

## Synthesis and characterization of nanosized ZrTiO<sub>4</sub> powders prepared by the sol-gel method

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**Abstract:** Ceramic ZrTiO<sub>4</sub> powders were prepared by a modified sol-gel method using zirconium oxychloride and titanium tetraisopropoxide. In situ high temperature X-ray diffraction results show that crystallization of the amorphous gel starts at 400 °C. Single-phase ZrTiO<sub>4</sub> nanoparticles were obtained after heat treatment at 450 °C for 1 h. An average particle size of 46 nm has been determined by nitrogen adsorption analysis. After pressing these sinteractive powders, pellets with controlled pore size distribution were obtained by sintering at temperatures as low as 400 °C. The analysis of pores by mercury porosimetry show an average porosity of 45 %. Pressing and sintering the nanosized powders prepared by that modified sol-gel technique produced pellets that are good candidates to be used in humidity sensing devices.

### Introduction

Ceramic materials based on zirconium titanate (ZrTiO<sub>4</sub>) are extensively used in humidity sensors [1-3], resonators for microwave telecommunications [4-6], catalysis [7-9], and optical devices [10]. Other materials, based on zirconium titanate, have found applications as high temperature pigments and ceramic composites [11]. Classical ZrTiO<sub>4</sub> synthesis involves a solid state reaction of a stoichiometric mixture of zirconium and titanium oxides at temperatures above 1400 °C [12]. More recently, the preparation of agglomerated 0.5-3.0 μm single phase ZrTiO<sub>4</sub> particles at 1300 °C from the precursor oxides was reported [13]. Solid state reactions involve grinding and thorough mixing of precursor powders followed by high temperature prolonged sintering; the results are usually low specific surface area powders. The sol-gel technology may overcome these problems because highly sinteractive (high specific surface area) powders may be prepared, requiring much lower sintering temperature [14]. A number of ZrO<sub>2</sub>-TiO<sub>2</sub> binary oxides prepared by the sol-gel technique have been reported [15-18]. Fully crystalline and stoichiometric ZrTiO<sub>4</sub> have been obtained with a crystallization temperature of 400 °C by preparing TiO<sub>2</sub> and ZrO<sub>2</sub> gels and mixing them on a 1:1 ratio [15]. The low temperature synthesis of ZrTiO<sub>4</sub> from different precursors with a Zr:Ti concentration ratio of 1:1 has been reported [17], with ZrTiO<sub>4</sub> phase formation around 700 °C.

Taking advantage of the sol-gel method, the low temperature preparation of ZrTiO<sub>4</sub> ceramic nanoparticles was successfully achieved and is here described. The material was prepared by a modified sol-gel method, in which the titanium alcoxide is hydrolized in the presence of zirconium oxychloride, as opposed to hydrolising in pure acidic water. Our aim using this modified approach is to ensure the maximum contact between titanium and zirconium, thus leading to lower formation temperatures for ZrTiO<sub>4</sub>. These materials are more homogeneous, crystallize at a lower temperature and are more sinteractive than the ones obtained by the conventional solid state synthesis.

## Experimental

### *Ceramic powder preparation*

The starting materials were a solution of zirconium oxychloride  $ZrOCl_2 \cdot 8H_2O$  and titanium tetraisopropoxide  $Ti[OCH(CH_3)_2]_4$  - Alfa Aesar. The zirconium oxychloride was prepared by dissolving, in hydrochloric acid, hydrous zirconium oxide  $ZrO_2 \cdot nH_2O$  (>99%) produced at IPEN-Brazil. For the preparation of the ceramic powders in the nominal composition  $ZrO_2:TiO_2$ , titanium tetraisopropoxide was slowly added to a zirconium oxychloride solution (pH  $\sim 0.5$ ) under continuous stirring at room temperature. The suspension was stirred for approximately 7 days. The solution, milky with a white precipitate at the beginning, was translucent after long time stirring. The obtained sol was then dried at approximately 40 °C for another 7 days. A yellowish transparent glassy material was then obtained and ground to obtain the amorphous  $ZrTiO_4$  ceramic powder.

Some specimens were also prepared by the polymeric precursor technique and by mixing the oxides. The specimens were sintered in air at different temperatures for obtaining specimens with different pore volume content [3].

### *Characterization*

The stoichiometry of the powders was analyzed by X-ray fluorescence. Standard compositions of  $(ZrO_2)_x(TiO_2)_{1-x}$  ( $x=0, 0.25, 0.50, 0.75$  and 1) were prepared for XRF measurements. The relative concentrations of Ti and Zr in the powders obtained by the sol-gel technique were determined as 50.1% and 49.9%, respectively.

Thermogravimetric analysis (Shimadzu model TGA-50) was carried out in the dried powder under synthetic air in the room temperature - 800 °C range, with a 20 °C  $min^{-1}$  heating rate. Differential Scanning Calorimetry analysis (Shimadzu model DSC-50) was carried out in the 25-475 °C at the same rate. Simultaneous thermogravimetric and differential thermal analysis was also carried out under synthetic air from room temperature to 800 °C at 10 °C  $min^{-1}$  heating rate using a Netzsch STA 409E equipment.

The specific surface area of the powders was evaluated by gas adsorption analysis by the BET method using a Micromeritics ASAP 2000 equipment.

Scanning electron microscopy experiments were carried out on powder suspensions in a LEO 440 SEM equipment for observing particle shape and to evaluate average particle size.

X-ray diffraction analysis was performed in all powders with  $CuK\alpha$  radiation in the 20-80°  $2\theta$  range in a Bruker-AXS D8 Advance X-ray diffractometer. High temperature *in situ* X-ray diffraction experiments were performed in the same diffractometer in a  $\theta$ - $\theta$  configuration with an Anton Paar HTK-16 sample chamber and a Braun PSD detector.

Powder density was evaluated by mercury porosimetry with a Micromeritics Autopore III porosimeter. The pore size distribution and the apparent density of the pellets were evaluated in the 360  $\mu m$  - 0.003  $\mu m$  (30 Å) range using mercury pressure up to 414 MPa.

## Results and Discussion

### *Powder analysis*

Figure 1 shows the thermogravimetric analysis of the zirconia-titania powder prepared by the sol-gel technique.

A significant mass loss is measured from room temperature to approximately 600 °C due to the removal of water, organic substances, and chloride. The remaining material corresponds to 42.9% of the mass before heating. The mass loss occurs in at least three steps: 33.8% from RT to 384 °C, 20.1% in the 384-417 °C range, and 3.2% in the 417-600 °C range. The sharp feature of the mass loss in the second step might be associated to the exothermic crystallization process. Carefully controlled differential scanning calorimetry experiments, as

shown in the inset of Figure 2, did not allow for determining unambiguously the expected exothermic peak of the crystallization process.

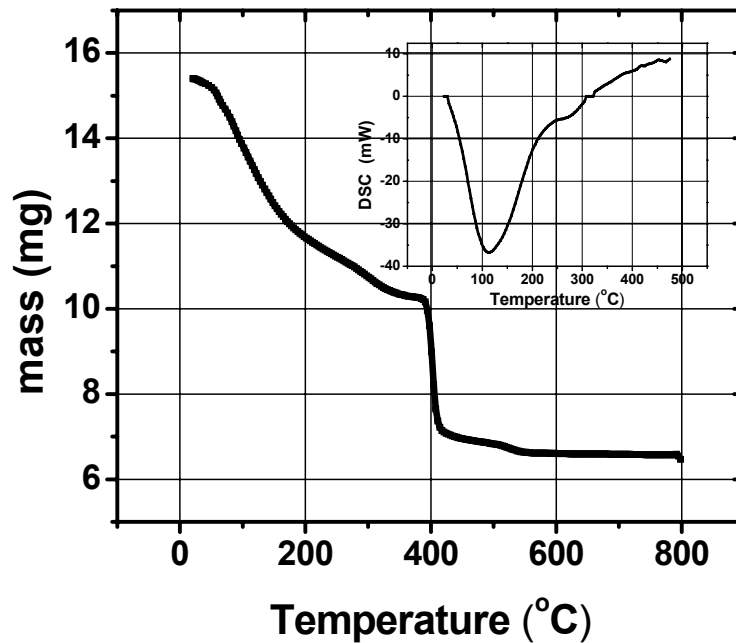


Fig. 1: Thermogravimetric analysis of the  $\text{ZrTiO}_4$  powder prepared by a sol-gel technique and dried at  $35\text{ }^\circ\text{C}$ ; heating rate  $20\text{ }^\circ\text{C min}^{-1}$ .

High temperature *in situ* X-ray diffraction analysis (see below) helped to determine accurately the crystallization temperature. The temperatures  $450\text{ }^\circ\text{C}$  and also  $600\text{ }^\circ\text{C}$  were chosen as calcination temperatures for the powders prepared by the sol-gel technique.

Figure 2 shows X-ray diffraction patterns of the powders obtained by the sol-gel technique after calcination at  $450\text{ }^\circ\text{C}$  for 1 h (Figure 2a) and at  $600\text{ }^\circ\text{C}$  for 1 h (2b). For comparison purposes, the diffraction pattern of a powder obtained by the polymeric precursor technique and calcined at  $730\text{ }^\circ\text{C}$  for 1 h is also shown (Figure 2c). The diffraction patterns of Figures 2a and 2b show that the powders are crystallized in the  $\text{ZrTiO}_4$  structure according to ICDD file #80-1783. Only the reflections due to the  $\text{ZrTiO}_4$  phase are identified in powders obtained by the sol-gel technique and calcined at  $450$  and  $600\text{ }^\circ\text{C}$ . Similar results are obtained in powders prepared by the polymeric precursor technique. Moreover, the crystallization occurs at a temperature lower than that of the powders obtained by the polymeric precursor technique [3]. Most of the methods for obtaining  $\text{ZrTiO}_4$  crystalline powders require temperatures close to  $700\text{ }^\circ\text{C}$  [19].

High temperature X-ray diffraction experiments were performed for crystallization studies. Figure 3 shows the dependence of the intensity of the (111) reflection ( $2\theta = 30.498^\circ$ , ICDD file # 80-1783) on the temperature upon heating the  $\text{ZrTiO}_4$  amorphous ceramic powder from  $27\text{ }^\circ\text{C}$  to  $800\text{ }^\circ\text{C}$ . Data were collected at the following temperatures:  $27, 100, 200, 250, 300, 350, 400$  to  $500\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C}$  increment, and  $550$  to  $800\text{ }^\circ\text{C}$  at  $50\text{ }^\circ\text{C}$  increment. The heating rate for reaching each temperature was set at  $4\text{ }^\circ\text{C s}^{-1}$ . The inset shows the (111) reflection at all these temperatures. Figure 3 shows that crystallization starts at approximately  $400\text{ }^\circ\text{C}$ .

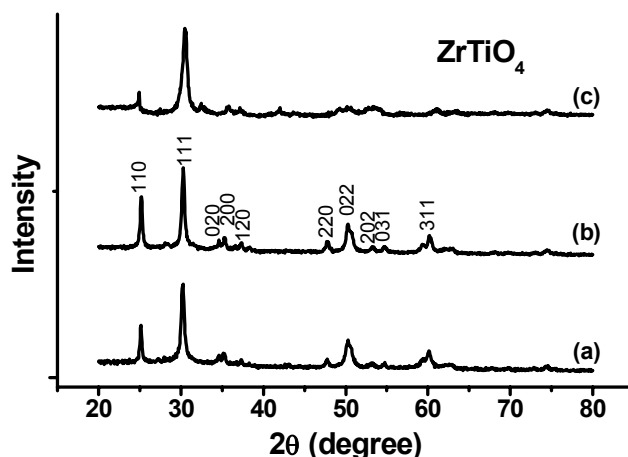


Fig. 2 X-ray diffraction patterns of the  $\text{ZrTiO}_4$  powders obtained by the sol-gel technique and calcined at 450 (a) and 600 °C (b) for 1 h; for comparison purposes, the X-ray diffraction pattern of the powder obtained by the polymeric precursor technique and calcined at 730 °C for 1 h is also shown (c) [3]. Indexation according to ICDD file 80-1783.

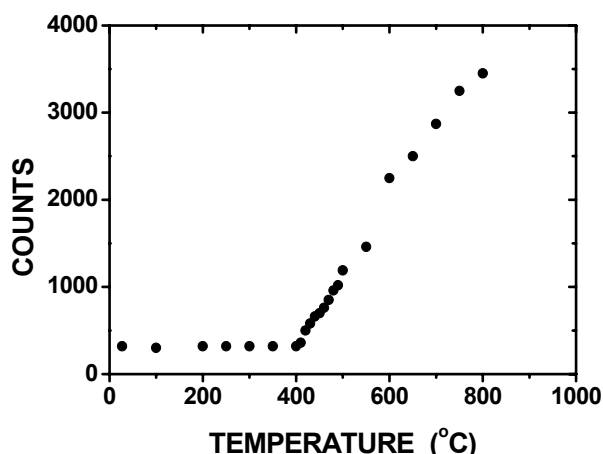


Fig. 3 High temperature *in situ* X-ray diffraction data: intensity of the (111) reflection of  $\text{ZrTiO}_4$  powders obtained by the sol-gel technique as a function of temperature in the 27-800 °C range.

Figures 4a and 4b show the results of the scanning electron microscopy experiments on powders calcined at 450 and 600 °C, respectively, for 1 h. Both powders consist of large agglomerates probably resulting from the high combustion heat produced during the thermal decomposition of the powders, these agglomerates are composed of clusters of submicron sized particles.

A detailed analysis of the powders was done to find the average equivalent diameter of the agglomerated particles. The BET method for the determination of the specific surface area by nitrogen gas adsorption analysis was applied. The results show that the specific surface area of  $\text{ZrTiO}_4$  powder after calcination at 450 and 600 °C are 43 and 38  $\text{m}^2 \text{g}^{-1}$ , respectively. Using the equation  $D (\mu\text{m}) = 6 / (\rho \cdot S)$ , the equivalent spherical diameter of the particles  $D$  was evaluated;  $\rho$ , determined by mercury porosimetry, and  $S$  stand for the  $\text{ZrTiO}_4$  density ( $\text{g cm}^{-3}$ ) and the specific surface area ( $\text{m}^2 \text{g}^{-1}$ ), respectively.

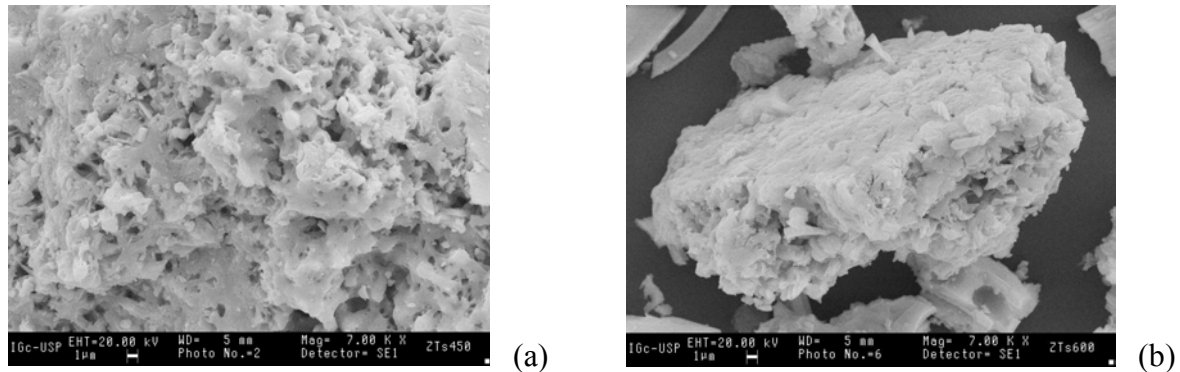


Fig. 4 Scanning electron microscopy micrographs of the  $ZrTiO_4$  powders obtained by the sol-gel technique: a) calcination temperature  $450^\circ C$  for 1h (7000X); b)  $600^\circ C$  for 1 h (7000X).

These results are shown in Table 1. Particles treated at 450 and 600 °C show no apparent modification in their average size. The specific surface area shows a slight decrease with consequent increase in the apparent density and in the average size of the particles probably due to particle sintering and pore elimination. Table 1 also shows values of the mean crystallite size  $L$  of these powders, determined using the Scherrer equation [20]. The mean crystallite sizes are of the same order of magnitude (approximately half) of the values of the average particle sizes determined by gas adsorption analysis. This means that the nanoparticles obtained by the modified sol-gel technique here described may be single crystalline, provided further cominution of the dried gel is done.

Table 1. Specific surface area  $S$ , apparent density  $\rho$ , average equivalent diameter  $D$ , and crystallite size  $L$  of the powders obtained by the sol-gel technique after calcination at  $450^\circ C$  and  $600^\circ C$ .

Temperature of calcination	$S$ ( $m^2/g$ )	$\rho$ ( $g/cm^3$ )	$D$ (nm)	$L$ (nm)
$450^\circ C$	43	3.00	46.5	20.5
$600^\circ C$	38	3.19	49.5	21.5

#### *Analysis of the sintered pellets*

The powders calcined at  $600^\circ C$  were pressed and heat treated at 300 and  $400^\circ C$  for 3 h. Figure 5 shows the X-ray diffraction patterns of these pellets. There is a partial decomposition of the  $ZrTiO_4$  phase to monoclinic zirconia (Figs. 5a and b). As the temperature is lower than the calcination temperature, mechanical stresses during pressing could be the main reason for that decomposition. Similar results have been observed in nanosized tetragonal zirconia particles submitted to mechanical stress by grinding [21]. In the same figure, the X-ray diffraction patterns of  $ZrTiO_4$  specimens obtained by solid state synthesis, Figure 5d and 5e, and by the polymeric precursor technique, Figure 5c, are also shown. The pellets prepared using powders obtained by the polymeric precursor technique and sintered at  $1150^\circ C$  (Figure 5c) are  $ZrTiO_4$  single phase. The pellet obtained by solid state synthesis and sintered at  $950^\circ C$  have two phases: monoclinic zirconia and rutile  $TiO_2$ . The  $ZrTiO_4$  phase is found only after sintering at  $1050^\circ C$  and higher temperatures, becoming  $ZrTiO_4$  single phase only after sintering at  $1250^\circ C$  (Figure 5e), in agreement with reported results [22].

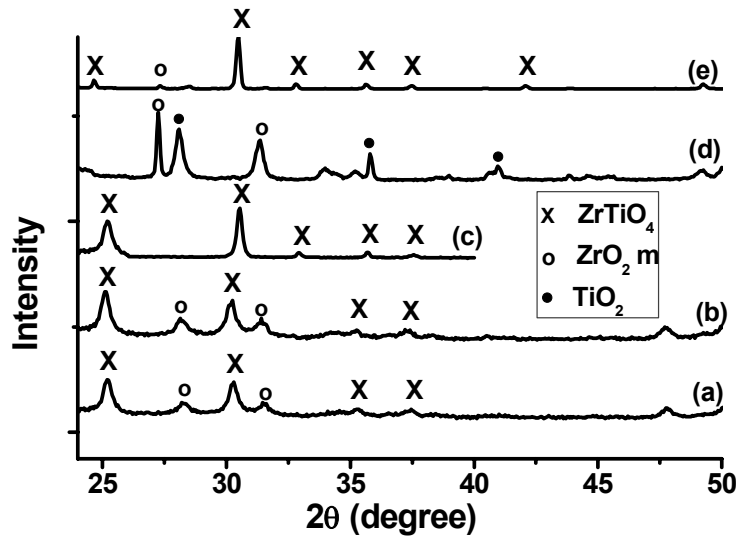


Fig. 5 X-ray diffraction patterns of pellets sintered at 300 (a) and 400 °C (b) for 1 h, prepared with powders obtained by a sol-gel technique. Also shown the X-ray diffraction patterns of pellets sintered at 1150 °C for 1 h from powders prepared by the polymeric precursor technique (c) and sintered at 950 °C (d) and 1250 °C (e) for 1 h from powders prepared by the solid state synthesis.

The application of the  $ZrTiO_4$  sintered pellets we are looking for is as humidity sensing main component. Therefore, one of the main requirements is a large distribution of pores for accommodation of water species for changing the electrical resistivity. Figure 6 shows the results of the pore size distribution analysis of the pellets sintered at 300 and at 400 °C, prepared from powders obtained by the sol-gel technique. Pore distribution is about the same for both specimens, with approximately 45% pore volume and similar size distribution. Both specimens have also a large pore density in the region 50 - 300 Å. This is important for designing ceramic humidity sensors because the larger is the pore density in that range, the better is the linearity and the sensitivity of the sensor [23].

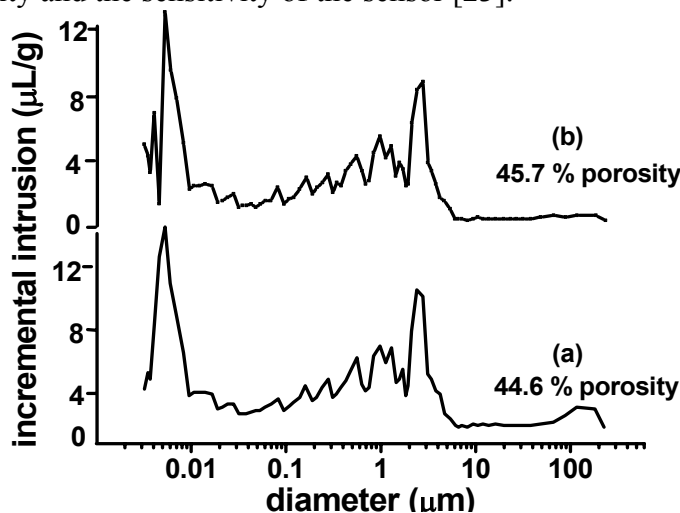


Fig.6 Pore size distribution in ceramic pellets obtained by sintering at 300 and 400 °C for 1 h pressed powders prepared by a sol-gel technique.

## Conclusions

A successful preparation of clustered nanosized particles of  $ZrTiO_4$  ceramic powders by a modified sol-gel technique allowed for sintering at relatively low temperatures porous

ceramic pellets. The crystallization temperature of the powders was accurately determined as 400 °C by *in situ* high temperature X-ray diffraction. The average size values of the nanoparticles is approximately twice that of the crystallite size value. The sol-gel technique is an appropriate technique for preparing sinteractive ceramic nanoparticles

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