



Electric conduction properties of boron-doped ceria

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ABSTRACT

In the present study, the effect of the addition of boron on the electrical conduction properties of nanocrystalline cerium oxide (CeO_2) was investigated. Pellets consisting of pure CeO_2 and a mixture of CeO_2 and 10 mol.% of boron oxide (B– CeO_2 samples) were sintered at 800 °C as well as 1100 °C and their electrical conduction properties investigated by impedance spectroscopy at different temperatures and oxygen partial pressures. The nanocrystalline B– CeO_2 samples exhibit a higher electronic grain boundary conductivity and higher activation energy compared to a pure CeO_2 sample (1.41 eV for B– CeO_2 vs. 1.21 eV for pure CeO_2). According to electron energy-loss spectroscopy analysis, (i) boron can be detected only at the grain boundaries and (ii) cerium cations are lightly reduced at the grain boundaries. The results are consistent with both the formation of a space charge layer with a positive space charge potential but also with conduction along a glassy cerium-boron-oxide phase.

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1. Introduction

Cerium oxide (CeO_2) is a material of great interest as electrolyte for solid oxide fuel cells (SOFC) thanks to its high conductivity at intermediate temperatures [1]. Its perceptible electronic transference number, a disadvantage for SOFC application, makes it interesting also for different applications, e.g. catalysis and oxygen membranes. Notably, there have been evidences of significant changes of the mixed electronic/ionic conductivity in ceria nanocrystals [2]. In this case, it was assumed that the overall conductivity of doped oxide ceramics (in the case of weak acceptor doping) turns from ionic into electronic upon grain size reduction into the nanometric range. This could be fully explained in the framework of the space charge model, as, within the space charge regions – in proximity of the grain boundaries (GB) – electrons are accumulated and oxygen vacancies depleted [3–5].

In this context, an intriguing aspect is represented by the question whether it could be possible to modify the space charge potential – and therefore the GB conduction properties – in order to tune the electrical conductivity of CeO_2 according to the desired field of application.

A number of different approaches have been reported in the literature. For example, Avila-Paredes and Kim [6] induced the segregation of different transition metals at the GB of gadolinium-doped CeO_2 by long-term annealing and proved that indeed the presence of dopants at the GB reduces the space charge potential.

Litzelman et al. [7] investigated nanocrystalline CeO_2 thin films locally doped via in-diffusion along the GB; the decreased electrical conductivity was explained in terms of reduced space charge potential due to the presence of dopants at the GB.

The aim of the present contribution is to modify the electrical conduction properties of the GB of nanocrystalline CeO_2 by local doping with B_2O_3 . The low melting point oxide, namely B_2O_3 , was mixed with the pure CeO_2 powder, pressed into pellets and then sintered, with the purpose of obtaining a nanocrystalline material, in which the GB were enriched of boron.

2. Experimental section

The CeO_2 powder was synthesized starting from cerium nitrate hexahydrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich; purity 99.99%) calcined for 10 h at 400 °C in air. Part of the so-obtained powder was mixed with 10 mol.% B_2O_3 (Alfa Aesar, purity 99.999%) in a zirconia vibration mill for 1 h. Both compositions, i.e. pure CeO_2 and B– CeO_2 , were isostatically cold pressed (500 MPa, 5 min) and then sintered at 800 °C for 30 min or at 1100 °C for 6 h in air. The density of the samples (with a final diameter of ~5 mm and a thickness of ~1 mm) was about 90% of the theoretical density. Upon sintering, the samples underwent X-ray diffraction analysis (XRD) using a XRD diffractometer (Xpert, Philips, 3710 HTK, $\text{CuK}\alpha = 1.54056 \text{ \AA}$). The average grain size was 30 nm for pure CeO_2 (800 °C), 60 nm for B– CeO_2 (800 °C), 65 nm for pure CeO_2 (1100 °C) and >1 μm for B– CeO_2 (1100 °C).

The electrical conduction properties of the samples were determined using an impedance spectrometer Solartron SI 1260 (AC voltage of 0.2 V, frequency range from 1 MHz to 1 Hz) in different oxygen/nitrogen mixtures with $p\text{O}_2$ varying from 1 to 10^{-4} atm and

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temperatures between 550 °C and 350 °C. For each pO_2 , the samples were first equilibrated at 550 °C for 30 h. Then the impedance spectra were collected during cooling at temperature steps of 30 °C and holding time (at each temperature) of 2 h. The pO_2 values were monitored using a zirconia-based oxygen sensor operating at 900 °C.

HRTEM was performed using a JEOL ARM 1250 transmission electron microscope operating at 1250 kV with a point resolution of 1.2 Å. TEM specimens were prepared following the tripod polishing process followed by a final ion thinning step (Argon gas at 1.5 keV).

EELS was carried out using a scanning transmission electron microscope (STEM) operating at 100 kV, and equipped with a parallel electron energy-loss spectrometer (GATAN UHV Enfina) [8,9]. Core-loss spectra of Ce–N₄₅ edge (onset at ~110 eV), B–K edge (at ~196 eV), and O–K edge (at 532 eV) were acquired simultaneously. Core-loss spectra for Ce–M₄₅ edges at ~883 and 901 eV, respectively, were also collected.

The Ce–M_{5,4} spectra were treated as follows. First, the intensity background was subtracted from the edge signal. The multiple scattering contribution was then removed from the spectra that were taken from areas thicker than 0.5 λ , with λ being the electron mean free path for inelastic scattering. Finally, the intensity values of M₅ and M₄ edges were obtained by integrating the area under the peak [10].

3. Results and discussion

3.1. Impedance spectroscopy analysis

Fig. 1 summarizes the typical impedance spectra collected in a pure O₂ atmosphere from pure CeO₂ and B–CeO₂ samples sintered at 800 °C for 30 min (Fig. 1a and b) as well as 1100 °C for 6 h (Fig. 1c and d).

We start with analyzing the data of the samples sintered at 1100 °C, in which it is possible to distinguish between bulk and GB contribution as a consequence of the larger grain size. These spectra

were fitted using an equivalent circuit composed of 2 RQ elements, in the case of pure CeO₂, which take account of bulk and GB contribution, and 3 RQ elements for B–CeO₂, in which the third RQ element corresponds to the electrode contribution.

Q is the constant phase element defined as $C = (R^{1-n}Q)^{1/n}$, with C being the capacitance and n an additional fitting parameter ranging between 0.75 and 1. The results are summarized in Fig. 2a while the pO_2 dependence plots are depicted in Fig. 2b and c.

The measured activation energy of the bulk of pure CeO₂ $\bar{E}_b^{(p)}$ is 0.97 eV whereas the activation energy of GB $\bar{E}_{GB}^{(p)}$ is found to be 1.60 eV (the bar denotes here all quantities relative to the samples sintered at 1100 °C). Both bulk and GB conductivities exhibit pO_2 dependence, although for the bulk this starts to be significant at pO_2 lower than 10^{-2} atm. The bulk electronic conductivity $\bar{\sigma}_{b,e}^{(p)}$ shows a pO_2 dependence equal to $-1/4$, which implies extrinsic electronic behavior that can be attributed to the presence of a low concentration of acceptor dopants. This observation is important since it allows us to treat these results according to the Mott–Schottky model.

Here, it is worth noting that since the average grain size of this sample is still quite small (~65 nm) $\sigma_b^{(p)}$ can result from the superposition of an ionic (actual bulk) and an electronic contribution due to the parallel GB (see also Ref. [5]). If we extrapolate the electronic contribution (slope = $-1/4$) down to $\log pO_2 = 0$ (see the gray line in Fig. 2b), $\bar{\sigma}_{b,e}^{(p)}$ is equal to 4×10^{-6} 1/Ohm cm, which is almost the half of the measured value $\bar{\sigma}_b^{(p)}$ (7.6×10^{-6} 1/Ohm cm), and therefore the ionic conductivity $\bar{\sigma}_{b,i}^{(p)}$ is 3.6×10^{-6} 1/Ohm cm.

The B–CeO₂ sample exhibits a bulk activation energy $\bar{E}_b^{(B)}$ of 0.69 eV and $\bar{E}_{GB}^{(B)}$ of 1.67 eV. Notably, the bulk conductivity $\bar{\sigma}_b^{(B)}$ is nearly independent of pO_2 , whereas $\bar{\sigma}_{GB}^{(B)}$ exhibits a pO_2 dependence equal to $-1/6$. The value of $\bar{E}_b^{(B)}$ corresponds to the characteristic enthalpy of oxygen vacancy mobility in CeO₂. Note that the experimental value of $\bar{\sigma}_b^{(B)}$ is in good agreement with the calculated value of $\bar{\sigma}_{b,i}^{(p)}$. This suggests that, even upon sintering at 1100 °C, the addition of boron has no effect on the conduction properties of the bulk and, therefore,

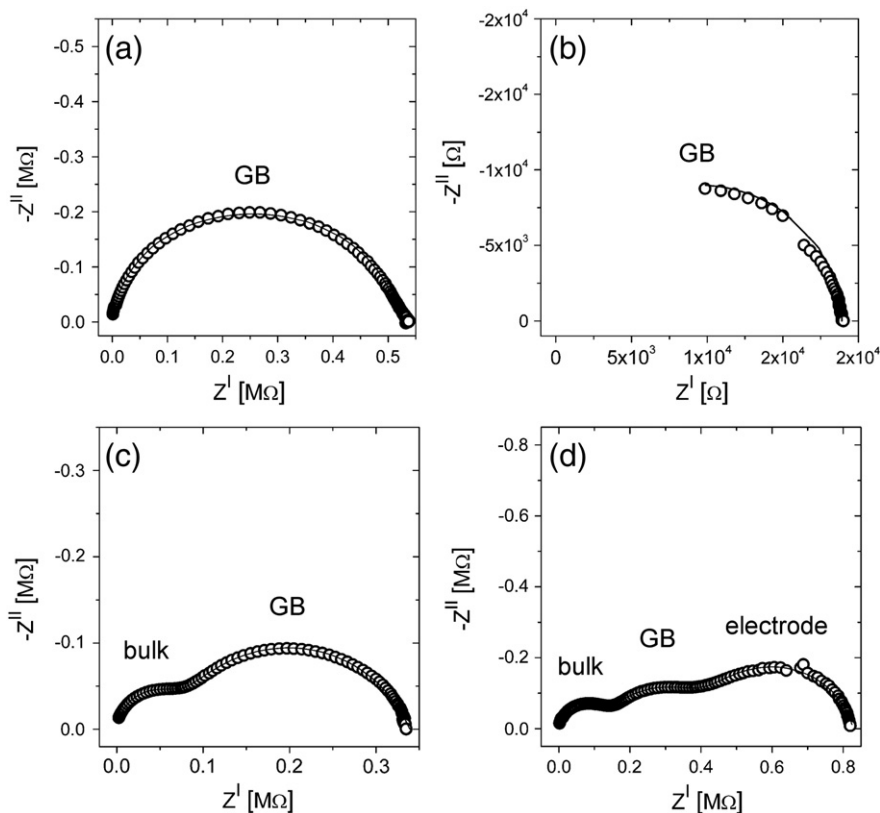


Fig. 1. Impedance spectra acquired in pure O₂ from (a) pure CeO₂ 800 °C; (b) B–CeO₂ 800 °C; (c) pure CeO₂ 1100 °C and (d) B–CeO₂ 1100 °C.

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