

# Synthesis and Characterization of Nanocrystalline Powders for Partially Stabilized Zirconia Ceramics

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## Abstract

*In this work, wet-chemical methods to obtain yttria or calcia-doped zirconia powders for partially stabilized zirconia ceramics are presented. They are based on pyrolysis of nitrate solutions with the addition of citric acid or glycine as a fuel. Powders were characterized by X-ray diffraction and scanning electron microscopy, finding that tetragonal and cubic phases are stabilized at room temperature because of the small crystallite size (about 10–20 nm). Ceramic samples obtained after uniaxial pressing and sintering in air were characterized by density and Vickers microhardness measurements in order to evaluate the final material performance. © 1998 Elsevier Science Limited. All rights reserved*

## 1 Introduction

It is well-known that zirconia-based ceramics are widely used because of their electrical and mechanical properties. On the one hand, they exhibit a high ionic conductivity at elevated temperatures and they are applied in electrochemical cells such as fuel cells, oxygen sensors or oxygen pumps.<sup>1</sup> On the other hand, the discovery by Garvie, *et al.*<sup>2</sup> of transformation toughened zirconias (as  $Y_2O_3$ , CaO or MgO-doped partially stabilized zirconia ceramics) generated a big technological interest, resulting in the development of new materials, as  $ZrO_2-Al_2O_3$  or  $ZrO_2$ -mullite composites.<sup>3</sup>

Partially stabilized zirconia (PSZ) ceramics are useful because of both types of properties. In the case of electrochemical cells, the high sensitivity of

fully stabilized zirconia (cubic phase) to thermal shock has been a serious problem, which could be overcome by the use of PSZ cells. They also have important engineering applications because of their very high strength and fracture toughness. These exceptional mechanical properties are attained by a process known as ‘transformation toughening’. Briefly, this effect is due to the ability of zirconia precipitates to transform from tetragonal to monoclinic phase under the influence of a propagating crack.<sup>3</sup>

PSZ ceramics generally consist of a matrix of cubic phase zirconia with a dispersion of tetragonal and/or monoclinic precipitates, as in calcia-doped PSZ (Ca-PSZ) or magnesia-doped PSZ (Mg-PSZ). Cubic grains are bigger than tetragonal or monoclinic ones, often causing an important porosity. In the case of yttria-doped PSZ (Y-PSZ), sintering can be performed at lower temperatures, allowing fine grains so that high strength ceramics can be produced. In Y-PSZ ceramics a second tetragonal phase, called  $t'$ , has been found. It is generally called as ‘non-transformable’ because of its resistance to undergo the transformation to monoclinic symmetry. This  $t'$  phase exhibits a higher yttria content than the conventional  $t$  one, so it has a smaller tetragonality (smaller  $c/a$  ratio) and for this reason it is very difficult to discriminate between  $t'$  and cubic phases.<sup>4</sup>

There are several methods for the preparation of powders but the advantages of wet-chemical methods are now well established. Such powders are generally homogeneous in composition, very reactive and able to be sintered at lower temperatures than those usually employed, yielding materials with higher density and improving mechanical and electrical properties. The aim of this work is to propose a method based on the gellification by citric acid or glycine of a zirconyl nitrate solution,

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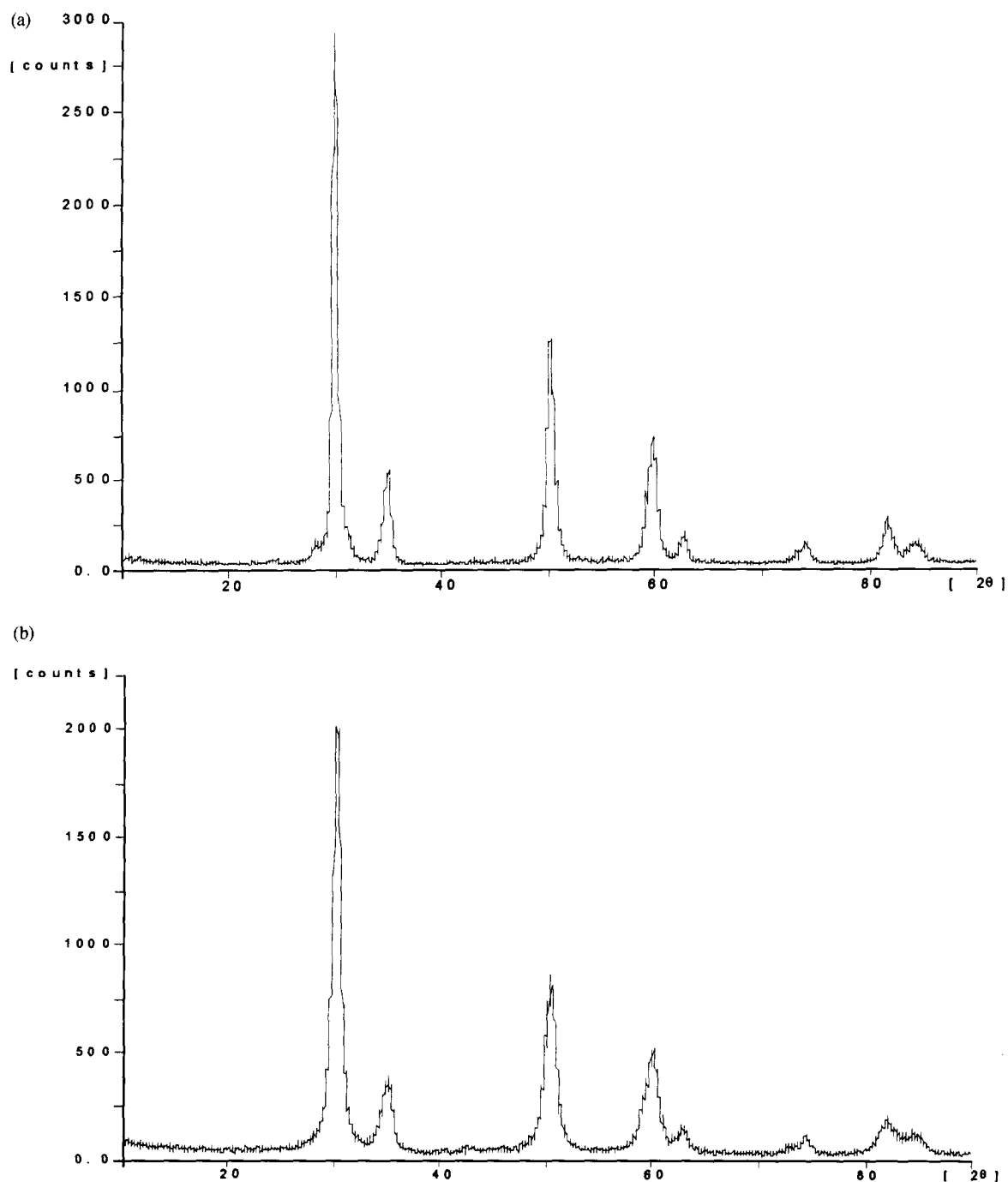


Fig. 1. Typical XRD spectra of milled powders: (a) Y-PSZ, (b) Ca-PSZ.

followed by a pyrolytic process. This method has been employed to obtain nanocrystalline Y-PSZ and Ca-PSZ powders, allowing the stabilization at room temperature of the high temperature tetragonal and cubic phases because of the small crystallite size (about 10–20 nm). In the case of Y-PSZ powders, ceramics samples were obtained in order to evaluate final material performance.

## 2 Experimental Procedure

Merck zirconium oxychloride and Riedel-de Haën yttrium oxide (or Merck calcium oxide), in a ratio corresponding to the final composition of  $ZrO_2$ –

5.0% mol  $Y_2O_3$  (or  $ZrO_2$ –8.0% mol CaO) were dissolved in an excess of Merck nitric acid. Chlorine was eliminated through evaporation thus obtaining a nitrate solution with a nitric acid excess

Table 1. Powder characterization results

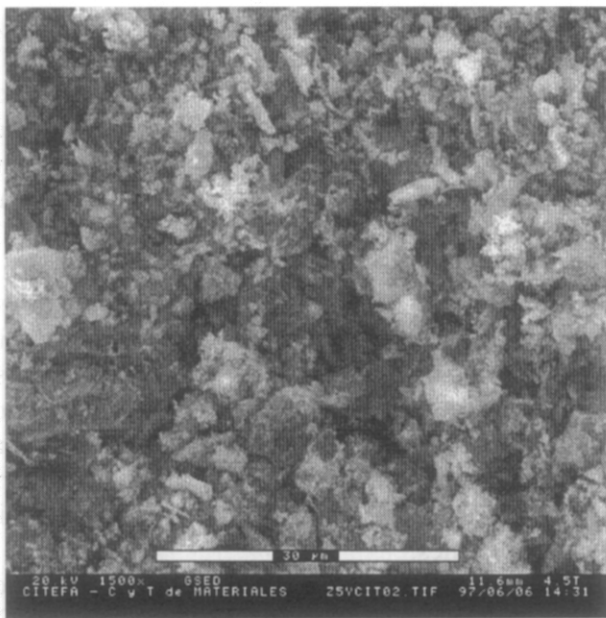
Powder and method	Crystallite size (nm)	Monoclinic content (%)
Y-PSZ, citric acid	16 ± 1	2–3
Y-PSZ, glycine	15 ± 1	Absent
Ca-PSZ, citric acid	10 ± 1	Absent
Ca-PSZ, glycine	14 ± 1	1–2

(it is not possible to use commercial zirconyl nitrate because of the difficulties to control the initial water content of this salt). After a dilution to the original volume, Merck citric acid and glycine (in a proportion of 1–2 mol of those additives per mol of metal atom) were added to form two different solutions. The pH of the citric solution was adjusted between 6 and 7 by using a diluted solution (1:1) of Merck ammonium hydroxide, while this step was intentionally omitted in the glycine solution to avoid an early precipitation. All mentioned reagents were p/a grade.

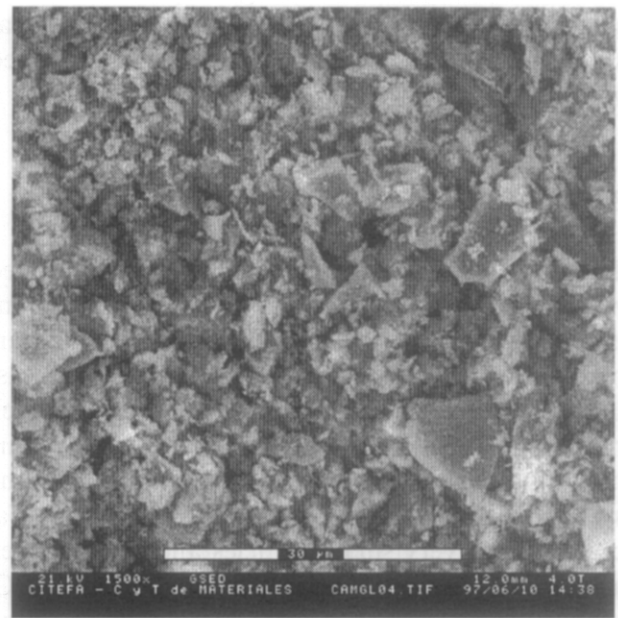
These solutions were then evaporated on a hot plate (300°C) and concentrated until a gel consistency was reached. Further heating desiccates it

causing a violent autoignition burning to gray ashes. They were then heated at 350°C in an open-air oven for an hour to eliminate the carbonaceous impurities and, after a calcination at 700°C for 2 h, a white, pure material with a foamy aspect was obtained. Finally, It was milled with zirconia balls in ethanol, giving a fine white powder.

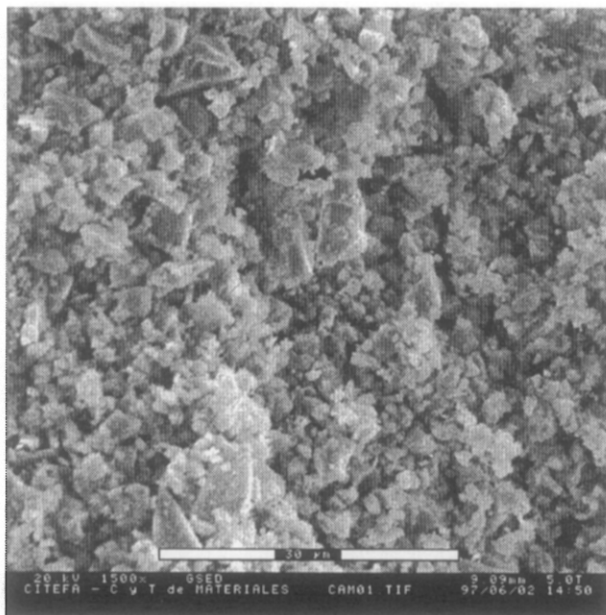
The powders were characterized by X-ray diffraction (XRD) using a PW 3710 Philips diffractometer (Cu  $K\alpha$  radiation) to identify the phases and to determine the crystallite size by using the standard X-ray line broadening method<sup>5</sup> ( $Al_2O_3$  powder with particles greater than 25  $\mu m$  was used to determine instrumental broadening). In order to distinguish the existing phases, spectra



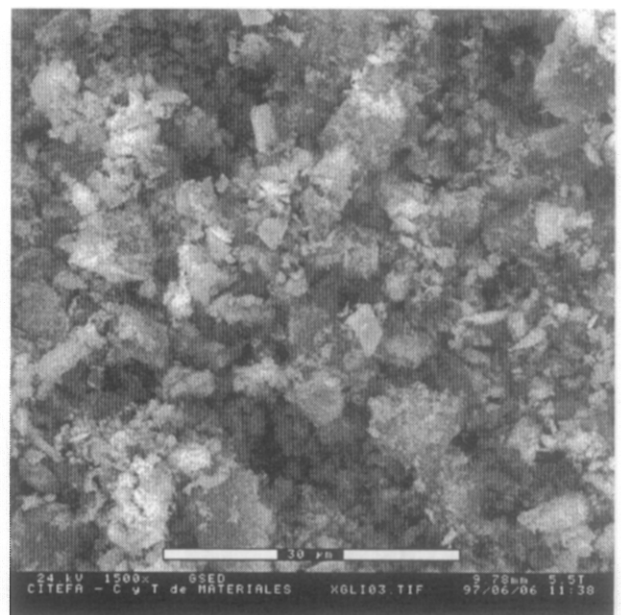
(a)



(a)



(b)



(b)

**Fig. 2.** ESEM micrographs showing aggregates in citric acid method powders: (a) Y-PSZ, (b) Ca-PSZ. The bar corresponds to 30  $\mu m$ .

**Fig. 3.** ESEM micrographs showing aggregates in glycine method powders: (a) Y-PSZ, (b) Ca-PSZ. The bar corresponds to 30  $\mu m$ .

of the angular regions 26–33° and 71–76° were used, the first one to determine monoclinic content and the second one to identify high temperature phases.<sup>3,4</sup>

Observations of the powder morphology were performed in an ElectroScan 2010 environmental scanning electron microscope (ESEM) and the composition was verified by energy dispersive analysis with the EDAX microprobe of a Philips 515 electron scanning microscope (SEM).

Y-PSZ cylindrical specimens (1.0 cm diameter and 0.2–0.3 cm height) were uniaxially pressed at 200 MPa and sintered in air at 1500–1600°C for 4 h. The phases in these samples were identified by XRD (the same angular regions were studied) and their microstructure was imaged by ESEM. Density was evaluated by weight and dimension measurements, and their microhardness was performed with a Leco H-400-G Vickers indenter.

### 3 Results and Discussion

The proposed method for yttria or calcia-doped zirconia powders involves a combustion mechanism, producing  $\text{NO}_x$  gasses and heat. An exothermic redox reaction takes place with a fast increment in the temperature of the system, which burns until the reactants are fully consumed. During this pyrolytic process, the temperature of the system reached 400–500°C. Then, the material cracked into very small particles and, finally, grey ashes were obtained. Heating them in air at 700°C, carbonaceous impurities were eliminated, resulting in white, light aggregates with a tree-like aspect.

Figure 1(a) and (b) shows typical XRD spectra of the Y-PSZ and Ca-PSZ powders after milling. Peaks of tetragonal and cubic phases could not be resolved because of their overlapping by broadening. In spite of being stable at room temperature, only a small amount of monoclinic phase was found in some powders. Average crystallite sizes were between 10 and 16 nm (Table 1). These nanocrystalline particles allowed tetragonal and cubic phases stabilization at room temperature. Crystallite size depends strongly on calcination temperature, especially if it is above 800°C. For example, Y-PSZ powders calcinated at 900°C showed crystallite sizes about 40 nm.

ESEM micrographs of powders obtained via citric acid are shown in Fig. 2(a) and (b). Very small agglomerates were found, specially in Y-PSZ powder which exhibited aggregates smaller than 1–2  $\mu\text{m}$ . Figure 3(a) and (b) shows micrographs of powders obtained via glycine showing bigger aggregates, some of them about 4–5  $\mu\text{m}$ . The average agglomerate size was smaller than 1  $\mu\text{m}$  in all the powders.

In citric acid Y-PSZ ceramic samples, *t* and *t'* phases were found, and the presence of cubic phase could not be clearly established, as can be seen in Fig. 4. Monoclinic phase was not found in these specimens, while in glycine materials important amounts (about 20%) of monoclinic phase were found (Table 2). This is probably related with the lower values of density and hardness obtained in glycine ceramics.

Figure 5 shows the typical microstructure of citric acid Y-PSZ samples. Small grains (0.3–0.4  $\mu\text{m}$ ) are probably of *t* symmetry, while the

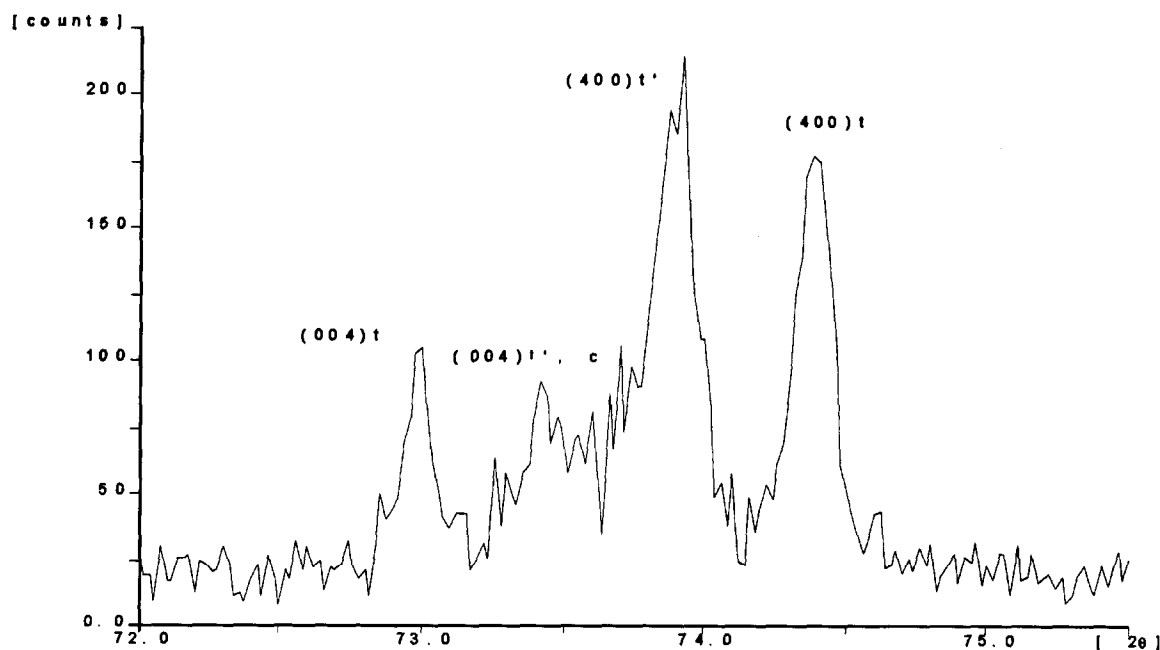
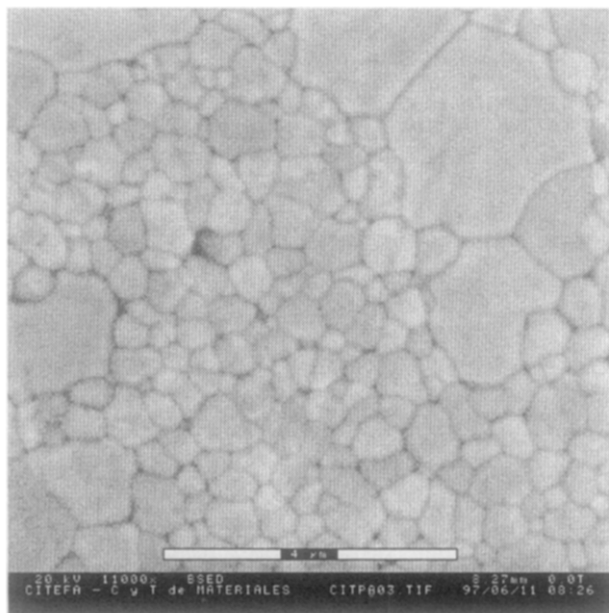


Fig. 4. XRD spectrum of a Y-PSZ ceramic obtained from the citric acid method powder, showing the high-angle region after  $\text{K}\alpha_2$  stripping.

**Table 2.** Y-PSZ ceramic characterization results

Specimen and method	Monoclinic content (%) (% theoretical)	Density (% theoretical)	Microhardness (GPa)
Y-PSZ, citric acid	absent	96 ± 2	9.5 ± 0.3
Y-PSZ, glycine	20 ± 2	93 ± 2	7.8 ± 0.3

**Fig. 5.** Typical ESEM micrograph of a citric acid Y-PSZ ceramic. The bar corresponds to 4  $\mu\text{m}$ .

greater ones (2–4  $\mu\text{m}$ ) correspond to t' or c phases. Glycine Y-PSZ samples were similar, with greater t or m grains, about 0.5–0.6  $\mu\text{m}$ , which might account for explain the high monoclinic content.

#### 4 Conclusions

A wet-chemical method to synthesize yttria or calcia-doped zirconia powders for partially stabilized zirconia ceramics by pyrolysis of nitrate solutions with organic fuels has been proposed. It is an inexpensive method, which can be used to prepare other nanocrystalline oxide ceramics.

Powder characterization has demonstrated that this method results in good quality nanocrystalline Y-PSZ or Ca-PSZ powders with crystallite sizes of 10–16 nm, allowing the stabilization of high temperature tetragonal and cubic phases. Ceramic specimens with high values of density and hardness were obtained.

It is interesting to mention that these highly reactive powders can be used to make very small grained ceramics by means of fast-firing.<sup>6</sup> In this way, high-density materials can be obtained without grain coarsening. This can be useful for Ca or Mg-PSZ ceramics because it is possible to obtain them without very high sintering temperatures (in this case, a thermal treatment in the single-phase cubic region is not required because the powder already has the right composition) and without forming monoclinic phase because of grain coarsening. Further work will be carried out to assess this point.

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