze-drying precursor method. The sintering conditions were optimized by adding $Zn(NO_3)_2{\cdot}6H_2O$ as sintering additive. The materials are thoroughly characterized by different structural and microstructural techniques, including X-ray diffraction, scanning and transmission electron microscopy, and thermogravimetric-differential thermal analysis. The addition of Zn favours the phase formation and densification at lower sintering temperatures; however, it leads to the segregation of a Zn-rich secondary phase, with general formula $BaLn_2ZnO_5$ (Ln=Y, Gd and Yb), which is identified and quantified for the first time. All samples with Zn as sintering aid exhibit cubic structure; however, the samples without Zn crystallize with orthorhombic or cubic structure, depending on the composition and thermal treatment. The electrical properties are studied by impedance spectroscopy. A deep analysis of the bulk and grain boundary contributions to the conductivity has revealed that the bulk conductivity remains almost unchanged along both series over Yb-doping; however, the grain boundary resistance decreases. The highest conductivity values are found for the intermediate members of both series, $BaCe_{0.6}Zr_{0.2}Y_{0.1}Yb_{0.1}O_{3\text{-}\delta}$ and $BaCe_{0.6}Zr_{0.2}Gd_{0.1}Yb_1O_{3\text{-}\delta}$, with 33 and 28 mS cm^{-1} at 750 °C, respectively.

1. Introduction

Solid oxide fuel cells and electrolysis cells are efficient devices that produce energy and hydrogen gas, respectively. They are formed by two porous ceramic electrodes separated by a dense electrolyte, which could be an oxide-ion or proton conducting material. In particular, proton conducting solid oxide cells (PC-SOC) have the advantage to operate at lower temperatures than the traditional oxide ion conducting cells (400–700 °C), due to the fact that the proton mobility is higher than the oxide ions at intermediate temperatures. The reduction of the operating temperature has several benefits, such as reduction of compatibility issues and longer durability of the cells components.

Most of the electrolytes for PC-SOCs are based on perovskite-type materials, such as $BaCeO_3$ and $BaZrO_3$. The highest conductivities are observed for doped-$BaCeO_3$, ~0.01 S cm^{-1} at 600 °C; unfortunately, they have poor chemical stability in the presence of CO_2. On the contrary, $BaZrO_3$-based electrolytes exhibit improved stability in CO_2 and H_2O environments; however, extremely high sintering temperatures, as high as 1700 °C, are necessary to achieve densification, which is unsuitable from an industrial point of view. Therefore, a compromise solution has been proposed by preparing compounds containing both cerium and zirconium, combining the conductivity and stability properties of cerates and zirconates, respectively. [1–6]. In order to increase the conductivity, $BaCe_{1\text{-}x\text{-}y}Zr_xLn_yO_{3\text{-}\delta}$ (BCZ) materials are doped with trivalent cations, such as Ln = Y^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Yb^{3+}, Tb^{3+} and Dy^{3+} [5,7–20]. In general, Y^{3+} is the most widely used aliovalent dopant for both $BaCeO_3$ and $BaZrO_3$ electrolytes. However, the highest values of proton conductivity in $BaCeO_3$ series have been reported for Gd-doping, because this substitution produces a smaller lattice distortion of the cell with a higher free volume for oxygen diffusion [20,21].

Co-doping with aliovalent elements is an alternative strategy to improve the properties of $Ba(Ce,Zr)O_3$ based electrolytes. For instance, Yang et al. have studied the effect of Y and Yb co-doping in $BaCe_{0.7}Zr_{0.1}Y_{0.2-x}Yb_xO_{3-\delta}$ $(0 \le x \le 0.2)$ series [22]. The maximum conductivity value, about 60 mS cm^{-1} at 750 °C, was found for x = 0.1. In addition, these materials showed high tolerance to sulphur and

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coking poisoning, due to an improvement of the catalytic activity towards sulphur oxidation and hydrocarbon cracking and reforming.

Different synthetic methods have been used to improve the properties of $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$, such the Pechini method [23,24], attrition milling [11], coprecipitation [25], direct current sintering [26], and atmospheric plasma spray [27]. However, sintering temperatures above 1500 °C are still necessary to achieve densification of these materials, but lead to BaO evaporation and the segregation of CeO_2 [28]. In order to reduce the temperatures, transition metals, such as Co, Fe, Ni and Zn, have been used as sintering aids [29–34]. Among them, Zn^{2+} has shown to be the most effective because allows reducing the sintering temperature to 1000–1200 °C without altering significantly the transport properties of the parent compound [32–35]. However, the addition of Zn leads to the segregation of minor secondary phases, which are still unidentified. Moreover, the origin of these impurities and how to avoid their formation is still unclear.

In this work, a co-doping strategy with Y^{3+}, Yb^{3+} and Gd^{3+} was employed to obtain two series of compounds $BaCe_{0.6}Zr_{0.2}Y_{0.2-x}Yb_xO_{3-\delta}$ and $BaCe_{0.6}Zr_{0.2}Gd_{0.2-x}Yb_xO_{3-\delta}$ ($0 \le x \le 0.2$). The materials are synthesized by both solid state reactive sintering and freeze-drying precursors. Dense ceramic pellets without and with Zn addition are prepared, and the structural and electrical properties are investigated by X-ray diffraction, scanning and transmission electron microscopy and impedance spectroscopy.

2. Experimental

2.1. Synthesis and sintering conditions

Materials with composition $BaCe_{0.6}Zr_{0.2}Y_{0.2-x}Yb_xO_{3-\delta}$ and $BaCe_{0.6}Zr_{0.2}Gd_{0.2-x}Yb_xO_{3-\delta}$ (x = 0, 0.05, 0.10, 0.15 and 0.20) were prepared by a freeze-drying precursor method (FD) from: $Ba(NO_3)_2$, $Ce(NO_3)_3{\cdot}6H_2O$, $ZrO(NO_3)_2{\cdot}6H_2O$, $Y(NO_3)_3{\cdot}6H_2O$, $Gd(NO_3)_3{\cdot}6H_2O$ and $Yb(NO_3)_3{\cdot}5H_2O$ (Sigma-Aldrich, purity > 99%). The precursor solutions were obtained by dissolving the different reagents in water. An ethylenediaminetetraacetic acid (EDTA) solution was added as a complexing agent in a 1:1 ligand: metal molar ratio. The solutions were frozen in liquid nitrogen, followed by dehydration by vacuum sublimation in a Scanvac Coolsafe freeze-dryer. Further experimental details on the freeze-drying process are given elsewhere [20,31]. The amorphous precursor powders were initially calcined at 300 °C for 1 h to prevent rehydration, at 800 °C for 1 h to eliminate carbonaceous species, and subsequently at 1100 °C for 1 h to obtain the crystalline materials. The resulting powders were reground for 2 h at 200 rpm in a Fritsch ball mill (model Pulverisette 7, zirconia balls and vessel) without and with 4 mol% of $Zn(NO_3)_2{\cdot}6H_2O$ (1 wt% ZnO) as sintering aid in absolute ethanol media. It has to be commented that this is the optimum Zn-content to obtain dense ceramics without altering significantly their transport properties [31,36]. The powders were pressed into pellets at 500 MPa (10 mm diameter and 1 mm of thickness) and sintered at 1500 °C for 1 h for samples without Zn and 1200 °C for 15 min, 5 and 10 h for samples with Zn. The pellets were slowly cooled to room temperature at 5 °C min^{-1} and finely ground into powders before further characterization. Hereafter, the series of compounds $BaCe_{0.6}Zr_{0.2}Y_{0.2-x}Yb_xO_{3-\delta}$ and $BaCe_{0.6}Zr_{0.2}Gd_{0.2-x}Yb_xO_{3-\delta}$ are labelled as YYb_x and $GdYb_x$, respectively, where x represents the ytterbium content.

For the sake of comparison, some of these materials were prepared by reactive sintering method (SSR) to compare their properties with those obtained by freeze-drying precursors. For this purpose, the reagents: $BaCO_3$, ZrO_2, CeO_2 and Ln_2O_3 (Ln=Y, Gd, Yb) (Sigma-Aldrich, purity > 99%) were mixed in the ball mill in absolute ethanol media and then dried in a muffle furnace. The resulting powder mixture was pressed into pellets and sintered at 1500 °C for 5 h. Several regrinding and thermal treatments were used to achieve single phase materials. The relative density of the pellets was lower than 85% so that they were structurally characterized but not electrically analyzed.

2.2. Structural and thermal characterization

All compounds were analyzed by laboratory X-ray powder diffraction (XRPD) at room temperature. The patterns were collected on a PANalytical Empyrean with CuK_α radiation. The overall measurement time was approximately 4 h per pattern over the 10–70° (2θ) angular range, with a 0.017° step size. Phase identification and structural analysis were performed with X'Pert HighScore Plus and the GSAS suite programs, respectively [37,38].

Thermogravimetric analysis (TGA) data were recorded on a SDT-Q600 analyzer (TA Instruments) under wet (~ 2 vol% H_2O) air at a heating/cooling rate of 5 °C min^{-1} from room temperature to 950 °C. Two heating and cooling cycles were performed to test the reproducibility of the measurements.

2.3. Microstructural and electrical characterization

The microstructure of the ceramics was observed by scanning electron microscopy (SEM) (Jeol JSM-6490LV). Grain size of the dense pellets was estimated from the SEM micrographs, using the linear intercept method [39]. Energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED) were performed with a high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (FEI, Talos F200X).

For the electrical characterization, platinum ink (METALOR® 6082) was coated on both sides of the pellets, followed by heating at 750 °C for 1 h in air to form the electrodes. Impedance spectra were acquired using a frequency response analyzer (Solartron 1260) in dry and wet air (2 vol%. of H_2O, bubbling through water at room temperature). The spectra were recorded on the cooling process from 750 to 100°C with a stabilization time of 30 min between consecutive measurements. The resistance and capacitance values of the different processes were deconvoluted by fitting the data with equivalent circuit models using the ZView program [40].

3. Results and discussion

3.1. Single phase formation and optimization of the synthesis temperature

XRPD patterns of a representative sample with composition $YYb_{0.1}$, prepared by freeze-drying precursors and calcined at different temperatures, are shown in Fig. 1. Different compounds are identified after calcining the precursor powders at 800 °C, including a $Ba(Ce,Zr)O_{3-\delta}$ (BCZ) perovskite-related phase, and impurities of $BaCO_3$ (PDF 00-001-0506) and CeO_2 (PDF 00-001-0800). At 1100 °C the main phase is the BCZ perovskite, with a very small amount of unreacted $BaCO_3$. Finally, pure compounds are obtained after calcining at 1500 °C for 1 h. Fig. S1 (Supplementary information) displays the XRPD patterns of the remaining members of YYb_x and $GdYb_x$ series at 1500 °C. No secondary phases are detected for all compositions; however, the patterns show a different degree of peak splitting, depending on the phase composition, indicating that the samples crystallize with different symmetry, either cubic or orthorhombic.

Fig. 1 also compared XRPD patterns of $YYb_{0.1}$ prepared without and with Zn. The sample without Zn shows peak splitting due to the orthorhombic distortion of the unit cell, as it was mentioned before; however, the sample containing Zn as sintering aid crystallizes with a cubic structure.

The same materials were prepared by solid state reactive sintering under similar experimental conditions at 1500 °C for 10 h. In this case, the peak splitting is more important, indicating a less symmetric unit cell of the materials. Moreover, the lattice distortion decreases when the materials are milled, homogenized, and calcined again at 1500 °C (Fig. S2). This indicates that the cation composition in the bulk material