

Effect of CuO on microstructure and conductivity of Y-doped BaCeO₃



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ABSTRACT

Effect of CuO additions on sinterability and conductivity of BaCe_{0.85}Y_{0.15}O_{2.925} was studied. Two different amounts, 0.75 and 1.5 wt% with respect to the pure powder, were considered. Microstructural characterization showed that for smaller additions Cu was completely incorporated on B-site of the perovskite, while formation of the secondary phase Y₂BaCuO₅ was detected when higher amount of CuO was added. Enhanced cations diffusivity at grain boundary is responsible for a pronounced reduction of sintering temperature and grain growth. Density as high as 96–97% of theoretical value was obtained when sintering at 1000 °C for 2 h.

As long as Cu is incorporated in the perovskite, higher conductivity and lower activation energy of grain core were found. In addition, total conductivity of 0.75 wt% doped material was limited by fine grain size that resulted in apparent poor conductivity of the grain boundary.

On the contrary when Cu segregates in the Y₂BaCuO₅ phase, overall conductivity increased mostly because of the contribution from the electronic conductivity of that phase.

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1. Introduction

Barium cerate substituted on the B-site with trivalent yttrium ions (BCY) is one of the perovskite oxides with highest proton conductivity at temperatures ranging from 500 to 650 °C [1,2]. For this reason it is a good candidate as electrolyte material for protonic solid oxide fuel cells (p-SOFC) operating at intermediate temperatures. Its use is also considered to be promising for solid oxide electrolysis cell (SOEC) [3–5]. BCY not only shows high proton conductivity (about 10 mS/cm at 600 °C), but also a mixed, protonic-anionic conductivity, depending on the operative conditions like temperature, partial pressure of gases and thickness of electrolyte [6]. This type of double conductance was recently investigated as particularly suited for a new type of cell architecture, called ‘dual membrane’ (DM) [7,8,9] which allows to separate the three main gas streams (hydrogen, oxygen, and water vapour) with considerable advantages over traditional SOFC architectures, especially in SOEC mode [10]. BCY suffers from a poor stability in presence of CO₂ due to tendency of Ba to form BaCO₃. Nevertheless, due to the high potentiality of this material, some efforts have been doing to overcome the problem [11,12].

Generally, the preparation of dense BCY requires sintering at temperatures in the range 1400–1600 °C. Several syntheses [13] were studied to obtain a very fine powder that could sinter at lower temperature, but not always high surface area powders gave good results. Another widely used strategy to reduce sintering temperature is the

introduction of small amounts of sintering aids into the starting powder. In most cases their effect is based on the formation of thin liquid layer at the grain boundary followed by dissolution of intergrain neck, rearrangement of wetted grains and enhanced mass transfer through the liquid phase that promotes the densification at lower temperature. [14,15]. Several attempts are presented in literature on different materials with different sintering aids [13]. In particular, copper oxide is a favourable sintering additive for the Ba-containing ceramics, because in such systems, along with the low-temperature melting of Cu₂O at about 1030 °C, two binary oxides BaCuO₂ and Ba₂CuO₃ melting in air at about 1000 and 800 °C, respectively, can form. In addition, BaCuO₂ and CuO can form a eutectic mixture at about 900 °C. Analysis of the phase diagram of BaO–CuO system showed that the system BaO–CuO is characterized by the relatively low temperature of the liquid phases' appearance in a wide range of the component ratio. Nevertheless results presented on BCY are still lacking in clarity about the effect of CuO on structure and conductivity.

In this work we started from a very fine BCY powder prepared by a modified solid-state process [16] and combined the effect of CuO sintering aid. Sinterability, structure, microstructure and conductivity were studied for different CuO contents.

2. Experimental

Fine powder was prepared by solid state synthesis starting from ultrafine BaCO₃ (Solvay Bario e Derivati), nanocrystalline CeO₂ (VP AdNano® Ceria 50, Evonik Degussa) and Y(NO₃)₃·6H₂O (Aldrich). An aqueous solution of Y(NO₃)₃·6H₂O was prepared and CeO₂–BaCO₃ mixture was added in the right ratio to obtain the stoichiometry of

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BaCe_{0.85}Y_{0.15}O_{2.925}. PolyAcrylic Acid (Acros Chimica, MW 2000) was added as dispersant. The slurry was mixed in a PE bottle in presence of zirconia grinding media, freeze dried and then power sieved. More details on preparation are reported elsewhere [16]. CuO sintering aid (Aldrich), 0.75 or 1.5 wt% to BCY powder, and a PVA binder (Aldrich) average molecular weight: 85,000–124,000, 1 wt% to BCY powder, were ball milled with BCY in isopropanol into a PE bottle in presence of zirconia grinding media. Then powders were freeze dried and sieved. Phase composition was analysed by XRD (CubiX, Panalytical). Powders were uniaxially pressed as pellet and sintered in air at 1000 °C ≤ T ≤ 1500 °C for 2 ≤ h ≤ 10. The density of sintered ceramics was measured by Archimede's method. Microstructure of powders and ceramics was characterized by SEM (1450VP, LEO). The chemical composition was determined by an energy-dispersive electron microprobe (INCA 300, Oxford Instruments). The electrical characterization of pellets was performed by an impedance meter (FRA Solartron 1260 + Dielectric Interface Novocontrol BDC) in the ranges 10⁻¹–10⁶ Hz, 20 °C ≤ T ≤ 700 °C, under wet (3 at.%) Ar-5%H₂. The impedance diagrams were fitted with equivalent circuits using the ZView (Scribner Associates Inc.). Pt electrodes (Pt-Ink, Metalor) were painted on pellets by slurry coating and cured at 1000 °C.

3. Results and discussion

3.1. Structural and microstructural properties

In order to reveal the influence of CuO as sintering aid, density measurements and microstructure analysis in different conditions of temperature and CuO amount were performed. As reported in a previous paper [16], the modified solid state route used in the preparation of BaCe_{0.85}Y_{0.15}O_{2.925} powder (BCYN) allowed to reach about 96% of theoretical density [17] at 1250–1280 °C, without any sintering aid, thanks to the nanocrystalline form of reactants and the efficient mixing process. Addition of 0.75wt CuO (BCY-C0.75) to BCYN resulted in a further significant enhancement of sintering properties, with a relative density value equal to 96–97% already at T = 1000 °C and to 98% at T = 1100 °C. Increasing the amount of CuO to 1.5 wt% (BCY-C1.5) had a quite negligible effect on sinterability for both sintering at T = 1000 °C and T = 1100 °C. SEM images confirmed a very high density for all samples. Furthermore, the grain size is substantially independent from the amount of CuO. For both concentrations, at lower temperature (1000 °C) samples were characterized by a fine and homogenous microstructure with submicron grains of 0.3–0.5 μm (Fig. 1 on the left). Increasing temperature to 1100 °C, microstructure showed a bimodal distribution; some regions with small grain of about 0.5 μm can be observed in a matrix consisting of grains of 1–1.5 μm (Fig. 1 on the right). A similar bimodal distribution was detected also in pure BCYN, sintered at temperatures ≥ 1280 °C, but with smaller grain sizes.

Therefore, in general CuO acts as sintering and grain growth promoter through diffusion along grain boundaries, as higher concentration of Cu is likely to be located at grain boundaries. At higher temperature, grain growth through bulk diffusion is also activated resulting in the reported bimodal distribution in both BCYN and BCY-C. The images collected on polished surfaces confirmed the high density of samples. EDS analyses indicated that for BCY-C0.75 the average composition is close to nominal, without formation of other phases. On the contrary, in both BCY-C1.5 samples sintered at T = 1000 °C and T = 1100 °C a second phase was revealed clearly visible in Fig. 2 as dark spots.

XRD patterns confirmed what observed by SEM: all samples show orthorhombic perovskite-type structure (*Pmncn* space group, ICSD 78538). Moreover, in BCY-C0.75 no additional diffraction peaks of CuO or other Cu-containing phases were detected. This indicates that Cu is predominantly incorporated in the perovskite structure and highly distributed at grain boundaries as an oxide. Conversely, in BCY-C1.5 samples both sintered at T = 1000 °C and T = 1100 °C a secondary phase is present, identified as Y₂BaCuO₅ (orthorhombic, *Pnma* space group, ICSD 62903). The inset in Fig. 3 focuses on the region where the most intense peaks of the secondary phase (Y₂BaCuO₅) are located. In BCYN and BCY-C0.75 samples, small deviations from the baseline are visible. In BCYN it could be attributed to small amounts of barium carbonate and cerium oxides, deriving from the spontaneous decomposition of the perovskite in air. For BCY-C0.75 they could also suggest the presence of a small quantity (below 1 wt.%) of the same secondary phase.

Being the theoretical density of this secondary phase, as calculated from ICSD data, close to the one of BCY, its effect was neglected also on calculation of relative density of BCY-C1.5. It is also important to observe that because of the limited resolution of XRD, the formation of a small quantity (up to 1 wt.%) of Y₂BaCuO₅ distributed at grain boundaries cannot be excluded even in BCY-C0.75.

Patterns were also analysed by the Rietveld method, as implemented in the Fullprof software, to check for dependence of the unit cell volume of the perovskite phase on Cu addition. As an example, the Rietveld refinement for BCY-C0.75 is reported in Fig. 4. Lattice parameters and unit cell volume are reported in Table 1 as function of CuO content with-in the reliability factors R_f, R_{wp}, R_p. Parameters b and c are constant within the error. Only for parameter a and cell volume there is a slight increase with increase of CuO content. These results are quite unexpected due to the smaller size of Cu²⁺ (73 pm, coordination VI) cations with respect to Ce⁴⁺ (87 pm, coordination VI) and Y³⁺ (90 pm, coordination VI) but could be explained as the combined effect of lattice contraction due to small cations incorporation and lattice expansion due to oxygen vacancies formation like in the case of Zn incorporation in to BaCe_{0.9}Gd_{0.1}O_{3-δ} ceramics [18]. The values of reliability factors R_f, R_{wp}, R_p are quite large because only the main phase orthorhombic perovskite-type structure was considered for refinement.

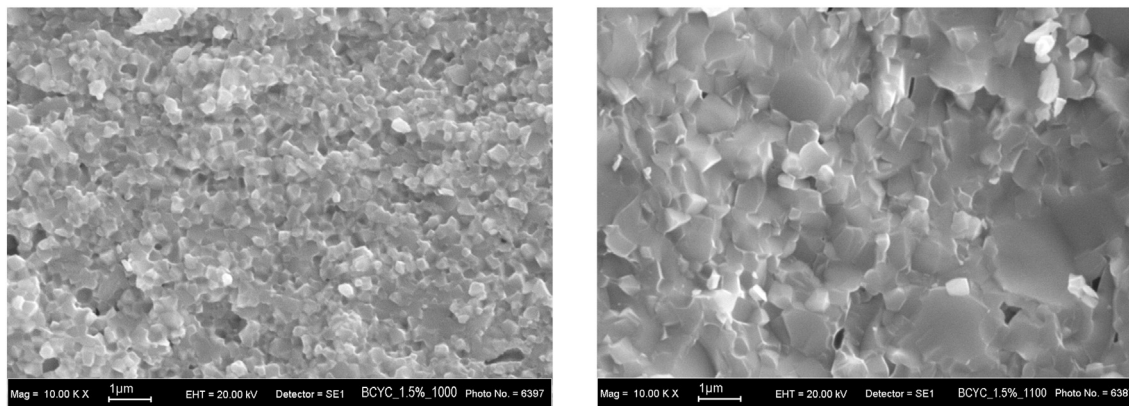


Fig. 1. SEM images of sample BCY-C1.5 sintered at T = 1000 °C (on the left) and at T = 1100 °C (on the right).

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