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On the use of NiO as sintering additive for $BaCe_{0,9}Y_{0,1}O_{3-\alpha}$

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ABSTRACT

The effect of nickel oxide addition on the densification behaviour and electrical conductivity of $BaCe_{0,9}Y_{0,1}O_{3-\alpha}$ (BCY10) is investigated. Small addition (4 mol%) of this sintering aid reduces the sintering temperature by 200 °C and promotes the densification. 95% of the theoretical density was reached after sintering at 1250 °C for 10 h in air. Addition of NiO has no detrimental effect on the total conductivity of BCY10 in wet hydrogen. Nevertheless, the activation energy of the recorded blocking effect is higher than that of the bulk contribution, indicating different electrical properties between grains and internal interfaces in pure and NiO doped BCY10.

1. Introduction

In the field of SOFC, many investigations are dedicated to decrease the operating temperature (down to 600 °C) as well as to reduce cost and improve both efficiency and durability of systems. Thus, researches are mainly focused on the optimization of the microstructure or on the use of new electrolyte materials efficient at low temperatures. For the latter, some rare earth based perovskites (ABO_3) such as $BaCeO_3$ or $BaZrO_3$ are recently attractive candidates for applications in intermediate temperature fuel cells. They are regarded as promising electrolyte materials for Proton Ceramic Fuel Cell (PCFC) [1,2]. In these materials, the oxygen sublattice exhibits a strong basic behaviour [3,4] due to the difference of electronegativity between anions and cations. The introduction of protons into the perovskite ceramics results from an equilibrium between water vapour (acid behaviour) and oxygen vacancies. The net reaction demonstrating the interaction of oxygen vacancies with water vapour producing proton charge carriers can be written [5]:

$$H_2O_{(g)} + V_O^{\bullet\bullet} + O_O^{\times} = 2(OH_O^{\bullet}) \quad (1)$$

Since water absorption is very sensitive to the point defect thermodynamic in the case of intrinsic behaviour, substitution by heterovalent ions, Y^{3+} or rare earth ions (RE^{3+}), up to 15 mol% is generally performed on B sites of the perovskite so that an extrinsic behaviour, which enhances the proton defect concentration within the material [4–6]. Among all of these acceptor doped oxides, $BaCe_{0,9}Y_{0,1}O_{3-\delta}$ (BCY10) has been identified by many authors as exhibiting one of the highest proton conductivities (10^{-2} S/cm at 600 °C in wet hydrogen) [7].

A major obstacle for application of perovskite-based proton conductors in PCFC is the required high sintering temperature, generally above 1400 °C [7–11]. This is not really consistent with a low cost process or with a fine tuned porosity for the electrodes in case of co-sintering. The introduction of additives is considered to be the most effective simple method to lower the sintering temperature.

It has been shown that small additions of some metal transition oxides (cobalt, nickel, copper, zinc, titanium or iron) enhances the sintering of doped barium cerates and zirconates [12–15]. For instance, the sintering temperature of $BaCe_{0,9}Gd_{0,1}O_{3-\alpha}$ has been reduced by 150 °C and the relative density was increased up to 95% after the addition of 1 mol% NiO [15]. Since a cermet based on nickel is routinely used as an anode material in fuel cells, the effect of NiO addition on the microstructure of BCY10 has been investigated. Since the total conductivity of doped-barium cerate ceramics depends on the grain size [16,17], like other ionic ceramic conductors, the electrical properties of pure and NiO doped BCY10 were determined and compared.

2. Experimental

2.1. Starting powders

BCY10 powders were produced by following thoroughly the oxalate co-precipation procedure described by Almeida de Oliveira

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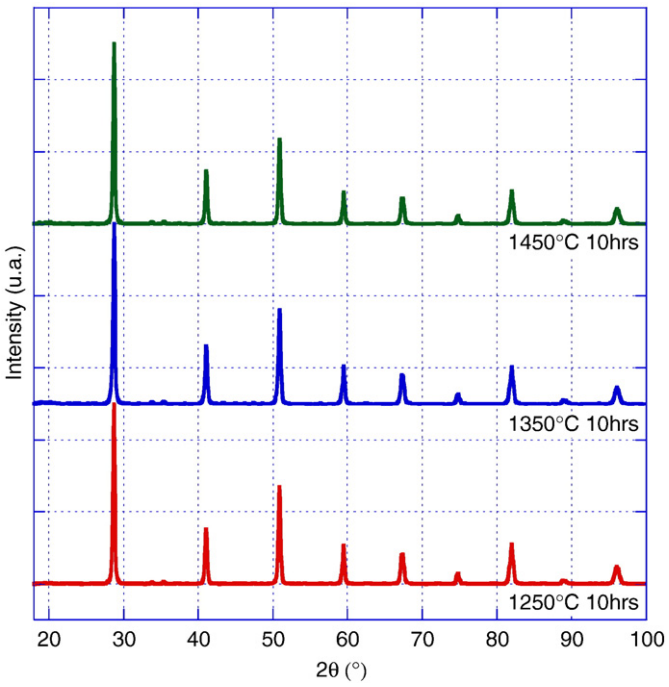

Fig. 1. Normalized – diffractogram of BCY10 – 4 mol% NiO sintered at 1250 °C, 1350 °C, and 1450 °C for 10 h in air.

et al. [18]. The as-calcined powder was a pure single perovskite phase from X-ray diffraction analysis (XRD), and exhibited a BET surface of 2.3 m^2/g. The crystallite size was determined to be about 150 nm. These crystallites were agglomerated within large anisotropic platelets (5 μm*1 μm*1 μm). A commercial NiO powder (Novamet A Type) was used as sintering additive (average grain size of 5 μm).

2.2. Sample preparation

Mixtures of BCY10-NiO with a varying molar ratio of NiO (0.04 mol%; 0.4 mol%; 4 mol%) were prepared by grinding in a mortar the appropriate amount of each component. The as-obtained powders were uniaxially pressed into cylindrical green pellets (16 mm in diameter) at 400 MPa for 5 min. Green pellets were sintered at 1250 °C, 1350 °C and 1450 °C for 10 h in air, on a buffer powder layer to prevent any reaction of BCY10 with alumina, zirconia or platinum sintering supports [19–21]. The chosen dwell time was required to suppress open porosity. For comparison, all investigated samples were sintered simultaneously with pure BCY10 green pellets obtained according to the same pressing procedure.

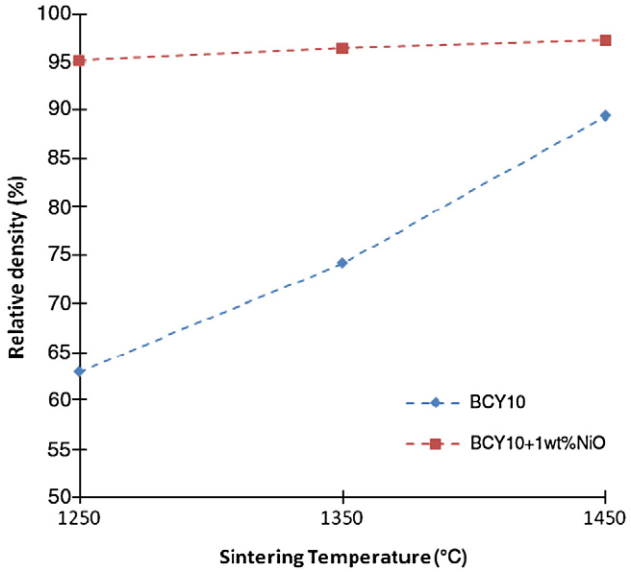

Fig. 2. Relative density vs sintering temperature for pure BCY10 and 4 mol% NiO doped BCY10.

2.3. Characterization

X-Ray Diffraction has been carried out to check the phase purity and the cell parameters, using a BRUKER D500 diffractometer in θ–2θ configuration, with Cu Kα radiation. Lattice parameters were calculated using *cellref* freeware and considering an orthorhombic description and Pmcn space group (# 62) of the crystalline structure.

Densification studies of the samples were performed both by direct density measurements and by image analysis of polished cross section micrographs, using a ZEISS DSM 982 Gemini SEM (Scanning Electron Microscope). An EDX analysis (Energy Dispersive X-ray spectrometry) was performed in SEM mode.

Average quantifications have been achieved by EPMA-WDS via a CAMECA SX50 electron-probe. $BaSO_4$, CeO_2, Y_2O_3, and NiO samples have been use for calibration before quantification.

A transmission electron microscope (FEI TECNAI 20F ST) in STEM mode (Scanning Transmission Electron Microscopy) was used to perform EDX analyses in order to investigate any chemical difference between bulk and grain boundaries of the investigated samples. Electrical measurements were achieved by impedance spectroscopy

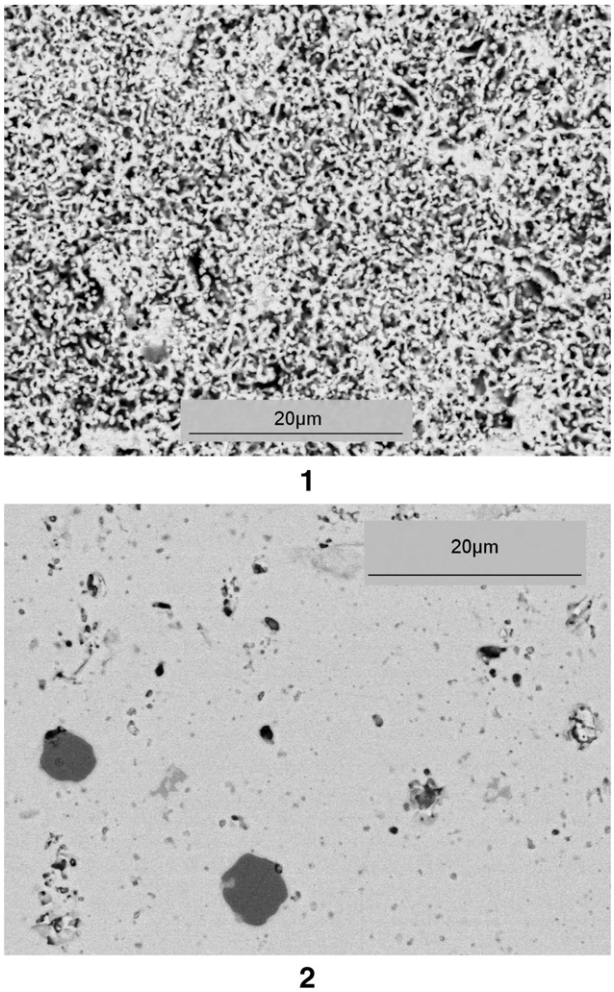

Fig. 3. BSE-SEM micrographs of two samples sintered at 1250 °C for 10 h in air: 1: pure BCY10. 2: 4 mol% NiO doped BCY10 (undissolved NiO grains appear in grey).