

# Heat-stimulated transformation of zirconium dioxide nanocrystals produced under hydrothermal conditions

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Processes occurring during the thermal treatment of nanocrystalline zirconium dioxide are reviewed. Changes in the dimensions and structure of  $\text{ZrO}_2$  that occur depend upon the calcination conditions used.

**Keywords:** zirconium dioxide,  $\text{ZrO}_2$ , hydrothermal synthesis, phase formation, formation mechanism.

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## 1. Introduction

Many publications (see, e.g., [1–12]) have studied the formation of various structural forms of  $\text{ZrO}_2$  nanocrystals and have analyzed the reasons for the relatively high stability of the thermodynamically non-equilibrium modifications in nanocrystalline zirconium dioxide at relatively low temperatures. Publications [1–3] link this peculiarity of zirconium dioxide nanocrystals to a dimensional effect. Publications [4–12] examined the impact of the methods and parameters of  $\text{ZrO}_2$  nanocrystal synthesis on their structure, morphology and properties. Studies on the mechanism for nanocrystalline zirconium dioxide formation [4, 5, 14, 15] and its behavior during heating [3, 7, 16] indicated that a more detailed analysis was needed of the impact of the reaction system prehistory on the process of  $\text{ZrO}_2$  nanoparticle crystallisation.

The study of zirconium dioxide nanocrystals by comprehensive thermal analysis [16–19] has revealed a number of unusual effects in their behavior. Numerous publications [16–19] that have used this method to study the processes occurring in  $\text{ZrO}_2$  particles obtained by different methods have reported an intensive exothermic effect in the 200–500°C temperature range which was accompanied by a loss of mass. The appearance of an exothermic effect in the 400–500°C temperature range is explained in publications [15–18] by the crystallisation of X-ray amorphous  $\text{ZrO}_2$ . The authors of publications [19, 20] attribute the exothermic effect to oxidation of carbon-containing compounds because nanocrystalline  $\text{ZrO}_2$  was produced using zirconium oxalate, butanediol or other organic reagents. Publications [4, 5, 7, 8, 16, 21–27] explain the stabilization of the tetragonal (pseudo-cubic) modification of zirconium dioxide in the low-temperature range by the inclusion of water into the nanoparticle structure, while removal of water during heating initiates a structural rearrangement, accompanied by an exothermic effect.

The lack of a clear interpretation of the reasons for structural changes in the zirconium dioxide-based nanocrystals, including those accompanied by an exothermic effect with a simultaneous loss in mass during heating, requires a detailed study of these transformations.

## 2. Experimental methods

Zirconium dioxide nanocrystals were produced by hydrothermal processing of zirconium oxyhydroxide precipitated from a  $\text{ZrOCl}_2$  solution by the technique described in [28].

The “isothermic calcination-quenching” method, using a specially designed furnace to ensure high sample heating and cooling rates, studied the structural change kinetics in the condition and dimensions of the zirconium dioxide nanocrystals depending on temperature and heat treatment duration.

The X-ray diffraction study was made on a DRON-3M diffractometer,  $\text{CuK}\alpha$ -radiation. Quantitative analysis of the tetragonal ( $t\text{-ZrO}_2$ ) and monoclinic ( $m\text{-ZrO}_2$ ) forms of zirconium dioxide and precise determination of the position of the diffraction maximums were conducted using the method of an internal reference introduction ( $\alpha\text{-Al}_2\text{O}_3$ ). The size and shape of the crystallites were determined in accordance with the recommendations of publication [9] based on the data on expansion of the X-ray diffraction line and high-resolution transmission electron microscopy (Jeol JEM-200).

### 3. Results and discussion

Based on X-ray phase analysis (Fig. 1), the nanoparticles produced under hydrothermal conditions consisted of two structural modifications:  $t\text{-ZrO}_2$  and  $m\text{-ZrO}_2$ . Quantitative calculation of the  $t\text{-ZrO}_2$  and  $m\text{-ZrO}_2$  content, performed by the technique described in publication [28], showed that  $80\pm 5\%$   $t\text{-ZrO}_2$  and  $20\pm 5\%$   $m\text{-ZrO}_2$  are present in the system.

It should be noted that this ratio of  $t\text{-ZrO}_2/m\text{-ZrO}_2$  is fairly stable and typical for the technique used to obtain the nanoparticles, as confirmed by the results of previous studies [4, 5, 7, 14-16, 25, 27, 28].

The dimensions of  $\text{ZrO}_2$  nanocrystals, which were determined by both transmission electron microscopy (Fig. 2) and based on data from the expansion of the X-ray diffraction lines (Fig. 1) for  $t\text{-ZrO}_2$  and  $m\text{-ZrO}_2$ , essentially coincided and were  $20\pm 3$  nm, on the basis of which it can be concluded that the nanoparticles produced under hydrothermal conditions were monocrystalline. Structural analysis results for individual nanoparticles by high-resolution transmission electron microscopy also attest to the monocrystalline nature of the produced zirconium dioxide nanoparticles and the fusion on the edges of individual nanocrystals. It is noted that the resulting  $\text{ZrO}_2$  nanocrystal dimensions are reproduced fairly consistently when  $\text{ZrO}_2$  nanocrystals are synthesised under hydrothermal conditions, as follows from the results of previous studies (see, e.g., [5, 9, 14, 28]). The dimensions of the  $\text{ZrO}_2$  nanocrystals may be reduced somewhat to 15–18 nm by reducing the duration of hydrothermal treatment [5], however in this case, zirconium oxyhydroxide is generally not completely dehydrated [5]. We therefore used such hydrothermal processing conditions for zirconium oxyhydroxide which result in its complete dehydration with the formation of  $\text{ZrO}_2$  nanocrystals, according to the data of publication [5].

The results from the kinetic study of the change in zirconium dioxide nanocrystal structure and size when heated in the “isothermic calcination-quenching” mode are shown in Fig. 2. Three temperature regions with varying nanoparticle behavior are isolated, based on analysis of the resulting dependences of the quantity of tetragonal modification and particle size of zirconium dioxide on the temperature and duration of treatment (Fig. 2). This temperature ranges to  $500^\circ\text{C}$ , from  $600$  to  $800^\circ\text{C}$  and from  $900$  to  $1100^\circ\text{C}$ .

After thermal treatment of the nanoparticles at temperatures up to  $500^\circ\text{C}$ , there are no noticeable changes in the structure or particle size of  $\text{ZrO}_2$  (Fig. 2). It is also precisely in this temperature range that significant exothermic effects are observed, accompanied by simultaneous water release [16]. Since the total quantity of crystalline  $\text{ZrO}_2$ , the ratio of metastable tetragonal and monoclinic zirconium dioxide modifications, and the sizes of the nanocrystals during thermal treatment in the examined temperature range do not essentially

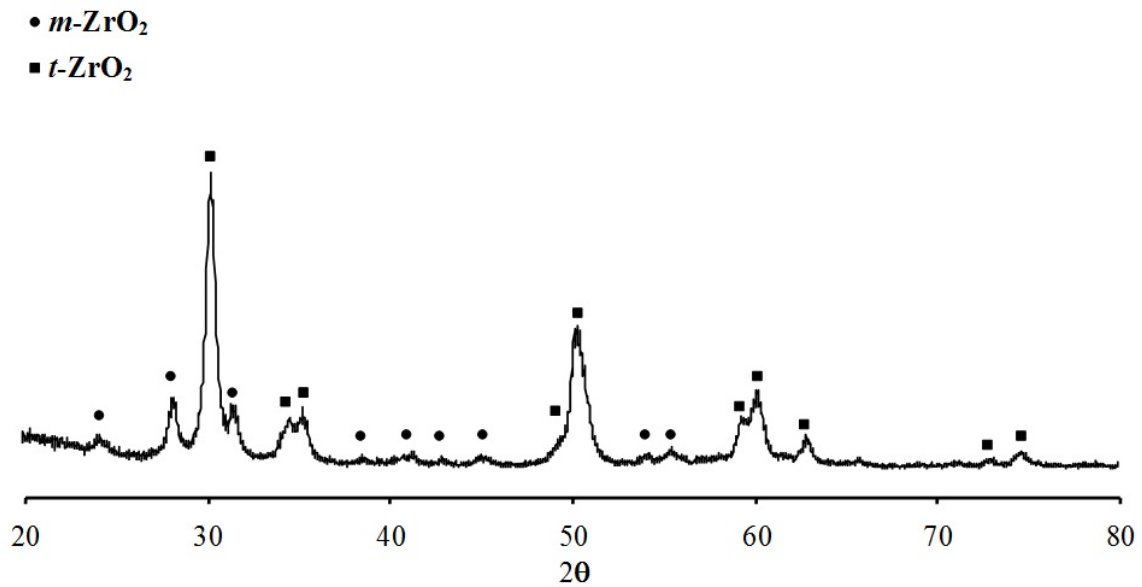


FIG. 1. X-ray diffraction of the nanocrystalline zirconium dioxide, obtained by hydrothermal synthesis

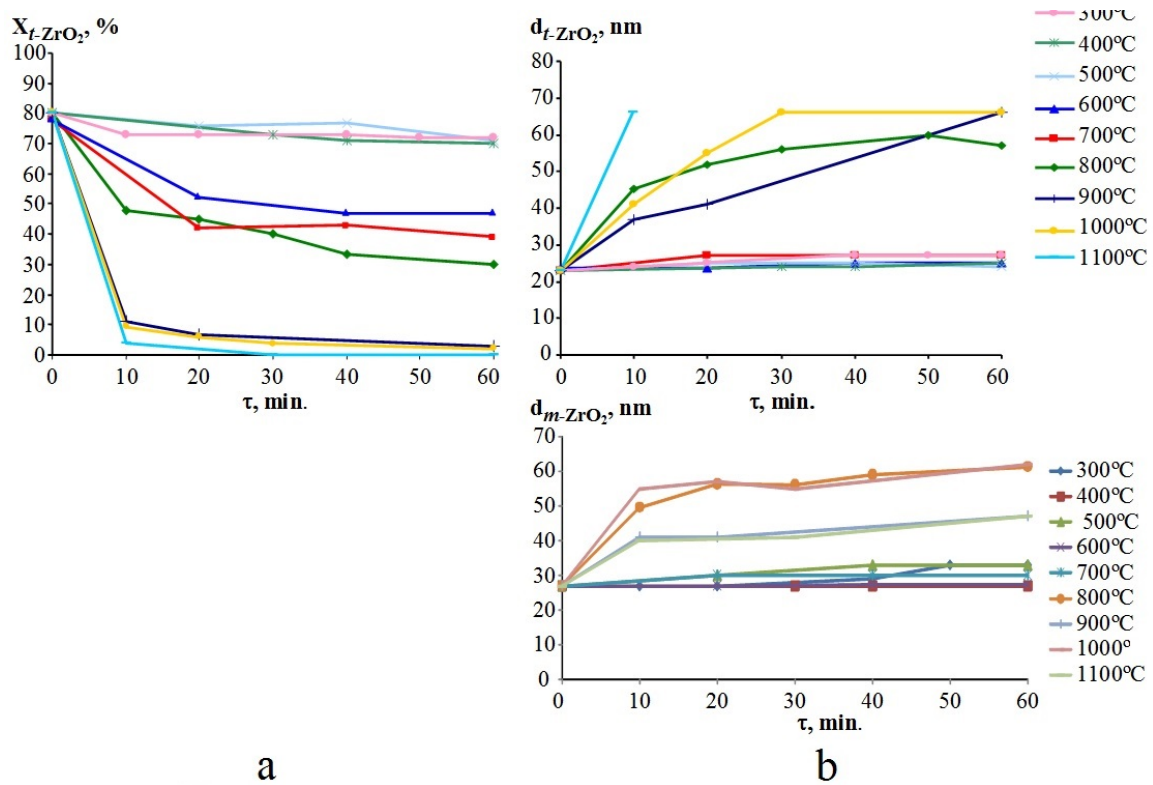
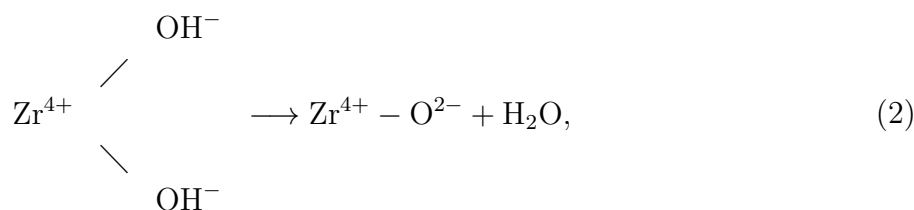


FIG. 2. The dependence of the amount of  $t\text{-ZrO}_2$  (a) and crystallite size  $t\text{-ZrO}_2$  and  $m\text{-ZrO}_2$  (b) of the duration and temperature of heat treatment

change (Fig. 2), there are no grounds to classify the observed thermal effects as crystallization of amorphous zirconium dioxide, polymorphous transition  $t\text{-ZrO}_2 \rightarrow m\text{-ZrO}_2$  or change in surface energy because of growth in nanoparticle grains. The process leading to heat release could be structural rearrangement in the nanocrystals, which does not cause transformation of one polymorphous modification of zirconium dioxide nanoparticles into another, and linked, for example, to relaxation processes in nanoparticle sublattices, primarily and apparently in the anion sublattice. The structural changes in the anion sublattice may be initiated, in particular, by certain dehydration reactions in the nanocrystals:



which alter the anion sublattice structure, and consequently, create conditions for the occurrence of relaxation processes, which reduce the system internal energy, i.e., occurring with an exothermic effect. The presence of structural changes in the nanocrystals, accompanying the dehydration process is confirmed by data indicating a change in the position and ratio of the intensity of X-ray diffraction lines in  $t\text{-ZrO}_2$ .

<b>t-ZrO<sub>2</sub></b>	<b>h k l</b>	<b>d/n</b>	<b>h k l</b>	<b>d/n</b>
Standard (24-1164)		2.995		2.635
Original sample	1 0 1	2.971	0 0 2	2.601
Sample after heat treatment at 500°C		2.951		2.592

The proposed interpretation of  $t\text{-ZrO}_2$  nanocrystal behavior in the 500°C temperature range correlates with previous zirconium dioxide structural study results indicating that its structure in the planes (1 0 1) coincides with the  $t\text{-ZrO}_2$  structure [29]. The difference in the structure between zirconium X-ray amorphous hydroxide and tetragonal dioxide, according to publication [28-30] is that in the first case, the planes (1 0 1) are arranged randomly. Since, according to data [10, 11, 26], during zirconium hydroxide dehydration under hydrothermal conditions, the formed  $\text{ZrO}_2$  nanoparticles inherit the structure of the hydrate precursor, one can thus hypothesize that the formed  $t\text{-ZrO}_2$  nanoparticles also inherit the random arrangement of anions between the planes (1 0 1). This random atom arrangement in the anion sublattice will thus be stabilized by the presence of water in it [2, 7, 14, 16], while the dehydration processes (1) and/or (2) initiate a more orderly arrangement of  $\text{O}^{2-}$  ions, which, apparently, also causes the corresponding exothermic effects [16].

Heat treatment in the 600–700°C temperature range results in a noticeable increase in the amount of  $\text{ZrO}_2$  monoclinic modification (up to 50%), while the particle size does not essentially change. Mass loss by the sample due to water release during  $t\text{-ZrO}_2 \rightarrow m\text{-ZrO}_2$  transformation, which is slight in this temperature range, is only about 0.5 mass% [16]. At the same time, as shown by the nanoparticle study using high-resolution transmission electron microscopy, after heat treatment of nanoparticles in this temperature range, their morphology changes significantly (Fig. 3). They are converted from essentially non-faced particles into well-faced particles with the characteristic shape for crystallites of the relevant

structural modifications (Fig. 3). This is apparently caused by activation of atom movement in the nanoparticles in this temperature range. We also note that an increase in the percentage of *m*-ZrO<sub>2</sub> nanoparticles to 50% without a change in their mean size was observed previously [29] for the behavior of zirconium dioxide nanoparticles by thermal radiography when heated to 800°C.

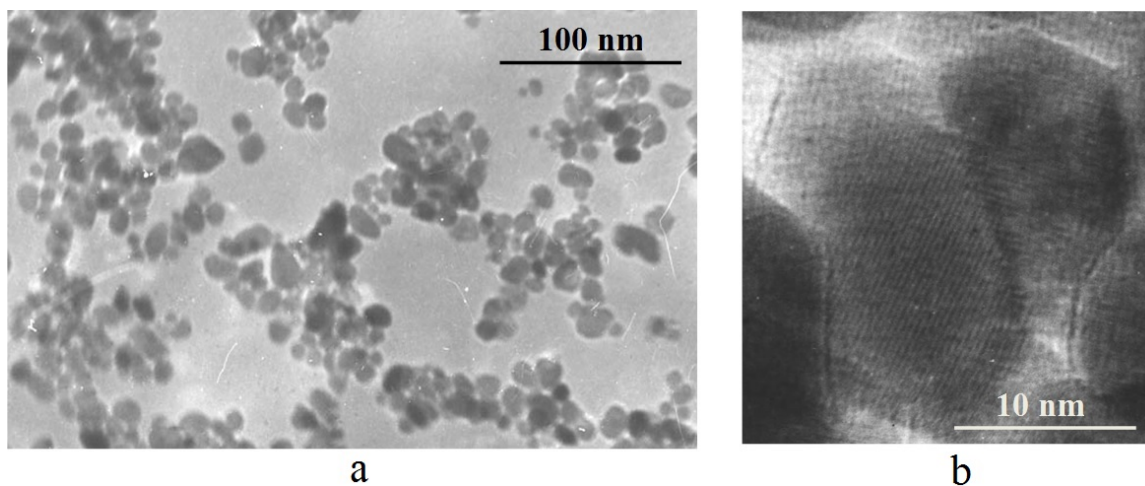


FIG. 3. Microphotographs of ZrO<sub>2</sub> nanocrystals, obtained in hydrothermal conditions (a) and after heat treatment at 700°C

It follows from the kinetic studies (Fig. 2) that for the 900–1100°C temperature range, structural transformation *t*-ZrO<sub>2</sub> → *m*-ZrO<sub>2</sub> ends completely, while the size of the *m*-ZrO<sub>2</sub> nanocrystals more than doubles to 50–60 nm (Fig. 2). Based on thermal analysis, in addition to the exothermic conversion, a slight water release is observed here, leading to mass loss by the sample of about 0.1 mass% [16]. It is noted that in the 900–1000°C temperature range, in addition to the growth of *m*-ZrO<sub>2</sub> nanocrystals, there is a growth of *t*-ZrO<sub>2</sub> nanocrystals (Fig. 2). This type of change in the nanoparticle dimensions is apparently due to activation of mass transfer at these temperatures both between the nanoparticles of one structural modification and transfer of matter from the non-equilibrium structural modification of *t*-ZrO<sub>2</sub> at this temperature to equilibrium *m*-ZrO<sub>2</sub>.

The findings, as well as the fact that *t*-ZrO<sub>2</sub> → *m*-ZrO<sub>2</sub> transformation may occur essentially without a change in particle size supports the weak impact of the dimensional effect on nanoparticle *t*-ZrO<sub>2</sub> stability at low temperatures, as indicated in a number of publications [1, 2]. The stabilizing effect of the water, localized in the anion sublattice of the zirconium dioxide nanoparticle is the primary factor which determines the stability of *t*-ZrO<sub>2</sub> nanoparticles at temperatures up to 500°C.

#### 4. Conclusion

It has been shown that the occurring changes in ZrO<sub>2</sub> nanoparticles in the 300–500°C temperature range are linked to the release of water, accompanied by an exothermic effect, to all appearances determined by structural re-arrangement in the *t*-ZrO<sub>2</sub> nanocrystals, initiated by dehydration, and resulting in a more orderly arrangement of the atoms in the anion sublattice.

The *t*-ZrO<sub>2</sub> → *m*-ZrO<sub>2</sub> transition in the 600 to 800°C temperature range essentially occurs without a change in nanocrystallite size, but with a noticeable water loss. Removal of the stabilizing water from the *t*-ZrO<sub>2</sub> structure also results in a transition of the metastable

tetragonal modification of zirconium dioxide to that of the monoclinic ZrO<sub>2</sub> modification which is stable at these temperatures.

In the 800 to 1100°C temperature range, mass transfer from the non-equilibrium *t*-ZrO<sub>2</sub> nanocrystallites to the *m*-ZrO<sub>2</sub> equilibrium phase makes a significant contribution to the increase in the percentage of *m*-ZrO<sub>2</sub> nanocrystals.

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