

Characterization and creep properties of proton-conducting Yb-doped barium cerate

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Abstract

Polycrystals of Yb-doped barium cerate with composition $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ have been synthesized via a solid-state reaction route. The ceramic has a single orthorhombic perovskite phase, and the crystallographic unit cell is almost unperturbed with respect to undoped BaCeO_3 . The compound exhibits a homogeneous distribution of equiaxed and submicron grains. The high-temperature mechanical properties have been studied for the first time. Mechanical tests were carried out in compression between 1100 and 1250 °C in air at constant initial strain rate. A gradual brittle–ductile transition was observed with increasing temperature and/or decreasing strain rate. Grain boundary sliding is the main deformation mechanism in the ductile region. In this regime, the true stress–true strain curves display an unusual behavior, with an initial strength drop followed by an extensive steady-state stage. This behavior is accompanied by the emergence of new, fine grains along the boundaries and triple junctions of the original grains during deformation.

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1. Introduction

In the last few years, perovskite-structured oxides of generic formula ABO_3 , where A^{2+} and B^{4+} denote site cations (for example, BaCeO_3 , SrCeO_3 and SrZrO_3) are receiving increasing attention because of their remarkable proton conducting performance at intermediate temperatures.^{1–5} This property is of prime importance for practical applications in the field of electrochemical energetics, particularly as electrolytes in solid oxide fuel cells (SOFCs). These devices can electrochemically convert hydrocarbons with high efficiency and low emissions. Substitution of B^{4+} -site by trivalent ions in these perovskite oxides causes the formation of oxygen vacancies, which allow for protonic conduction (hydrogen ion transport) upon exposure to water vapor at relatively high temperatures. Due to the higher mobility of protons compared to oxygen ions, the operating temperature of SOFCs can be safely reduced without lowering performance. Such a device could compete with conventional energy conversion devices if the requirements of long-term durability and reliability are met.

Trivalent cations such as Y^{3+} , Yb^{3+} , Nd^{3+} and Gd^{3+} -doped barium cerates are a prototype of this class of proton conducting oxides. They exhibit one of the highest proton and ionic conductivities at elevated temperatures, as well as an excellent chemical stability over a large range of temperatures and oxygen partial pressures.^{4–6} Most of the investigations on doped-barium cerates are concerned with their processing, structure, defect chemistry and conductivity characteristics. Very few studies, in contrast, have focused on the high-temperature mechanical properties of these solid-state proton conductors.^{7–9} These properties are, however, of special relevance in the design of SOFCs and other high-temperature operating devices because at the working conditions, deformation, mechanical degradation and failure determine the material behavior and ultimate overall performance. In addition, high-temperature plastic deformation is usually controlled by diffusion, and can thus provide basic information about mass transport in the compounds. Since sintering and grain growth are governed by diffusional processes, such information can be used to devise optimum processing schedules.

Furthermore, it has been usually assumed that the trivalent dopants exclusively occupy the Ce^{4+} -site, which introduces oxygen vacancies into the perovskite structure and furthers the protonic conductivity. Recent studies,^{10–12} however, indicate

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that dopant partitioning can occur, such that a non-negligible concentration of trivalent ions resides onto the Ba^{2+} -site; this site transfer consumes oxygen vacancies, which is unfavorable for the ulterior water/proton uptake. These studies also showed that partitioning is restricted for small ionic radii dopants (compared to Ce^{4+}). In this sense, Yb^{3+} has essentially the same ionic radius than Ce^{4+} (0.87 \AA^{13}), and is therefore expected to lead to the ideal (maximum) oxygen vacancy content available for proton conductivity. To our knowledge, there are no studies on the microstructural characterization of ytterbium-doped barium cerate ceramics and their high-temperature mechanical properties. Therefore, the objective of this work was twofold: to synthesize Yb-doped BaCeO_3 with perovskite structure by solid state reaction and characterize the crystallographic structure and microstructure, and to investigate its mechanical behavior at elevated temperatures by means of compressive creep tests at constant initial strain rate in order to assess the strength of the material.

2. Experimental procedure

2.1. Sample preparation

Polycrystalline $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ (BC5Yb) was produced via a solid-state reaction route. Commercial powders of BaCO_3 , CeO_2 and Yb_2O_3 (Aldrich, purity >99.0%) were weighted in the required stoichiometric ratio, mixed and ground in agate media for 1 h using a planetary ball mill. The resulting powder was calcined for 10 h at 1200°C in air and then carefully reground. At this point, the crystal structure of the powder was checked by X-ray diffraction (see below), which confirmed the presence of a single orthorhombic perovskite phase. Green pellets were obtained by uniaxial pressing at 150 MPa and isostatic pressing at 210 MPa. A two-step sintering process was performed on the pellets in air atmosphere at low heating and cooling rates: a first step at 600°C for 2 h to eliminate water and hydroxides formed during intermediate stages, and a second sintering step at 1550°C for 10 h. The final density of the samples, determined using Archimedes' method, was about 90–95% of the theoretical value of barium cerate (6360 kg/m^3). Osman et al.⁶ reported a density of 91% in $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ prepared via a sol-gel method and sintered at 1500°C for 10 h; the final grain size was not reported.

2.2. Crystal structure determination

The structural analysis of the crystalline phases in the calcined powders and sintered pellets was performed on X-ray powder diffractograms obtained using a Bruker AXS D8 Advance X-ray diffractometer in Bragg-Bentano configuration with $\text{Cu K}\alpha$ radiation (X-ray Laboratory, CITIUS, University of Sevilla, Spain). A continuous scan mode was used to collect 2θ data from 10° to 120° in steps of 0.02° and a counting time of 10 s/step. X-ray tube voltage and current were set at 40 kV and 30 mA, respectively. Collected X-ray spectra were processed by the Le Bail refinement method using the TOPAS 4.2 Bruker AXS software package.

2.3. Mechanical tests and microstructural studies

Specimens of $5 \text{ mm} \times 3 \text{ mm} \times 3 \text{ mm}$ in size were cut from the sintered pellets with a low-speed diamond saw and used for mechanical testing. Compression tests were carried out at temperatures T between 1100 and 1250°C ($0.74T_m < T < 0.82T_m$, where $T_m = 1850 \text{ K}$ is the melting temperature of BaCeO_3) at constant cross-head speed. Experiments were performed in air atmosphere because Park et al.⁷ found that the high-temperature deformation of $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ ($x = 0.05\text{--}0.20$) was independent of testing atmosphere. The specimens were sandwiched between CSi pads in order to reduce the friction with the alumina push rods of the deformation machine, which tends to cause plastic constrictions at the ends of the specimen. The recorded data, load vs. time, were plotted as $\sigma - \varepsilon$ curves, where ε is the true strain ($\varepsilon = \ln(l_0/l)$, with l_0 and l the initial and instantaneous length, respectively) and σ is the true stress ($\sigma = \sigma_0 \exp(-\varepsilon)$, with σ_0 the initial stress). Samples were typically deformed to total strains of 50%. At test completion, the specimen height was measured and compared with the value expected from the cross-head speed applied during the test; differences smaller than 1% were found in all cases. On the other hand, the previous equation for true stress is valid for homogeneous deformation at constant volume. This assumption has been proven to be valid for specimens deformed in the ductile region (see below). The data were analyzed using the standard high-temperature power law for steady-state deformation:

$$\dot{\varepsilon} = A\sigma^n d^{-p} \exp\left(\frac{-Q}{RT}\right) \quad (1)$$

where A is a parameter depending on the deformation mechanism, d is the grain size, n is the stress exponent, p is the grain size exponent, Q is the activation energy for flow and R is the gas constant.

The microstructural characterization of as-fabricated and deformed polycrystals was carried out using conventional (SEM) and high-resolution (HRSEM) scanning electron microscopy (Microscopy Service, CITIUS, University of Sevilla, Spain). To reveal grain boundaries, longitudinal sections were cut from the samples and mechanically polished using up to $1 \mu\text{m}$ grade diamond paste, and then thermally etched at 1200°C for 2 h in air. The relevant morphological parameters, grain size d (taken as the equivalent planar diameter $d = (4(\text{grain area})/\pi)^{1/2}$) and form factor F (defined as $F = 4\pi(\text{grain area})/(\text{grain perimeter})^2$) were measured by using a semiautomatic image analyzer. Fracture surfaces of samples that either failed during testing or were intentionally broken at room temperature were also characterized by HRSEM.

3. Results and discussion

The calcined powder as well as the sintered pellets were identified by X-ray diffraction as being pure orthorhombic perovskite phase, with space group $Pm\bar{c}n$. Fig. 1 shows the X-ray diffractogram of the sintered BC5Yb ceramic; the peak positions correspond to the orthorhombic structure of undoped BaCeO_3 (ICSD pattern No. 01-082-2425¹⁴). The lattice param-

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