

DEHYDRATION AND CRYSTALLIZATION PROCESS IN SOL–GEL ZIRCONIA Thermal and spectroscopic study

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Abstract

Sol–gel zirconia was characterized using high-resolution thermogravimetry (Hi-Res TG) and differential scanning calorimetry (DSC) and compared with X-ray diffraction, Raman scattering, and UV-Vis spectroscopy. $\text{ZrO}_{2-x}(\text{OH})_{2x} \cdot y\text{H}_2\text{O}$ annealed below 400°C show typical behavior of amorphous material. As the annealing temperature is increased, the tetragonal and monoclinic phases crystallize. Typical Hi-Res TG curve shows that the samples are continuously dehydrated in a long temperature range, between room temperature and 600°C. The total mass loss relative to the initial mass is of about 29%. The DSC analysis coupled with TG and structural information, indicate that the exothermic processes about 355 and 447°C can be related to the nucleation process of the formation of tetragonal zirconia, with bulk crystallization at 447°C.

Keywords: sol–gel zirconia Raman study, sol–gel zirconia TG-DTA, sol–gel zirconia UV-Vis, sol–gel zirconia XRD

Introduction

The great variety of applications that display zirconia, has increased the attention to investigate the factors controlling its structure [1, 2]. Pure ZrO_2 present three types of crystalline structures: tetragonal, monoclinic and cubic, and they are determined by different factors used in their synthesis. In sol–gel zirconia preparation tetragonal phase is stable and is transformed into monoclinic through different ways, like in conventional microcrystalline zirconium oxide [3–7].

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The formation of tetragonal zirconia from amorphous material is well documented and its characterization is mainly made by XRD studies [8]. However, little evidence is given concerning thermal process involved in the formation of tetragonal zirconia, and about its transformation into monoclinic crystalline phase. DSC and TG techniques have been successfully used to analyze dehydration process in various compounds as oxide powders [9, 10], minerals [11] and pharmaceutical hydrates [12]. With the aim of contribute to the identification of zirconia crystalline phases by thermal analysis, in the present work the evolution of the formation well characterized zirconia obtained from zirconium alkoxides is reported. XRD, Raman, and UV-Vis spectroscopy supported TG and DTA results.

Experimental

ZrO₂ was prepared by sol-gel method. A solution of 29 cm³ of zirconium *n*-butoxide (80% Strem chemicals) and 143 cm³ of ethanol (99.8% Baker) was added drop-wise during 2 h into 31 cm³ of water until a final molar ratio of H₂O/Zr(But)₄=20/1 and EtOH/Zr(But)₄=5/1 were obtained. The synthesis process is obtained under constant stirring and at a reflux temperature of 60°C during 24 h until the gel was formed. The gel was then dried at 70°C during 12 h in the air. Samples were studied both in the freshly prepared state (*RT*) and after annealing in air in a thermally regulated Lindberg furnace for 4 h at 200, 400, 600, 800 and 900°C and then cooled to room temperature.

The powder XRD spectra were taken at room temperature and after annealing process. The diffractograms were obtained on a Siemens D-5000 X-ray diffractometer with a CuK_α radiation source (with a wavelength of 0.15418 nm). The samples were prepared by softly compacting the powder in the specimen holder. An on-line automatic search system (PDF Data-base) facilitated that observed data match with JCPDS standards.

Thermal analysis were done in flow of N₂ (100 cm³ min⁻¹) on a thermobalance (TA Instrument, mod. TG-2950). The programmed heating rates were 5, 10, 15, and 20°C min⁻¹. The mass of the samples used was between 10 and 15 mg. Each experiment was at least repeated four times. The differential scanning calorimetry (DSC) curves were obtained in a (TA Instruments DCS-2920). The samples were heated from *RT* to 500°C in a N₂ atmosphere at a heating rate of 10°C min⁻¹, with isotherms of 5 min before the start of the process.

Raman spectroscopy measurements were performed at room temperature on a computerized Spex 1403 double monochromator in combination with the 514.5 nm line of an Argon laser (Lexel lasers) at a power level of 50 mW at the laser head. Raman spectra were taken directly from zirconia powder or aggregates in back scattering geometry.

UV-Vis spectra were obtained using the diffuse reflectance technique on a Varian Cary III equipped with an integrator sphere.

Results and discussion

X-ray diffraction

The diffractogram of the solids samples $\text{ZrO}_{2-x}(\text{OH})_{2x}\cdot y\text{H}_2\text{O}$ annealed below 400°C show only wide bands (data not shown), which is a typical comportment of amorphous material. As the annealing temperature increases to 400°C , metastable tetragonal phase begins to crystallize as it can be seen in Fig. 1a (reflection at 30.3° , indexed as 011). Small diffraction peaks, indicated by an asterisk (Fig. 1b), are attributed to the monoclinic phase (reflections at 28.6° , indexed as 111 and 31.8° , indexed as 111) and can be observed at 600°C . They are more intense at 800°C , nevertheless, the tetragonal phase is still present at this temperature. A Rietveld analysis was performed to precise the proportion of each phase. At 400°C , the sample is in a mixture of amorphous and tetragonal phases. Using the Scherrer equation, it is possible to estimate the average crystallite size $D(\text{nm})$ in function of the annealing temperature. The percentages of each phase were calculated in function of the amount of tetragonal phase (100%, $D=10.5\text{ nm}$) existing in the sample at 400°C . At 600°C there is a mixture of tetragonal (78.9%, $D=30.9\text{ nm}$) and monoclinic (21.1%, $D=5.3\text{ nm}$) phases and, at 800°C the content of monoclinic phase was increased (23.3%, $D=25.9\text{ nm}$). It can be observed that the zirconia is nanostructured and the crystallite size increases as the annealing temperature increases.

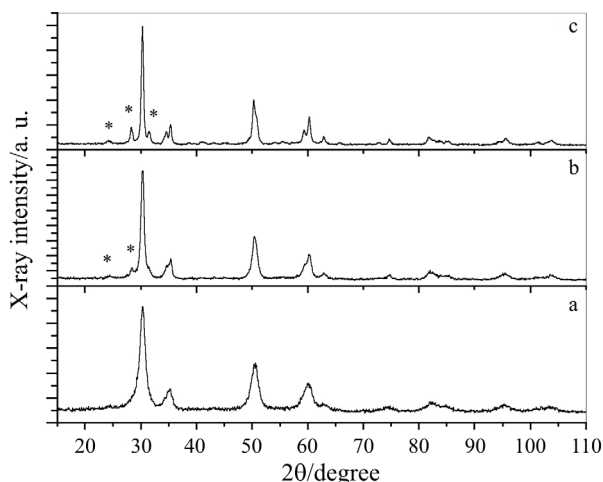


Fig. 1 X-rays diffractograms of zirconia at different annealing temperatures: a – 400°C , b – 600°C and c – 800°C . The monoclinic diffraction peaks are indicated by an asterisk

Thermal study

Typical TG curves of the $\text{ZrO}_{2-x}(\text{OH})_{2x}\cdot y\text{H}_2\text{O}$ are shown in Fig. 2. It can be observed a continuous dehydration and residual ButOH release process between RT and

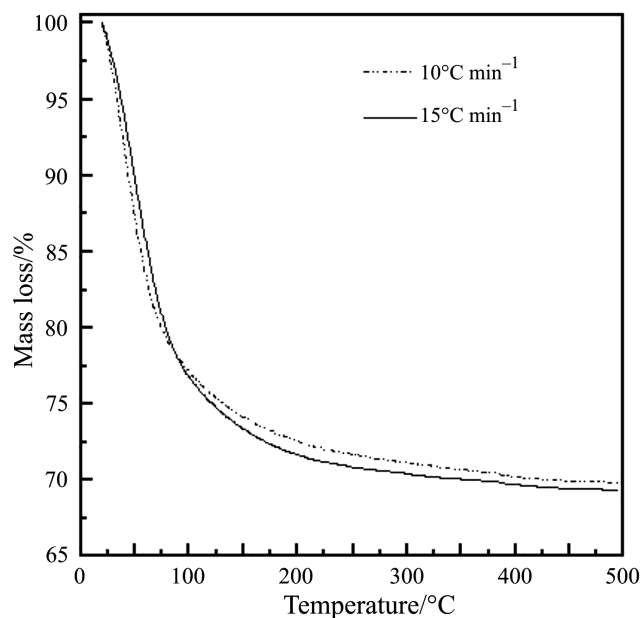


Fig. 2 Typical TG curve during dehydration process of $\text{ZrO}_{2-x}(\text{OH})_{2x.y}\text{H}_2\text{O}$ at 10 and $15^\circ\text{C min}^{-1}$

500°C that can be divided into two steps. The main mass loss (22.5%) is between RT and 100°C . A second mass loss of 7.5% is observed between 100 and 500°C . No change in TG was observed after 500°C . The last process (7.5%) corresponds to the formation of H_2O by condensation of surface $-\text{OH}$ groups, where can be situated the sites for the promotion of the nucleus formation of the tetragonal phase.

DSC analysis (Fig. 3), coupled with the previous TG show that the endothermic peak at 60°C is a consequence of the physical water desorbed as observed previously, while the exothermic processes at 355 and 447°C are related to the crystallization of the ZrO_2 . The presence of the thermal event at 355°C can be related with the initial formation of nucleus of the metastable tetragonal phase of ZrO_2 , as observed by X-ray scattering (Fig. 1), while, at 447°C the bulk crystallization process occurs. The total enthalpy change for those two processes is 16.2 kJ mol^{-1} , similar to previous works [13]. As was observed in TG analysis no change in DSC curve is observed after 500°C .

Raman scattering

Amorphous, monoclinic, tetragonal and cubic phases have been observed on zirconia. These phases may be identified from one another by means of Raman scattering. On the basis of experimental results [14, 15] tetragonal zirconia is expected to yield a spectrum consisting of six bands with frequencies at about 146, 267, 315, 456, 607 and 645 cm^{-1} . Monoclinic zirconia shows fourteen bands around 158, 177, 190, 221,

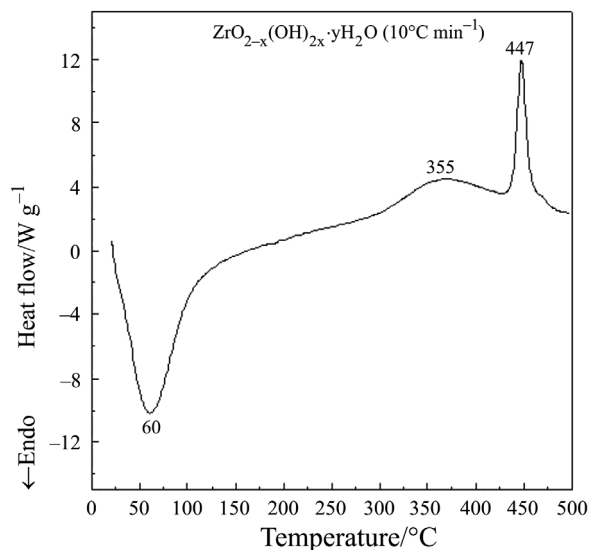


Fig. 3 DSC profile of $\text{ZrO}_{2-x}(\text{OH})_{2x} \cdot y\text{H}_2\text{O}$ between RT and 500°C at 10°C min⁻¹

306, 333, 347, 381, 475, 500, 537, 558, 615 and 638 cm⁻¹. In the case of the amorphous sample a broad band is generally observed at about 550 cm⁻¹.

In Fig. 4 the Raman spectra in the 100–750 cm⁻¹ region of the zirconia at different annealing temperatures from the fresh sample to 900°C are presented. Between room temperature and 400°C no peak is observed in agreement with X-ray diffraction results. It seems that some broad bands are existing suggesting a beginning of crystallization of the tetragonal phase inside the amorphous material at 400°C. At 600°C the tetragonal phase is clearly evidenced with bands at 150, 271, 323, 463 and 648.5 cm⁻¹. At 800°C we have a mixture of monoclinic and tetragonal phases where the bands at 174, 184, 217, 330, 344, 472, 500, 534, 557, 612 and 636 cm⁻¹ are due to the monoclinic phase and the bands at 141, 262 and 307 cm⁻¹ are due to the tetragonal phase, in agreement with X-ray diffraction. At 900°C the monoclinic phase is largely predominant in the sample. Some small bands or shoulders can be observed due to residual tetragonal phase.

UV-Vis

In Fig. 5 the UV-Vis spectra of pure zirconia are presented in function of the annealing temperature. The band gap is determined from the equation:

$$\alpha(h\nu) = A(h\nu - E_g)^{m/2}$$

where $\alpha(h\nu)$ is the absorption coefficient at the $h\nu$ energy photon, E_g the band gap, m a coefficient which is 1 for a direct transition and 4 for an indirect transition [16]. From the spectra a straight line is extrapolated to zero absorbance where $E_g = h\nu$.

The band gap varies from 5.0 eV for the fresh sample to 3.3 eV for the sample annealed at 800°C. The thermal treatment favors greatly the semiconducting proper-

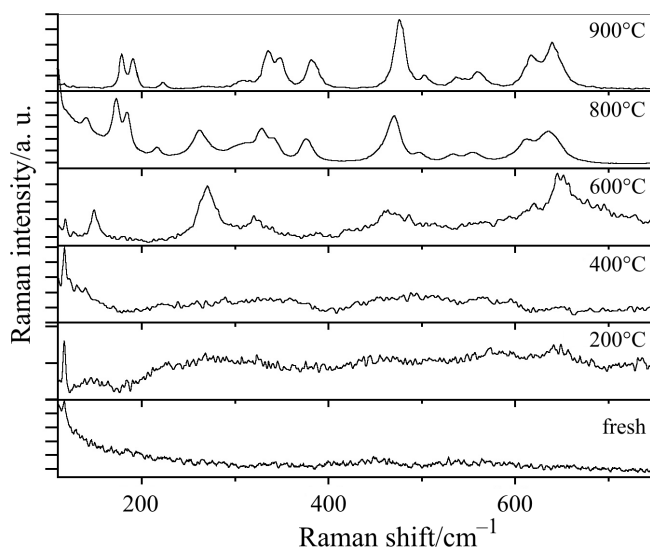


Fig. 4 Raman spectrum of sol-gel ZrO₂ at increasing annealing temperatures in the 100–800 cm⁻¹ region

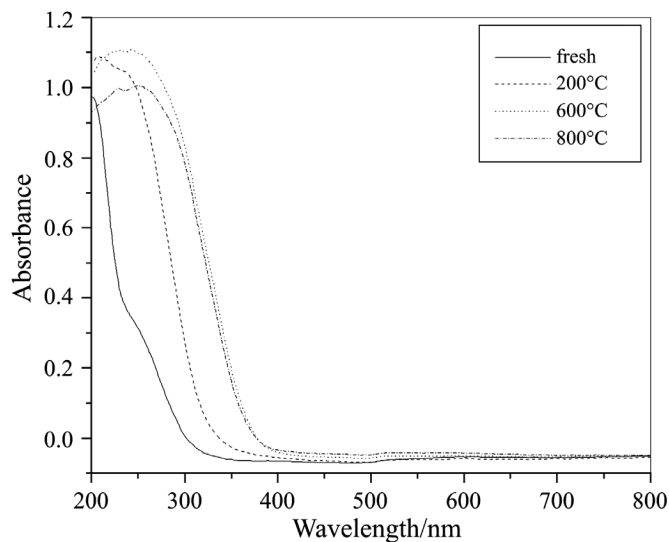


Fig. 5 UV-Vis absorption spectra of ZrO₂ sample at different annealing temperatures

ties of the material. This effect is correlated with the formation of defects in the materials due to oxygen vacancies caused by oxygen surface desorption, phenomenon in which due to the continuity of the process the energy involved cannot be detected by thermal analysis.

Conclusions

The XRD spectrum of the sol-gel $\text{ZrO}_{2-x}(\text{OH})_{2x}y\text{H}_2\text{O}$ obtained in this work when it is annealed below 400°C show typical behavior of amorphous material. As the annealing temperature is increased above 400°C , metastable tetragonal phase is crystallized. The formation of monoclinic zirconia at 600°C in mixture with tetragonal phase is identified by Raman spectroscopy. Hi-Res TG curves show that the samples are continuously dehydrated in a long temperature intervals, between room temperature and 600°C . The total mass loss mass is of about 30%. The DSC and TG analysis compared with XRD results indicate that the exothermic process about 355 and 447°C can be associated to the nucleation process of tetragonal phase and the bulk crystallization of this phase in ZrO_2 . After 500°C the transformation of tetragonal zirconia into monoclinic cannot be observed by TG-DSC, showing that this transformation is continuous and with low energy no detectable by DSC. The transformation of $\text{ZrO}_{2-x}(\text{OH})_{2x}y\text{H}_2\text{O}$ in tetragonal zirconia and his transformation into monoclinic during the sol-gel zirconia evolution is proved. No evidence of $\text{ZrO}_{2-x}(\text{OH})_{2x}y\text{H}_2\text{O}$ direct transformation to monoclinic phase is obtained. As annealing temperature increases, the material changes from isolating to semiconducting one as it can be observed with the band-gap variation with the annealing temperature. This evolution of the material is correlated to the existence of the monoclinic phase.

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