ELSEVIER

Thermochimica Acta 259 (1995) 225–234

thermochimica
acta

The effect of mechanical treatment of zirconium(IV) hydroxide on its thermal behaviour

G. Štefanić [a], S. Popović [b], S. Musić [a,*]

[a] Ruder Bošković Institute, P.O. Box 1016, 41001 Zagreb, Croatia
[b] Department of Physics, Faculty of Science, University of Zagreb, P.O. Box 162, 41001 Zagreb, Croatia

Received 18 November 1994; accepted 29 January 1995

Abstract

Precipitated zirconium(IV) hydroxide was ball-milled at room temperature for 1, 3, 9, 35 and 60 h. The samples were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD).

DSC curves of the samples, obtained by ball-milling for 1, 3 and 9 h, showed two exothermic peaks due to crystallization of tetragonal ZrO_2 as determined by XRD and FT-IR. These two exothermic peaks were ascribed to the heterogeneity of the zirconium(IV) hydroxide structure caused by ball-milling. The samples, obtained by ball-milling for 35 and 60 h, showed only one exothermic peak. Three important phenomena, as a consequence of the ball-milling of zirconium hydroxide, were observed: (a) dehydration, (b) an increase in the activation energy of the crystallization and (c) a decrease in the enthalpy of crystallization of t-ZrO_2 from ball-milled zirconium hydroxide. The present study indicated that the process of crystallization of t-ZrO_2 from zirconium(IV) hydroxide is more complex than a simple structural (topotactic) rearrangement.

Keywords: DSC; FTIR; TGA; XRD; Zirconium hydroxide

1. Introduction

The mechanism of the precipitation of amorphous zirconium hydroxide and its thermal behaviour have been investigated extensively [1–7]. These investigations have

---

* Corresponding author.

SSDI 0040-6031(95)02279-1

indicated that the pH of precipitation and the time required to attain the final pH are important factors determining the structural type of ZrO_2 formed from zirconium hydroxide heated up to 400°C [1–4]. Clearfield [5–7] suggested that major species in the solutions of zirconium salts are tetrameric zirconium units $[Zr(OH)_2 \cdot 4H_2O]_4^{8+}$ which undergo polymerization on addition of base or on aging of the solution at elevated temperatures. If the process of polymerization is fast (rapid addition of base), only a few tetrameric units can be linked by hydroxyl bridges, yielding an amorphous gel. A slow process of polymerization generates two-dimensional sheets of $Zr(OH)_4 \cdot xH_2O$ that link together with the release of water, thus forming the fluorite structure. The formation of metastable tetragonal zirconium oxide, t-ZrO_2, by thermal decomposition of zirconium hydroxide at ~400°C is well known, but the mechanism of this process is still the subject of discussion. A detailed description of this will be published elsewhere [8].

In the present paper we emphasize three theories. The first suggests that t-ZrO_2 is stabilized due to impurities remaining in the crystal lattice [5, 9]. In the second theory, proposed by Garvie [10, 11] and supported by Bailey et al. [12], the stabilization of t-ZrO_2 is interpreted in terms of its low surface energy. In the third theory, proposed by Livage et al. [13] and supported by other researchers [14–16], the formation of metastable zirconia is described as being a result of structural similarities between t-ZrO_2 and the amorphous zirconium hydroxide precursor.

Mechanochemical treatment of solid samples, used in the present work, is a frequently utilized method for the activation of metal hydroxides or oxyhydroxides in the synthesis of the corresponding metal oxides [17–19]. In many cases, such phase transformations can be attained at room temperature by simple grinding in a planetary ball-mill. For instance, α-Fe_2O_3 was obtained after grinding δ-FeOOH for 8 h [17]. The grinding period needed for the complete transformation of δ-FeOOH into α-Fe_2O_3 was shorter than in the case of β-FeOOH or γ-FeOOH as the starting material, thus indicating a certain structural relationship between δ-FeOOH and α-Fe_2O_3.

Tsuchida and Ichikawa [19] investigated the effect of ball-milling γ-$Al(OH)_3$ (gibbsite), α-$Al(OH)_3$ (bayerite) and γ-AlOOH (boehmite). All these three compounds converted to an amorphous phase without dehydration, gibbsite and bayerite after 4 h and boehmite after 8 h of grinding. The DTA endotherms, typical for the dehydration of hydrated aluminas, gradually diminished on grinding and broad endotherms of the amorphous phase appeared at ~150 to 200°C. All amorphous hydrated aluminas obtained by mechanochemical treatment showed the same conversion route upon heating: amorphous alumina $\rightarrow \eta$-phase $\rightarrow \alpha$-Al_2O_3. The temperature of this conversion is decreased by more than 200°C in relation to the conversion into α-Al_2O_3 from the initial crystalline phases.

The mechanochemical treatment of monoclinic zirconium oxide, m-ZrO_2, was performed by Bailey et al. [12] and Scian et al. [20]. They found that the transformation m-$ZrO_2 \rightarrow t$-ZrO_2 occurred when the particle sizes were sufficiently small. However, Murase and Kato [21] observed the transformation t-$ZrO_2 \rightarrow m$-ZrO_2 when t-ZrO_2, prepared by thermal decomposition of zirconium hydroxide, was ball-milled in different atmospheres.

The aim of the present work was to investigate the effect of ball-milling amorphous zirconium(IV) hydroxide on the crystallization of t-ZrO_2, and to obtain more information on the nature of this process.

2. Experimental

Analytically-grade salt, $ZrO(NO_3)_2 \cdot 2H_2O$, was dissolved in doubly distilled water. Amorphous zirconium hydroxide was precipitated at pH ~ 10.5 by the addition of NH_4OH solution under vigorous stirring. The precipitate (sample Z_0) was separated from the mother liquor and then washed with doubly distilled water. The solid phase was separated from an aqueous phase by a Sorvall RC2-B ultra-speed centrifuge (max. 20000 rpm). This procedure was repeated until a neutral pH was obtained. A Radiometer instrument, pHM-26, was used to measure pH. Using this washing procedure, the impurities (NO_3^-, NH_4^+) were removed, preventing their possible influence on the formation of metastable t-ZrO_2.

Sample Z_0 was dried at 50°C and subjected to mechanical treatment at room temperature using a Fritsch (Pulverisette 5) planetary ball-mill with agate bowl and balls (99.9% SiO_2). The notation of the samples and the ball-milling conditions are given in Table 1. Differential scanning calorimetry was performed with a scanning rate of 20°C $\min^{-1}$ using a Perkin-Elmer instrument, model 7. During the measurement procedure, circulating water was used as a coolant. The flow of nitrogen ensured a constant purging of the sample holder during the measurement. Thermogravimetric analysis was performed using standard instrumentation. X-ray powder diffraction measurements were performed at room temperature with a Philips diffractometer, model MPD 1880. FT-IR spectra were recorded in the far infrared region at room temperature using a Perkin-Elmer spectrometer, model 2000. The FT-IR spectrometer was coupled with a personal computer loaded with an IR Data Manager. The samples were pressed onto the surface of polyethylene foil.

Table 1
The results obtained from DSC thermograms of ball-milled samples

Sample	Time of ball-milling/h	Dehydration		Crystallization		
		Enthalpy/ (kJ mol^{-1})	Maximum/ (°C)	Enthalpy/ (kJ mol^{-1})	Maximum 1/ (°C)	Maximum 2/ (°C)
Z_0	0	39.4	88	−21.6	448	
Z_1	1	29.8	131	−19.4	447	468
Z_3	3	18.6	133	−14.9	449	487
Z_9	9	12.3	137	−12.9	452	508
Z_{35}	35	4.8	128	−11.3		563
Z_{60}	60	6.4	131	−11.1		575

3. Results and discussion

Fig. 1 shows the DSC curves of samples Z_0, Z_3, Z_9, Z_{35} and Z_{60}. The DSC curve of sample Z_0 showed two peaks. The first broad, strong endothermic peak, corresponding to dehydration, had its maximum at 88°C, beginning at ~50°C and ending at ~250°C. The second sharp, strong exothermic peak, corresponding to crystallization of ZrO_2, had a maximum at 448°C, starting at ~425°C and ending at ~475°C. Sample Z_1 showed a thermogram very similar to sample Z_0. The intensity of the dehydration peak was little decreased, while a shoulder appeared at the high-temperature side of the crystallization peak, indicating the appearance of a new exothermic peak.

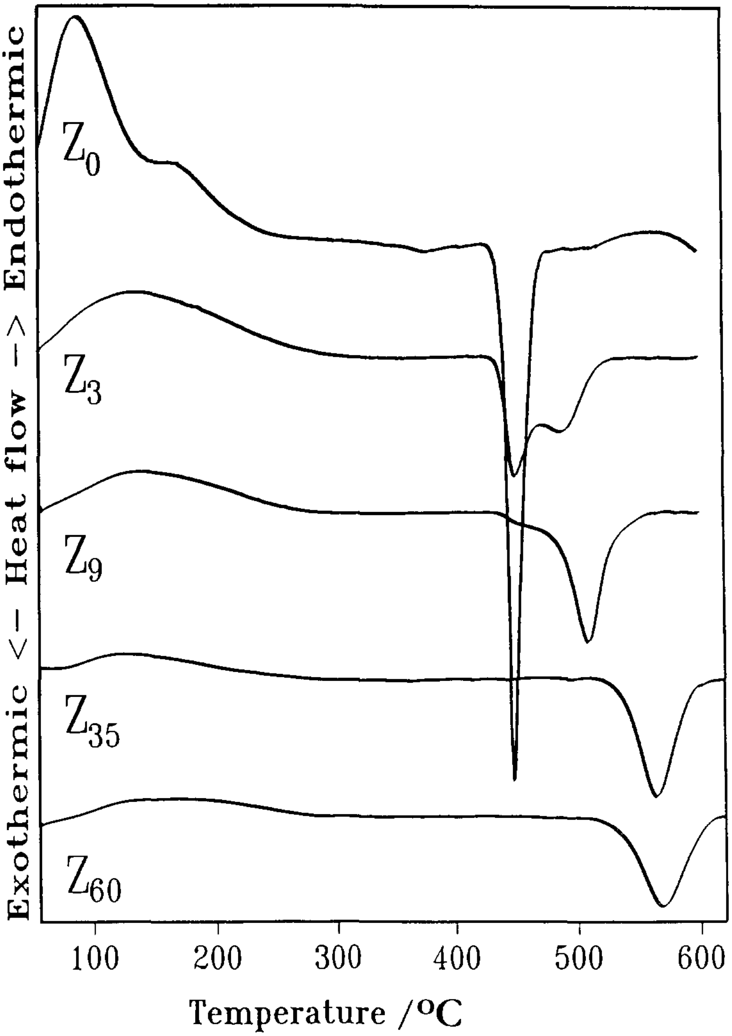

Fig. 1. DSC thermograms obtained from zirconium hydroxide mechanically treated for different times.

Sample Z_3 showed two separate exothermic peaks, the first beginning at 431°C and ending at 475°C, with the maximum at 449°C, which is close to the position of the exothermic peaks of samples Z_0 and Z_1, very probably corresponding to the same crystallization process. The second peak, of less intensity than the first, begins at 470°C and ends at 530°C, with the maximum at 487°C. DSC measurements with sample Z_3 and other samples which exhibited a further decrease in the endothermic peak intensity, indicated that dehydration of the samples took place during the ball-milling. Sample Z_9 also showed two exothermic peaks, but the first one, corresponding to that of sample Z_0 and Z_1, was very small and broad. The second peak showed an increased intensity, and was shifted to a higher temperature. Samples Z_{35} and Z_{60} exhibited only the second exothermic peak which was further shifted to higher temperatures.

In order to clarify the nature of the first and second exothermic peaks, we used sample Z_3, which was characterized by distinctly separated peaks of similar intensities. Sample Z_{3a} was obtained by heating sample Z_3 inside the DSC instrument, using the same scanning rate as before, up to the saddle point at 470°C. Sample Z_{3b} was obtained in a similar way, but the heating was performed up to 600°C. This temperature was high enough to ensure that the process causing the appearance of the second exothermic peak took place. Fig. 2 shows characteristic parts of the X-ray diffraction patterns of samples Z_3, Z_{3a} and Z_{3b}.

According to the X-ray diffraction pattern, sample Z_3 was amorphous with no indication of crystallinity. Sample Z_{3a} was metastable t-ZrO_2, but the presence of a small fraction of an amorphous phase could not be excluded. Surprisingly, sample Z_{3b} was also metastable t-ZrO_2, exhibiting diffraction lines that were sharper and more intense than sample Z_{3a}. No diffraction lines characteristic for other ZrO_2 polymorphs were present.

FT-IR spectra of samples Z_0, Z_1, Z_3, Z_{3a}, Z_{3b}, Z_9, Z_{35} and Z_{60}, recorded in the far-infrared region from 700 to 70 cm^{-1}, showed a broad band with a transmittance minimum at $\sim 480\,cm^{-1}$. FT-IR spectra of samples Z_3, Z_{3a} and Z_{3b} are shown in Fig. 3. Samples Z_{3a} and Z_{3b} also showed shoulders at 595 and 353 cm^{-1} and one very broad band with a transmittance minimum at $\sim 187\,cm^{-1}$. This is in agreement with the spectrum of t-ZrO_2 described in the literature [8, 22]. These results confirmed that both exothermic bands obtained by DSC belonged to the crystallization of metastable t-ZrO_2.

Srinivasan et al. [3] found that the transformation from amorphous zirconium hydroxide to m-ZrO_2 showed approximately the same exothermic peak as the transformation to t-ZrO_2. This means that conclusions cannot be drawn concerning the type of phase transformation on the basis of the DSC curves alone, as discussed previously. Samples Z_0, Z_1, Z_9, Z_{35} and Z_{60}, when heated inside the DSC up to 600°C, showed FT-IR spectra similar to that of sample Z_{3b}, with no bands characteristic for m-ZrO_2 [8, 23], so that both exothermic peaks can be ascribed to the formation of t-ZrO_2.

The relation between the ball-milling time and the temperature of t-ZrO_2 crystallization, including both exothermic peaks, is shown in Fig. 4. This relation indicates clearly that grinding amorphous zirconium hydroxide shifts the crystallization onset to higher temperatures, i.e. increases the activation energy needed for the crystallization. On the

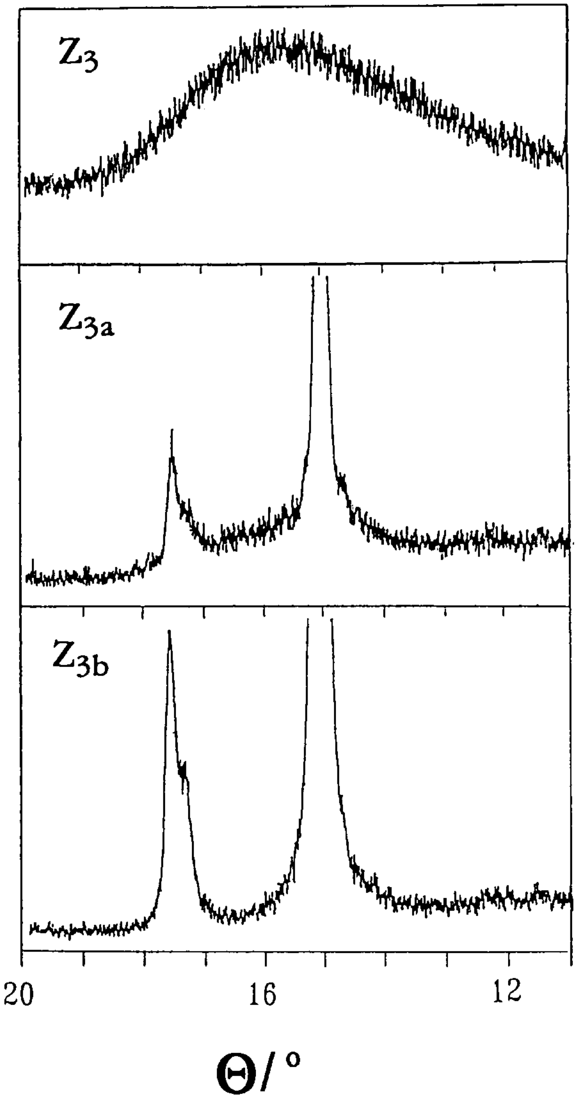

Fig. 2. X-ray powder diffraction patterns of samples Z_3, Z_{3a} and Z_{3b}.

basis of the present experiments, it can be concluded that the process of ball-milling induces a structural change in zirconium hydroxide showing a certain structural similarity with t-ZrO_2, which is in agreement with the conclusions of other researchers [3, 13–16]. It may be supposed that this structural similarity results from a short-range order, because XRD and FT-IR did not detect any crystalline phase; see, for example, Fig. 2, sample Z_3. The existence of two exothermic peaks can be ascribed to heterogeneity of the sample structure due to mechanical treatment. For shorter milling times, only

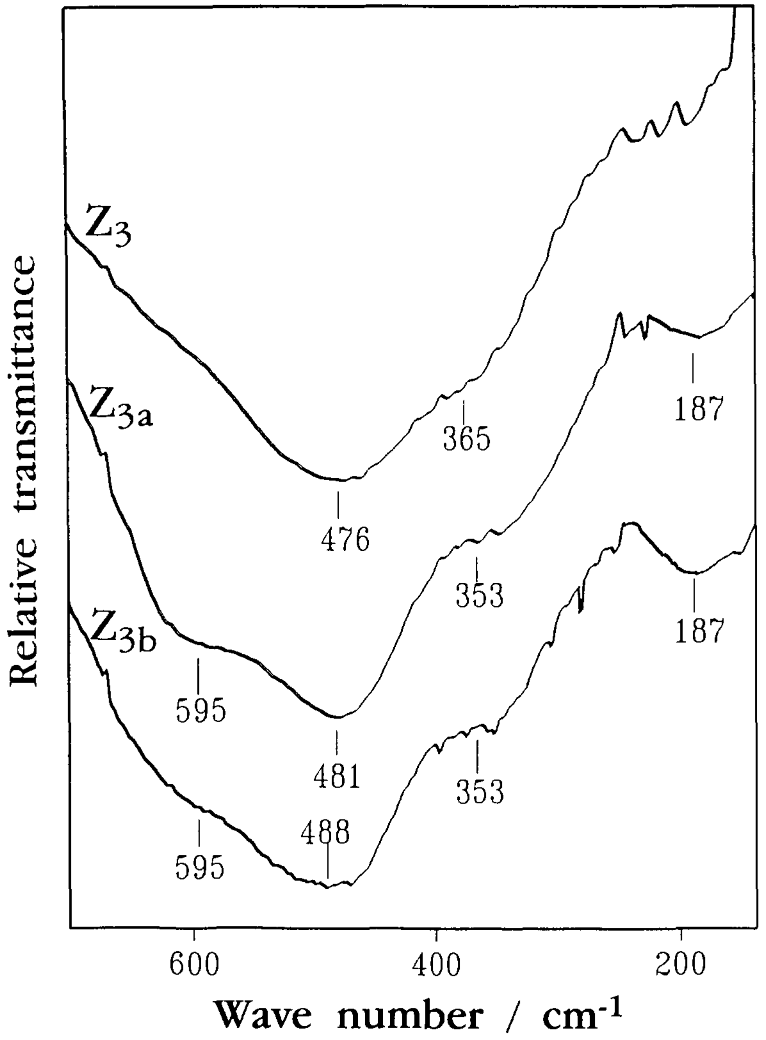

Fig. 3. FT-IR spectra of samples Z_3, Z_{3a} and Z_{3b}.

the outer part of the particles was influenced. With a prolonged time of mechanical treatment, the entire volume of the particles became changed, so that samples Z_{35} and Z_{60} exhibited only one exothermic peak. The curve in Fig. 4 shows the saturation which is reached for a prolonged ball-milling time.

In the present study, three important phenomena that result from the ball-milling of zirconium hydroxide, were observed: *the dehydration, an increase in the activation energy needed for the crystallization, and a decrease in the crystallization enthalpy* (ΔH_c). The last phenomenon is shown in Fig. 5. In the early stages of ball-milling, ΔH_c rapidly decreases. For a prolonged ball-milling time, saturation is reached, as shown in Fig. 4.

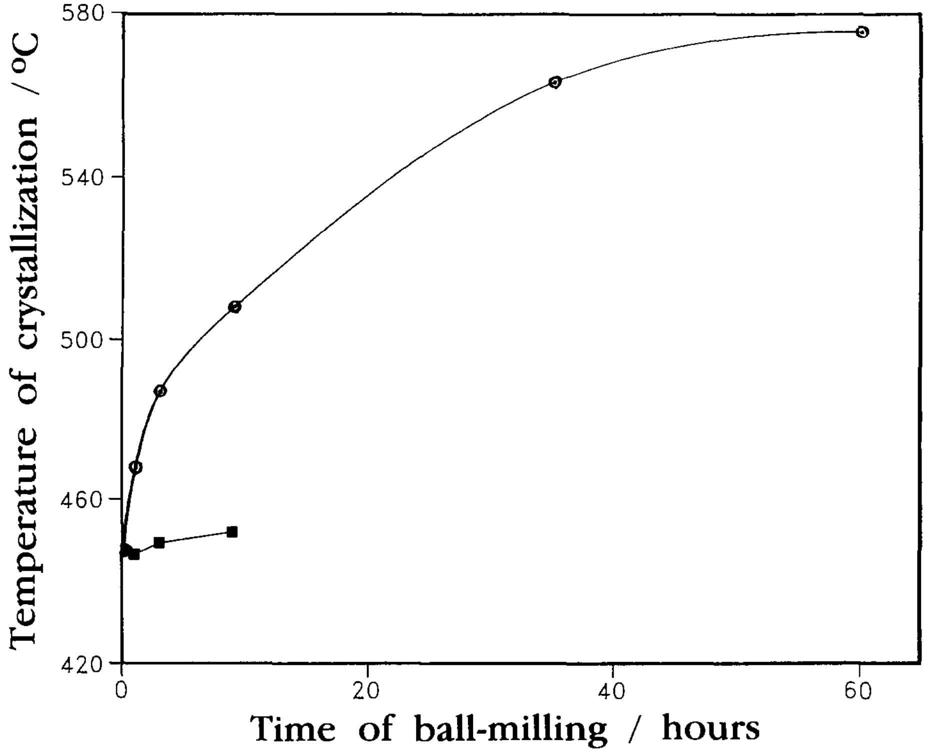

Fig. 4. The temperature of crystallization of t-ZrO_2 as a function of the time of ball-milling of zirconium hydroxide: ■ = peak maximum 1; ⊙ = peak maximum 2.

Changes of enthalpy during the process of crystallization (ΔH_c) and dehydration (ΔH_d) are shown in Table 1. For the starting sample Z_0, a value of $\Delta H_c = -21.6\,\mathrm{kJ\,mol^{-1}}$ was obtained, this being similar to the result of Srinivasan et al. [3] ($-23.2\,\mathrm{kJ\,mol^{-1}}$), slightly higher than the result of Torralvo et al. [24] ($-19\,\mathrm{kJ\,mol^{-1}}$), and much smaller than the result of Livage et al. [13] ($\sim -30\,\mathrm{kJ\,mol^{-1}}$). The smaller value obtained by Torralvo et al. [24] was probably caused by a much higher drying temperature, 350°C, which induced a slow process of crystallization.

In our case there are two possible explanations for the decrease in crystallization enthalpy. The first possibility, which takes into account the decrease of ΔH_c as a result of dehydration, is based on the topotactical rearrangement in the zirconium(IV) hydroxide matrix, as suggested by Tani et al. [15]. The second possibility is that the mechanical treatment causes a change in the short-range order of a small part of the zirconium hydroxide. In both cases the mechanical treatment of zirconium hydroxide may induce the formation of small number of very fine t-ZrO_2 crystals, which are not detected by XRD and FT-IR. In order to find out which of these possibilities can be accepted and to establish the relation among the three phenomena, observed as

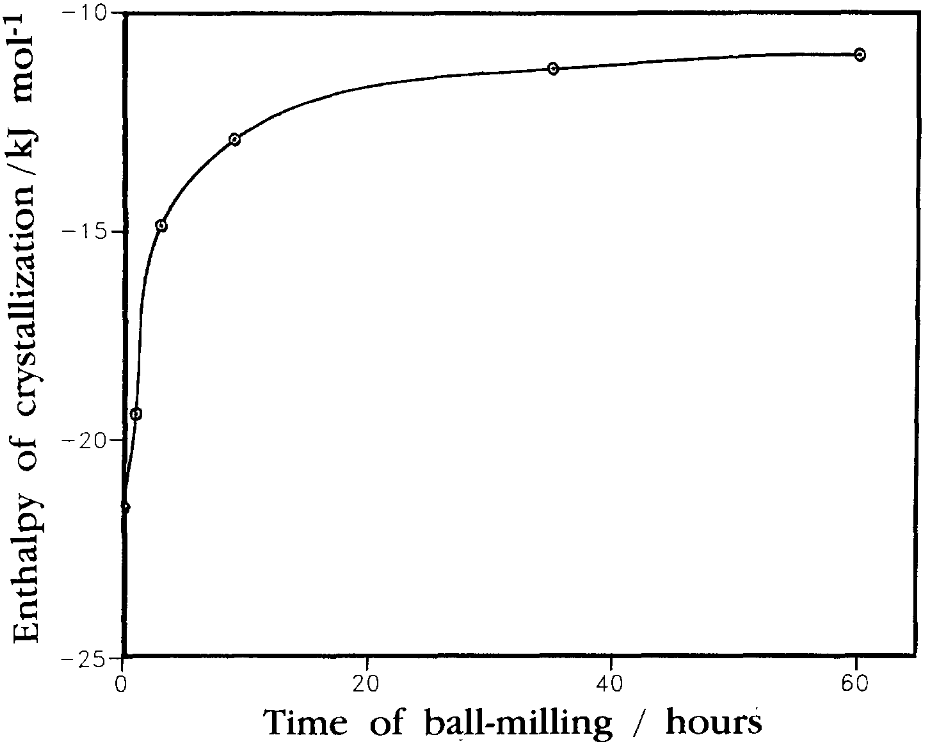

Fig. 5. The enthalpy of crystallization of t-ZrO_2 as a function of the time of ball-milling of zirconium hydroxide.

a consequence of the ball-milling, sample Z_0 was heated at 300°C for 2 h. In this way, the dehydration of the sample took place without ball-milling. The DSC thermogram of this sample showed a small endothermic peak beginning at 50°C and ending at 130°C, which disappeared when heating inside the DSC instrument was repeated. After that, the thermogram obtained showed no features in the region of dehydration, while the peak of crystallization appeared at the same place as for the original sample Z_0, with the intensity lowered by about 1 $kJ\,mol^{-1}$, in accordance with the results of Torralvo et al. [24].

The presence of the small dehydration peak in the first DSC thermogram was explained by TGA analysis of sample Z_0, which showed a small increase in weight from room temperature to 50°C due to its hygroscopic nature. From 50°C to 400°C, there was a continuous loss of weight as a result of dehydration. Further heating to a temperature of ~850°C showed a very small loss in weight, so that at the crystallization temperature of ~450°C, no change of weight was observed. The present DSC and TGA measurements showed that dehydration has no influence on the increase in activation energy and the decrease in the heat flow of crystallization. The results of this study evidently indicate that the crystallization of metastable t-ZrO_2 from zirconium(IV) hydroxide is a more complex process than a simple structural (topotactic) rearrangement.

References

[1] B.H. Davis, J. Am. Ceram. Soc., 67 (1984) C-168.
[2] R. Srinivasan, R.J. DeAngelis and B.H. Davis, J. Mater. Res., 1 (1986) 583.
[3] R. Srinivasan, M.B. Harris, S.F. Simpson, R.J. DeAngelis and B.H. Davis, J. Mater. Res., 3 (1988) 787.
[4] T. Mamott, P. Barnes, S.E. Tarling, S.L. Jones and C.I. Norman, J. Mater. Sci., 26 (1991) 4054.
[5] A. Clearfield, Inorg. Chem., 3 (1964) 146.
[6] A. Clearfield, Rev. Pure Appl. Chem., 14 (1964) 91.
[7] A. Clearfield, J. Mater. Res., 5 (1990) 161.
[8] G. Štefanić, S. Musić, S. Popović and K. Furić, Croat. Chem. Acta, in press.
[9] R. Cypres, R. Wollast and J. Raucq, Ber. Dtsch. Keram. Ges., 40 (1963) 527.
[10] R.C. Garvie, J. Phys. Chem., 69 (1965) 1238.
[11] R.C. Garvie, J. Phys. Chem., 82 (1978) 218.
[12] E. Bailey, D. Lewis, Z.M. Librant and L.J. Porter, Trans. J. Br. Ceram. Soc., 71 (1972) 25.
[13] J. Livage, K. Doi and C. Mazieres, J. Am. Ceram. Soc., 51 (1968) 349.
[14] G. Keramidas and W.B. White, J. Am. Ceram. Soc., 57 (1974) 22.
[15] E. Tani, M. Yoshimura and S. Somiya, J. Am. Ceram. Soc., 66 (1983) 116.
[16] F.-C. Wu and S.-C. Yu, J. Mater. Sci., 25 (1990) 970.
[17] I.M. Imenez Mateos, I. Morales and I.L. Tirado, J. Mater. Sci. Lett., 5 (1986) 1295.
[18] E. Mendelovici, R. Villalba, A. Sagarzazu, Mater. Res. Bull., 17 (1982) 241.
[19] T. Tsuchida, N. Ichikawa, React. Solids, 7 (1989) 207.
[20] A.N. Scian, E.F. Aglietti, M.C. Caracohe, P.C. Rivas, A.F. Pasquevich and A.R. L. Garcia, J Am. Ceram. Soc., 77 (1994) 1525.
[21] Y. Murase and E. Kato, J. Am. Ceram. Soc., 62 (1979) 527.
[22] C.M. Phillippi and K.S. Mazdiyasni, J. Am. Ceram. Soc., 54 (1971) 254.
[23] N.T. Mcdevitt and W.L. Baun, J. Am. Ceram. Soc., 47 (1964) 622.
[24] J. Torralvo, M.A. Alario and J. Soria, J. Catal., 86 (1984) 473.