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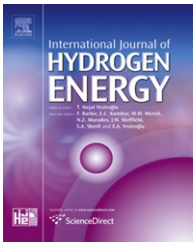

# Influence of Pr substitution on defects, transport, and grain boundary properties of acceptor-doped $BaZrO_3$

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ABSTRACT

We report on effects of partially substituting Zr with the multivalent Pr on the conductivity characteristics of acceptor (Gd) doped $BaZrO_3$-based materials. $BaZr_{0.6}Pr_{0.3}Gd_{0.1}O_{3-\delta}$ was sintered 96% dense at 1550 °C with grains of 1–4 μm. The electrical conductivity was characterised by impedance spectroscopy and EMF transport number measurements as a function of temperature and the partial pressures of oxygen and water vapour. $H_2O/D_2O$ exchanges were applied to further verify proton conduction. The material is mainly a mixed proton–electron conductor: the *p*-type electronic conductivity is ~0.004 and ~0.05 S/cm in wet $O_2$ at 500 and 900 °C, respectively, while the protonic conductivity is $\sim 10^{-4}$ S/cm and $\sim 10^{-3}$ S/cm. The material is expectedly a pure proton conductor at sufficiently low temperatures and wet conditions. The specific grain boundary conductivity is essentially equal for the material with or without Pr, but the overall resistance is significantly lower for the former. We propose that replacing Pr on the Zr site reduces the grain boundary contribution due to an increased grain size after otherwise equal sintering conditions.

## 1. Introduction

$BaZrO_3$ is among state-of-the-art electrolyte materials for proton conducting solid oxide fuel cells (PC-SOFCs) [1–3]. It exhibits high grain interior proton conductivity ($\sim 10^{-2}$ S/cm) combined with chemical and mechanical stability. However, the combination of low specific grain boundary conductivity (see for instance Refs. [3–7]), and slow grain growth, yields relative high grain boundary resistances that limit the overall dc conductivity. Moreover, $BaZrO_3$-based materials require very high sintering temperatures to be dense (1600–1700 °C) [8,9]. This complicates fabrication of $BaZrO_3$-based fuel cell assemblies and is believed to cause partial evaporation of barium, which has been reported to decrease the conductivity [10].

The origin of the high grain boundary resistivity in oxide ion conductors has been discussed using a space-charge layer model [11–14]. Analyses of impedance measurements of nanocrystalline ceria have shown the existence of space charge layers at the grain boundaries with strong depletion of oxygen vacancies and high *n*-type conductivity [11]. A similar model has also been applied to account for the behaviour of Y-doped $BaZrO_3$ [7] with the conclusion that protons are depleted in a space-charge layer enriched in electrons and the acceptor dopant ($Y_{Zr}^{/}$).

Compositional modifications have been pursued to decrease the sintering temperature and increase the grain size to lower the overall resistance of the material. Partial substitution of the Zr by Ce lowers the grain boundary resistance but

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at the cost of chemical stability towards acidic – notably $CO_2$-containing – environments [9,10,15,16]. More recently, it has been reported that additions of small amounts of NiO [17], ZnO [18] or Co [19] decrease the sintering temperature. The influence of these sintering additives on the electrical properties is yet not well investigated, but some authors report that a decrease of the ionic conductivity is noticeable for the cobalt or nickel doped barium zirconate [19].

The aim of this contribution is to investigate the influence of Pr substitution for Zr in Gd-doped $BaZrO_3$. Under oxidising atmospheres, the end member acceptor-doped $BaPrO_3$ behaves as a *p*-type conductor [20–24] with minor contributions from protons and oxygen vacancies [24]. Materials with such relatively high electronic conductivity generally exhibit lower grain boundary resistances than typical $BaZrO_3$-based materials, which are purer proton conductors [25]. It was shown that Pr substitution in $BaZrO_3$ increases sintering and grain growth rates [26,27] which may lower the overall grain boundary resistance of ceramic materials. The defects and transport properties in $BaZr_{0.9-x}Pr_xGd_{0.1}O_{3-\delta}$ have not been reported earlier in detail, and we here present a study for the case of $x = 0.3$. This composition has a relatively low Pr content in order to both increase the proton conductivity relative to electronic conductivity, and to increase the chemical stability compared to the Zr-free materials, as $BaPrO_3$ is known to be unstable in wet and/or reducing gases, and $CO_2$ [20,21,24]. It is of particular interest whether Pr by its multivalent character influences the grain boundary conductivity.

## 2. Experimental

### 2.1. Sample preparation

Nanopowders of $BaPr_{0.3}Zr_{0.6}Gd_{0.1}O_{3-\delta}$ (hereafter abbreviated as **Pr30**) were prepared by an EDTA-based combustion synthesis as described in more detail before [27]. The combusted precursor was calcined at 1200 °C, ball milled with agate mortar and balls at 250 rpm for 1 h in acetone, and then dried at 80 °C for 30 min. Green bodies of ~57% of the relative density were obtained by uniaxial pressing at ~140 MPa. Sintering was performed at 1550 °C for 5 h, yielding samples with ~96% of the theoretical density.

### 2.2. Conductivity

The electrical conductivity of **Pr30** was measured in a ProboStat™ sample holder (NorECs, Norway) by the 2-electrode 4-wire setup. The sintered specimens were polished prior to the conductivity measurement in order to remove impurities and non-stoichiometries at the surface. Pt electrodes (Ferro 6512-0410 Pt ink) were then painted on each side and fired at 1000 °C for 1 h. Impedance spectra were obtained using a frequency response analyser (Solartron 1260) in the frequency range 0.1 Hz–1 MHz at an AC voltage of 500 mV RMS. Complex impedance spectra were analysed using the equivalent circuits fitting tool in the ZView software [28]. A capacitance of 5 pF [29] for the empty sample holder was taken into account to obtain accurate grain interior capacitances. Specific grain boundary conductivities were calculated using the brick layer model, explained in detail by Haile et al. [30]:

$$\sigma_{gb} \approx \frac{L}{R_{gb}S} \cdot \frac{C_{gi}}{C_{gb}} \tag{1}$$

where $\sigma_{gb}$ is the specific grain boundary conductivity, $L$ and $S$ are the thickness of the sample and electrode area, respectively, $R_{gb}$ is the measured resistance corresponding to the grain boundary contribution, $C_{gi}$ and $C_{gb}$ are the capacitances of grain interior and grain boundary, respectively.

Additionally, a 4-point electrode setup with Pt wires in a van der Pauw configuration was employed in order to rule out possible conductivity limitations by the 2-point setup, in particular at high temperatures under oxidising conditions.

Conductivity isotherms (from 1100 to 400 °C) were measured versus the partial pressure of oxygen ($pO_2$) in the range ~$10^{-5}$–1 atm under wet conditions (~2.5% $H_2O$) and, moreover, versus the partial pressure of water vapour ($pH_2O$) in the range ~$3 \times 10^{-5}$ to ~0.025 atm in both $O_2$ and Ar. Additional $pO_2$ dependencies were recorded under more reducing conditions at 700 °C. The conductivity was monitored versus time at each new set of conditions to ensure that proper equilibrium was achieved. $D_2O/H_2O$ shifts were carried out in Ar to clarify the role of protons.

Complex impedance sweeps were recorded under isobaric conditions in wet (~2.5% $H_2O$) air and Ar from 900 to 150 °C, in temperature intervals of 50 or 100 °C. Additionally, sweeps in wet (~2.5% $H_2O$) 5% $H_2$/Ar (reducing) were recorded from 600 to 150 °C.

EMF measurements were performed to extract transport numbers using a ~96% dense specimen with the setup and procedure described in Refs. [31,32]. A thick gold gasket was placed between the specimen and the support tube for sealing, which was accomplished by annealing at ~1060 °C. The open-circuit voltages (OCV) resulting from differences in the gas composition and chemical potentials across the specimen were measured with an Agilent/HP 34401A multimeter.

We should mention that several specimens were used for this study, and measurements were reasonably reproducible under inert and oxidising conditions. Also, there was no difference in the values obtained between a 4-point and a 2-electrode setup, as opposed to earlier reported Gd-doped $BaPrO_3$, where the 2-electrode setup gave higher resistances due to formation of insulating layers in the sample underneath the electrodes [33].

## 3. Results and discussion

Fig. 1 shows a SEM micrograph representative of the surface of a well-sintered $BaZr_{0.6}Pr_{0.3}Gd_{0.1}O_{3-\delta}$. The relative density is 96% and the grain size ~1–4 μm, both high compared to traditional $BaZrO_3$-based materials without Pr. In this respect, it is interesting to note that an equivalent composition using Ce instead of Pr is reported to reach only 80% relative density after sintering at 1650 °C ($BaZr_{0.6}Ce_{0.3}Y_{0.1}O_{3-\delta}$) [16], or 80–93% obtained at 1500–1600 °C for $BaZr_{0.8-x}Ce_xY_{0.2}O_{3-\delta}$ [15]. This indicates that Pr improves sintering and grain growth of $BaZrO_3$-based materials more effectively than Ce.