# Sol-gel processing and crystallization of yttria-doped zirconia

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## Abstract

$ZrO_2$–$Y_2O_3$ (5%) gel was synthesized by the hydrolytic polycondensation reactions of zirconium propoxide and yttrium chloride. The transformation of the gel on heating, examined by differential thermal analysis, thermogravimetric analysis and X-ray diffraction, is reported and discussed. The studied gel crystallizes directly into metastable tetragonal phase at low temperatures. This phase keeps stable up to a temperature of 1200°C.

*Keywords:* Crystallization; DTA; Sol-gel processing; TGA; XRD; Yttria-doped zirconia

## 1. Introduction

The great potential offered by the mechanical and electrical properties of zirconia and zirconia-containing ceramics has led to much work on fabrication procedures capable of providing homogeneous and reproducible materials with closely defined microstructures [1].

Zirconia exhibits polymorphism: it exists in three different crystalline forms, namely monoclinic (m), tetragonal (t) and cubic (c). The m→t phase transformation is observed at 1150°C and the t-phase reverts to the m-phase at about 950°C on cooling. Since the m-phase has a larger volume than the t-phase, the t→m transformation invariably causes cracking of bulk $ZrO_2$; the martensitic transformation under such conditions is deleterious. To stabilize the high-temperature t-phase at room temperature, CaO, $Y_2O_3$ or MgO are usually added to zirconia in appropriate proportions.

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The current processes for producing high-quality ceramic products involve preparation of submicron size particles of homogeneous composition, adoption of an appropriate powder processing technique to reduce or eliminate particle agglomeration, and controlled thermal treatment of the compacted products. A sol-gel approach represents a valid alternative to these procedures [2–7]. The application of the sol-gel method allows fabrication of gel-glass which can subsequently be converted into sintered ceramics by a suitable thermal treatment.

In a previous paper [8], we reported the non-isothermal crystallization of zirconia gel-glass. The results of this study show that the zirconia gel-glass crystallizes directly into the metastable t-phase at comparatively low temperatures and that the transformation into the stable m-phase occurs by heat treatment at 750°C for 1 h. The kinetic parameters obtained for the crystals growth of the t-phase, $E = 338 \text{ kJ mol}^{-1}$ and $n = 2.7$, suggest that in zirconia gel-glass a bulk crystallization is dominant.

In this work, 5 mol% yttria-doped zirconia gel was prepared and its crystallization behaviour was studied with the aid of X-ray diffraction and differential thermal analysis.

## 2. Experimental

Zirconia gel containing 5% $Y_2O_3$ was prepared using zirconium propoxide, $Zr(OC_3H_7)_4$, and yttrium chloride, $YCl_3$, analytical grade reagents as starting materials. Alcoholic solutions of zirconium propoxide were prepared in a dry box at room temperature. To control the $Zr(OC_3H_7)_4/H_2O$ ratio, absolute ethanol obtained by distillation of commercial anhydrous ethanol with metallic sodium, was used. Acetylacetone was also added to control the hydrolytic activity of zirconium alkoxide. The preparation procedure flow chart and the molar ratios employed are reported in Fig. 1. The hydro-alcoholic solution of $YCl_3$ was slowly added to the solution of $Zr(OC_3H_7)_4$ and then stirred with a magnetic stirrer. Under these conditions, complete gelation occurred in about 30 min, giving a clear pale yellow gel. The gelled system was held for one day more at room temperature before drying. After complete drying at 50°C for one day, yellow pieces of dry gel were obtained.

The nature and temperature of the various reactions that occur during heating of the dried gel (volatilization, pyrolysis, etc.) were determined using simultaneous thermogravimetric (TGA) and differential thermal analysis (DTA). A powdered sample, 20 mg, of the dried gel, was subjected to TGA/DTA (Stanton-Redcroft analyser) runs in nitrogen at a heating rate of 10°C min$^{-1}$ from room temperature to 800°C, using powdered $Al_2O_3$ as a reference material.

In addition, DTA runs were carried out on the small bulk samples (about 50 mg) of the dried gel in nitrogen at a heating rate of 10°C min$^{-1}$ from room temperature to 1200°C. Powdered $Al_2O_3$ was added to improve the heat transfer between bulk samples and the sample-holder of the DTA apparatus. A Netzsch thermoanalyser High Temperature DSC 404 was used, with powdered $Al_2O_3$ as a reference material.
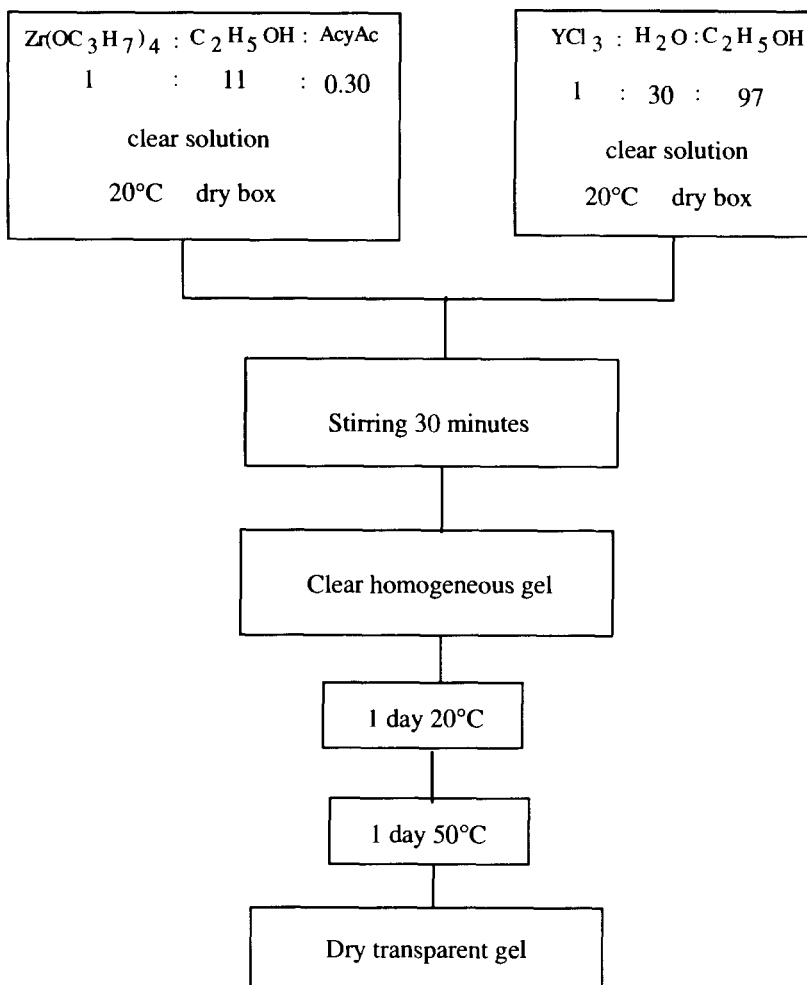
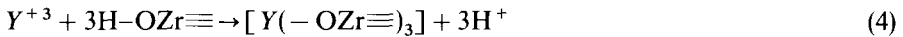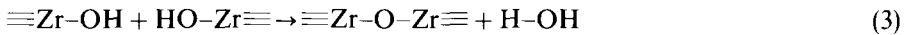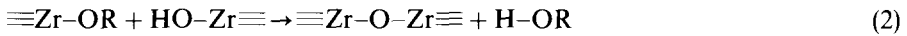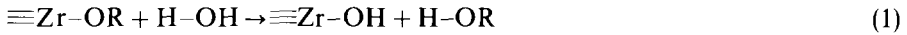Fig. 1. Flow diagram of the gel preparation procedure.

The amorphous nature of the dried gel and the identification of the phase crystallizing during the DTA runs were ascertained by X-ray diffraction using a Philips diffractometer. Powders of each sample were scanned from $2\theta = 5$ to $60°$ using Cu K$\alpha$ radiation. The grain size, $D$ (in angstroms), was evaluated from the broadening of the line (111) of the t-phase using the Scherrer formula

$$D = \frac{0.9\,\lambda}{B\cos\theta}$$

where $\lambda$ is the X-ray wavelength, $\theta$ the Bragg angle and $B$ the peak width at half the peak height.

## 3. Results and discussion

Gelation is the result of hydrolysis and condensation reactions according to the following equations

$$\equiv \text{Zr–OR} + \text{H–OH} \rightarrow \equiv \text{Zr–OH} + \text{H–OR} \tag{1}$$

$$\equiv \text{Zr–OR} + \text{HO–Zr}\equiv \rightarrow \equiv \text{Zr–O–Zr}\equiv + \text{H–OR} \tag{2}$$

$$\equiv \text{Zr–OH} + \text{HO–Zr}\equiv \rightarrow \equiv \text{Zr–O–Zr}\equiv + \text{H–OH} \tag{3}$$

$$Y^{+3} + 3\text{H–OZr}\equiv \rightarrow [Y(-\text{OZr}\equiv)_3] + 3\text{H}^+ \tag{4}$$

At room temperature, the hydrolysis reaction (Eq. (1)) is much faster than the condensation reactions (Eqs. (2) and (3)), so that the number of Zr–O–Zr bridges formed are insufficient to give gelation, and precipitation of hydrated zirconium oxide–alkoxide aggregates occurs. However, the use of acetylacetone [2] allows: (a) the control of the hydrolysis reaction rate of zirconium alkoxide so that soluble polymeric intermediates are obtained, which then undergo further polymerization to form gel; (b) the introduction of the $Y^{+3}$ cation into the zirconia network according to Eq.(4).

The TGA and DTA curves of the dried gel and of the dried gel heated for 3 h at 340°C are reported in Fig. 2(a) and (b), respectively. A large endothermic peak, from room temperature to about 250°C, appears on the DTA curve in Fig. 2(a), with a maximum at about 105°C, and a simultaneous weight loss in the TGA curve. The weight loss in this temperature range was 20.5%. These effects were due to the evaporation from open pores of water and alcohol physically trapped in the gel. At higher temperatures, the DTA curve of the dried gel shows an exothermic hump, from 250°C to about 360°C, with a maximum at about 340°C, and a simultaneous weight loss occurs in the TGA curve, from 20.5 to 28.0%. These effects are due [7, 8] to the pyrolysis of residual organic groups in the gel, which had not reacted by the end of the drying step and consequently did not evaporate from the gel before calcining. Finally, the DTA curve of the dried gel exhibits an exothermic peak with a maximum at 473°C that can be attributed to the growth of tetragonal zirconia crystals, as shown by the XRD pattern of the sample heated in the DTA furnace until the temperature of the DTA crystalliza-tion peak, reported in Fig. 3, trace (c). As the TGA curve of the dried gel exhibits a further weight loss, from 28 to 32%, in the temperature range corresponding to the first part of the DTA crystallization peak, and in order to detect the glass transition temperature on the DTA curve, the dried gel was heat-treated for 3 h at 340°C in the DTA furnace. This heat treatment does not produce crystallization, as shown by the XRD pattern of the sample heated in the DTA furnace for 3 h at 340°C reported in Fig. 3, trace (b), but strongly affects the DTA/TGA curves. The DTA curve of the heat-treated gel-glass, reported in Fig. 2(b), does not show any appreciable effects until 350°C, even if, simultaneously, on the TGA curve of Fig. 2(b) a small but gradual weight loss (6%) was observed. This behaviour is probably due to the slow removal of water physically adsorbed after the heat treatment. An exothermic hump appears on the DTA curve of Fig. 2(b), just before the sharp exothermic peak with a maximum at 459°C. As the XRD pattern of the sample heated in the DTA furnace up to this
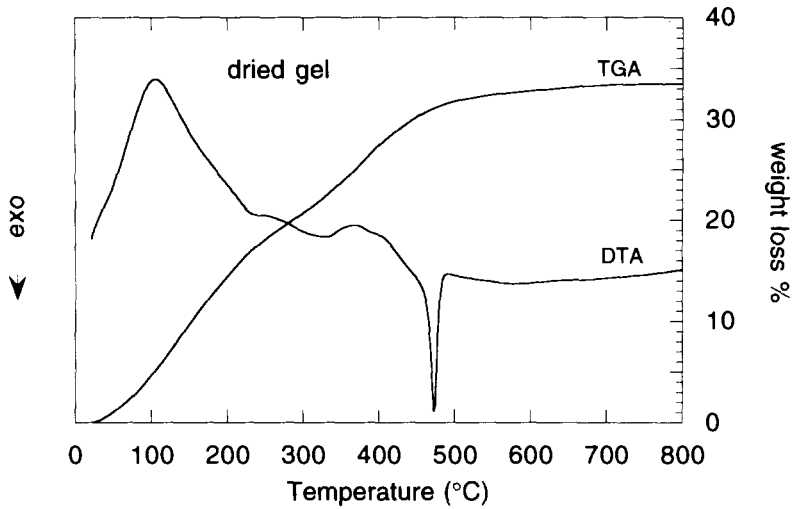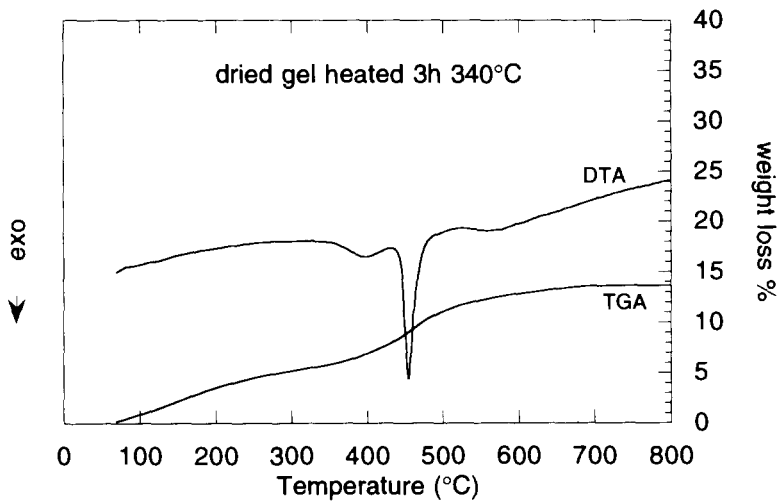
Fig. 2. DTA and TGA curves recorded in nitrogen at 10°C min⁻¹: (a) dried gel, (b) dried gel heated for 3 h at 340°C.

exothermic peak has the same look of that reported in trace (c) of Fig. 3, it can be attributed to the crystallization, even if simultaneously a weight loss, from 6 to 12%, occurs on the TGA curve. Moreover, no slope change attributable to the glass transition temperature was detected on the DTA curve of the heat-treated gel. These results can be interpreted as being due to the overlapping of three processes in the same
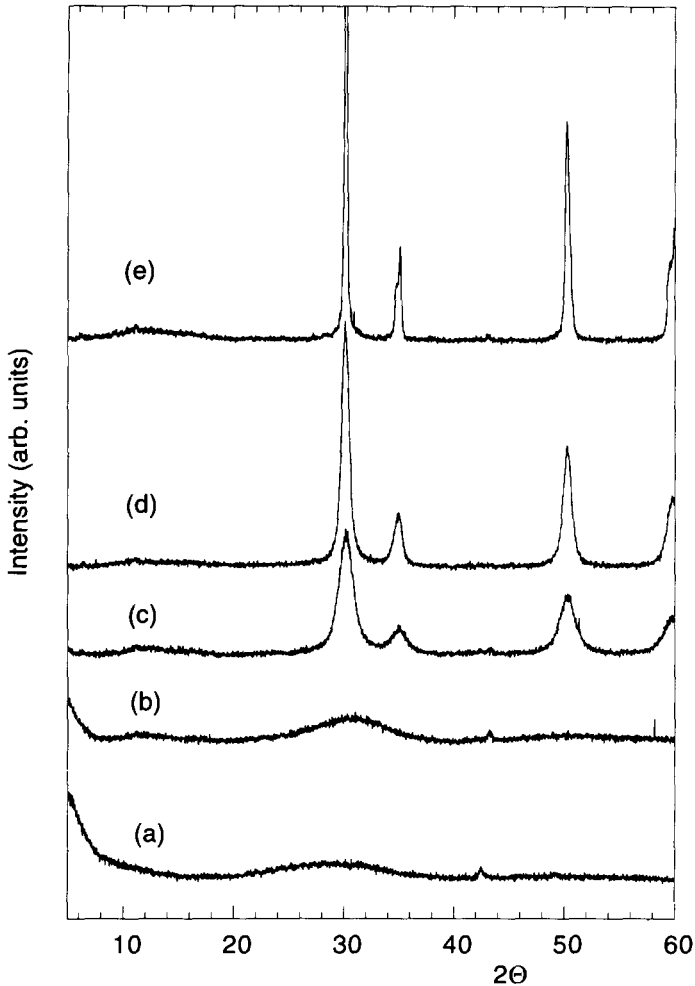
Fig. 3. Powder X-ray diffraction patterns: (a) dried gel, (b) dried gel heated for 3 h at 340°C, (c) a sample of dried gel heated in the DTA furnace up to the temperature of the exothermic crystallization peak, (d) a sample of dried gel heated for 14 h at 800°C, (e) a sample of dried gel heated for 14 h at 1200°C.

temperature range: first, the decomposition of some of the products of the hydrolysis and polycondensation reactions (organic molecules, zirconium oxy-hydroxide, zirconium oxy-chloride) [7]; second, the gel-glass transformation; and third, the crystallization of tetragonal zirconia crystals.

The studied gel-glass crystallizes directly into the metastable t-phase at low temperatures and the t-phase is stable up to 1200°C. Long heat-treatments (14 h) at 800 and 1200°C do not produce the transformation into the thermodynamically stable m-phase, as shown by the XRD patterns of the samples, heated in the DTA furnace for 14 h at 800°C (d) and 14 h at 1200°C (e), reported in the traces (d) and (e) of Fig. 3. The above heat-treatments only cause an increase of the crystal mean size from 66 to 220 Å.
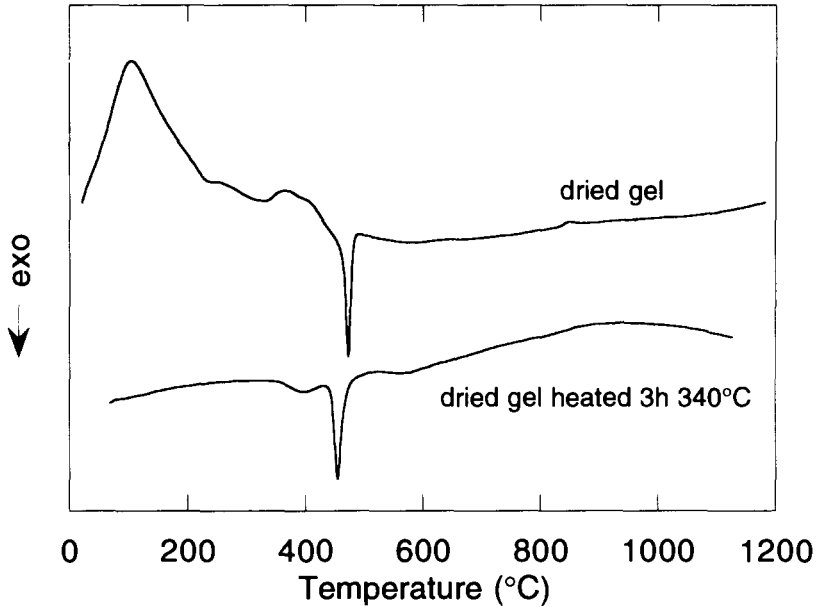
Fig. 4. DTA curves recorded in nitrogen at 10°C min⁻¹.

The DTA curves in Fig. 4 show that the heat-treated dried gel devitrifies at a lower temperature (459°C) than the dried gel (473°C). As it was shown in Ref. [9] that the higher the number of nuclei, the lower the temperature of the DTA crystallization peak, the above result suggests that during the heat-treatment at 340°C, a large number of nuclei are formed and that this temperature is very close to the glass transition temperature value.

## 4. Conclusions

The bulk dried gel of $ZrO_2$–$Y_2O_3$ (5%) prepared contains water and organic residues that are lost on heating. The temperature necessary for the gel to glass conversion is very close to the glass transition temperature of the glass being formed, and therefore during the heat treatment, a high number of internal nuclei are formed. The studied gel-glass crystallizes directly into the metastable tetragonal phase and the addition of yttrium makes the t-phase of zirconia stable from room temperature to 1200°C.

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