

PHASE EVOLUTION IN ZIRCONIA BASED SYSTEMS

O. Yu. Kurapova^{1,2,3,4} and V. G. Konakov^{1,2,3,4}

¹Institute of Chemistry, St. Petersburg State University, St. Petersburg, Russia

²Institute for Problems of Mechanical Engineering, St. Petersburg, Russia

³Science and Technical Center "Glass and Ceramics", St. Petersburg, Russia

⁴St. Petersburg State Polytechnical Institute, St. Petersburg, Russia

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Abstract. Data on phase formation and transition in both pure zirconia and zirconia based systems are systematized and critically considered in this review; the point of essential interest is the presence and possible stabilization of metastable zirconia at low temperatures. The effect of system prehistory, i.e. the synthesis conditions, further post-treatment, and thermal evolution is discussed; the conclusion about the drastic effect of sample prehistory on the phase evolution in zirconia based systems is done. It is also showed that phase formation in zirconia systems follows the Ostwald step rule.

1. INTRODUCTION

High temperature oxygen conducting membranes gain much attention for modern technologies of petroleum products conversion, organic synthesis, engines engineering, pharmaceutical drug synthesis, etc. For this reason, oxygen pumps [1-3] and the transport of oxygen ions in high temperature ion conducting membranes based on zirconia [4-6] and rare-earth elements are of great importance. The present review is devoted mainly to the thermal evolution of cubic ZrO_2 -based solid solutions with the well-known conductivity mechanism [7-10].

The point of especial interest is the presence and stabilization of metastable zirconia modifications (i.e. cubic or tetragonal) and its solid solutions in the range of temperatures and concentrations wider than that determined for the equilibrium phase diagrams. Tetragonal and cubic zirconia-based materials are used as refractories [11,12], solid oxide fuel cells (SOFC) manufacturing [13,14], oxygen sensors [4-6,15], and biomaterial in optics and medicine [16]. Ceramics with the maximal value of

conductivity can be manufactured from the zirconia powders with the cubic structure, that are stable at 800-1000 °C [17].

Pure zirconia and systems on its base seem to be widely investigated; they appear to be a model for different fundamental and applied researches. The mechanism and kinetics of phase transitions in ZrO_2 and its solid solutions were studied in details in [18,19]; as well as physical, chemical, and mechanical properties of the materials on its base [20]. It is known that monoclinic zirconia is the most thermodynamically stable phase; however, less stable modification of ZrO_2 (cubic or tetragonal) could form during amorphous gel crystallization [21].

At the ambient pressure of 1 atm, zirconia exhibits three polymorphic modifications [22]. Monoclinic ZrO_2 (*m*- ZrO_2 , $\rho = 5.83 \text{ g/sm}^3$) is thermodynamically stable from room temperature and up to 1170 °C, when it undergoes the transformation to the tetragonal phase (*t*- ZrO_2 , $\rho = 6.1 \text{ g/sm}^3$). Tetragonal ZrO_2 exists up to 2370 °C. In the range from 2370 °C to the melting temperature, the phase with the highest symmetry (i.e. cubic) is stable (*c*- ZrO_2 , $\rho = 6.09 \text{ g/sm}^3$). The number of publications, cover-

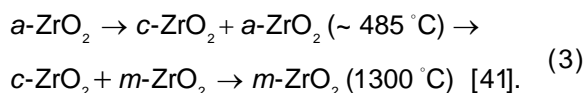
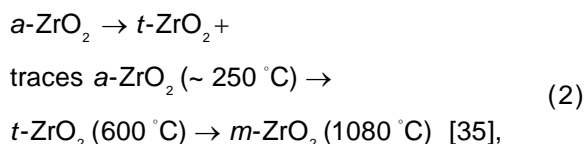
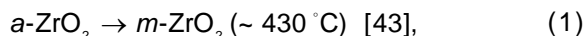
Corresponding author: O.Yu. Kurapova, e-mail: glasscer@yandex.ru

ing the problem of the stabilization of high temperature zirconia modifications and the manufacturing of novel materials on their base, is constantly increasing [23,24]. However, still there is no common opinion on the factors affecting exact phase formation and stability of zirconia.

It should be mentioned that metastable *t*-ZrO₂ was obtained for the first time by O. Ruff and F. Ebert via hydrolysis in 1929 [25]. Basing on the estimates of the excess in the *t*↔*m* transition free energy, R. Garvie in 1978 considered that the existence of tetragonal zirconia depends on the crystallite size in the precursor powder [25]. However this explanation contradicts the experimental data obtained later [26-28].

The investigations of ceramic systems on the nanoscale range showed that the significant dependence of the final phase composition on the precursor powder dispersity; sometimes, the achieved final phases contradicts conventional equilibria phase diagrams data. The mean size of precursors also affects the mechanism and kinetics of phase formation in zirconia systems [30]. According to the literature, the stabilization of high temperature zirconia phases at low temperatures can be reached by proper method of precursor synthesis [31], the reasons for such stabilization also can be the presence of residual OH- groups and impurities up to high temperatures [32], vacancies in structure [33], etc. At the same time, this question is still open to argue.

Such chemical routes as sol-gel synthesis (i.e. hydrolysis of alkoxides, reversed co-precipitation), allows one to manufacture metastable *t*- and *c*-ZrO₂ at the temperatures rather lower than that typical for the equilibrium phase diagrams [20]. Depending on the precipitation conditions, all three modifications can be obtained via crystallization of the amorphous precursors (*a*-ZrO₂) at <500 °C. Schematically, all the transitions can be ascribed as following:



The initial conditions of sol-gel synthesis (i.e. the nature and concentration of initial salts and the

precipitant, pH of the medium, temperature, outer fields, etc.) affect the crystallization temperature and zirconia thermal evolution. Further dehydration predetermines the degree of final agglomeration, i.e. the further phase evolution in zirconia systems with the temperature. The features of zirconia hydroxide formation during sol-gel synthesis, its dehydration and thermal evolution are studied in details and presented in [29,37,38]. To date, the investigation of mechanism and kinetics of tetragonal to monoclinic transformation in both pure zirconia and its tetragonal solid solutions is the point of interest for most papers in this field. However, in terms of practical applications, cubic solid solutions are more attracting. The present paper is devoted to the systematization and critical review of the data concerning the effect of sol-gel synthesis conditions and further post-treatment on the mean size of the agglomerates and crystallites in precursor powders and phase formation in zirconia based systems with temperature. In this work the emphasis was made on the thermal evolution of cubic zirconia based solid solutions.

2. CRYSTALLIZATION TEMPERATURE

The direct crystallization of tetragonal and cubic zirconia and its solid solutions remains one of both the most perspective and complicated areas in modern science. As it was widely shown [31,39], the temperature of phase transition in precursors depends on its dispersity and synthesis method. For instance, the formation of the metastable cubic solid solution in precursors with a final composition 8 mol.% Y₂O₃-25 mol.% TiO₂ - 67 mol.%ZrO₂ obtained by the solution pyrolysis takes place at ~ 650 °C. To compare, the crystallization of the amorphous precursors with the same composition, obtained by reversed co-precipitation from diluted salts solution, was observed at ~460 °C [31].

It has well known that the crystallization from amorphous to tetragonal zirconia obtained by hydrolysis of alkoxides takes place at about 250 °C [35,40]. According to XRD data, see [20], pure *t*-ZrO₂ is stable up to 1400 °C. Up to date, the metastable modification can not be quenched and slowly transforms to monoclinic on cooling. It is interesting to note that tetragonal ZrO₂ cannot be produced by the reversed co-precipitation. Herein, the crystallization occurs at ~440-485 °C and followed by competitive formation of cubic and monoclinic modifications [36,41]. *m*-ZrO₂ forms are thermodynamically stable at ~1000-1200 °C.

As it was shown in [42], the concentration of oxygen vacancies in ZrO_2 structure significantly affects the phase stability and the crystal domain size in zirconia precursors. It is known that the partial or complete stabilization of cubic or tetragonal modifications is possible by the addition of different stabilizing dopants (Y^{3+} , Ca^{2+} , Mg^{2+} , Sc^{3+} , etc.). The solid solution forms via the mechanism of vacancies. The nature of the cation predetermines both the temperature of phase transition from amorphous precursor to crystalline solid solution and the stability of the solid solution formed. The effect of yttria concentration on the crystallite size in zirconia precursor was studied in [43]; the increase in the crystallite mean size that was observed with the decrease in Y_2O_3 concentration was referred to the tendency to the Geimholz energy decrease.

As it is known, zirconia always contains the isomorphs admixture of HfO_2 with the concentration of 0.5-4 mol.% [44]. The presence of hafnia leads to the shift in the crystallization temperature to lower values. However, this amount is not enough for cubic or tetragonal solid solution stabilization in low temperature region. It is interesting that the significant amount of both cationic and the anionic vacancies was observed in the lattice of pure zirconia which was synthesized by different methods [45]. According to the authors, the vacancies as well as small crystallite size play an important role in the formation and full stabilization of tetragonal zirconia up to high temperatures.

The advantages of the materials based on double and triple systems over pure ZrO_2 were discussed in [46]. As it was shown, cubic zirconia ceramics doped by yttria, calcia, and magnesia possesses high anionic conductivity at the elevated temperatures, chemical stability, and hardness. Thereby, these systems were studied in detail. For example, a partial substitution of ZrO_2 to TiO_2 in Y_2O_3 - ZrO_2 system leads to the decrease in crystallite size and the increase in crystallization temperature [46]. Herewith, the cubic field in $8Y_2O_3$ - $xTiO_2$ - $(92-x)ZrO_2$ (mol.%) system is between 0 and 10 mol.% of TiO_2 . The addition of the third component (as TiO_2 , Al_2O_3 , CeO_2) results in elevated hardness (toughness) of ceramics without the significant decrease in anionic conductivity. The sensor properties of solid electrolytes with composition of $8Y_2O_3$ - $(92-x)ZrO_2$ - $xTiO_2$ ($x = 5$ -10 mol.%) are comparable to those for yttria-zirconia ones and overcome them in the hardness. These ceramics membranes are recommended for oxygen partial pressure measurements in the gas ambience at >500 °C [36].

3. BASIC TERMS OF HIGH TEMPERATURE ZIRCONIA MODIFICATIONS STABILIZATION

So far, there exist a number of hypotheses explaining the preferable crystallization of metastable zirconia to thermodynamically stable form at given temperature and pressure and its thermal evolution. For the first time, the occurrence of metastable phases was mentioned by Ostwald during the study of the crystallization from the solutions. Basing on experimental observations, he postulated his famous empiric Step Rule [47], which states the following: if the reaction results in several products (several polymorphs), thermodynamically less stable phase appears at the first steps, this is due to higher velocity of its crystallization. This unstable phase passes through a number of intermediates (which are also metastable) and, finally, transforms into thermodynamically stable form at given temperature and pressure. The qualitative justification of this rule was made in [48] via matching the velocities of the phase crystallization and the absolute values of Gibbs energy of formation ($|\Delta G_{form}^0|$). The higher is the value of $|\Delta G_{form}^0|$ for the given phase, the faster the crystallization of this phase occurs; thus, the more probable the process is. There are many points of view on the occurrence and the stabilization of metastable phases in time and temperature ranges. However, most of hypotheses explain the stabilization of metastable polymorphs in terms of free energy excess.

When it comes to zirconia, the works of R. Garvie remain the most referred [26,49]. Among the factors affecting the phase formation in zirconia based systems, he emphasizes the role of the specific area and the excess of free energy (comparing to that for a single crystal). His assumption was as following "...the high temperature polymorph of a crystal could be stabilized at temperatures below its normal transformation temperature at some critical crystallite size if the high temperature polymorph had a reduced surface free energy with respect to the low temperature structure" [26]. It means that the crystallites in *t*- and *c*- ZrO_2 are smaller than in *m*- ZrO_2 and the specific area of high temperature polymorphs is lower than that for low temperature, i.e. tetragonal ZrO_2 is stable when the crystallites are small and the specific area (S_{spec}) is high. Consequently, a certain excess of free energy should exist. The crystallites grow upon heating following the diminishing of both the S_{spec} and free energy. When the size of crystallites overcomes 30 nm, the tetragonal phase transforms to monoclinic.

The difference between free surface energy of the nanocrystalline tetragonal and monoclinic zirconia was calculated on the base of the experimental data. Its value was shown to be 6.7 kcal/mol. Then, using the data obtained, the heat transition was determined. Its match with the calculated value confirmed R. Garvie's hypothesis. Thermodynamics of tetragonal to monoclinic transformation is described in detail in [26]. According to this work, both hydrostatic and nonhydrostatic stresses significantly influence the microcrystal size-transformation temperature relationship.

The effect of crystallite size on phase formation both in pure zirconia and its solid solutions was studied carefully in [50]; it was demonstrated that the diminishing of the crystallite size in the material leads to the stabilization of high symmetric zirconia based solid solutions. The nanosized precursors of Al_2O_3 - ZrO_2 system were used as a model. The authors assume that the cubic zirconia solid solution stabilization is due to nanosized powders with the excess of free energy, comparable to the energy of first order phase transition. Pure stable tetragonal zirconia with crystallite size 18-25 nm was obtained at ≤ 800 °C in [20]. Similar results were reported for Y_2O_3 - ZrO_2 [51], CaO - ZrO_2 [31], etc.

It should be mentioned that the pure monoclinic zirconia with the crystallite size in the powder of 4-6 nm without any admixtures of high symmetric phase was obtained in [28]; the results of some experimental work also contradict Garvie's hypothesis.

4. CRYSTALLITE SIZE ESTIMATION

Conventionally, Scherrer equation is used for the estimation of the crystallite size (d_{xrd}) in zirconia systems, see as R. Garvie [26,49], R. Srinivasan [27,40], J. Livage [29]:

$$d_{\text{xrd}} = \frac{K\alpha}{\beta \cos \theta}, \quad (4)$$

where d_{xrd} is a coherent scattering region – CSR (i.e. the size of crystallites), θ - Bragg angle of diffraction, K – Scherrer constant, set by the shape of crystallite (1 is the recommended value), α – the wavelength of the incident radiation ($\alpha = 1.5406$ Å), θ – corrected half height width of the peak.

One shouldn't expect the exact correlation of d_{xrd} results obtained by different authors. Except the crystallite size itself, the instrumental error, lattice defects and strains, the choice of the standard, and

the texturing also significantly affect on the broadening of diffraction spectra. Here, it seems to be more correct to generalize the Garvie's assumption about the d_{xrd} limit of 30 nm to some critical crystallite size limit, up to which the degradation of metastable ZrO_2 occurs.

The crystallite size can be also estimated using BET theory (d_{BET}), as follows

$$d_{\text{BET}} = \frac{6 \cdot 10^{-4}}{\rho S_{\text{BET}}}, \quad (5)$$

where d_{BET} is the diameter of spherical crystallite (nm), ρ – the theoretical density of the phase, S_{BET} – the specific surface of the sample according the BET theory (m^2/g). The value of d_{BET} is close to the characteristic particle size of dispersed phase.

In [52], yttria precursor was obtained by reversed co-precipitation, treated by different ways (i.e. freeze-drying, pan-drying, drying at room conditions, washing by ethanol, isobutanol, acetone), and calcined at 800 °C. In all the cases, the correlation of both estimates was observed. The smallest crystallites were obtained using freeze-drying. The proximity of these values is, likely, due to the fact that the crystallization at 800 °C has been almost completed and the active caking hasn't yet started.

Notable, that in [53] the values of d_{xrd} and d_{BET} turned to be completely equal due to the correct synthesis and post-treatment conditions. The amorphous gel with the average agglomerates of 250 nm and primary crystallites of 3-4 nm was produced by means of reversed co-precipitation from 0.1 M solution. The particle size of dispersed phase (d_{BET}) of precursor after pan-drying at 150 °C and under the pressure of 1 kg/cm² matched the size of ACS in all the range of thermal treatment. The crystallization occurred at the temperature lower than equilibria phase diagram states and was followed by the formation of the metastable zirconia based cubic solid solution.

Referring to the literature [26-28], the critical size of crystallites is not a unique cause of metastable zirconia stabilization. Some authors consider that the stabilization of high temperature polymorph is due to the impurities (i.e. OH^- , SO_4^{2-} , NH_4^+ groups) in the structure of synthesized gel and, then, post-treated precursors [33,54]. The cubic zirconia was obtained in thin films via evaporation [55]; *c*- ZrO_2 stabilization at both low and average temperatures was attributed to the grain size. The presence of moisture accelerated the degradation of zirconia to its monoclinic modification.

All the factors discussed above affect the transition amorphous phase transition to the crystalline ZrO_2 simultaneously. Thus, it is not possible to determine clearly the nature of the metastable zirconia formation and the mechanism of crystallization at low temperatures. At the same time, the initial conditions of precursor synthesis govern the crystallite size, the specific area, the impurities in the powder, and the grain size in final material. For example, pure tetragonal zirconia or its mixture with monoclinic phase can be obtained via thermal treatment of the amorphous zirconia hydroxide, pyrolysis of initial zirconia salts, milling of $m-ZrO_2$ in a stirred media mill, spark plasma synthesis, etc. [56].

A comparative study of the available methods of zirconia based precursors was performed in [20,31]. It was shown that sol-gel synthesis is prior to commonly used methods; it allows to manufacture the powders characterized by the given agglomerate size and controlled phase composition. The homogeneous mixing of the reagents provides high uniformity of components distribution during all the ceramics synthesis [37,57]. That is why sol-gel synthesis following by different post treatment of gels is so widely used for different oxide materials manufacturing.

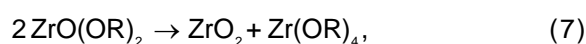
Following dehydration and thermal treatment of the amorphous precursor promotes the formation of tetragonal or cubic zirconia at the temperatures lower than the equilibria phase diagram states. It should be mentioned that the data for all the equilibria diagrams was obtained by annealing and quenching method. The presence of short-range order in amorphous zirconia was determined via small angle X-ray scattering [34]. Basing on the data obtained, it was assumed that the structural similarity of high temperature modifications of ZrO_2 and amorphous phase induces the crystallization of tetragonal zirconia. The topotactic mechanism of crystallization was proposed in [56], where the nucleation of the crystalline phase takes place on the nuclei, presenting initially in amorphous phase. To date, the topotactic transition involves a structural change to a crystalline solid, where the rearrangement of the initial to final lattice is minimal i.e. proceeding with minimal activation energy. This assumption is in accordance with Ostwald Step Rule, discussed above and is confirmed by thermal evolution of the various zirconia systems.

The reversed co-precipitation from solutions and hydrolysis of the alkoxides are usually used to obtain zirconia and its solid solutions [17]. In both

cases, the synthesis involves following steps: preparing of the mixed solution of the initial salts (or alkoxides), the chemical reaction, and following formation of the hydroxide. The common stages are: homogenization of initial reagents, its conversion to the gel and then to a sol.

5. SOL-GEL SYNTHESIS BASED ON HYDROLYSIS OF ALKOXIDES

The addition of water to the alkoxides solution induces the hydrolysis, followed by the condensation at low temperatures, according to the reaction [21]:



where R is $-OCH_2CH_3$, iso- or n- $O(CH_2)_2CH_3$ or other soluble alkoxide. The hydrolysis results in hydroxylated M-OH groups. Latter acts as active centers of the reaction of polycondensation, which, likely, proceeds in accordance to the mechanism of the alkoxylation [17]. The conditions and the environment of the synthesis deeply affect the structure of amorphous precipitate. It varies from the three-dimensional network, built from small particles of dispersed phase to the disordered gel with some fragments of structure [57]. The variety of gel structures forming during sol-gel synthesis are depicted in Fig. 1.

The increase in the annealing temperature induces the crystallization of amorphous ZrO_2 . Here, the formation of high symmetric zirconia modifications (i.e. tetragonal) is predominant to the modification of low symmetry (monoclinic) [21]. Monoclinic ZrO_2 appears at about 600 °C and its amount increases with temperature. As it reported in [20], the tetragonal modification exists up to 1400 °C.

A detailed study of zirconia phase composition, obtained by hydrolysis of zirconium n-propoxide at pH = 5, was performed in [59]. High temperature *in situ* XRD analysis showed that the tetragonal/monoclinic modification ratio is ~90:10%; it remains constant up to ~750 °C. The degradation of tetragonal ZrO_2 takes place with the temperature; it leads to following formation of monoclinic phase. Their amount becomes equal at ~1300 °C.

Overall, the evolution of zirconia, derived by the hydrolysis of alcoxides, can be ascribed as follows:

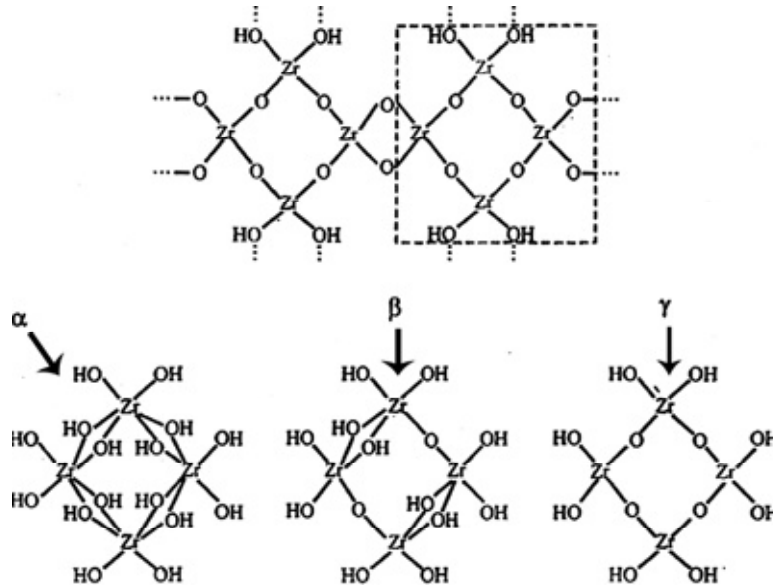
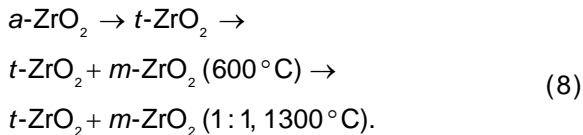


Fig. 1. The structure of gel, forming during sol-gel synthesis according to [53].



According to the reference data, $t\text{-ZrO}_2$ stabilization is due to small crystallites in the precursor. At it is noticed in [60], the conditions of synthesis, mentioned above, are quiet universal and allow to obtain the crystallite solid solutions and such zirconia compounds, as for example TiZrO_4 , at the temperatures lower than equilibrium one. Only monoclinic modification exists in the samples cooled down to 30°C . It is, likely, because pure metastable zirconia can not be quenched and ultimately transforms to equilibrium monoclinic phase.

6. SOL-GEL SYNTHESIS BASED ON REVERSED CO-PRECIPIATION FROM THE SALT SOLUTIONS

This way of synthesis is based on precipitation or the co-precipitation of hydroxides or, more often, mixed hydroxides from the solution by the help of some third compound. The precipitant is usually the alkali or ammonia solution. The ammonia is favorable due to easier removal from the gel during its filtration and drying. The special facility for the gaseous ammonia transmission through the solution of salts was highlighted in [37]. However, the use of aqueous ammonia solutions appears to be technically easier. Both hydrolysis and the co-precipitation from salt solutions result in the amorphous gel of zirconia hydroxide or its mixture with doping oxide.

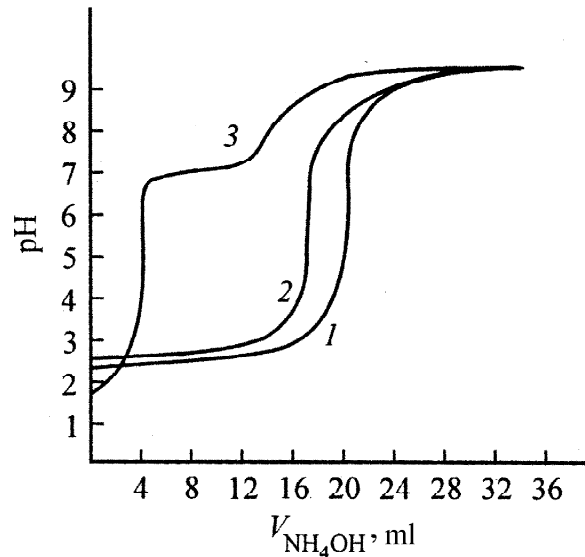
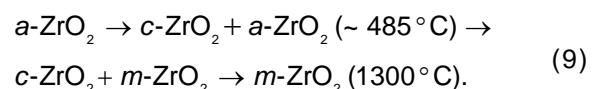


Fig. 2. Titration curves for $\text{ZrO}(\text{NO}_3)_2$ (1) $\text{Y}(\text{NO}_3)_3$ (2), $\text{HfO}(\text{NO}_3)_2$ (3) according to [30].

The crystallization of pure nanosized zirconia, obtained by reversed co-precipitation from the diluted salts solution with following gel freeze-drying results in the mixture of cubic and monoclinic modification [36,41]. Here, the competitive phase formation is observed; it depends on powder calcination temperature, see the scheme below:



Pure monoclinic zirconia is observed at 1300°C . The addition of the dopant to zirconia results in the stabilization of cubic solid solution up to $\sim 1000^\circ\text{C}$:



As it can be seen from the examples above, the prehistory of the system drastically affects on the mechanism and kinetics of phase formation as well as on physical and chemical properties of final powders. The phase formation in zirconia and zirconia systems does not follow strictly the data reported by equilibrium phase diagrams [61]. Let us discuss the interrelations between the pH and the nature of the medium, the concentration of initial reagents and precipitant, impurities, influence of outer fields, the addition of surfactants, and following dehydration, and the temperature of phase transitions and phase formation in zirconia systems with the temperature.

6.1. pH effect

In the aqueous media, the presence of hydrogen and hydroxide ions governs the character and the direction of the chemical deposition reactions. McInnes showed that the pH value in practice should serve as the acid or base feature of the solution and there is no need to consider it from the strict point of the theory of the solutions. For zirconia hydroxide (IV), as for all the compounds of transition metals, the pH of the solution is a key factor during the deposition process. It is known, that in acidic medium the Zr^{4+} ion undergoes the hydrolysis following polymerization [37].

The pH-metric titration of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ aqueous solution was performed in [44, 59]. As it can be seen from Fig. 2, the formation of the precipitate starts at $\text{pH} = 2.3$. The hydrolysis is induced by the dissolution of the initial hydrate (or the salt of zirconium). For example, 0.01 mole of HCl appears in the solution due to the dissolution of 0.01 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. Mention that the increase in the salts concentration leads to the inhibition of hydrolysis due to the high initial acidity of the solution and a slight decrease in the particle size in the dispersed phase [20]. A particular study of the effect of increase of $[\text{H}^+]$ concentration occurring during the hydrolysis of ZrOCl_2 solution on the particle size of the dispersed phase was done in [62,63].

Slow addition of the base to the initial solution causes the increase of the polymerization degree. The precipitation is completed when the equivalence point ($\text{pH} = 9$) is reached [59]. In the same work, the investigation of hafnia precipitation was performed. It was shown that the precipitation of tetrameric $\text{Hf}_4(\text{OH})_{16} \cdot (\text{H}_2\text{O})_8$, which is isomorphic to

$\text{Zr}_4(\text{OH})_{16} \cdot (\text{H}_2\text{O})_8$ starts at $\text{pH} 2.5$, and the precipitation of $\text{Y}(\text{OH})_3$ – just about 8 pH units i.e. in order to reach homogeneity the precipitation should be reversed.

In the work [37] NaOH solution was used to neutralize the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution in order to reach $\text{pH} 4, 6, 8$. All the suspensions were left for a week. In order to remove Cl^- , the precipitate obtained was filtered and then washed. The gel obtained was dried at 120°C during 48 hrs. The acidic medium of synthesis favored the formation of monoclinic zirconia after calcination. Metastable $t\text{-ZrO}_2$ was obtained via the precipitation in alkaline medium. The existence of metastable modification is, likely, due to the absence of the polymerization in the alkaline mediums and diversity of precursors obtained. Indeed, the specific area of precursors, obtained at $\text{pH} 8$, was significantly higher than that for the precursors, obtained at $\text{pH} 4$ and 6 .

At the same time according to [21], slight acidification of the solution of alkoxides by nitric acid (0.125 M) induces the shift of zirconia crystallization to low-temperature region. This data is in accordance with the Garvie's hypothesis about stabilization of the metastable zirconia in acidic medium due to the free energy excess [26]. Herewith, the exothermic effect of crystallization on DSC curves of precursor, derived in the acidic medium, is sharper than that for precursor, derived without the addition of HNO_3 .

The coagulating effect of various ionic mediums on the initial gel is different [57]. Indeed, the tendency to the solvation of the secondary particles of the precipitate, i.e. the structure and the composition of the final precipitate, is in dependence of the adsorption of H^+ and OH^- on the surface. Here, the effect of cations on the coagulating properties of the medium is more significant than the effect of anions. Thus, according to Debye–Hückel theory the minimal ionic force (i.e. the neutral solution) and lower density distribution should be reached. On the other hand, the precipitation of $\text{Zr}(\text{OH})_4$ takes place just after $\text{pH} 9$.

6.2. Temperature effect

The effect of the precipitation temperature on the phase transition temperature amorphous gel \rightarrow crystalline solid solution is highlighted in the literature [23,44,57]. In [23], the co-precipitation was performed at three different temperatures: ambient temperature (20°C), 0 , and -5°C . The precursors with the final composition $8\text{Y}_2\text{O}_3 \cdot x\text{HfO}_2 \cdot (92-x)\text{ZrO}_2$, $x = 5\text{--}10$ mol.% were used as model system. The precipi-

tates of the amorphous hydroxides were treated at 300 °C during 1 hour. According to DSC data, the similar tendency was observed for all the compositions, i.e. the crystallization temperature decreased from 480-500 to 460 °C with the decrease in the synthesis temperature from 20 to -5 °C. It is, likely, due to the elimination of the agglomeration with the temperature. The formation of metastable cubic solid solution without the admixtures of low symmetric phases has been observed already at 550 °C.

The authors noticed that the stoichiometric mass loss during thermal treatment of hydroxides was observed just in case of samples obtained at 0 °C, while for other samples the mass loss was lower than theoretical. Based on the data obtained, the precipitation at 0 °C was chosen as optimal. This conclusion matches the recommendations given in papers [44, 57].

6.3. Initial salts concentration

It is well known that the effect of supersaturating is observed (i.e. much nuclei are formed simultaneously) in case when the chemical precipitation is performed from concentrated homogeneous solutions [57]. In such systems, the following growth of the particles by the mechanism of isothermal recondensation is complicated because of the low concentration of monomer. The higher is the supersaturation, the smaller the nuclei and the faster coagulation are. It leads to the agglomeration of the particles of dispersed phase and, thus, the shift of crystallization to the high temperature region.

The systematic investigation of the effect of the initial salts concentration on the agglomerates size and the temperature of crystallization in zirconia systems was performed in [53]. The precursors with the final composition 0.08 mol.% Y_2O_3 -0.92 mol.% ZrO_2 were obtained by reversed co-precipitation. The

concentration of the initial salts solution was varied from 0.01 to 1.2 M. Decimolar solution of ammonia was used as the precipitate. The mixture was added to the precipitate with the rate of 1-2 ml/min. The temperature of the medium was 1-2 °C. The precursors were systematically investigated by BET, laser scattering, and DSC. The specific area increases and the crystallization temperature decreases with the dilution of the solution (see Table 1).

As it can be seen from the table, the minimum of crystallization temperature corresponds to the concentration of 0.01 M. However, in this case the precipitation lasts up to 10 hours. That is why the solutions with a concentration of 0.1 M are optimal for the precipitation. The shift of the crystallization temperature in 200 °C corresponds to the increase of the concentration, the increase is two orders of magnitude here [64]. Similar results were obtained for the Ce_2O_3 - ZrO_2 system; the concentration was varied from 0.001 to 1.5 M and pure zirconia, derived by hydrolysis from mixed alcohol-water solutions with the concentration of initial salt 0.05-0.2 M [21]. As it was observed for yttria-zirconia precursors, the crystallization temperature decreased with the decrease in initial alkoxides concentration, while the dispersity of powders increased significantly. Crystallization occurred at about 400 °C and was followed by the formation of *t*- ZrO_2 . Tetragonal phase was shown to be stable up to 1400 °C. These observations are in accordance with the literature, see refs. [40,59].

6.4. The effect of the medium

The medium of sol-gel synthesis predetermines the structure of the final precipitate. Water is commonly used as a medium in the case of co-precipitation. The addition of different surfactants allows to stabilize the particles of dispersed phase and, thus, to

Table 1. The dependence of the average agglomerate size and the crystallization temperature of powders on the concentration of the initial solution, see [53].

Concentration of the solution, M	Average agglomerate size, nm	Specific area, m ² /g	Temperature of crystallization, °C
0.01	42	140.15	429
0.05	58	97.4	444
0.1	96	62.1	474
0.4	510	14.0	639
0.6	815	13.8	675
0.8	2400	11.4	685
1.2	10000	-	727

eliminate agglomeration. When it comes to hydrolysis, the polymers and acids, forming the chelate complex with zirconia ions, are used as surfactants. On the first stage, the substitution of alkoxide by the chelate ligand (usually, an acid residue) takes place [59]. Then, the ligand splits out and Zr-OH bond forms. Latter reduces the hydrolysis rate and leads to the formation of gel characterized by high dispersity. Careful observations of the effect of precipitation parameters on the thermal evolution of zirconia were carried out in [65]. The optimal conditions of hydrolysis leading to pure t -ZrO₂ formation are specified as follows: hydroxypropyl cellulose is an effective steric stabilizer for ZrO₂ nanoparticles; the proper molar ratio of water and alkoxide. It was shown that the stabilizer concentration and its molecular weight also affect the tetragonal/monoclinic phase ratio. According to authors of [65], the phase formation in zirconia is following an empiric Ostwald Step Rule. The crystallization is multidomain process when the nucleation of both tetragonal and monoclinic phases occur simultaneously. The nanocrystallites of tetragonal phase are formed; they are covered by some amount of monoclinic phase, but the amount of this phase is negligible, so it is not detected by XRD. The amount of the monoclinic phase increases with the temperature as follows: amorphous ZrO₂ → tetragonal ZrO₂ → tetragonal + monoclinic ZrO₂ → monoclinic ZrO₂, the synthesis conditions strictly affect the temperatures of phase transitions and phase composition of particles.

Steric stabilization of dispersed phase during coprecipitation is commonly reached by the addition of sodium laurel sulfate (SLS) [66]. However, most of surfactants can not be removed by simple cycle of washing and filtration and the final gel will contain undesirable organic admixtures. The use of alcohol-water mediums is more favorable as alcohols are easily removed by following dehydration of precursors. To date, the addition of alcohol to the water significantly decreases the dielectric constant of the solution. The effect of salting out is observed because of the decrease in the solubility of the initial salts. According to the data reported in [20],

salting out effect induces the nucleation in hybrid water-alcohol solutions. The growth of nuclei is due to either the deposition of tetrameric zirconia complexes or the agglomeration of primary particles. The final agglomerates are the microspheres with the diameter less than 100 nm.

When it comes to hydrolysis, different alcohols play the role of the medium. Alcohol promotes the growth of particles of dispersed phase (i.e. agglomeration), but, in the acidic mediums, it inhibits the polymerization [20]. Therefore, the nature of alcohol is one of the key factors affecting the phase evolution of the system. Nucleophilic alcohol attacks the electrophilic center of alkoxide. The length of carbon chain affects the degree of hydrolysis, i.e. the structure of final gel. In [20], zirconia n -propoxide was dissolved in three different alcohols (methanol, ethanol, propan-2-ol). It was concluded that the shorter is the carbon chain, the deeper hydrolysis proceeds and, the crystallization of amorphous precursor results in monoclinic zirconia. Phase transition temperatures and the type of zirconia modification are listed in Table 2 together with the alcohols applied. Ethanol is, obviously, a better stabilizer of the tetragonal modification, whereas the use of methanol results in monoclinic zirconia. Here, the occurrence of two tetragonal zirconia is discussed. Authors believe that the use of ethanol and methanol induces the formation of t_1 and t_2 zirconia forms. Indeed, the two t -ZrO₂ with the lattice parameters $a = 3.64 \text{ \AA}$, $c = 5.22 \text{ \AA}$, and $a = 5.17 \text{ \AA}$, $c = 5.24 \text{ \AA}$ were founded in PDF database by the authors of present review. The second modification corresponds to the formulae Zr_{0.95}O₂ and is questionable to exist. The latter parameters of this structure were computed, but there is no experimental support for this calculations. As it can be seen, the values of latter parameters are close to each other and the structure is depleted by zirconium. This data is, likely, obtained using the assumption that the part of Zr⁴⁺ ions is removed from the cubic ZrO₂ lattice in order to get tetragonal modification. This assumption is reasonable from mathematic point of view, however, it can not be realized in practice.

Table 2. The dependence of the temperature of crystallization and the type of polymorphic modification of zirconia on the nature of the medium according to [20].

	Temperature of crystallization	Polymorphic modification of ZrO ₂
Methanol	485	monoclinic
Ethanol	250	tetragonal (t1)
Propanol-2	350	tetragonal (t2)

Using the data of small angles scattering and TEM [20], it was proved that the crystallization of zirconia occurs in two steps. At ~250 °C the organics (alcohol) is removed from the structure of the precursor. In case of ethanol it, likely, causes the simultaneous crystallization of tetragonal ZrO₂, whereas in propanol medium the crystallization occurs at 350 °C. The final formation of *t*-ZrO₂ takes place at about 450 °C when the all the hydroxyl is removed. The significant amount of *m*-ZrO₂ forms with the increasing of the temperatures and results in pure monoclinic modification at 1000 °C.

6.5. Precipitation rate

A comprehensive study of hydrolysis and polymerization in the aqueous zirconium salts solutions was performed in [54,67]. It was shown that the final gel structure is strongly affected by pH, procedure duration, and precipitation temperature. The amorphous [Zr(OH)₄*xH₂O]_n gel with ordered structure was obtained when the solution of initial salt was added to the precipitant quiet slowly (with the rate of ~1-2 ml/min) and the pH value was kept in the region 7-11. The local oversaturation during the rapid addition of salts solution to the precipitant leads to the formation of disordered structures. Following thermal treatment of gels resulted in different phase evolution of the precursors: cubic or tetragonal are obtained from initially ordered gels, while thermodynamically stable monoclinic ZrO₂ is obtained using disordered gels.

6.6. The effect of ultrasound

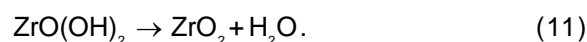
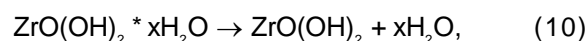
The effect of ultrasound on the phase evolution in ceramic oxides with temperature is poorly investigated. Ultrasound is usually used either to break primary agglomerates during the coprecipitation process or to increase the dispersity of the final powders. The elevation of the solution temperature, the intensification of mixing, and the plenty of cavitation bubbles is observed as a result of ultrasound application to the suspension. It causes the generation of additional nuclei centers [67]. The blast wave is formed during the collapse of bubbles, which, likely, prevents the direct contact of particles and, consequently, the uprising of the dispersity of the final powders and the shift in crystallization temperature to the low-temperature region.

However, in contrast to the thesis above, the agglomeration of the particles of dispersed phase was observed in [69] when the precipitation was

performed in the ultrasonic field (power 50 Wt, frequency 35 kHz) The average agglomerate size without the application of the ultrasound was 250 nm, and for the samples obtained under ultrasound – 750 nm. The temperature of cubic solid solution formation also shifted to the high temperature region. Authors explain this phenomenon by means of the degradation of solvate shells and coagulation of the neutral particles in order to reduce the excess of free surface energy.

6.7. The effect of post-treatment

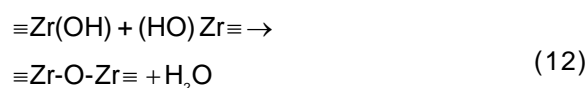
The post-treatment involves the dehydration of gel obtained by sol-gel synthesis, following sol formation with empiric formulae ZrO(OH)₂*xH₂O [37,58]. The formation of anhydrous ZrO₂ is followed by simultaneous and continuous change of the dispersed phase composition according to the reactions:



The investigation of gel dehydration was performed in [36,41,42,67]. The major mass loss was observed on the DSC curves in the region of 100-400 °C; it was referred to water removal. This assumption was proved by the agreement of the values of enthalpy of dehydration and the heat of water evaporation. As it was noted in [42,67], the temperature of endothermic effect on DSC curves, the activation energy of dehydration, and kinetic constant of the process are quiet low and do not depend on the concentration of the dopant.

According to paper [33], dehydration in all zirconia systems passes gradually and finishes at ~ 1000-1100 °C. One can assume that the structure of the agglomerate surface that causes the retention of water up to high temperatures. Some authors consider that the stabilization of *t*-ZrO₂ and *c*-ZrO₂ up to 1100 °C is due to the presence of hydroxyl in the precursor.

The preservation of the initial structure and high dispersity of the gel during its treatment and following thermal evolution allows to broaden the region of the stabilization of metastable zirconia. The high temperatures impact leads to both dehydration and simultaneous condensation according to the reaction:



The latter cause the formation of oxygen bridges between the particles and, hence, hard agglomeration. The mean size of agglomerates in the precursor dried at room temperature (i.e. without any post-treatment) is 3-5 μm [31]. In order to diminish the degree of agglomeration of final powders such "mild treatment" methods as freeze-drying [33,58], pan-drying [69], azeotropic pan-drying [50], and hydrothermal treatment are used.

The original way of pan-drying was proposed in [69]. Here, the drying of thin layers of gel produced by sol-gel synthesis was carried out under the pressure of 1 kg/cm². This approach allows to eliminate the growth of hard 3D agglomerates; these agglomerates possess low strength and can be easily broken mechanically.

The method of azeotropic pan-drying is also of interest. The basics of this method discussed in [36]; it is the combination of azeotropic distillation and pan-drying discussed above. As it turns, the powders with the highest dispersity are manufactured by use of the hybrid methods. The dependence of dispersity on the number of drying cycles passes through the maximum. The mean size of agglomerates reaches its minimum (250 nm) after 2 cycles of the treatment.

Usually, spontaneous crystallization is observed during the thermal treatment of powders at temperatures about 500 °C; commonly, is not followed by significant mass loss (<0.6 wt.%) [68]. This phenomena is widely discussed in the literature and is called «glow crystallization». So far, the mechanism of the crystalline solid solutions formation is determined. The Avrami equation was used to study the crystallization kinetics as well as the effect of the precursor composition on phase transition temperature and kinetic constants. SEM data shown that the growth of $[\text{Zr}(\text{OH})_4 \cdot x\text{H}_2\text{O}]_n$ with the temperature of post-treatment takes place because of the unification of hydroxyls and the rejection of dispersed water molecules. According to [43], this fact means that the crystallization follow the interfacial control mechanism, when the nuclei are forming and growing just on the surface; bulk diffusion here is negligible.

Table 3 shows the phase evolution of ZrO_2 the Al_2O_3 - ZrO_2 and CaO - ZrO_2 systems during their thermal treatment at 800 – 1600 °C. Note, that the precursors were synthesized by reversed coprecipitation. Data from [36,41] is compared in this table with the data of equilibrium phase diagrams for these systems.

Table 3. XRD data for Al_2O_3 - ZrO_2 and CaO - ZrO_2 systems (*m*- ZrO_2 – monoclinic zirconia, *c*- ZrO_2 – cubic solid solution, *t*- ZrO_2 – tetragonal solid solution).

Composition of the powder, mol. %	Temperature	Phase composition	Data from [69,70]
ZrO_2	800 °C	<i>c</i> - ZrO_2 + <i>m</i> - ZrO_2	<i>m</i> - ZrO_2
	1000 °C	<i>m</i> - ZrO_2 + <i>c</i> - ZrO_2 (traces)	<i>m</i> - ZrO_2
	1300 °C	<i>m</i> - ZrO_2	<i>t</i> - ZrO_2
8 Al_2O_3 -92 ZrO_2	800 °C	Al_2O_3 + <i>m</i> - ZrO_2	<i>c</i> - ZrO_2
	900 °C	Al_2O_3 + <i>m</i> - ZrO_2	<i>c</i> - ZrO_2 + <i>t</i> - ZrO_2
	980 °C	Al_2O_3 + <i>m</i> - ZrO_2	<i>t</i> - ZrO_2
	1600 °C	Al_2O_3 + <i>t</i> - ZrO_2	<i>m</i> - ZrO_2
11 Al_2O_3 -89 ZrO_2	900 °C	Al_2O_3 + <i>m</i> - ZrO_2	<i>m</i> - ZrO_2 + <i>c</i> - ZrO_2
	1600 °C	Al_2O_3 + <i>t</i> - ZrO_2	<i>m</i> - ZrO_2
5 CaO -95 ZrO_2	800 °C	<i>c</i> - ZrO_2 + <i>m</i> - ZrO_2	CaZr_4O_9
	1000 °C	<i>c</i> - ZrO_2 + <i>m</i> - ZrO_2 + <i>t</i> - ZrO_2	CaZr_4O_9 - <i>t</i> - ZrO_2
	1300 °C	<i>c</i> - ZrO_2 + <i>m</i> - ZrO_2 + <i>t</i> - ZrO_2	<i>t</i> - ZrO_2
9 CaO -91 ZrO_2	800 °C	<i>c</i> - ZrO_2	CaZr_4O_9
	1000 °C	<i>c</i> - ZrO_2 + <i>t</i> - ZrO_2	<i>t</i> - ZrO_2 - CaZr_4O_9
	1300 °C	<i>c</i> - ZrO_2 + <i>m</i> - ZrO_2	<i>c</i> - ZrO_2 + <i>t</i> - ZrO_2
12 CaO -88 ZrO_2	800 °C	<i>c</i> - ZrO_2 + <i>m</i> - ZrO_2	CaZr_4O_9
	1000 °C	<i>c</i> - ZrO_2 + <i>m</i> - ZrO_2	<i>t</i> - ZrO_2 - CaZr_4O_9
	1300 °C	<i>c</i> - ZrO_2 + <i>m</i> - ZrO_2	<i>c</i> - ZrO_2 + <i>t</i> - ZrO_2
15 CaO -85 ZrO_2	800 °C	<i>c</i> - ZrO_2 + <i>m</i> - ZrO_2 (traces)	CaZr_4O_9
	1000 °C	<i>c</i> - ZrO_2 + <i>m</i> - ZrO_2 (traces)	<i>t</i> - ZrO_2 - CaZr_4O_9
	1300 °C	<i>c</i> - ZrO_2 + <i>m</i> - ZrO_2	<i>c</i> - ZrO_2 + <i>t</i> - ZrO_2

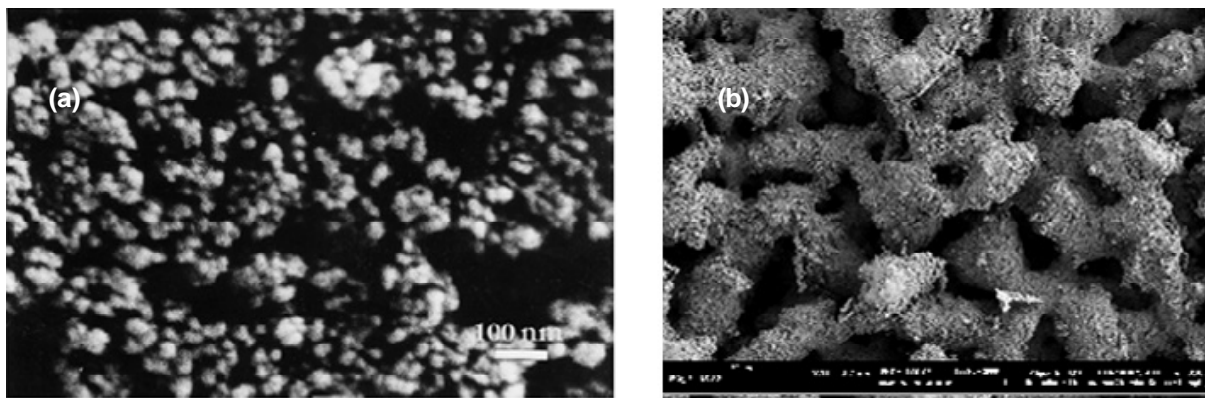


Fig. 3. The structure of precursor after treatment a) globular structure, b) sponge-type structure. Data from [41,53].

As it can be seen from the table, due to the proper choice of synthesis, cubic solid solution can be stabilized in the wider region of temperatures and compositions than the equilibrium phase diagram states [70]. Authors believe that the occurrence and stabilization of cubic ZrO_2 at the temperatures lower than that for equilibria is due to the small size of crystallites [36].

The comprehensive study of the effect of different treatment methods on the structure and the phase formation in the precursors during its thermal post treatment showed that the mild dehydration induces slow crystallization followed by tetragonal [71] or cubic [52] zirconia formation already at 280-350 °C. It should be mentioned that this crystallization is accompanied by exothermal effect on DSC curve in the region of 280-360 °C.

In case of freeze-drying, the direct removal of the disperse phase (water) from the solid to gaseous phase eliminates the number of contacts between the particles and preserves the initial structure of precipitate. The crystallization, likely, occurs on the surface of particles of dispersed phase at 500 °C. This conclusion is based on the investigation of phase evolution in precursor with the composition of 9 mol.% CaO-91 mol.% ZrO_2 obtained by co-precipitation method with following freeze-drying. "Glow crystallization" takes place at ~500 °C and is, likely, bulk process. It is necessary to note that the growth of crystallites is "frozen" up to 800 °C, this fact agree with the data reported in [33,71]. The processes of dehydration, crystallization, and re-crystallization occur simultaneously up to 1000 °C and result in transformation of sponge-type structure to the globular, made of close-packed small crystallites (see Fig. 3).

7. CONCLUSIONS

The present paper reviews the effect of synthesis conditions and the post treatment on the phase composition in zirconia systems. It is shown that the direct crystallization of metastable zirconia and its solid solutions can be reached varying of synthesis conditions and dehydration. The possibility to obtain t - ZrO_2 by reversed co-precipitation technique is not mentioned in the literature. The following basic conditions should be mentioned.

1. The concentration of initial salts and precipitant during sol-gel synthesis. These factors dramatically affect the mean size of agglomerates in the final powder, and, in turn, the temperature of phase transition from amorphous precursor to crystalline zirconia or its solid solution. The influence of nature of the medium and pH on the crystallization temperature is less significant.
2. The type of polymorphic modification of zirconia, occurring during the crystallization, is predetermined by pH of medium.
3. The phase evolution in zirconia based systems during their thermal treatment follows the empiric Ostwald Step Rule. The set of interconnected factors (i.e. the critical size of crystallites, high dispersity of final powders, the presence of hydroxyl and impurities up to high temperatures, etc.) affect the stability of metastable zirconia at the low temperatures and, so far, it is not possible to distinguish the most important one.

To summarize, more and more experimental facts go against the hypothesis of Garvie stating about the critical crystallite size effect on the stabilization of metastable zirconia. The data highlighted above show that the thermal evolution of pure both zirconia and zirconia based systems

produced by sol-gel synthesis, more likely, follows the Ostwald Step Rule. In case of sol-gel synthesis, the transition amorphous phase → metastable crystalline ZrO₂ occurs at the temperature much lower than the equilibrium phase diagram states. The region of stability of the metastable polymorphs depends on the size of crystallites, the dispersity of final powder, hydrostatic stresses, the presence of impurities in structure, etc. As they all are deeply interconnected, so far it is not possible to distinguish the one which is the most dramatic. Hence, there is no common theory describing the occurrence and further thermal evolution of pure metastable zirconia and its solid solutions. At the same time, the proper choice of precursor synthesis conditions allows to control the size of crystallites, the specific area, grain size in the final ceramics, i.e. allows the direct crystallization of metastable phases.

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