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Physico-chemical characterization of highly pure nanocrystalline doped TZP

F. Boulc'h, E. Djurado *, L. Dessemond, J. Fouletier

Laboratoire d'Electrochimie et de Physico-Chimie des Matériaux et des Interfaces, BP 75, 38402 St Martin d'Hères, France

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Abstract

Yttria and scandia doped nanocrystalline tetragonal zirconia ceramics have been prepared from sintering of spray-pyrolysis powders. The average primary crystallite size after sintering has been found equal to 70 nm from X-ray diffraction line broadening while aggregated particle size of 300 nm has been characterized by scanning electron microscopy (SEM). No trace of segregated Si has been detected in the grain boundaries using wavelength dispersion scanning (WDS). Impedance diagrams show two well-resolved components in the 300–700°C range. Small size of crystallites and existence of nanoporosity give rise to a large grain boundary contribution compared to microcrystallized zirconia.

Keywords: Fuel cells; Grain boundaries; Ionic conductivity; Powders: chemical preparation; ZrO_2

1. Introduction

At present, efforts are focused on lowering solid oxide fuel cells (SOFC) operating temperature from above 900°C to below 750°C (IT–SOFC). Moderate operating temperatures, however, require a significant decrease of electrolyte resistance. Due to its remarkable mechanical properties[1] and a higher ionic conductivity in the low temperature domain compared to cubic zirconia,[2,3] tetragonal zirconia is considered as a promising candidate to be used as an electrolyte in IT–SOFC. Furthermore, it is expected that nanostructured materials (i.e. grain size less than 100 nm) may exhibit enhanced ionic conduction along the grain boundaries as previously shown by Mondal et al. in nearly pure tetragonal zirconia ceramics.[4] Up to now, very little data are available in the literature[2,5] about the role played by grain boundaries in the total conductivity of completely pure nanocrystalline tetragonal zirconias. In this context, we have investigated pure tetragonal yttria and scandia doped zirconias which present nanometric crystallite sizes.

The present article mainly reports the preparation of nanometric yttria and scandia doped tetragonal zirconias by spray-pyrolysis. Structural characteristics of the powdered and the sintered material are presented. Their electrical properties were investigated by impedance spectroscopy in air and in the 300–700°C range.

2. Experimental

Two nanometric powdered batches constituted of 2.5 mol% Y_2O_3 (2.5Y–TZP) and 5 mol% Sc_2O_3 nominal content (5Sc–TZP) doped zirconia were synthesized by spray pyrolysis using a 1.7 MHz ultrasonic atomizer.[6] Pellets used for impedance measurements were prepared by isostatic pressing at 300 MPa and sintering at 1500°C/2 h in air (heating and cooling rate: 10°C/min). Densities were measured from specimen dimensions and weight. Microstructure and composition of powders and sintered disks were examined using SEM (Jeol JSM-35) equipped with an energy dispersive X-ray analyzer (EDX-PGT). Wavelength dispersion scanning (WDS) investigations in ceramics were performed using electron probe micro-analysis (CAMECA SX50) (200 nA, 15 kV). X-ray characterization was carried out using a Siemens D500 diffractometer (Cu$K_{\alpha 1}$ radiation, $\lambda = 1.5406$ Å). Silicon was used as internal reference for all scans (0.004°, 2θ steps, 5 s counting time). Average crystallite size was calculated using the Debye–Scherrer formula, corrected

* Corresponding author. Tel.: +33-0-4-76-82-66-84; fax: +33-0-4-76-82-66-70.

E-mail address: elisabeth.djurado@lepmi.inpg.fr (E. Djurado).

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with silicon for the 111 peak of tetragonal zirconia. Simultaneous thermogravimetric and differential thermal analyses (TG/DTA) were carried out in dry air, using a Setaram TGA 24S16 instrument (temperature range: 30–1300°C, heating and cooling rates: 10°C/min). Impedance spectroscopy measurements were carried out on symmetrical cells in dry air flow (10 ml/min) between 300 and 700°C. Platinum coatings were deposited on both sides of the pellets by sputtering (Plassys MP 300) at room temperature. The electrodes were contacted by platinum grids and wires. The impedance diagrams were recorded under zero dc bias conditions in the 5–1.3×10^7 Hz frequency range using a Hewlett-Packard impedance meter (4192 ALF). The amplitude of the measuring signal was 200 mV in order to obtain well defined diagrams. All the diagrams were normalized to a unit geometrical factor. Accordingly, the determined conductances are conductivities. Electrode characteristics were well-separated from the electrolyte impedance. For the sake of clarity, the electrode contributions have been substracted from the experimental diagrams.

3. Results and discussion

2.5Y–TZP and 5Sc–TZP powders which were successfully prepared by spray-pyrolysis crystallized into the tetragonal monophase [Fig. 1(a)]. Microscopic examinations show submicronic spherical particles [Fig. 2(a)], dense and homogeneous in chemical composition consisting of primary nanocrystallites of 6.4±0.2 nm for 2.5Y–TZP and 6.0±0.1 nm for 5Sc–TZP. No trace of the monoclinic form was detected by XRD. If one compares the thermal stability of two different scandia doped zirconia, respectively 2 and 5 mol%, exothermal effect assigned to the appearance of monoclinic zirconia is only observed for 2 mol% on cooling while both samples contain 5 wt.% OH amount (Fig. 3). We have previously reported perfect thermal stability of nanometric 2.5Y–TZP in air since it reversibly remains tetragonal using TG/DTA in the 30–1300°C range.[7] Indeed, it is necessary to introduce a larger amount of scandium which presents a smaller ionic radius (0.87 Å) compared to that of yttrium (1.015 Å) in order to stabilize tetragonal

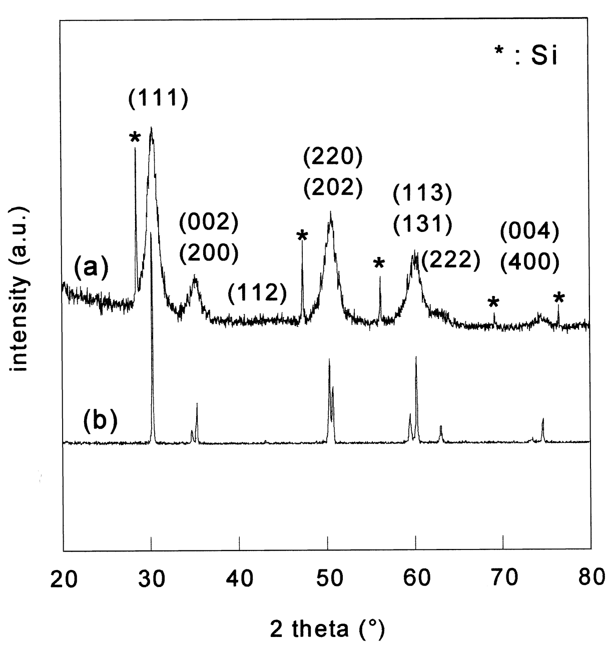

Fig. 1. Typical X-ray diffraction pattern of 5Sc–TZP: (a) as-prepared powder; (b) ceramic.

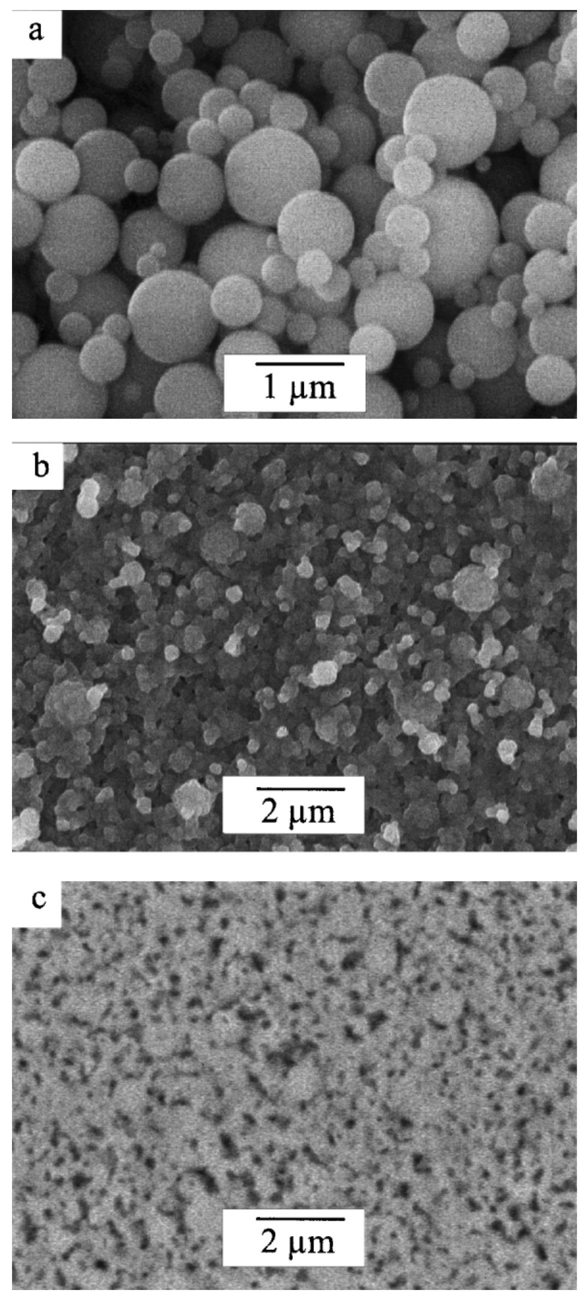

Fig. 2. Morphology of 5 Sc–TZP: (a) powders; (b) ceramic; (c) polished ceramic observed by SEM.

phase. So, the cumulative effect of the dopant steric effect with small crystallite size becomes predominant in stabilization of doped tetragonal zirconia.

With conventional sintering, ceramics prepared from spray-pyrolyzed nanometric powders successfully lead to only 70 nm primary crystallites even after sintering at 1500°C/2 h compared to 80 nm found by Mayo et al.[8] on 3Y–TZP sintered at 1100°C for 1 h. Densities of 2.5Y–TZP and 5Sc–TZP pellets are found to be 96% of the theoretical density. A unimodal distribution of 300 nm average aggregate size was determined by SEM [Fig. 2(b)]. Stoichiometry has been found the same as that of precursor solution within experimental error for 2.5Y–TZP using WDS while only 2.30(3) Sc at.% has been measured in 5Sc–TZP ceramic instead of 3.20 expected. A

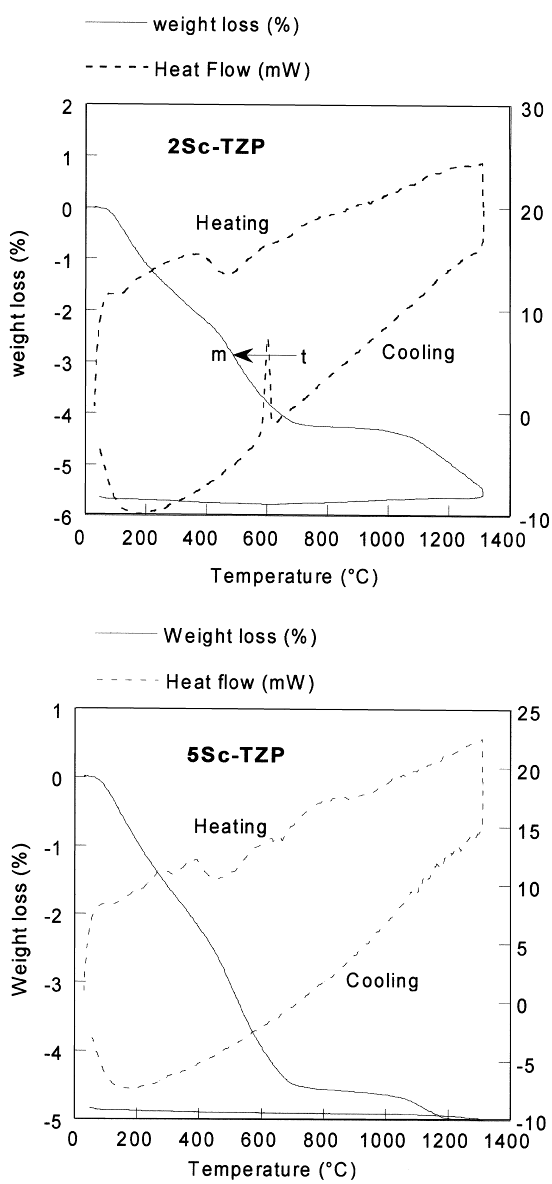

Fig. 3. Simultaneous TG/DTA on 2 Sc–TZP and 5Sc–TZP in the 30–1300°C range in air (10°C min^{-1}).

splitting of TZP diffraction lines is now clearly observed for both batches. The unit-cell parameters changed from $a = 0.50961(4)$ nm and $c = 0.51771(2)$ nm for 2.5Y–TZP to $a = 0.5085(2)$ nm and $c = 0.51620(9)$ nm for 5Sc–TZP. Whatever the nature of dopants, c/a ratio has been found to be 1.015 ± 0.001. Moreover, purity of yttria and scandia doped zirconia samples was verified by WDS: both batches contain only traces of Hf impurity and above all they have been found free of silicon.

The observed separation of the electrolyte impedance from the electrode characteristics indicates that the platinum electrodes perfectly match the outer surface of the pellets. Moreover, this ensures that no additional microstructural defect response, apart from the low frequency blocking effect (LF), was described. All the electrolyte diagrams were easily well separated into two semicircles within an accuracy of 5% (Fig. 4). After impedance spectroscopy, Raman spectrometry (Fig. 5) reveals monophased tetragonal zirconia and no degradation of microstructure has been detected by SEM micrograph. Therefore, the high frequency semicircle (HF) can be regarded as the specific contribution of tetragonal zirconia grain. At 400°C, the specific conductivity σ_b is 6×10^{-5} S cm^{-1} and 1.3×10^{-4} S cm^{-1} for, respectively, 2.5Y–TZP and 5Sc–TZP and, at 600°C, it is respectively 1.7×10^{-3} cm^{-1} and 2.7×10^{-3} S cm^{-1}. As already reported for microcrystalline samples,[9] the specific conductivity of scandia doped zirconia is higher.

Within the investigated temperature range, the related activation energies are 0.94 eV for both samples. The

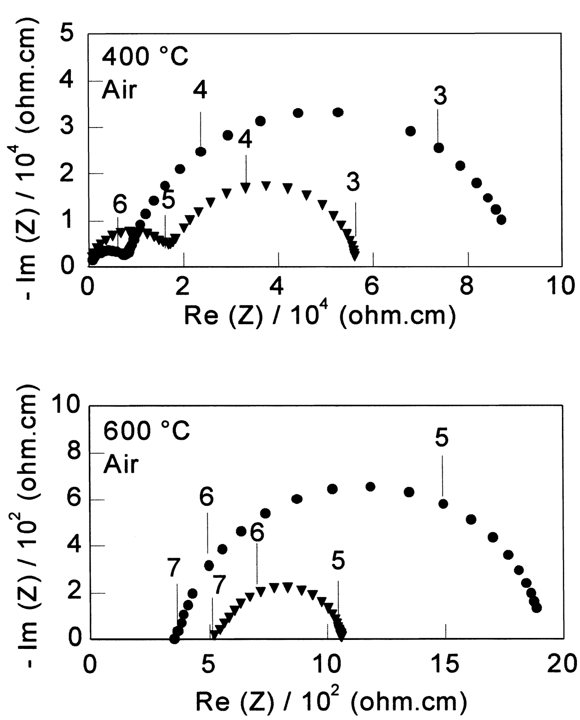

Fig. 4. Electrolyte impedance of 2.5Y–TZP (▼) and 5Sc–TZP (●) at 400°C and 600°C in air. The numbers on diagrams indicate the logarithm of the measuring frequency.

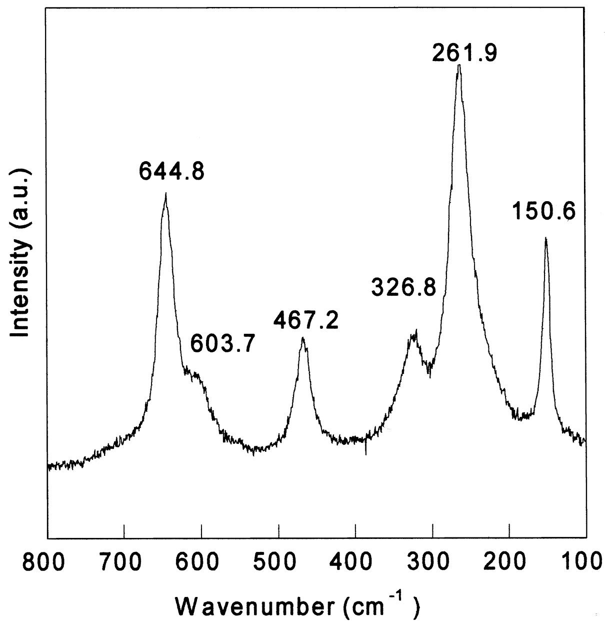

Fig. 5. Raman spectrum of 5Sc–TZP after impedance measurements.

HF semicircle depression angle is always lower than 10°. This value is fairly low and indicates a good homogeneity of the electrical properties of the grains and therefore of their composition, in agreement with SEM and EDX investigations.

Because of nanometric grain size, a large blocking effect is expected. For instance, the average blocking factor α_R has been found to be about 0.8. It is worth noting that it is lower than ones previously determined for nanocrystalline tetragonal zirconia.[3,4] For both specimens, blocked capacitances are 2.7×10^{-9} F at 400°C and 2.3×10^{-9} F at 600°C. Activation energies calculated from the Arrhenius diagram of the blocked conductivity σ_{bl} are 1.25 and 1.09 eV for, respectively, yttria and scandia doped zirconia. These values are found similar to the specific ones. Consequently, the blocking effect is geometric in nature. The LF semicircle depression angle (< 10°) further suggests the homogeneous microstructure of investigated samples. However, a multitude of interaggregate nanoporosities has been observed [Fig. 2(c)]. If one refers to the high purity of studied samples, this porosity is expected to play a significant role in the recorded blocking effect.

4. Conclusion

In the present work, pure tetragonal and nanocrystallized doped zirconia powders of quite exceptional quality have been synthesized by spray pyrolysis with homogeneity in chemical composition and good thermal stability in the 300–700°C temperature range in air. Microstructural results mainly show good homogeneity in composition in both ceramics and good homogeneity in aggregate size (≈300 nm) of 70 nm primary crystallites. Impedance spectroscopy measurements confirm this excellent quality of TZP ceramics free of silicon traces. Moreover, interaggregate nanoporosities contribute to the predominant low frequency contribution in impedance diagrams. No microstructural degradation of ceramics has been detected by SEM after impedance measurements.

Our future experiments will aim at enhancing the grain boundary conductivity focusing on the shrinkage of deleterious nanoporosities with minimal grain growth. Different densification methods will be used such as hot isostatic pressing and dynamic compaction.

References

1. He, Y. J., Winnubst, A. J. A., Burggraaf, A. J., Verweij, H., van der Varst, P. G. and de With, B.G., Grain-size dependence of sliding wear in tetragonal zirconia polycrystals. *J. Am. Ceram. Soc.*, 1996, **79**, 3090–3096.
2. Weppner, W., Tetragonal zirconia polycrystals- a high performance solid oxygen ion conductor. *Solid State Ionics*, 1992, **52**, 15–21.
3. Ramamoorthy, R., Sundararaman, D. and Ramasamy, S., Ionic conductivity studies of ultrafine-grained yttria stabilized zirconia polymorphs. *Solid State Ionics*, 1999, **123**, 271–278.
4. Mondal, P., Klein, A., Jaegermann, W. and Hahn, H., Enhanced specific grain boundary conductivity in nanocrystalline Y_2O_3-stabilized zirconia. *Solid State Ionics*, 1999, **118**, 331–339.
5. Badwal, S. P. S., Zirconia-based solid electrolytes: microstructure, stability and ionic conductivity. *Solid State Ionics*, 1992, **52**, 23–32.
6. Djurado, E. and Meunier, E., Synthesis of doped and undoped nanopowders of tetragonal polycrystalline zirconia by spray-pyrolysis. *J. Solid State Chemistry*, 1998, **141**, 191–198.
7. Djurado, E., Dessemond, L. and Roux, C., Phase stability of nanostructured tetragonal zirconia polycrystals versus temperature and water vapor. *Solid State Ionics*, 2000, **136–137**, 1249–1254.
8. Mayo, M. J., Processing of nanocrystalline ceramics from ultrafine particles. *Int. Mater. Rev.*, 1996, **41**, 85–115.
9. Badwal, S. P. S., Effect of dopant concentration on electrical conductivity in the Sc_2O_3–ZrO_2 system. *J. Mater. Sci.*, 1987, **22**, 4125–4132.