

## Short range investigation of sub-micron zirconia particles

**M C Caracoche, J A Martínez**

Departamento de Física, IFLP, Facultad de Ciencias Exactas, CICPBA, Universidad Nacional de La Plata, Argentina

**P C Rivas**

IFLP-CONICET, Facultad de Ciencias Agrarias y Forestales, Universidad Nacional de La Plata, Argentina

**F Bondioli, V Cannillo**

Dipartimento di Ingegneria dei Materiali e dell' Ambiente, Facoltà di Ingegneria, Università di Modena e Reggio Emilia, Italy

**A M Ferrari**

Dipartimento di Scienza e Metodi dell' Ingegneria, Università di Modena e Reggio Emilia, Italy.

E-mail: [cristina@fisica.unlp.edu.ar](mailto:cristina@fisica.unlp.edu.ar).

**Abstract.** The Perturbed Angular Correlations technique was used to determine the configurations around Zirconium ions and their thermal behavior in non-aggregated sub-micron zirconia spherical particles. Three residues containing- Zr surroundings were determined for the non-crystalline starting particles, which were identified under the assumption of a certain chemical reactions sequence during synthesis. While the one made up mainly by hydroxyl groups was common to both samples, the two involving mainly organic residues were particle size dependent. Upon crystallization, both samples stabilized in the t'- and t- tetragonal forms and the Xc-cubic form but their amounts and temperatures of appearance were different. On heating, the structure of the smaller particles became gradually monoclinic achieving total degradation upon the subsequent cooling to RT.

### 1. Introduction

A growing demand for improved performance of ceramics in loadbearing and functional applications has raised the importance of chemical purification and processing of the starting powders. In particular, ceramic powders with high purity consisting of sub-micron spherical, unagglomerated, monosized particles are desirable for making high quality advanced ceramics. In the present paper, configurations around Zr(Hf probes) in spherical sub-micron zirconia particles and their thermal evolution have been determined using the Perturbed Angular Correlation (PAC) nuclear technique. From PAC spectra, the quadrupole parameters of the electric field gradient (EFG), i.e. the quadrupole frequency, the asymmetry parameter and the frequency distribution width, are obtained. Due to the extremely localized character of the EFG ( $\propto r^{-3}$ ), several non-equivalent lattice sites as well as their relative fractions can be determined. Hyperfine interactions of equilibrium and metastable phases of zirconia are already known [1-2].

## 2. Samples preparation and characterization

Zirconia particles were obtained by the sol-gel method using tetra-*n*-propylzirconate (TPZ), capronic acid (CA) and ethanol (EtOH). Synthesis was performed by slow addition of an alcoholic solution containing CA (0.016 M) and TPZ (0.1M), previously reacted for 30 min at room temperature, to a mixture of EtOH and water (50:1 molar ratio). Particle precipitation was carried out at 40 °C for 35 min under vigorous magnetic stirring. After evaporation of volatiles (12h at 100 °C), particles showing different sizes and size distribution were obtained depending on the water concentration (0.35 M or 0.6 M) [3]. Particle morphology was examined by transmission electron microscopy, TEM (JEM 2010). To estimate the particle size distribution, image analysis was carried out on TEM micrographs. The specific surface area of the powders was obtained by the B.E.T. method (Gemini 2360). Residual carbon content was determined using a Carlo Erba CHNS-O analyzer. X-ray diffraction (XRD) data were collected at room temperature by a Philips 3710 diffractometer over the 20-80° 2 $\theta$  range. The diffractometric thermal behavior of the powders was investigated using a Philips X'Pert Pro in the 20-1000°C temperature range. The bulk thermal behavior of the synthesized samples was studied by thermogravimetric and differential thermal analyses in air at a heating rate of 10 °C/min, using a simultaneous TG/DTA apparatus (Netzsch STA409). For the PAC experiment, Hf probes were produced by thermal neutron irradiation of the samples. Measurements were carried out at RT and at increasing temperatures up to 1000 °C. A final RT measurement was also performed.

## 3. Results

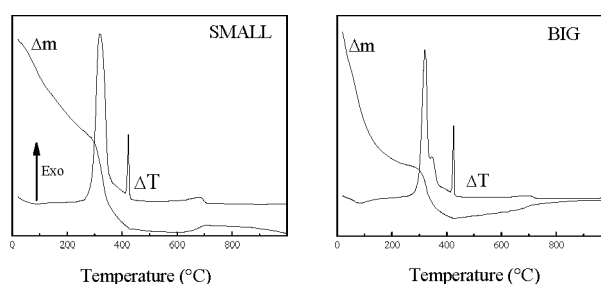
Average particle diameters determined out of TEM images, specific surface areas and residual

**Table I.** Results obtained by TEM, BET and Elemental analysis.

Sample	TEM mean particle diameter (nm)	B.E.T. specific surface area (m <sup>2</sup> /g)	Carbon content (wt%)
SMALL	220 ± 40	102.9	7.2
BIG	550 ± 60	9.6	10.8

carbon content of the powders are reported in Table I. TEM micrographs revealed non aggregated spherical sub-micron particles and narrow size distributions for both samples. Particles prepared with the lower water concentration exhibited greater sizes. According to their relative mean particle sizes, the two powder samples investigated were named SMALL and BIG.

DTA curves (figure 1) evidence the organic residues elimination (a double peak for BIG) over

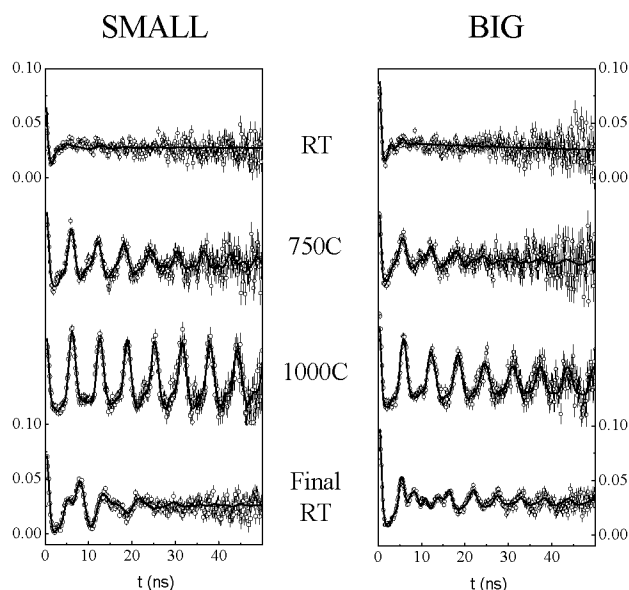


**Figure 1.** TG-DTA results obtained for both samples.

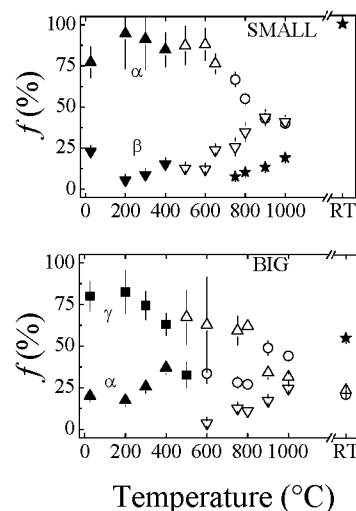
300 °C and the exothermic crystallization peak at about 430 °C. Close to 700 °C a change in the baseline can be observed too. Except for the crystallization peak, DTA signals are simultaneous with TG mass changes. Mass losses up to crystallization sum up 23 and 33% for SMALL and BIG respectively, in similar proportions to the carbon content determinations (see Table I). Over 600 °C, both samples show an apparent mass gain. The starting diffractograms revealed the rather amorphous nature of the obtained particles. The crystalline oxygen defective tetragonal structure ZrO<sub>1.95</sub> in both samples was present at 500°C. At 600°C, the existence of a small amount of monoclinic phase in SMALL could be observed. Results at 700°C showed that the

defective tetragonal structure had transformed to the regular tetragonal  $\text{ZrO}_2$ . Figure 2 displays selected spin rotation curves and in figure 3 the thermal evolution of the relative fractions of the hyperfine components for BIG and SMALL is shown. PAC results for SMALL indicate, from RT to 400 °C, the presence of two interactions, hereinafter named  $\alpha$  (full up triangle) and  $\beta$  (full down triangle), being  $\alpha$  clearly dominant.

Between 500 and 650 °C the interactions describing the defective tetragonal  $t'$ -form [1] (open up triangle) and the cubic Xc-form [3] (open down triangle), replace the former ones. At higher temperatures it is seen that the  $t'$ -form has disappeared to give rise to the tetragonal t-form (open circle) and to increasing amounts of both the Xc-form and of an interaction which depicts a



**Figure 2.** Selected PAC spectra obtained at indicated temperatures.



**Figure 3.** Relative fractions of the different hyperfine components.

somewhat distorted monoclinic phase (full star). At 1000 °C the sample is described by equal amounts of the tetragonal t- and cubic Xc-forms and 15% of the monoclinic polymorph. Upon cooling to RT the sample has become entirely monoclinic. PAC results in BIG show the presence of the  $\alpha$  interaction accompanied by a great amount of a new one hereinafter called  $\gamma$  (full square). At 500 °C  $\alpha$  has disappeared,  $\gamma$  is clearly decreasing and the appearance of a great amount of the  $t'$ -form is evidenced. The t- and Xc-forms are present from 600 °C on and over 800 °C they grow at the expense of the defective  $t'$ -form. Cooling down from 1000°C, the sample is half monoclinic and half tetragonal, exhibiting nearly equal amounts of both t- and  $t'$ -tetragonal configurations.

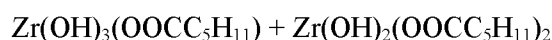
#### 4. Discussion

In order to discuss PAC results in the as-prepared samples and their thermal evolution, a simple model for the reactions occurred during synthesis will be assumed. According to Lerot et al.,[4] in the alcoholic solution of CA and TZP some substitutions of  $(\text{OC}_3\text{H}_7)$  by  $(\text{OOC}_5\text{H}_{11})$  groups could have taken place. Since the complete replacement was avoided due to the very low CA/TZP ratio employed, most probably the following reaction occurred:

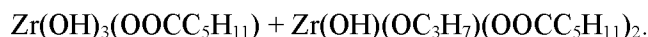


Lerot has also reported that the subsequent water addition causes the hydrolysis of exclusively the alkoxide groups. Thus, assuming that water has hydrolysed mainly zirconium-alkoxy

bonds belonging to the less acidified species, this process would have led for SMALL (abundant water) to the species:



and for BIG (scarce water) to the species:



Accordingly, PAC results evidence that the as-prepared SMALL and BIG samples exhibit a common interaction ( $\alpha$ ), the major amount of which was found in SMALL. Thus, it has been assumed that this interaction describes the configurations around Zr of the hydroxyl rich and common to both samples,  $\text{Zr(OH)}_3(\text{OCC}_5\text{H}_{11})$  species. In turn,  $\beta$  in SMALL would describe the configurations in the  $\text{Zr(OH)}_2(\text{OCC}_5\text{H}_{11})_2$  species and  $\gamma$  in BIG, would describe configurations typical of the  $\text{Zr(OH)(OC}_3\text{H}_7)(\text{OCC}_5\text{H}_{11})_2$  species, the richest one in organic groups. The higher carbon content determined in BIG supports the previous interpretation. On heating,  $\alpha$ ,  $\beta$  and  $\gamma$  interactions disappear over a thermal range fairly coincident with that over which the firing and crystallization of organic residues is revealed. Additionally, the two different carbon chains modeled for BIG match the firing of two different organic residues as suggested by the DTA. Regarding the crystalline forms, even when the  $t'$ -,  $t$ - and  $Xc$ - forms appear in both SMALL and BIG, their temperatures of appearance and thermal evolution are somewhat different. Relative to stabilization, some evidences must be pointed out. Upon crystallization the  $t'$ -form is predominant in both samples, as revealed by XRD and PAC results at 500°C. But distinctly, it disappears above 650°C in SMALL and is always present in BIG though reduced to a minor contribution above 800°C. The decrease in the amount of the  $t'$ -form is known to take place by the filling of oxygen vacancies [5] through atmospheric oxygen absorption, in agreement with the mass gain determined by TG and the change of the XRD pattern between 500 and 700°C. Knowing the role played by the surface in chemical reactivity, the particles of larger specific area, SMALL, are more proclive to absorb the oxygen that heals the stabilizing defects, thus leading to the  $t'$ - to  $t$ - destabilizing transformation. Once the regular  $t$ -form has appeared, the ordinary thermally induced- crystallite growth and stress elimination are most probably the cause for the occurrence of the distorted monoclinic form. This latter form can be thought as a monoclinic structure involving some types of defects as vacancies or residual hydroxyl groups that, as is occurs in the tetragonal phase[6,7], do not produce important crystallographic modifications. Finally, the complete degradation of SMALL when cooling down to RT is the expected consequence of the important amount of monoclinic phase preexisting at 1000°C. On the other hand, the lower reactivity in BIG seems to impede the oxygen absorption that causes the removal of  $t'$ -form. Thus, cooling down to RT, the formation of the monoclinic phase is hardened and only half of the sample becomes degraded.

## 5. Conclusions

The highly localized PAC technique allowed the determination of three different Zr surroundings in the non-crystalline starting structures. Assuming a plausible chemical sequence during synthesis, the one common to both samples was thought as involving mainly hydroxyl groups. The other two resulted from the presence of different organic residues and were present each one in each sample. In the bigger spheres, these organics rich configurations were predominant and probably consisting of two varieties of Zr-ligand bonds. Crystallization led to the formation of both tetragonal  $t'$ - and  $t$ - forms and the cubic  $Xc$ - form. The temperature of appearance, phase content and thermal behavior of the crystalline products depended on the different residues containing- precursors. The smaller particles degraded to the monoclinic phase gradually when heating and totally on cooling. On the contrary, the lower specific surface area of the bigger spheres favored the permanence of the oxygen defective  $t'$ - form on heating, thus leading to a partial degradation on cooling. According to these results, it seems that the smaller particles are less suitable for load bearing applications for which the tetragonal phase permanence is decisively required.

**References**

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