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Synthesis and Characterization of Crystalline Zirconium Titanate Obtained by Sol-Gel

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1. Introduction

Zirconium titanate (ZT)-based ceramic materials, ZrTiO4, have many attractive properties: high resistivity, high dielectric constant, high permittivity at microwave frequencies and excellent temperature stability for microwave properties (Bianco *et al*, 1999; Leoni *et al*, 2001). These materials have an extremely wide range of technological application, such as in microwave telecommunications (as capacitors, dielectric resonators in filters, and oscillators) (Navio *et al*, 1993; Navio *et al*, 1994; Azough *et al* 1996), in the manufacture of high-temperature pigments (Hund and Anorg, 1985; Dondi *et al*, 2006) in catalysis (as effective acid-base bifunctional catalysts and photocatalysts) (Tanabe, 1970; Araka and Tanabe, 1980), as structural ceramics (Parker, 1990) and, more recently, as biomaterial coated on 316L SS for biomedical applications (Devi *et al*, 2011).

The formation of $ZrTiO_4$ has been studied by several authors (McHale *et al*, 1989; Christoffersen *et al*, 1992a; Bhattacharya *et al*, 1996; Hom *et al*, 2001; Ananta *et al*, 2003; Kim *et al*, 2004; Troitzsch *et al*, 2005; Vittayakorn *et al*, 2006; Licina *et al*, 2008).

Zirconium titanate is normally synthesized by solid-state reaction of oxide mixtures between ZrO_2 and TiO_2 at elevated temperatures (1200-1600°C) and long heating times and also requires post treatment such as energy-intensive grinding/milling procedures for powder formation and this process usually leads to inhomogeneous, coarse, and multiphase powders of poor purity (Lynch, 1972; Swartz, 1982; McHale *et al*, 1983; McHale *et al*, 1986; Parker, 1990; Christoffersen *et al*, 1992b; Park et al, 1996; Stubicar *et al*, 2001; Troitzsch *et al*, 2004; Dondi *et al*, 2006). $ZrTiO_4$ ceramics have the orthorhombic structure of α-PbO_2 (Blasse, 1966; Newnham, 1967) and belongs to the space group Pbcn. Above 1200 °C the Zr ion and Ti ion of the high temperature normal phase are randomly distributed on octahedral site in α-PbO_2 type structure. (McHale *et al*, 1983; Christoffersen *et al*, 1992b; Azough *et al*, 1993; Ul'yanova *et al*, 1995). In contrast to the displaced transitions which take place at discrete temperature, $ZrTiO_4$ ceramics undergoes a continuous phase transition of the normal to incommensurate over the temperatures of 1200°C to 1100°C by increasing order in the Zr-Ti distributions.

The chemical preparation of reactive precursors offers advantages over traditional processing techniques because of the higher purity and better homogeneity obtained the

lower processing temperatures and improved material properties. Table 1 summarizes the procedures currently used to prepare pure $ZrTiO_4$ materials by non-conventional or chemical routes (Navio et al, 1992a; Pol *et al*, 2007).

Precursors	Preparation procedure	References
$Zr(SO_4)_2$, $Ti(SO_4)_2$	1.Coprecipitation of mixed oxides using concentrated ammonia water 2.Calcined precipitates shaped into pellets, pressed at 100 MPa, sintered at 1600 °C for 10 h and post-treated at 1500 °C for 5 h, quenched to room-temperature air and annealed at 700 °C for 3days	Ikawa *et al*, 1988; Ikawa *et al*, 1991
Zirconium isopropoxide titanium isopropoxide	1. Using 2-propanol as solvent, mixing for 5 h at 82 °C, hydrolysis with H_2O at room temperature and increased to 75 °C 2. Solid filtered, washed with hot water and dried at 120 °C under reduced pressure	Yamagushi *et al*, 1989
Zirconium propoxide titanium isopropoxide	Partial and controlled hydrolysis using CH_3COOH-propanol, and a ratio h = $[CH_3COOH]/[metal]$ $1 \leq h \leq 8$ If $h \leq 3$, homogeneous gels were obtained If $h > 3$, white precipitate $M(OR)_x(CH_3COO)_y$	Muñoz *et al*, 1990
Zirconium alcoxide, titanium alcoxide	Classical hydrolytic sol-gel, where metal alcoxides are dissolved in alcohol, after o gel is dried and calcined.	Hirano *et al*, 1991; Komarneni *et al*, 1999; Karakchiev *et al*, 2001
Zirconyl chloride	1. Mixing and precipitation with methanol, hydrogen peroxide solution and aqueous ammonia solution at pH 8-9 2. The gelled mass was washed with acetone, filtered and dried slowly for several days	Navio *et al*, 1992b
Zirconium oxychloride and titanyl chloride	Process involves hydrolysis of the starting salts, nucleation of zirconia and titania, nucleus growth, and the formation of $ZrTiO_4$ above 1150 °C.	Gavrilov *et al*, 1996
$Ti(OBut)_4$, $ZrOCl_2.8H_2O$ (Polymeric precursor)	Mixing with ethylene glycol, $Ti(OBut)_4$, $ZrOCl_2.8H_2O$ and citric acid, at 110-120 °C	Bianco *et al*, 1998
$TiCl_4$ and $ZrOCl_2$	Chemical precipitation using ammonia, produced ZT nanopowders	Leoni *et al*, 2001
Titanium sulfate, $ZrOCl_2.8H_2O$	Sol-gel process produced long $ZrTiO_4$ fibers	Lu *et al*, 2003

Table 1. Wet-chemical routes for synthesizing $ZrTiO_4$ materials

Actually the sol-gel processes were developed both in academic research and in industry, producing glasses by straightforward polymerization of molecular precursors in solution. Basically, sol-gel process carried out in a liquid medium. This process involves the evolution of inorganic networks through the formation of a colloidal suspension which is called sol and gelation of the sol to form a network in a continuous liquid phase which is denoted as gel. Three reactions generally describe the sol-gel process: (1) hydrolysis reaction, (2) alcohol condensation process, and (3) water condensation process. The sol-gel approach also provides an alternative and usual way for synthesis of nanomaterials. Combined with chemical nanotechnologies, remarkable progress has been achieved and sol-gel techniques have taken their place as a fundamental approach to the development of new nanomaterials. The sol-gel synthesis method has been used for the production of metal, metal oxide and ceramic nanoparticles with high purity and good homogeneity. If an organic surfactant is added to the sol as the structuring agent, it is even possible to obtain an ordered porous structure in two dimensions or three dimensions. The sol-gel process is considered as a low-temperature synthesis method that gives pure, homogeneous nanoparticles with good size distribution in the design of complex nanoarchitectures. Furthermore, many kinds of nanoparticles including oxides, sulfides, metals, and semiconductors with nanoporous structures can be synthesized through a precise heat treatment. The versatility of the process is largely due to the rich and varied chemistry of organometallic precursors, combined with the low processing temperature (Qiao *et al*, 2011).

Samples containing multi-phases are important from the technological perspective and are strongly superposed (Sham *et al*, 1998). Consentino *et al.* 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 *et al* 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*. Films of $ZrTiO_4$ were prepared, deposited between 450 and 550 °C. At 450 °C, a weak intensity peak at $2\theta = 30.48°$ indicates the presence of crystalline zirconium titanate, peaks at $2\theta = 32\text{-}35°$ 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 $2\theta = 32.6°$, 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 $2\theta = 33.06°$ associated with reflection (1 0 4) of Ti_2O_3. Peaks at $2\theta = 32\text{-}35°$ suggest the presence of phases for SnO_2, TiO_2 and ZrO_2, while a weak intensity peak indicates the crystallization of $Zr_{0.8}Sn_{0.2}TiO_4$ (0 0 2). (Bhattacharya *et al*, 1996; Troitzsch *et al*, 2005).

In this study, ZT powders were obtained from hydrolysis reactions of zirconium n-propoxide (NPZ) and titanium isopropoxide (tetra-isopropyl titanate – TPT). These reactions were performed by hydrolyzing the alkoxides separately, at the molar ratio of Zr:Ti of 1:1, in n-propanol, using the sol-gel process at ambient temperature (20°C) and

influence nitric acid, in order to verify the form of crystallization of $ZrTiO_4$ under these conditions. The results were compared to the previous work (Santos *et al*, 2010).

2. Materials and methods

The hydrolysis reaction to obtain zirconium titanate (ZT), $ZrTiO_4$, was performed with the alkoxides zirconium n-propoxide (NPZ) (Dupont), and titanium isoproxide (TPT) Dupont, deionized water in the presence of nitric acid (Merck). The solvent used was *n*-propanol (Merck).

2.1 Preparation of the zirconium titanate powders

The preparation of zirconium titanate powder from hydrolysis for alkoxides precursors, which was carried out separately, is illustrated in the block diagram reported in Figure 1. The synthesis performed with the mixture of alkoxides is described in Santos *et al*.
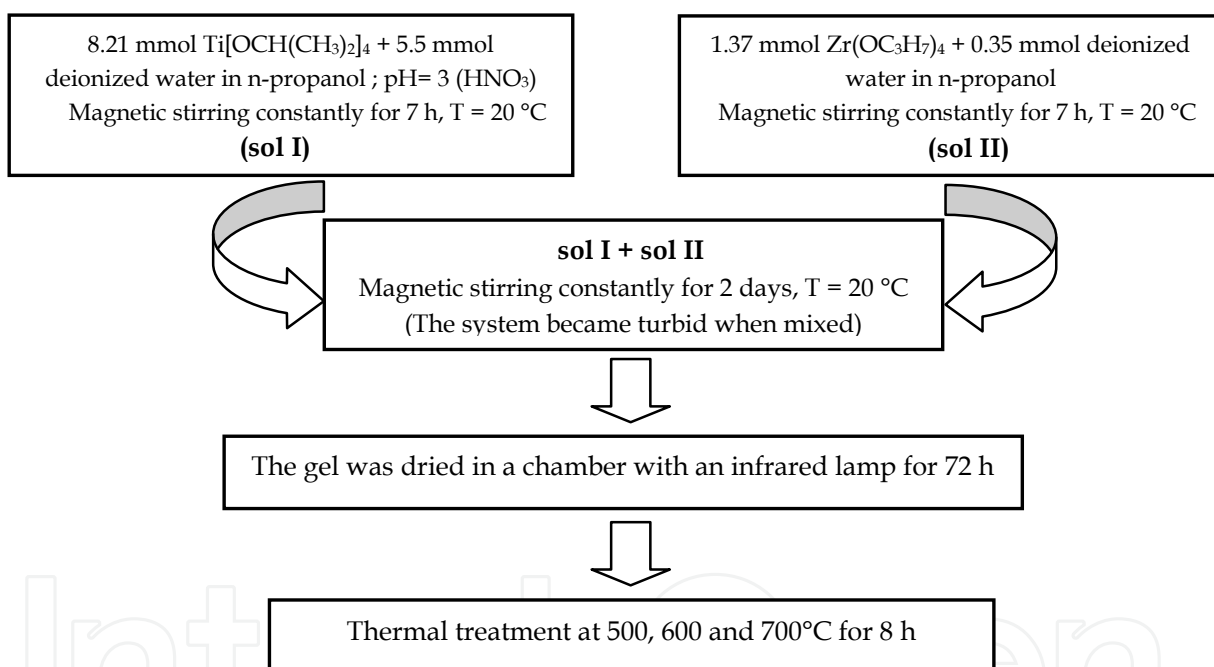
Fig. 1. Process of preparation of zirconium titanate powder from hydrolysis for alkoxides precursors.

2.2 Characterization methods

2.2.1 Thermal analyses

Thermogravimetric analyses (TGA) and thermodifferential analyses (DTA) of the powders were performed with an Harrop thermal analyzer, model STA 736, at a heating rate of 10 K· min^{-1} in air, with a 10 L·min^{-1} flow.

2.2.2 X-Ray diffraction

In order to determine the mineralogical phases by X-Ray Diffraction (XRD), a Philips X-Ray Diffractometer was used (model X'Pert MPD) equipped with a graphite monochromator and rotational anode, operated at 40 kV and 40 mV. The data were collected via Cu-K$_\alpha$ radiation at a step of 0.01° and time per step of 2 s, in order to determine the phases present in the samples.

2.2.3 Fourier transform infrared spectroscopy (FT-IR)

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 400–4000 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.

2.2.4 Particle size distribution by LASER diffraction spectrometry

The particle size distribution of agglomerates and particles of sintered powder was determined by a laser diffraction spectrometer Cilas, model 1180. The detection range of this equipment is between 0.04 and 2500 μm.

3. Results and discussion

Thermogravimetric and thermodifferential analyses are shown in Figures 2a for hydrolysis of alkoxides together and 2b for alkoxide hydrolysis separately. The curves obtained are very similar, initially, with a great loss of mass between approximately 40 °C and 200 °C, which is due, probably, to dehydration, accompanied by an endothermal peak due to the energy consumed to release volatiles. An exothermal mass can be seen in Figure 2a, at 703 °C. It is ascribed to crystallization of the orthorhombic phase of zirconium titanate. According to Khairulla and Phule (1992), the peaks by differential thermal analysis (DTA) at 350 and 550 °C are related to the removal of organic compounds and an exothermal event without loss of mass at approximately 710 °C is caused by the formation of the crystalline phase of $ZrTiO_4$. Macan *et al*[12], describe that a first loss of mass seen in the TGA and DSC curve as accompanied by an endothermal peak at 83 °C due to the evaporation of adsorbed water. Loss of mass diminishes constantly as temperature increases as a function of the slow degradation of residual organic matter, and the exothermal peak at 703°C is due to the crystallization of amorphous $ZrTiO_4$, confirmed in the preliminary research (Consentino *et al*, 2003).

In Figure 2b two exothermal peaks were observed, 261°C and 460 °C, accompanied by loss of mass, due to the burning of the remaining organic matter. Bhattacharya *et al* suggest that this inflexion is due to the removal of structural anionic species. As the temperature increases, decomposition reactions occur and a broad exothermic peak at 460 °C. The weight loss continues and stabilizes at about 500 °C. At 703°C no exothermal peak that could be attributed to the crystallization of zirconium titanate was observed. During the cooling process endothermal events occurred, with hardly any loss of mass at 1260, 948 and 897 °C, which may be related to crystalline phase transitions, as described by Park *et al* (1996) in the solid-state reaction of oxide mixtures between ZrO_2 and TiO_2 at elevated temperatures.
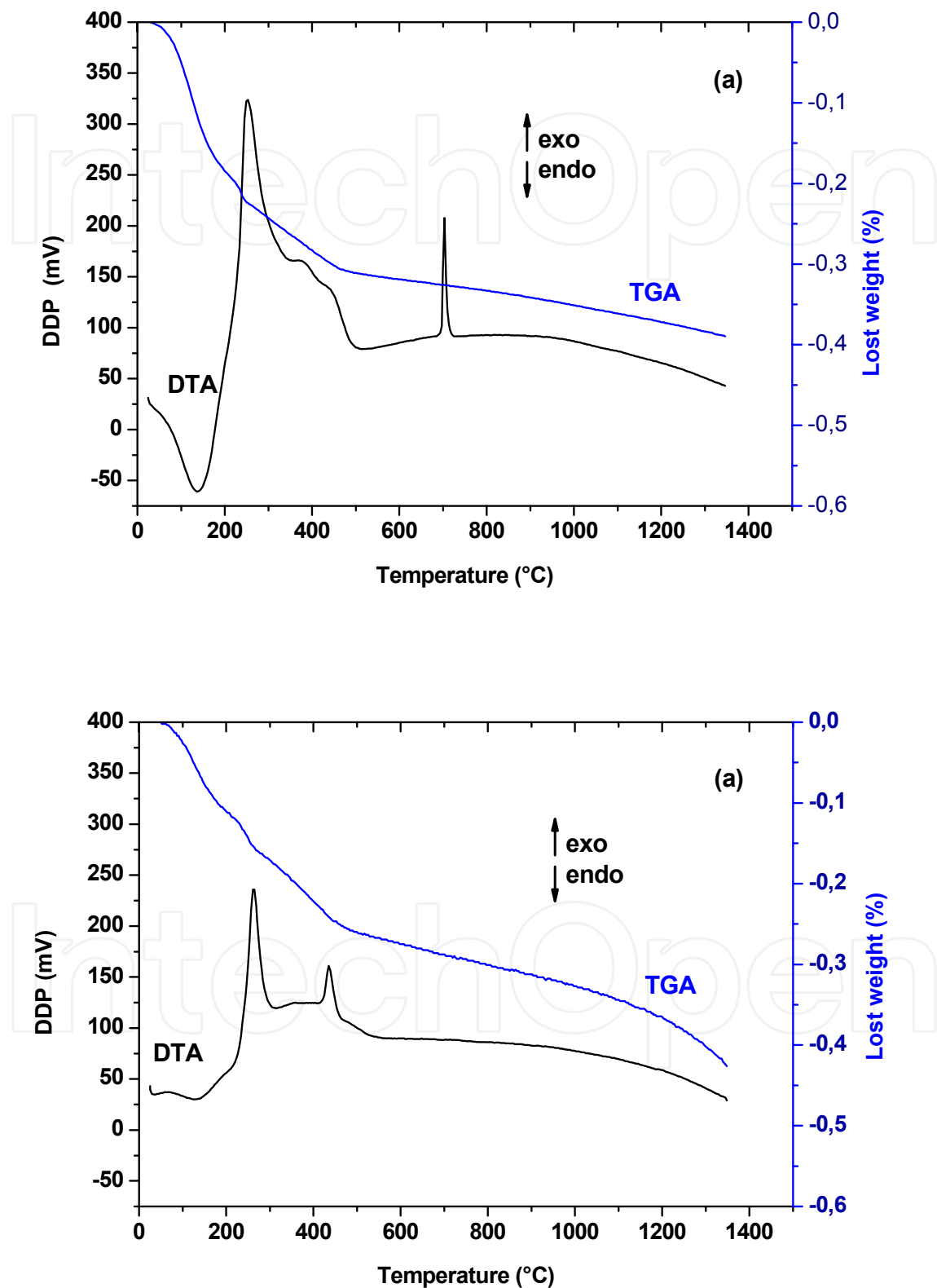
Fig. 2. Thermal analyses of powders after drying obtained by hydrolysis of the alkoxides, NTZ and TPT: (a) together (Santos *et al*, 2010) and (b) separately.

According to Navio *et al*, Figure 3 shows different structures for $ZrTiO_4$. The structure I could be postulated as the amorphous and it is expected to change to the structure II, III and IV (crystalline structures) as the temperature increases.
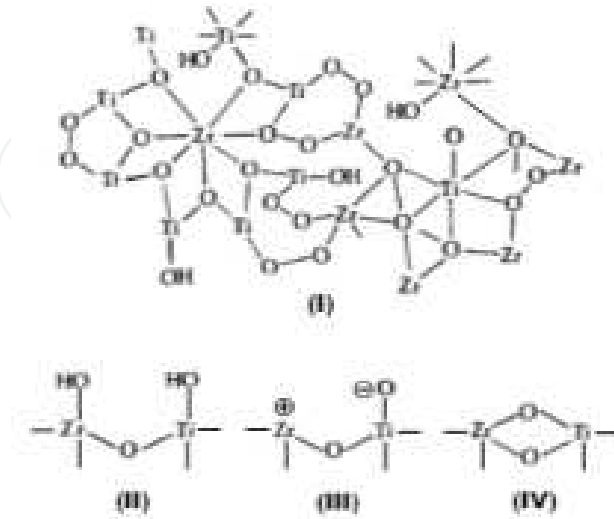

Fig. 3. Structures for $ZrTiO_4$. The structure I could be postulated as the amorphous and it is expected to change to the structure II, III and IV as the temperature increases (Navio *et al*, 1992b).
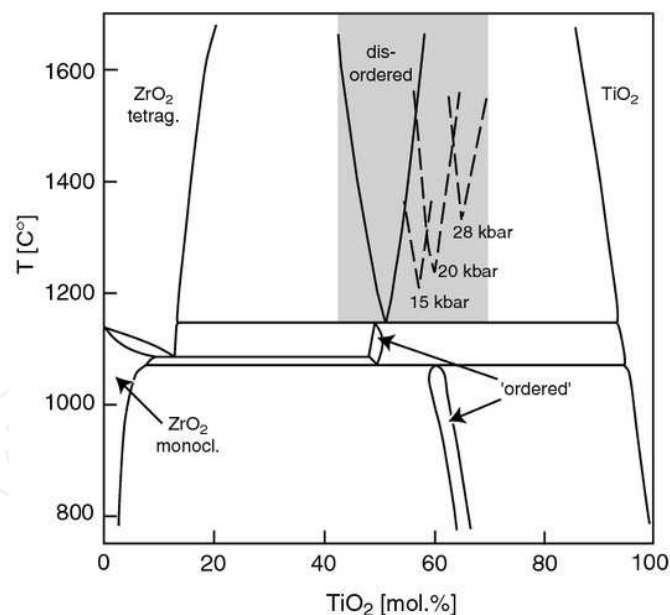
Fig. 4. ZrO_2-TiO_2 phase diagram (Troitzsch *et al*, 2005).

The ZrO_2-TiO_2 phase diagram, Figure 4, has been investigated by McHale and Roth (1986). Above 1100 °C there exists a stable solid solution, $Zr_{1+x}Ti_{1-x}O_4$, with approximate limits $-0.17 < x < 0.1$ ($x \sim -0.17$ corresponds to Zr_5-Ti_7O_{24}). At lower temperatures $ZrTiO_4$ is not thermodynamically stable, but a solid solution centered around the composition $ZrTi_2O_6$ is stable. However, a wide range of compositions in the solid solution $Zr_{1+x}Ti_{1-x}O_4$ can be

obtained in metastable form either by wet chemical methods (35-75 mol % Ti) or by quenching from high temperatures as the decomposition kinetics are very slow. The structure of $ZrTiO_4$ was first investigated in 1967. It was reported to be a close structural relative of columbite, $(Fe,Mn)Nb_2O_6$, a compound that has an α-PbO_2 substructure (Newnham, 1967).

The results of XRD of powders treated thermally at 500, 600 and 700 °C for 8 h are shown in Figure 5a (joint hydrolysis) (Santos *et al*, 2010) and 5b (separate hydrolysis). Figure 5a shows that below 700°C, the samples are amorphous. No presence of crystalline phases related to titania could be seen, probably because it presents in an amorphous form. The peak of orthorhombic $ZrTiO_4$ (2θ=30.595°) was observed in the diffractogram of the sample at 700 °C (López-López *et al*, 2010; Santos *et al*, 2010). López *et al.* prepared $ZrTiO_4$ films, deposited between 450 and 550 °C. At 450 °C, a weak intensity peak at 2θ = 30.48° indicates the presence of crystalline zirconium titanate, peaks at 2θ = 32-35° 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 2θ = 32.6°, 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 2θ = 33.06° associated with reflection (1 0 4) of Ti_2O_3. Peaks at 2θ = 32-35° suggest the presence of phases for SnO_2, TiO_2 and ZrO_2, while a weak intensity peak indicates the crystallization of $Zr_{0.8}Sn_{0.2}TiO_4$ (0 0 2) (López-López *et al*, 2008). Figure 5b shows that baddeleyite, JCPDS data for baddeleyite (13-0307), is formed at 2θ = 28.22°, at 600 °C and 700 °C from powder treated thermally at 500 °C. Besides the crystalline phase related to zirconium, the peak of titania, JCPDS data for anatase (04-0477), was observed in the anatase crystalline form and the peak of orthorhombic zirconium titanate, JCPDS data for zirconium titanate (34-415), at angles 25.2° and 30.6°, respectively.

Rodrigues et al (2010) reported the synthesis and characterization of nanostructures of sodium titanate/zirconium oxide obtained from the hydrothermal treatment of mixed oxide. Based on these results, we showed that the morphology and crystal structure of the productsobtained via hydrothermal treatment depend of the x value of the precursor $Ti_{1-x}Zr_xO_2$-nH_2O (Ti/Zr molar ratio). For example, for sample with x equal to 0, only the presence of sodium titanate nanotubes were observed, while for small x values (less than 0.50) the nanoparticles showed morphology of nanoribbons and the presence of the sodium titanate phase and tetragonal ZrO_2. For large values of x (greater than 0.50, high amount of zirconium) no morphological changes occurred and the tetragonal ZrO_2 phase was observed for samples. Furthermore, only for the product obtained from x equal to 0.15, we observed the presence of three-dimensional flower-like arrangements. Thus, the influence that the Ti/Zr molar ratio of the precursor plays on the phase and morphology of the hydrothermal products obtained is significant. Second Rodrigues, the preferential coordination of Zr^{4+} ion is between 7 and 8, while for Ti^{4+} it is always 6. The ionic radius of Zr^{4+} in ZrO_2 is 0.84 , assuming the coordination number equal to 8, and for the Ti^{4+} in TiO_2 it is 0.61 Å , assuming the coordination number equal to 6. This significant difference in the ionic radius results in the differences in behavior of incorporation of the Ti^{4+} into the lattice of the ZrO_2 and of the Zr^{4+} into the titanate lattice. When Zr^{4+} was introduced into the titanate structure this ion tends to interrupt the crystal arrangement of the titanate. On the other hand, the Ti^{4+} ion can
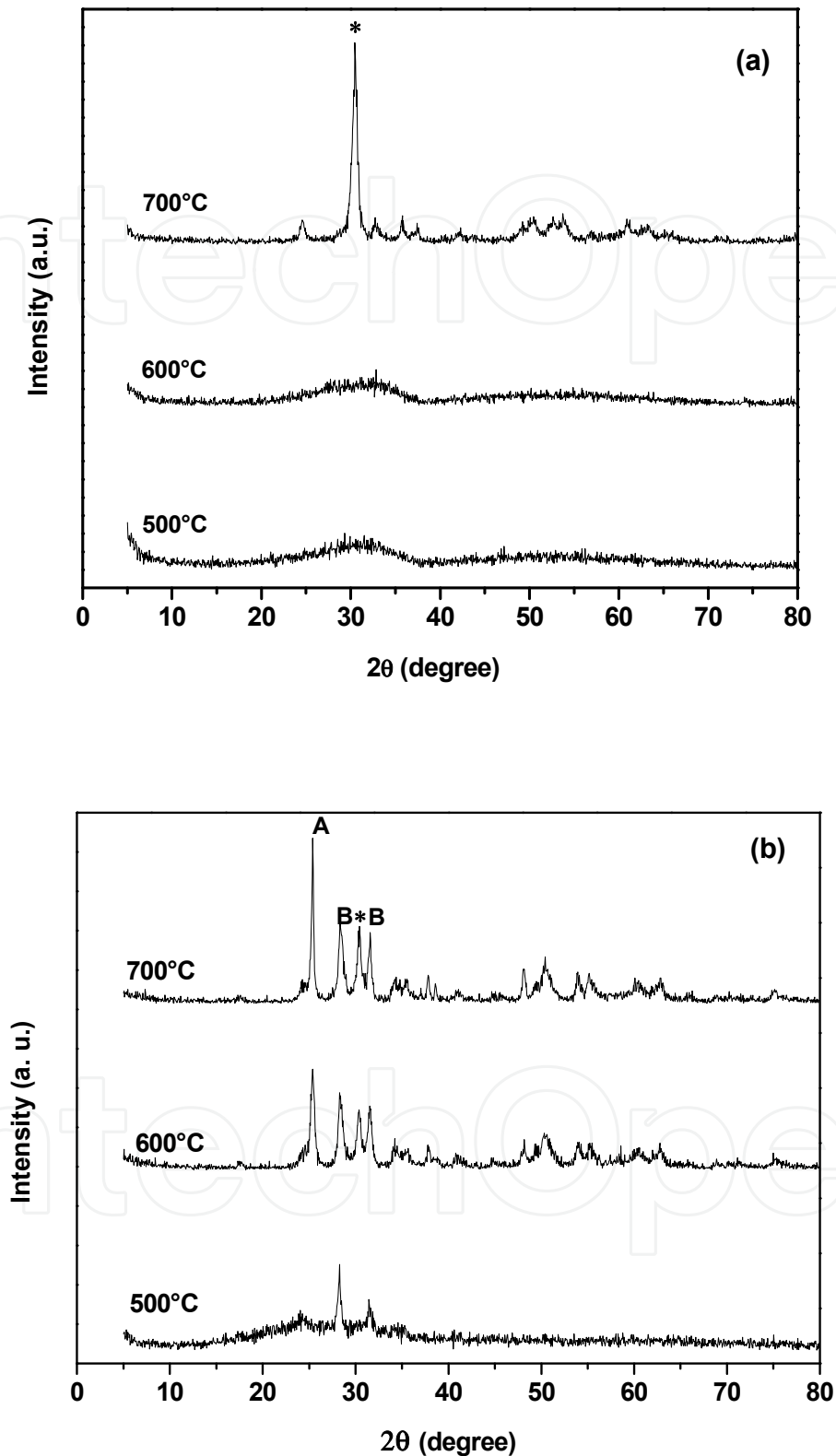
Fig. 5. Diffractograms of synthetized powders by hydrolysis of the alkoxides, after thermal treatment at 500, 600 and 700 °C for 8 h, NTZ and TPT: (a) together (*= ZT) (Santos et al, 2010) and (b) separately (A=anatase, B= baddeleyite, * = ZT).

be easily introduced into the ZrO_2 structure, because of its smaller radius and lower coordination number. However, because of its greater radius and coordination number Zr^{4+} ions could not be easily introduced into the titanate structure.

Figure 6 and 7 shows spectra obtained by means Fourier transform infrared spectroscopy (FT-IR) analysis of the dried and annealed ZT powders at different temperatures ranging from 100 °C to 800 °C with and without addition of nitric acid, respectively. 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 (Hao *et al*, 2004). According to Devi *et al* the bands between 3.500 and 3.300 cm^{-1} was assigned to fundamental stretching vibration of hydroxyl groups. Another peak related to hydroxyl group was found at 1.650 cm^{-1}. The set of overlapping peaks in the range of 810–520 cm^{-1} are related to Zr–O and Zr–O–Ti groups, respectively. From the above results it is indicated the presence of zirconium titanate on 316L SS (AISI stainless steel) substrate was confirmed. Similar results were also observed by Zhu *et al* (2009). The peaks between 500 and 710 cm^{-1} are related to Ti–O and Zr–O–Ti vibrations.

From the evaluation of the infrared spectra can be observed that the presence of nitric acid influences the absorption bands of OH, Zr–O and Zr–O–Ti. Hoebbel *et al* (1997) suggest that a low hydrolytic stability of metal oxide without functionality result in an additional, mostly indefinite number of H$^+$ groups, of the HNO_3 at the metal centres which causes a higher degree of hydrolysis reactions compared to stable complexes with a defined organic functionality.
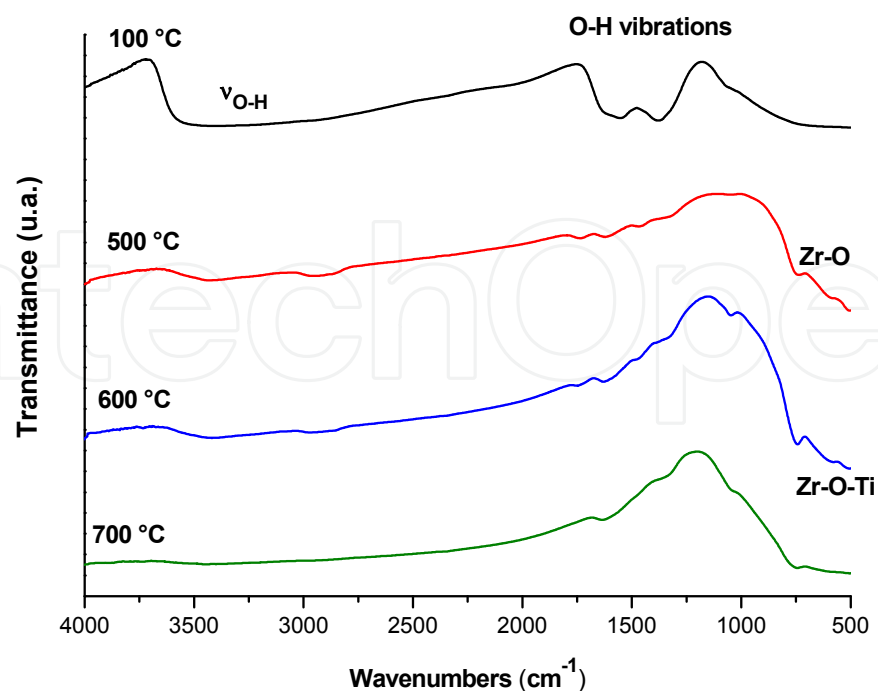

Fig. 6. FT-IR of the dried and annealed ZT powders at different temperatures ranging from 100, 500, 600 and 700 °C, with addition of nitric acid.
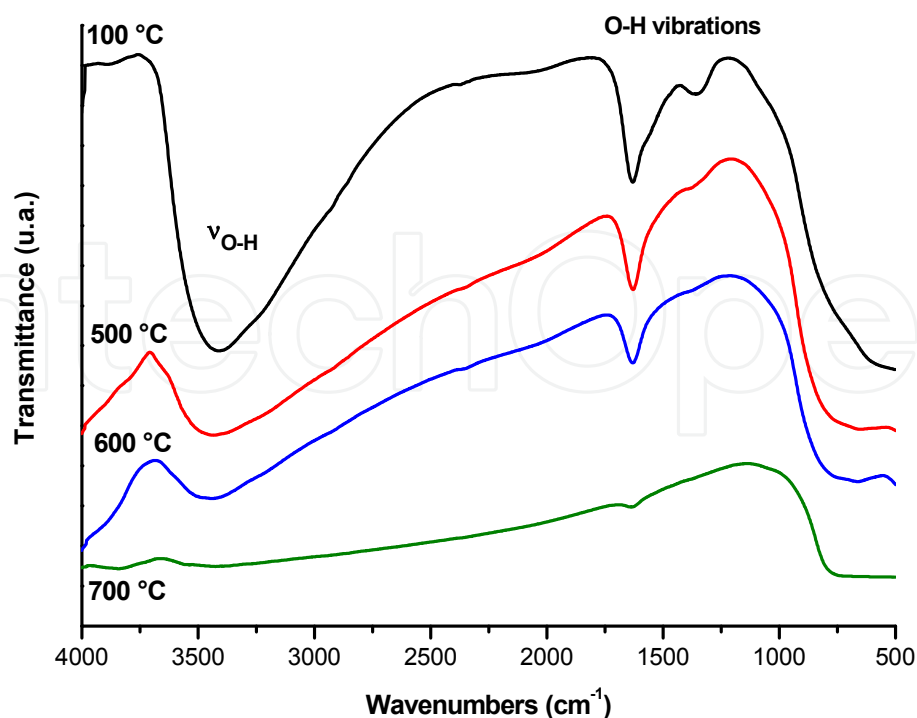
Fig. 7. FT-IR of the dried and annealed ZT powders at different temperatures ranging from 100, 500, 600 and 700 °C, without addition HNO_3.

With the thermal treatment at the temperatures evaluated in this study, the particle size increased. The mean size of the particle (D50) was 23 µm, determined by LASER diffraction spectrometry for powders after thermal treatment at 600°C. Generally in the sol-gel process, the particles are polydispersed and sometimes they can be multimodal, and/or nonspherical. In the sol-gel particles generally exhibit nanometer size, but in this work, the particle sizes presented in the order of micrometer size due to aggregation between the particles. Research on oxide-based materials have shown that dissolution reactions of titanium are initiated by the surface coordination of the material with H^+ and ligands that polarize, weaken and tend to break the metal-oxygen bonds of the surface (Blackwood *et al*, 2002). Therefore, durability of titanium oxide in acidic solutions can be envisaged as occurring by a parallel dissolution mechanism involving H^+ and ligands existing in solution. Unlike preferred complexing anions such as SO_4^{2-} or Cl^-, NO_3^- is a much weaker complexing agent, with very dilute HNO_3 known to be non-oxidising (Housecroft, 2005). The pronounced durability of zirconium oxide in nitric acid is well known for nanoparticles and films and can be extended here to zirconium titanate mesoporous materials from the results obtained (Gao *et al*, 1996; Andreeva *et al*, 1961). Moreover, Hoebbel *et al* suggest that a low hydrolytic stability of metal oxide complexes without functionality result in an additional, mostly indefinite number of H^+ groups at the metal centres which causes a higher degree of hydrolysis reactions compared to stable complexes with a defined organic functionality (Hoebbel *et al*, 1997).

It was possible to prepare $ZrTiO_4$ powders from zirconium *n*-propoxide and titanium isopropoxide, at a Zr:Ti molar ratio of 1:1, in propanol, with and without addition of nitric acid using the sol-gel process at ambient temperature (20 °C) and low thermal treatment.

Synthesis together with   the alkoxides was   obtained crystalline   orthorhombic   phase, confirmed by XRD and an exothermal peak without loss of mass by DTA analysis. When the synthesis was performed with separate alkoxides was   not   possible   to   obtain   only zirconium   titanate, probably due   to   the   fact formed crystalline   forms anatase, and baddeleyite observed by XRD, which competes with the formation of $ZrTiO_4$, which can be detected only at 700 °C. The $ZrTiO_4$ powders treated thermally at 700°C present. 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 700 °C they disappeared, indicating that the material structure no longer contains zirconium hydroxide. The sol-gel process was efficient in the   preparation of $ZrTiO_4$ using the two routes compared, but should be studied the addition of other acids, as nitric acid caused the aggregation of the powers.

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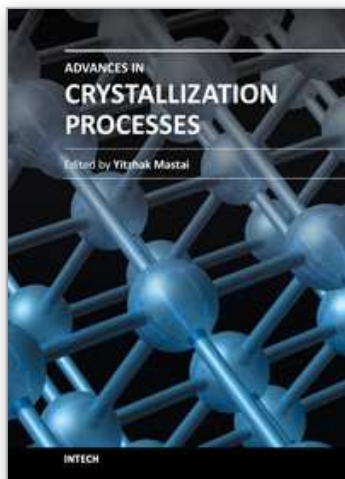
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Edited by Dr. Yitzhak Mastai

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