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# PAC characterization of Gd and Y doped nanostructured zirconia solid solutions

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#### Abstract

A perturbed angular correlation (PAC) study as a function of temperature has been carried out on spray pyrolysis-derived powders and compacts of  $2.5 \text{ mol}\% \text{ Y}_2\text{O}_3$ -ZrO<sub>2</sub> and  $2 \text{ mol}\% \text{ Gd}_2\text{O}_3$ -ZrO<sub>2</sub> nanostructured tetragonal zirconias. The powders undergo the ordinary thermal transformation between the two known defective *t'*- and regular *t*-tetragonal forms and also a partial and irreversible change to an ordered cubic configuration. The dynamical nature of the *t'*-form leads to an activation energy of about 0.15 eV for the oxygen vacancies movement. The as-obtained compacts do not exhibit any known cubic nanostructure but some additional contributions. In both of them a hyperfine component assigned to the orthorhombic phase is determined. In the smaller cation Y doped ceramic a small amount of monoclinic phase reflects an incomplete stabilization. © 2006 Published by Elsevier B.V.

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# 1. Introduction

Cubic  $Y_2O_3$  stabilized zirconia (8YSZ) is commonly used as electrolyte in high-temperature solid oxide fuel cell (SOFC). Zirconia presents different allotropic forms as a function of grain size, nature of the dopant (charge, ionic radius) and dopant content. It is well known that when zirconium is substituted by cations of lower valence an enhancement of the anionic conductivity is observed since mobile oxygen vacancies are created for charge compensation. The ionic conductivity of doped zirconia strongly depends on the crystal structure, the microstructure, the temperature and the grain size. Structural changes in zirconia ceramics characterized by an average grain size of 60 nm have been recently reported for rare-earth doping [1]. Internal tensile stresses as high as 1.3 GPa were previously quantified in tetragonal 3 mol% doped ZrO<sub>2</sub> when the dopant ionic radius increased from Sc, Yb, Y, Gd to Sm [2].

In this context, a systematic study of the influence of Y and some rare-earth (La, Pr, Sm, Gd, Dy and Er) dopant content and of their ionic radius size on the structural changes in nanocrystalline doped zirconia ceramics has been undertaken by our group. In this first work, the thermal stability up to 900 °C of two nanostructured tetragonal zirconias doped with, respectively, 2.5 mol%  $Y_2O_3$  and 2 mol%  $Gd_2O_3$  have been studied using mainly the perturbed angular correlations (PAC) technique. The aim is to determine the nanoconfigurations content and stability of powders and compacts as well as the sintering effect.

### 2. Experimental

Powder samples were prepared by spray pyrolysis [3] at 600 °C starting from a precursor solution based on zirconyl and yttrium or gadolinium nitrates dissolved in deionized

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water with a  $2.5 \times 10^{-2}$  mol L<sup>-1</sup> concentration. This solution was atomized using an ultrasonic atomizer, then pyrolysed in a tubular furnace. This method allowed dense and compositionally homogeneous nanocrystalline powders to be obtained at low temperature, with good purity, in which no amorphous phase was detected by either X-ray diffraction (XRD) or Raman spectroscopy. In the following, the powders will be referred to as ZYP and ZGdP, respectively, for 2.5 mol% Y<sub>2</sub>O<sub>3</sub> and 2 mol% Gd<sub>2</sub>O<sub>3</sub> doped ZrO<sub>2</sub>. The compacts were obtained by pressing the powders at 300 MPa and sintering for 2 h at 1500 °C in air. They will be referred, respectively, to as ZYC and ZGdC.

XRD data were collected on a Philips PW1710 diffractometer using Cu-K $\alpha$  radiation and a graphite monochromator. Data were recorded in the range 20°  $\leq$  $2\theta \leq 80^{\circ}$  in 0.02° steps with a counting time of 2 s per step. Average crystallite size was calculated from the half-width at half maximum (HWHM) of the (1 1 1) most intense line for stabilized zirconia ( $2\theta \approx 30^{\circ}$ , instrumental broadening of 0.1297°), using the Scherrer equation [4] and having taken into account the microstrain contribution. The interplanar spacing was also determined from the angular position of the same diffraction line. Diffractograms were obtained on the as-prepared powders, compacts and on the radioactive powders two years after the PAC experiments.

In order to anticipate eventual thermal changes and their nature, differential scanning calorimetry (DSC) experiments were carried out on the powders at  $30 \,^{\circ}C/min$  between room temperature (RT) and  $700 \,^{\circ}C$  in air using a Shimadzu 50 equipment.

A PAC experiment consists in the determination of the hyperfine interaction between nuclear moments and extranuclear fields by measuring the angular distribution of emitted radiations. The 133–482 keV  $\gamma$ – $\gamma$  cascade occurring during <sup>181</sup>Hf decay provides an adequate probe (the quadrupole moment of the intermediate nuclear state) to investigate the electric field gradients (EFG) in zirconia ceramics. Since zirconium contains natural Hf impurities, probes are directly obtained by irradiating the material with thermal neutrons. Data fitting of the experimental spin rotation curves  $A_2G_2(t)$  results in the determination of the quadrupole frequency  $\omega_0$ , its distribution width  $\delta$  and the asymmetry parameter  $\eta$  of the EFG acting on the probes. Possible dynamical effects are taken into account through a relaxation parameter  $\lambda$  associated to the changes of the EFG during the interaction time. Details can be found elsewhere [5,6].

PAC measurements were performed on both, powders and pellets, at RT 300, 500, 700, 900 °C and finally after cooling down to RT. The equipment consisted of four  $BaF_2$  detectors of 0.7 ns of time resolution.

### 3. Results and discussion

The XRD results of the as-prepared powders, of crystallite size  $\approx 60$  Å, indicate the presence of a single-phased tetragonal zirconia (Fig. 1(a)). Those obtained after

PAC measurements (Fig. 1(b)) reveal an increase in the crystallite size ( $\approx 250$  Å). Despite this grain size increase, tetragonal zirconia is still present in large majority. Interplanar spacings of the (111) reflection were determined to be 2.96 Å for ZYP and 2.97 Å for ZGdP. The respective values of ionic radii (Gd<sup>3+</sup> = 1.06 Å, Y<sup>3+</sup> = 1.02 Å), suggest the substitutional nature of the obtained zirconia solid solutions. Traces of monoclinic zirconia were also detected.



Fig. 1. (a) XRD patterns of the as-prepared powders. (b) XRD patterns of the powders after PAC measurements.



Fig. 2. DSC heating curves (solid lines) in ZYP and ZGdP powders. Dashed lines are manual base lines drawn to better understand the results.

XRD patterns and Raman spectra of compacts (not shown here) display undoubtedly tetragonal zirconia single phase.

DSC curves of the powders reveal the occurrence of some irreversible changes for temperature above 250 and  $450 \,^{\circ}$ C (see Fig. 2).

Regarding PAC results on the powders, shown in Fig. 3 (PAC spin rotation curves) and Fig. 4 (fitted quadrupole parameters), three already known interactions were determined over the whole thermal range investigated: the disordered configuration depicting the tetragonal defective t'-form [5] that involves nearest-neighbor oxygen vacancies created for charge compensation, the ordered configuration with quadrupole parameters similar to those of the equilibrium tetragonal phase [5] which depicts the regular tetragonal *t*-form and the ordered cubic nanoconfiguration Xc [6]. At RT, in agreement with XRD results, the two systems are described by tetragonal nanoconfigurations, only the t'-form in ZGdP and the t'-form and traces of the *t*-form in ZYP.

The thermal behavior of the quadrupole parameters is similar for the two powders. At low temperature the



Fig. 3. Spin rotation curves  $A_2G_2(t)$  determined for ZYP and ZGdP powders at increasing measurement temperatures.



Fig. 4. PAC results in Y and Gd doped powders. Symbols indicate:  $\bullet$ : *t*'-form,  $\circ$ : *t*-form and  $\blacksquare$ : Xc- form.

usually reported  $t' \rightarrow t$  exothermic transformation [7] occurs (about 20%), probably connected with the first DSC irreversible change. At higher temperatures, the appearance of the Xc-form reveals that a tetragonal to cubic partial (about 15%) phase transition has taken place. The quadrupole frequencies for the two tetragonal forms determined in ZGdP are slightly higher than those in ZYP. This fact, together with the evidence that the solid solutions are mainly substitutional, could be related to the larger ionic radius of  $Gd^{3+}$  as compared with that of  $Y^{3+}$ . On cooling, the transformations occurring upon heating do not revert (the relative fractions maintain their high temperature values). No monoclinic phase was detected contrary to XRD. This discrepancy could be due to ageing effects because XRD was performed a long time after PAC experiments.

Fig. 5 shows the PAC spectra for the compacts and Fig. 6, the thermal evolution of the relative fractions and quadrupole parameters fitted for the different interactions found. The presence of four interactions can be observed, three of them being common to both compacts: the major t'- (present in about 60%) and the *t*-tetragonal forms and a new one of quadrupole frequency similar to that of the monoclinic phase but of higher asymmetry parameter. This new interaction has been assumed to depict the orthorhombic zirconia phase (o-phase), which is crystallographi-



Fig. 5. Spin rotation curves  $A_2G_2(t)$  determined for ZYC and ZGdC compacts at increasing measurement temperatures.

cally related to the monoclinic polymorph. This latter was already found in some other doped zirconias in high temperature and pressure conditions [8]. The fourth interaction in ZYC corresponds to monoclinic zirconia, thus reflecting an incipient destabilization. In ZGdC, on the other hand, no assignment could be proposed for the additional contribution.

As temperature increases, all interactions in ZGdC remain, the only change observed being a pronounced  $t' \rightarrow t$  transformation from 700 °C. In ZYC two additional changes are detected: over 500 °C the o-phase disappears and at 900 °C (close to the temperature of the  $m \rightarrow t$  transition) the monoclinic phase assists the increase of the *t*-form. No transformation to any of the known cubic form occurs in either compact. Regarding the *t'*-form, the quadrupole frequency in ZYC and the asymmetry parameter in ZGdC are clearly different from those determined for the similar defective nanoconfiguration in the present as in other zirconia powders [5–7].



Fig. 6. PAC results in Y and Gd doped compacts. Symbols indicate  $\bullet$ : *t*'-form,  $\circ$ : *t*-form and  $\not\approx$ : monoclinic phase,  $\bullet$ : orthorhombic form and  $\triangleleft$ : unknown interaction.

On cooling, both compacts show that the transformation from the t'-form to the t-form partially reverts and in ZYC, the o-phase reappears.

All PAC results indicate that the defective t'-form is that which reflects the oxygen vacancies movement. In fact, doped zirconias with aliovalent oxides contain structural oxygen vacancies appeared for charge balance and it is already known that the vacancy-hopping causes EFG fluctuations in stabilized zirconias. Whenever the temperature dependence of the relaxation parameter  $\lambda$  follows an Arrhenius law, an activation energy for the jumping process can be derived [9]. In the powders, this process seems to obey a slow diffusion mechanism and the present preliminary results yield an activation energy of about 0.15 eV for vacancies moving over the high temperature range. For compacts, additional PAC experiments become essential to elucidate this point.

# 4. Conclusions

A PAC investigation between RT and 900 °C has been carried out on powders prepared by spray pyrolysis and compacts of 2.5 mol% Y<sub>2</sub>O<sub>3</sub> doped ZrO<sub>2</sub> and 2 mol% Gd<sub>2</sub>O<sub>3</sub> doped ZrO<sub>2</sub> nanostructured tetragonal zirconia solid solutions.

In the powders, the substitutional solid solution is mostly described by the tetragonal defective t'-form. When temperature is increased, this configuration partially and irreversibly transforms in two ordered forms of tetragonal (the *t*-form) and cubic (the  $X_C$ -form) structures. No monoclinic phase is observed except after a long ageing time. The dependence on the ionic radii could be reflected in the slightly more intense EFGs determined for the tetragonal forms in ZGdP. Oxygen vacancies seem to obey a slow diffusion movement involving a low activation energy.

The compacts differ from the powders in the atypical values of the t'-form hyperfine parameters, the absence of a cubic nanoconfiguration and the presence of small amounts of other contributions. The effects of high pressure and temperature inherent in their preparation is reflected, among others, by the fact that part of the lattice has become probably orthorhombic. The effect of the dopant cation size, in turn, could be related to the incomplete stabilization determined in the solid solution

of smaller dopant cation. Relative to the thermal evolution, except for the unavoidable t'-form to t-form transformation, the Gd doped compact evidences a more stable phase content.

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