

PREPARATION OF CRYSTALLINE $ZrTiO_4$ AT LOW THERMAL TREATMENT TEMPERATURES

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Abstract. $ZrTiO_4$ was obtained from zirconium n-propoxide and titanium isopropoxide, at the Zr:Ti molar ratio of 1:1, in propanol, through the sol-gel process at ambient temperature. $ZrTiO_4$ powders were treated thermally at 500 °C, 600 °C, and 700 °C for 12 h. The powders obtained were characterized by thermal analysis, XRD, FTIR, and BET. A large loss of mass was observed between 40 and ca. 200 °C, which is probably due to dehydration, confirmed in the spectrum FTIR. The exothermal peak at ca. 700 °C, without loss of mass, was attributed to the crystallization of the orthorhombic phase of $ZrTiO_4$ and confirmed by X-ray diffraction. The specific surface area of the $ZrTiO_4$ powders diminished by thermal treatment from $242 \pm 15 \text{ g.m}^{-2}$ (at 500 °C) to $62 \pm 6 \text{ g.m}^{-2}$ (at 800°C).

1. INTRODUCTION

Zirconium titanate ($ZrTiO_4$ -ZT) is a ceramic material which is widely used to manufacture electrical and optical devices, such as capacitors, piezoelectric sensors, ultrasonic motors and dielectric devices in microwaves, since it presents high permittivity in the microwave frequency. [1,2] The traditional preparation of ZT ceramics is based on solid state reactions between the TiO_2 and ZrO_2 powders at high temperatures (above 1400 °C). In order to improve the functional properties of the ceramic material, treatments consuming a high amount of energy after the reaction are generally necessary and expensive [2].

Chemical methods based on co-precipitation of the reactive precursors were developed to prepare powders with a high purity and low treatment cost after a reaction [3,4]. $ZrTiO_4$ crystallizes in the orthorhombic type structure α - PbO_2 . This phase is stable above 1100 °C and persists metastably at lower temperature because the ordering process is sluggish, being associated with a reconstructive transforma-

tion and driven by the respective preferences of the Zr and Ti ions for 8 (7)- and sixfold coordination, respectively [5]. Samples containing multi-phases are important from the technological perspective and are strongly superposed [6]. Consentino *et al.* [7] prepared ceramic powders from the mixture of zirconium oxychloride and titanium chloride in stoichiometric quantities in the presence of citric acid (60 °C) and ethylene glycol. By using this technique, the authors observed that after treated at 600 °C for 1 hour still amorphous. In 730 °C, had the crystalline phase of orthorhombic $ZrTiO_4$, contrary to reported by Karakchiev [8], which obtained zirconium titanate by sols hydrated in 1:1 ratio of Zr:Ti with the presence of TiO_2 as anatase, below 600 °C. At 600 °C this form disappears and gives way to the $ZrTiO_4$ peaks. The preparation of $ZrTiO_4$ and $Zr_{0.8}Sn_{0.2}TiO_4$ by pulsed laser deposition was reported by Viticoli *et al.* [9]. Films of $ZrTiO_4$ were prepared, deposited between 450 and 550 °C. At 450 °C, a weak intensity peak at $2\theta = 30.48^\circ$ indicates the presence of crystalline zirconium titanate, peaks at

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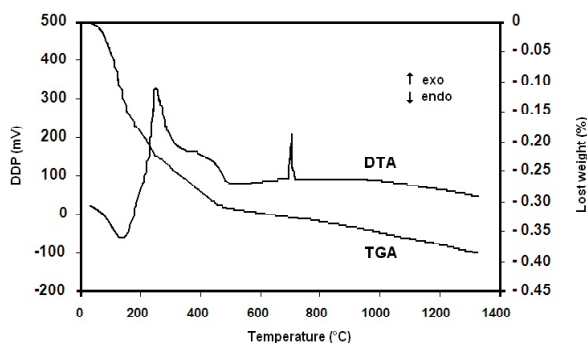


Fig. 1. Thermal analyses of the ZT sample obtained from the formulation containing NPZ and TPT.

$2\theta = 32\text{--}35^\circ$ also suggest the presence of phases for Ti_2O_3 , TiO_2 , and ZrO_2 . Raising the temperature to 550°C the intensity of reflections (1 1 1) characteristic of ZrTiO_4 and the reflections (0 2 0), (2 0 0), and (2 2 2) at $2\theta = 32.6^\circ$, 35.7° , and 63.3° can be identified. Under these conditions only the contributions of ZrTiO_4 can be observed, indicating the formation of a single crystalline phase of ZrTiO_4 . The crystallographic structure for the films deposited, containing tin presents an intense peak at 450°C at $2\theta = 33.06^\circ$ associated with reflection (1 0 4) of Ti_2O_3 . Peaks at $2\theta = 32\text{--}35^\circ$ suggest the presence of phases for SnO_2 , TiO_2 , and ZrO_2 , while a weak intensity peak indicates the crystallization of $\text{Zr}_{0.8}\text{Sn}_{0.2}\text{TiO}_4$ (0 0 2) [9,10].

In this work, ZT powders were obtained from zirconium propoxide (*n*-propyl zirconate – NPZ) and titanium isopropoxide (tetra-isopropyl titanate – TPT), at the Zr:Ti molar ratio of 1:1, in propanol, using the sol-gel process at ambient temperature (20°C).

2. EXPERIMENTAL

2.1. Preparation of ZT powders

Zirconium titanate powders were produced in the following manner. A mixture metal alcoxide solution (Zr:Ti molar ratio of 1:1) was made by combining zirconium propoxide (NPZ) and titanium isopropoxide (TPT) (Dupont) in propanol (Merck), nitric acid (Merck) under constant agitation (~ 860 rpm) for 15 min (solution pH = 6), at 20°C . Then deionized water was added slowly, and the mixture was agitated for 12 h. The gel formed looked like soft paraffin. The gels obtained were dried in a chamber with an infrared lamp for 72 h. After, the gels dried were annealed in air oven at different temperatures, ranging from 500°C to 800°C , for 12 h.

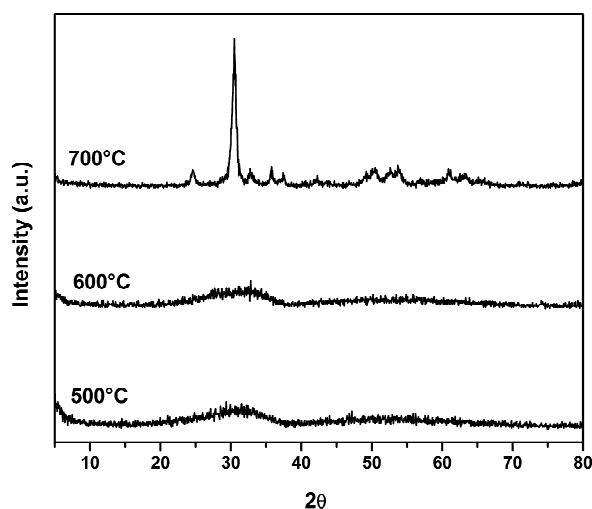


Fig. 2. X ray of ZT powders diffraction obtained by sol-gel process, after thermal treatment for 12 hours at different temperatures.

2.2. Characterization of ZT powder

Thermogravimetric (TGA) and thermodifferential (DTA) analysis of the zirconia powder were carried out with a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ until 1000°C , with a flux of O_2 and N_2 at the rate of $15\text{ mL}\cdot\text{min}^{-1}$ and $50\text{ mL}\cdot\text{min}^{-1}$, respectively. X-ray diffraction (XRD) was performed on synthesized and annealed powders for phase identification and examination at a rate of $1^\circ\text{C}\cdot\text{min}^{-1}$, using $\text{Cu K}\alpha$ radiation with a Philips X-ray diffractometer (model X'Pert MPD). Chromia was also employed as an external standard for correction due to instrumental broadening. The width of XRD peaks observed is a convolution of the factors such as inaccuracy of the instruments and physical factors [11].

Fourier transform infrared spectroscopy (FT-IR) analysis of dried and annealed powders were carried out in an Impact 400, Nicolet spectrometer in the wavenumber range $400\text{--}4000\text{ cm}^{-1}$ at resolution of 4 cm^{-1} for studying the chemical groups. For this analysis, KBr pellets were pressed to hold the samples to be analyzed.

The surface area was determined using Autosorb Quantachrome (New model 1200). This equipment calculates the total surface area of the sample by nitrogen adsorbed (m^2) from the adsorbed gas volume (V) depending on the relative pressure (P/P_0). The surface area is measured and then divided by the total weight of the sample tested (g) in order to obtain the specific surface area ($\text{m}^2\cdot\text{g}^{-1}$) [12].

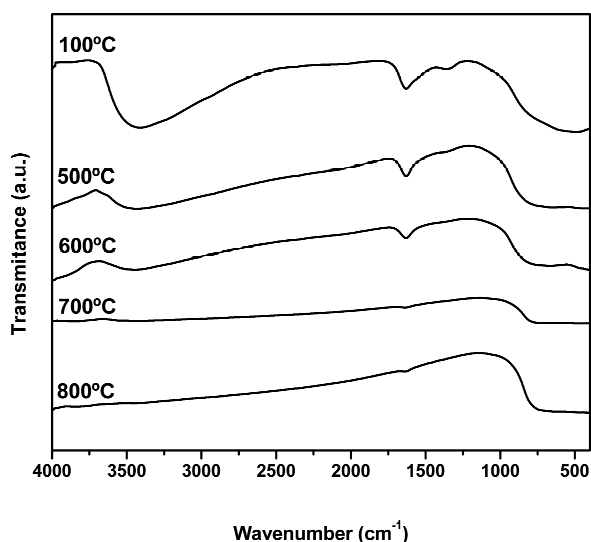


Fig. 3. FT-IR of the dried and annealed ZT powders at different temperatures ranging from 100 °C, 500 °C to 800 °C.

3. RESULTS AND DISCUSSION

Fig. 1 shows the TGA and DTA analysis of the ZT powder obtained using process sol-gel. A considerable weight loss can be observed in the range from 40 °C to 200 °C, probably due to dehydration. According Khairulla and Phule [13], the peaks in DTA at 350 and 550 °C are related to the removal of organic compounds. At approximately 710 °C an exothermal peak can be observed without loss of mass, which can be attributed to the crystallization of the orthorhombic phase of ZrTiO₄, confirmed by literature, [14] which can be proved by X-ray diffraction. Ananta *et al.* [15] studied formation and characterization of ZT powder in solid state, DTA analysis for mixture de ZrO₂-TiO₂ powder two exothermic peaks at 1150 and 1240 °C, which correspond to a phase transition.

Fig. 2 shows the powder diffractograms after thermal treatment at 500 °C, 600 °C, and 700 °C for 12 h. Below 700 °C the samples are amorphous. In this approach titanium isopropoxide was used, but the presence of crystalline phases referring to titania was not observed, probably because it presents in the non-crystalline (amorphous) form. This peak of orthorhombic ZrTiO₄ ($2\theta = 30.595^\circ$), JCPDS data for zirconium titanate (34-415), was observed in the diffractogram at 700 °C. These results are consistent with literature [7].

Fig. 3 shows spectra obtained by means Fourier transform infrared spectroscopy (FT-IR) analy-

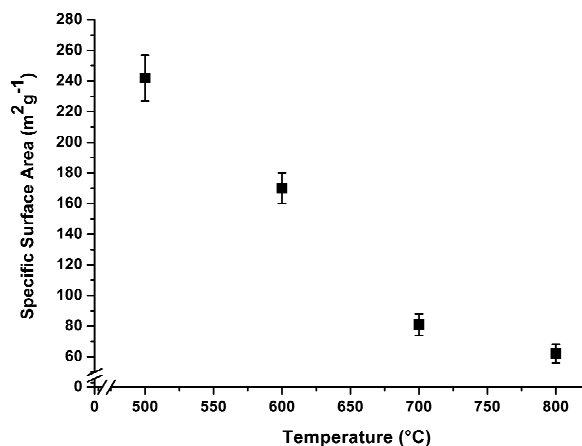


Fig. 4. Relationship between the specific surface area and thermal treatment temperature for composition Zr/Ti 1:1 annealed for 12 hours.

sis of the dried and annealed ZT powders at different temperatures ranging from 100 °C to 800 °C. The bands at 3380 cm⁻¹ and 1565 cm⁻¹ correspond to the vibration of stretching and deformation of the O-H bond due to the absorption of water and coordination water, respectively. As the annealing temperature increased, the formation of these bands gradually decreased, eventually disappearing. The absorption band at 466 cm⁻¹ can not be observed, this band is related to the vibration of the Zr-O bond in ZrO₂ [16].

The results of specific surface area (SSA) for ZT samples prepared from the sol-gel process (Fig. 4) showed that the temperature increase while the surface areas diminished [17]. This reduction in the specific surface area is probably due to the reduction of energy associated with the interface between particle and environment as a thermally activated natural phenomenon. The relationship between temperature and the specific surface area can be explained as a result of the mixture between the alkoxides. The BET surface area was 360 m²g⁻¹, for ZT powders prepared by controlled hydrolysis of mixtures of zirconium and titanium alkoxides and long chain carboxylates (lauric, palmitic or stearic acids) in the absence of solvent after calcination to 400 °C [18].

4. CONCLUSIONS

It was possible to obtain ZrTiO₄ powders from zirconium *n*-propoxide and titanium isopropoxide, at a Zr:Ti molar ratio of 1:1, in propanol, using the sol-gel process at ambient temperature (20 °C).

The ZrTiO₄ powders treated thermally at 700 °C present orthorhombic phase, confirmed by XRD and an exothermal peak without loss of mass by DTA analysis. The thermal analysis showed also a great loss of mass, between 40 and 200 °C approximately, probably due to dehydration. The peaks in DTA at 350 and 550 °C are related to the removal of organic compounds. The water loss was confirmed in the spectrum FTIR. It was observed that the formation of the bands related to the presence of hydroxyl group showed a decrease with the increase of annealing temperatures, and at 800 °C they disappeared, indicating that the material structure no longer contains zirconium hydroxide. The specific surface area of the ZrTiO₄ powders diminished by thermal treatment from 242±15 (12 h at 500 °C) to 62±6 (12 h at 800 °C).

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