DOPANT SEGREGATION IN NANOMETRIC TZP CERAMICS

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ABSTRACT

Dense, tetragonal single-phased and nanocrystalline zirconia ceramics containing 3 mol% R₂O₃ without impurities and with average grain sizes of 60 nm were prepared. Electrical properties were investigated by impedance spectroscopy, as the ionic radius increased from 0.098 nm to 0.109 nm, respectively from Yb³⁺, Y³⁺, Gd³⁺ to Sm³⁺. Conductivity variations were not due to these microstructure contributions but really due to an effect of R₂O₃ dopant. Segregation phenomenon has been put into perspective comparing these electrical data with those of air-quenched samples and it was fully related to the dopant ionic radius size.

INTRODUCTION

Necessary for application as solid electrolyte in solid oxide fuel cells operating at intermediate temperatures (IT-SOFCs) from 400 to 700°C are high ionic conductivity, good mechanical properties and long term stability. Tetragonal ZrO₂ (TZP) which is stabilized in small grains and with low R₂O₃ dopant contents presents (1) a large potential for making progress in the development of electrolytes for IT-SOFCs. Indeed, TZP is known to possess good mechanical properties (2,3). Recently, long-term stability has been demonstrated at 700°C in humid atmosphere (4). Moreover, enhanced ionic conductivity has been suggested when grain size is decreased down to 300 nm and for a lower yttria content (5). The oxygen-ion conductivity strongly depends on the microstructure (grain size, grain size distribution and porosity) of specimen, crystalline symmetry, purity, and vacancy content. At present, the grain boundary blocking contribution remains of great importance with comparison to the bulk if the grain size is reduced to the order of nanometer and for lower temperatures (6). This blocking contribution has been found to be larger than in coarse-grained materials (7). Without any impurity phases, the cause of this "intrinsic" blocking effect is still unclear.

This work is focused on the influence of the substitution of Zr⁴⁺ by a constant content of oversized R³⁺ doping from (Yb³⁺, Y³⁺, Gd³⁺ to Sm³⁺) on electrical properties and especially on the grain-boundary blocking contribution in nanometric ZrO₂ ceramics by using impedance spectroscopy. All ceramics will be referred to hereafter as 3R-TZP. In the first part, the grain boundary has been defined and its thickness found strongly related to the doping. Then, segregation phenomenon has been put into evidence in quenched samples and has been found doping size-dependent.
**EXPERIMENTAL**

**Physico-chemical Characterizations of Nanocrystalline 3R-TZP Ceramics**

Nanocrystalline powders of 3 mol% R₂O₃-doped ZrO₂ were produced by a spray-pyrolysis process using 1.7 MHz ultrasonic atomizer (8) and used to prepare single-phased tetragonal ceramics by isostatic pressing at 300 MPa and sintering at 1500°C for 2 hours in air. Oversized R³⁺ dopants from Yb³⁺, Y³⁺, Gd³⁺ to Sm³⁺ were selected for their lower valence (+3) compared to Zr⁴⁺ and for a systematic increase in their ionic radii respectively ranging from 0.098 nm to 0.109 nm.

X-ray diffraction was carried out at room temperature using a Siemens D500 diffractometer equipped with a linear detector (CuKα radiation, λ = 1.54Å, 0.04°, 20 steps, 5 s counting time). The average grain size was calculated by the Scherrer formula, corrected with silicon for the (111) peak of tetragonal zirconia. Position and Full Width at Half Maximum (FWHM) of XRD peaks were determined by a deconvolution of pseudo-Voigt-shaped peaks with Profile fitting software (Diffract-at, Socomb, Paris).

Raman spectrometry was performed using a DILOR XY confocal Raman spectrometer with the 514.5 nm line of an argon ion laser.

These materials were characterized by a high purity (no trace of silicon), a high degree of compositional homogeneity and only a 60 nm average grain size for all the series. This limited coarsening results from microstructure of powders which consist of nanocrystallites, conventionally called grains, aggregated in a crystallized envelope as shown by previous HRTEM observations (9). Density of 97% of theoretical was measured for all ceramics from the size and the weight of the pellets. Pore size was always found lower than 20 nm using a static volumetric method based on nitrogen adsorption/desorption.

For air-quenched samples, two firing cycles were carried out. First, the pellets were heated as previously up to 1500°C for 2h at a heating rate of 10°C/mn and then cooled down to room temperature at 10°C/mn. Then, they were subsequently heated up to a temperature lower or equal to 1500°C and then were air-quenched. 2.5Y-TZP ceramics were air-quenched from different temperatures: 1000, 1300 and 1500°C and 3Sm-TZP from 1500°C.

The microstructure of the disks was examined using scanning electron microscopy (SEM Jeol JSM-35) before and after air-quenching.

**Electrical Characterizations of Nanocrystalline 3R-TZP Ceramics**

The ac impedance diagrams were recorded on symmetrical cells (typically 6 mm in diameter, 2 mm thick) in dry air flow (80%N₂ / 20%O₂, 10 mL min⁻¹) between 300 and 700°C. Platinum coatings were deposited on both sides of the pellets by radio frequency magnetron sputtering (Plassys device) at room temperature. The electrodes were contacted by platinum grids. The impedance diagrams were recorded under ac conditions in the 5 to 1.3x10⁷ Hz frequency range using a Hewlett-Packard impedancemeter (4192LF). The amplitude of the applied voltage was 200 mV. The diagrams here reported
are normalized to a unit geometrical factor. The numbers on the presented diagrams indicate the logarithm of the measuring frequency. Data were fitted by a series association of two parallel circuits which were composed of a resistance and a constant phase element (CPE), using Zview software (version 2.1, Scribner Associates).

RESULTS AND DISCUSSION

All ceramics are characterized by the same microstructure (high purity, 60 nm-sized grains, density of 97% of the theoretical one) and are tetragonal single-phased for a constant 3R-TZP when the ionic radius is increased from 0.098 nm to 0.109 nm, respectively, from Yb$^{3+}$, Y$^{3+}$, Gd$^{3+}$ to Sm$^{3+}$. Accordingly, the recorded variations of conductivity should not be due to any microstructure change but more probably due to an effect of dopant ionic radius.

**Electrical Properties of 3R-TZP**

Whatever the dopant size and the thermal history, experimental impedance diagrams are composed of two fairly well separated semi-circles (Fig. 1). The high frequency one is related to the electrical properties of zirconia grains (bulk contribution) and the low frequency one describes the blocking effect due to internal interfaces.

![Figure 1: Impedance spectra recorded at 350°C for 3R-TZP: R= (●) Yb, (●) Sm.](image)

Arrhenius diagrams of bulk and blocking contributions are shown in Fig. 2 versus Yb, Y, Gd and Sm dopant. Bulk conductivity ($\sigma_b$) of zirconia matrix is increased when the dopant ionic radius is decreased (Fig. 2(i)), as already reported in the literature (10). The Yb$^{3+}$ dopant which presents the closest ionic radius to the Zr$^{4+}$ host cation (misfit equal to 0.014 nm), exhibits the highest conductivity. A 3.5-fold decrease of $\sigma_b$ was observed from ytterbia to samaria-doped zirconia at 300°C. The specific activation energy $E_b$, determined from the corresponding Arrhenius diagram, is an increasing function of the dopant size (0.80 to 0.92 eV).
Figure 2. Arrhenius diagrams of (i) bulk and (ii) blocking contributions of 3R-TZP: 
R= (•) Yb, (■) Y, (▲) Gd, (♦) Sm.

The relative variations of both specific conductivity and activation energy over the entire ionic radius range suggest that weaker interactions take place between oxygen vacancies and cationic defects such as Yb\textsuperscript{3+} than in other specimens. This result indicates an increase of mobile vacancies in ytterbium-doped TZP as shown by Kilner et al. in fluorite-type oxides (11). The larger the misfit (R\textsuperscript{3+}-Zr\textsuperscript{4+}), the larger the distortions of the unit cell and the larger the strain energy. An association enthalpy between oxygen vacancies and cationic defects is therefore increased as described in reference 11 in order to compensate an increase of strain energy. These results are in good agreement with calculations developed by Mackrodt (12) who demonstrated the importance of the compensation effect on association energy of cationic defaults. The same evolution of electrical properties was measured for the additional blocking contribution (see Fig. 2(ii)). Indeed, samaria-doped ZrO\textsubscript{2} specimen is characterized by the smaller intergranular conductivity over almost the entire temperature domain. Activation energies $E_{gb}$ are found slightly higher than $E_b$ and vary between 0.83 and 1.17 eV respectively for 3Yb-TZP and 3Sm-TZP. Variations of both blocking conductivity $\sigma_{gb}$ and corresponding activation energy $E_{gb}$ versus the dopant ionic radius compared to those of the specific contribution are quite similar. From these data, one can conclude that the bulk properties clearly influence the magnitude of the additional blocking contribution in oxygen ion conductors, as theoretically predicted by Fleig (13) and experimentally shown by Santos et al. (14). Therefore, the bulk conductivity mainly governs the blocking contribution, whatever the dopant nature.

**Particle or Grain-boundaries?**

Nanometric TZP ceramics, prepared by pyrosol, have been previously described by SEM (1) as aggregates of 600 nm average size, unimodally distributed, containing single
crystals of 60 nm in average deduced from x-ray diffraction. Both particle-boundaries and grain-boundaries could contribute to the recorded blocking effect in the series. In order to clarify this point, a comparison has been established between a 3Y-TZP prepared by pyrosol and a 3Y-TZP ceramic prepared by Santos et al. (14), characterized by 620 nm in grain size and density of 99% of theoretical and a low impurity content. By using the blocking resistivity per unit surface area of internal interfaces \( \rho_{bi} \) (19), one can compare the blocking process without referring to the grain size effect. \( \rho_{bi} \) values are found to be of the same order of magnitude, i.e. 0.72 and 0.68 \( \Omega \cdot \text{cm}^2 \), respectively for a 3Y-TZP sample (pyrosol) and for 3Y-TZP from Santos. Therefore, we can postulate that both samples present the same chemical features at blocking interfaces. Then, the influence of grain size can be evaluated from the blocking factor referred to as \( \alpha_R \) which represents the ratio of the blocking resistance to the total one (20).

Table 1. Comparison of \( \alpha_R \) for TZP characterized by different grain sizes.

| Samples                  | Relative density (%) | \( \alpha_R \) |
|--------------------------|----------------------|----------------|
| 3Y-TZP (14) - 620 nm     | 97                   | 0.30           |
| 3Y-TZP (this study) - 60 nm | 99                   | 0.86           |
| 2.9Y-TZP (7) - 50nm      | 96                   | 0.90           |

As shown in Table 1, \( \alpha_R \) value of 3Y-TZP (pyrosol) has been found closer to 2.9Y-TZP (7), this latter being characterized by 50 nm grain sizes. The blocking factor is far larger than for a 620 nm grain size 3Y-TZP (14). Accordingly, one can conclude that the recorded blocking effect mainly originates from boundaries between grains of 60 nm rather than from those between aggregated particles of 600 nm.

The analysis of the blocking semi-circle was performed according to the brick layer model (15). This approach is routinely employed to describe the frequency-dependent electrical behaviour of polycrystalline ceramics. The validity of the brick layer model for describing the grain boundary blocking effect has been recently discussed in the literature (16,17). The detailed analysis of Hwang et al. (18) has shown that this electrical approach was applicable to sufficiently dense nanocrystalline ceramics, as in this study.

Capacitances which were determined from the grain boundary semi-circle decrease when the dopant ionic radius is increased in the 300-500°C temperature domain (Fig. 3).
From these data, grain boundary thicknesses have been evaluated from 0.8 to 1.9 nm for Yb to Sm-doped ZrO$_2$ based on the hypothesis of similar dielectric constants for bulk and grain-boundary contributions (21). These values are in agreement with those already determined for zirconia based ceramics (22-27). Without any impurity phase, the calculated thicknesses cannot be related to a continuous amorphous grain boundary film. Indeed, grain boundaries free of second phases were found partly blocking (14, 22, 25). A strong yttrium segregation to the grain boundaries has been frequently observed and quantitatively measured, despite different grain sizes and impurity levels (28-33). Yttrium segregation was highly localized within a 1-2 nm layer at grain boundaries (26, 34). Accordingly, dopant segregation can be regarded as being most likely responsible for the blocking effect in pure polycrystalline zirconias (22, 36-38). An yttrium enrichment at grain boundaries even in the absence of a glassy intergranular film (24, 26) is in favour of this assumption. The dopant nature has been found the key parameter in the blocking contribution as far as the grain boundary thickness is increased.

**Segregation Phenomenon in 3R-TZP**

In order to put into perspective the segregation of R$^{3+}$ to the grain boundaries, air-quenching treatments have been undertaken on as-prepared 2.5Y-TZP ceramics from different temperatures. X-ray diffraction and Raman spectrometry confirmed the tetragonal single-phased zirconia in all specimens after these treatments and a very slight increase of grain size less than 5 % was detected. This slight increase in particle size was confirmed by SEM observations (see Fig. 4(a) and (b), (i)) and an increase of pore size was observed before and after quenching from 1500°C as shown by Figures 4(a) and 4(b), (ii). However, the total volume of pores was kept constant. Whatever the quenching temperature, same morphologies have been observed. At this stage, it is worth mentioning that the recorded variation of the magnitude of the low frequency blocking cannot be regarded as resulting from a varying density of microstructure defects (39).

Whatever the temperature, the conduction properties are enhanced after quenching (Fig. 5). The influence on the blocking effect is more pronounced, as already reported (40-42). The higher the quenching temperature, the lower the blocking effect. For instance, a 1.3-fold decrease of the grain boundary resistivity is measured at 350°C after quenching from 1500°C. Both activation energies $E_b$ and $E_{gb}$ remain unchanged indicating that conduction properties are not altered. Without silicon, the decreasing blocking effect cannot be related to a location of a grain boundary glassy phase to triple points or at external surfaces (43,44). Simultaneously, the grain boundary thickness monotonously decreases from 1.3 down to 0.9 for as-prepared and quenched samples, respectively. In the quenched samples, it is expected that the high temperature grain boundary structure can be preserved at lower temperatures, e.g. with a more homogeneous point defects distribution, as segregation effects are usually small at high temperatures (45). The decreasing blocking effect depression angle (from 20° to 10°) when the quenching temperature is increased from 1000°C to 1500°C is in agreement with a higher chemical homogeneity at grain boundaries (46). The recorded variation of the grain boundary thickness supports this assumption.
As mentioned above, the dopant nature is likely to influence the blocking contribution (Fig. 3). As a matter of fact, after quenching from 1500°C, only a 1.1-fold decrease of the grain boundary resistivity was detected in 3.5Sc-TZP (Fig. 6(a)) while a 1.5-fold decrease was measured in 3Sm-TZP at 300°C (Fig. 6(b)). Because of a larger Sm$^{3+}$-Zr$^{4+}$ misfit with comparison to Sc$^{3+}$-Zr$^{4+}$, Sm$^{3+}$ is expected to segregate at grain boundaries more strongly, as indicated by the highest grain boundary thickness.

Figure 4. SEM observations of 2.5Y-TZP (a) sintered at 1500°C/2h, (b) subsequently air-quenched from 1500°C, (i) as-prepared ceramics, (ii) polished ceramics.

Figure 5. Influence of quenching temperatures on impedance spectra of 2.5Y-TZP in air: ○ as prepared, + 1000°C, △ 1300°C, A 1500°C.
CONCLUSIONS

Segregation has been evidenced by impedance spectroscopy in nanometric 3 mol. % R₂O₃-doped ZrO₂ ceramics crystallizing in the tetragonal solid solution and presenting the same microstructure. The influence of an increase of the dopant ionic radius from Yb³⁺, Y³⁺, Gd³⁺ to Sm³⁺ in ZrO₂ has been investigated on grain-boundary contribution and has been directly related to an increase of grain-boundary thickness. Segregation phenomenon was put into perspective comparing impedance results for air-quenched samples. A larger segregation phenomenon has been found in TZP doped with a larger dopant ionic radius. EXAFS and STEM studies are in progress in order to quantify segregation of trivalent dopant in nanocrystalline ZrO₂.

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