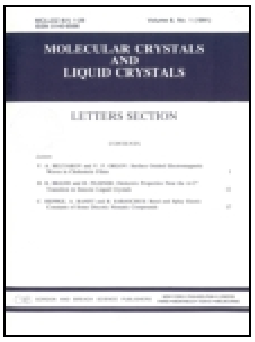

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Nonclassical Crystallization of Zirconium Dioxide and Derivatives in the Presence of Selected Polymers in Hydrothermal Conditions

BARTOSZ WÓJTOWICZ* AND WALDEMAR PYDA

AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Ceramics and Refractories, Cracow, Poland

In this work, the effects of selected polymers on zirconia crystallization under hydrothermal conditions were examined. The powders were crystallized by using different precursors, mineralizers, crystallization time and temperature. The resultant chemical composition, phase composition and morphology of the powders have been examined using SEM, TEM, XRD and XRF methods. Depending on the conditions of crystallization, the zirconia powders showed different morphologies i.e. 3D assemblies of plate-like or needle-like grains and hollow agglomerates. TEM revealed plate-like and needle-like particles that were composed of smaller primary plates of about 100 nm in size. The crystallization of an unknown phase composed of zirconium, oxygen, sodium and fluorine is reported.

Keywords Zirconia; nonclassical crystallization; hydrothermal crystallization; ceramic powder; powder morphology

Introduction

Zirconium oxide is one of the most important ceramic materials. Due to the transformation toughening mechanism [1], zirconia based materials show superb mechanical properties with K_{IC} exceeding 15 MPa·$m^{0.5}$ [2], bending strengths over 2 GPa and Weibull modulus over 10 [3]. Zirconia has high melting point, 2680°C, very good chemical resistance and low thermal conductivity. It is resistant to acids and reacts with strong bases in elevated temperatures. It can be dissolved in molten bases. Therefore, zirconia based polycrystals are often used as engineering materials, thermal barrier coatings [4] and refractory materials. Due to strong nonstoichiometry in the anionic sublattice zirconia is used in Solid Oxide Fuel Cells. Although zirconia was thoroughly examined during past several dozen years, some issues have not been fully explained, e.g. mechanism of stabilization of tetragonal phase of zirconia, and some have not been studied at all. The nonclassical crystallization belongs to them.

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*Address correspondence to Bartosz Wójtowicz, AGH University of Science and Technology, Faculty of Materials Science and 6 Ceramics, Department of Ceramics and Refractories, A. Mickiewicz Av. 30, 7 30-065, Cracow, Poland. Tel.: +48 012 617 3494; Fax: +48 012 633 46 30. E-mail: bartosz.wojtowicz@agh.edu.pl

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In classical crystallization theory–to simplify–crystals grow by joining atoms to the crystallization nuclei. In some conditions, crystals can grow in very different way–by joining whole crystallization nuclei or even larger crystallites. This is called the nonclassical crystallization, or in the case of mesocrystal formation as mesocrystallization [5]. When sides of crystals are aligned each other, an interesting phenomena occurs: the whole, big crystal, even over a dozen of cm in length, has the same properties as the small, building block. Such crystals are called mesocrystals. One can observe, for example, high mechanical durability and electromagnetic properties changed, i.e., a change in dielectric constant, both in value and Curie point [6, 7]. Using nonclassical crystallization one can also obtain biomimetic crystals [8].

In nature such crystals can be found for example in shells of snails. In the laboratory conditions, usually mesocrystals are obtained during the crystallization in the presence of water soluble polymers and ambient conditions. That is why the calcium carbonate is one of the most often researched compound in terms of nonclassical crystallization [9–11]. In the case of zirconia, one need hydrothermal conditions to crystallize it, so there is a number of factors the researcher must take into consideration. Thermal and chemical stability of the used polymer in the hydrothermal conditions are the most important ones. This is not trivial, because hydrothermal conditions are very aggressive even without the addition of acids, bases and mineralizers, and during the hydrothermal crystallization one of the above mentioned compound is usually present in the system. That is why chemical stability of polymer is very important. The thermal decomposition of polymer isn't desired because of changing the chemical composition of the system in a way which is very difficult to control and because of contamination of the resultant powder.

In this paper, for the first time, the results of examination of the influence of various water soluble polymers on the hydrothermal crystallization are reported.

Experimental

A flowchart of the experiment is shown in Fig. 1. In the typical experiment, a mineralizer was added to the polymer solution of concentration varying from 0.002 to 20 g/L. The amount of the mineralizer was calculated in such a manner that after the addition of the precursor the concentration of the mineralizer was 1M. Hydroxypropyl methylcellulose ($M_W = 100\,000$ Da), poly(vinyl alcohol) ($M_W = 14\,000$ Da and 72 000 Da) or poly(ethylene glycol) ($M_W = 4\,000$ Da) were used as the polymers, while sodium, potassium and ammonium fluorides and sodium hydroxide were used as the mineralizers. The aqueous solution of zirconium oxychloride or oxynitrate, being the precursor of zirconium oxide, was added to the solution of the polymer and the mineralizer. Despite being neutral in pH, the solutions of fluorides and polymer mixed together had a pH value of about 9, which was enough to form gel after addition of the zirconia precursor. After thorough stirring, the gel was moved to a PTFE container and put in an autoclave. The crystallization time varied from 0 h to 24 h, and the crystallization temperature varied from 140°C to 240°C under the autogenic vapour pressure. After the crystallization, the powder was washed several times with distilled water and with isopropyl alcohol, and dried overnight at 120°C. Several parameters of the resultant powders were examined, including the morphology (SEM; FEI NOVA Nano SEM 200, and TEM, FEI Tecnai), the chemical and phase composition (XRF, Axios mAX PANalytical; and XRD; X'Pert PANalytical), and the structure of the resultant phases (FTIR; MIR-FTS60v).

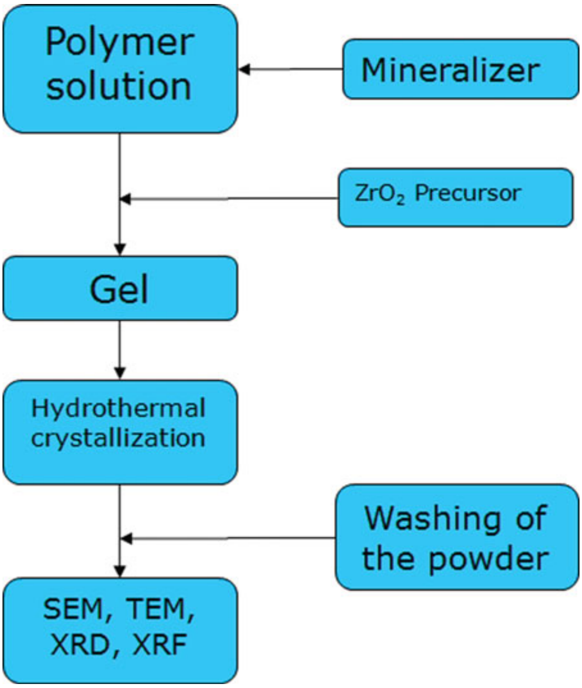

Figure 1. Flow chart of the experimental procedure.

All reagents were supplied by Avantor Performance Materials Poland, and were of analytical grade. No additional purification was used.

Results

The phase composition of the resultant powder without mineralizer as a function of temperature is shown in Fig. 2. The difference between powders crystallized from zirconium oxychloride and oxynitrate are shown in Fig. 3. The phase composition of powders obtained with the mineralizer addition is shown in Fig. 4. The phase composition of powders as a function of temperature in the range 180°C to 240°C with the addition of NaF is shown in Fig. 5, and the morphology of the resultant powders originated from the temperature range from 180°C to 240°C is shown in Fig. 6. TEM images of the resultant powders are shown in Fig. 7. FT-IR spectra of the new phase is shown in Fig. 8.

Discussion

XRD patterns of the powders obtained without an addition of mineralizer at different temperatures ranging from 140°C to 200°C in the environment of 2g/L HPMC solution are shown in Fig. 2. The powder crystallized at the temperature of 140°C is almost amorphous and the crystallinity of the powder increases with the temperature of crystallization. The obtained phase is the monoclinic polymorph of zirconium dioxide. This is typical behavior of hydrothermally crystallized powders. At the temperature of 200°C two powders have been crystallized in this part of the experiment: one using zirconium oxychloride as the precursor, and the other using zirconium oxynitrate. The difference in the XRD pattern

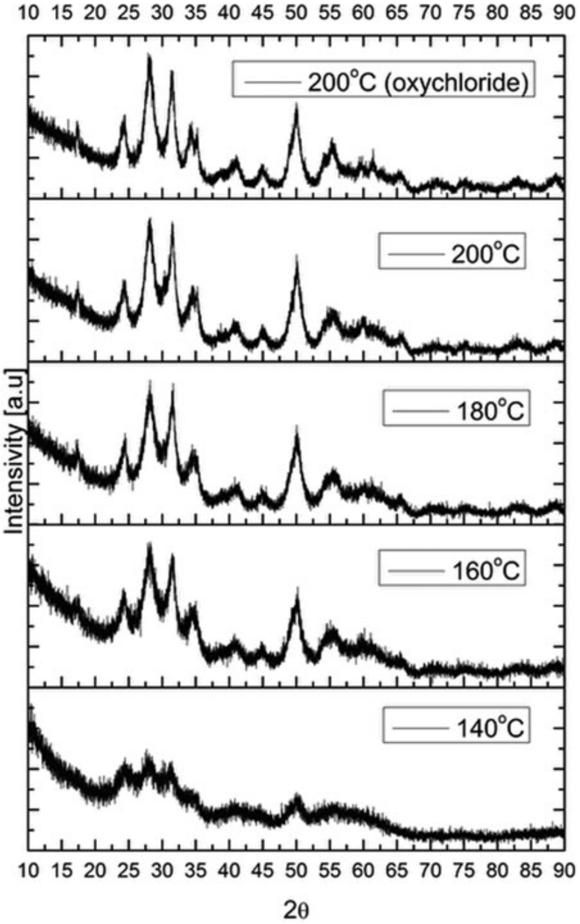

Figure 2. Phase composition of the resultant powders obtained without mineralizer as a function of temperature. All powders except of the top one were crystallized by using zirconium oxynitrate, while the top one was obtained using oxychloride.

is irrelevant, however, the difference in the macroscopic appearance of the powders can be clearly seen (Fig. 2). The powder prepared form oxychloride is black–chlorine ions quickened the decomposition of the polymer. The powder prepared from oxynitrate is grey, while pure zirconia is snow white. This suggests the presence of some organic impurities in the powder, originating from thermal decomposition of the polymer. The powders obtained from oxynitrate are grey only in the case when HPMC is present in the environment, when PEG or PVA are used the resultant powders are white. The reason is probably that HPMC has complicated, ring structure, while structures of both PEG and PVA are relatively simple. Basing on this observation, zirconium oxychloride has been rejected as the precursor, and the crystallization continued by using only zirconium oxynitrate.

The addition of the mineralizer to the crystallization environment gave interesting results (Fig. 3). When NaOH is added, the obtained phase is tetragonal polymorph of zirconia. Usually, at higher temperatures and without addition of the polymer, the result of crystallization in the 1M solution of NaOH is the monoclinic polymorph. However, at lower

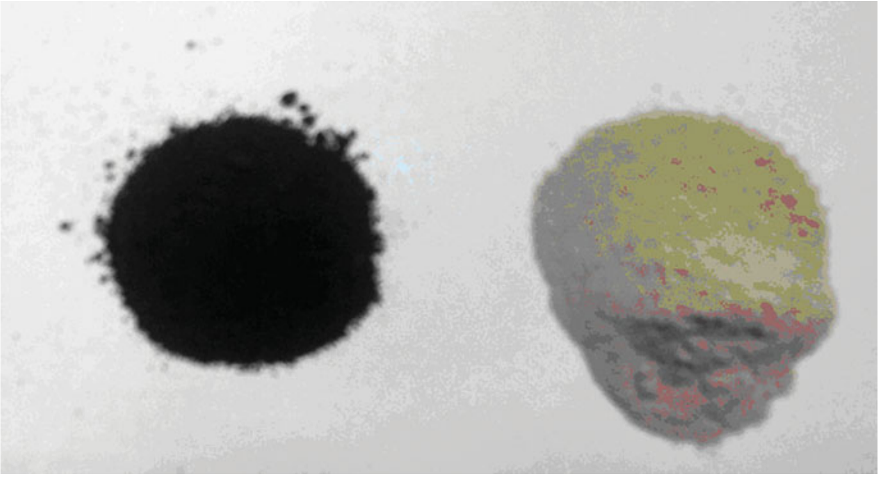

Figure 3. Left: powder obtained from oxychloride, right: powder obtained from oxynitrate. Crystallization conditions: 200°C, 2 h, HPMC 2 g/L.

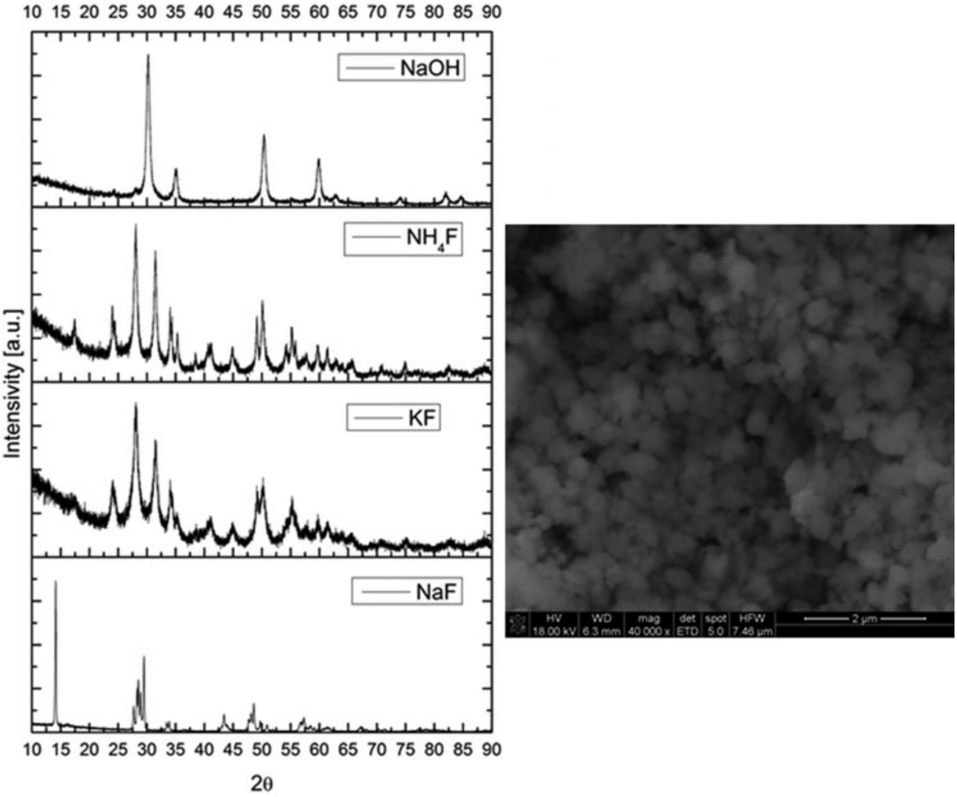

Figure 4. Left: phase composition of the powder crystallized at 140°C for 2 h in the presence of the different mineralizers, right: morphology of the representative sample of the powder crystallized in the presence of KF.

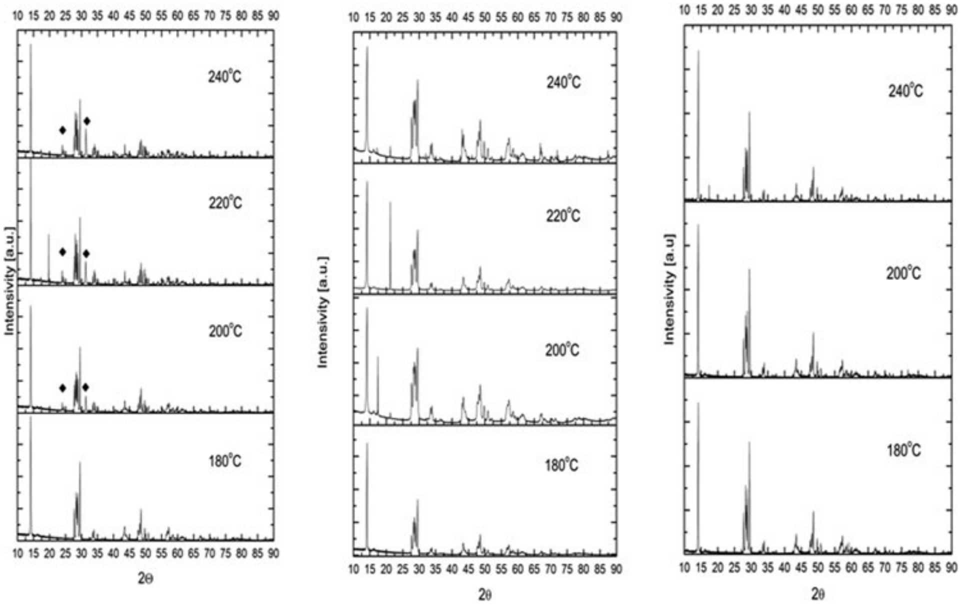

Figure 5. Phase composition of the powders as a function of temperature in the presence of selected polymers: left–PVA (M_W = 14 000 Da, c = 2g/L), middle–HPMC (c = 2g/L), right–PEG (c = 2g/L). Rhombus indicates peaks form the monoclinic polymorph of the zirconium dioxide.

temperatures the tetragonal phase is obtained. The addition of potassium and ammonium fluoride resulted in the monoclinic polymorph of zirconia with plate-like morphology of the crystallites. This is typical morphology of zirconia powders obtained in the presence of fluorides. The crystallinity of the powders is better when ammonium fluoride is used as a

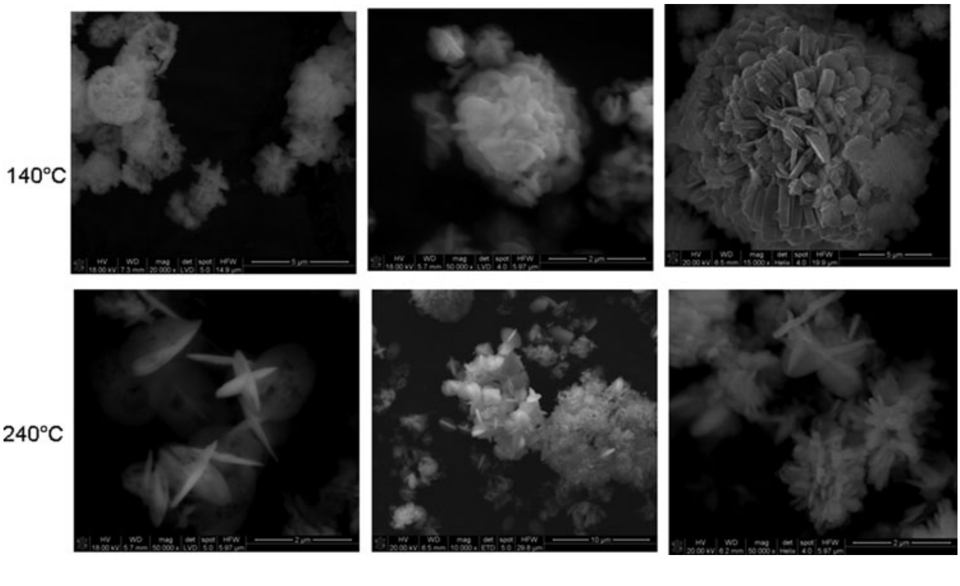

Figure 6. Morphology of the resultant crystals: left–in the presence of PVA (M_W = 14 000 Da, c = 2 g/L), middle–HPMC (M_W = 100 000 Da, c = 2 g/L), right–PEG (M_W = 4 000 Da, c = 2 g/L). Values on the left indicate crystallization temperature. Crystallization time.

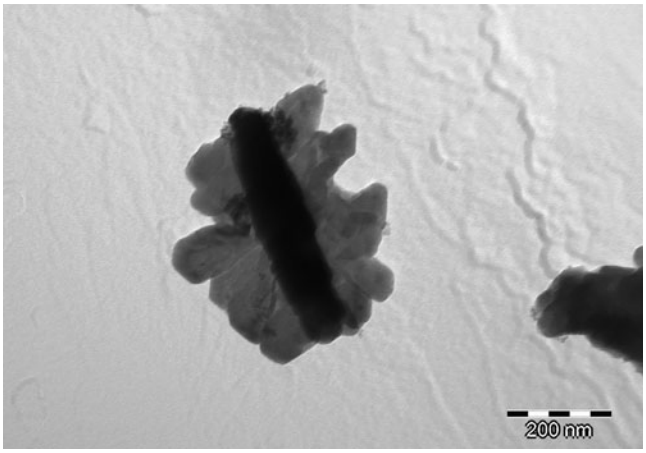

Figure 7. TEM image of the self-assembled aggregate of the new phase.

mineralizer (please note differences in the shapes of the groups of peaks about $2\theta = 35^\circ$ and $2\theta = 50^\circ$ - the peaks in the case of ammonium fluoride are more clearly visible).

The most interesting situation is when sodium fluoride was used as a mineralizer. Sodium fluoride is commonly used to obtain zirconia grains of the plate-like morphology. In this case, however, a completely new phase crystallizes, probably a hydride or hybrid organic/inorganic–a strong peak between $2\theta = 10^\circ$–15° could originate from chemically bound water or some organic. A IR spectra of the new phase can be seen in Fig. 8. The strong band at about 500 cm^{-1} and weaker one at about 750 cm^{-1} originates from Zr-O and Zr-O-Zr bonds, respectively. This suggests that the new phase is probably based on the zirconia structure. The chemical composition of the phase measured by the XRD technique is as follows: 47.39% Zr, 22.19% O, 14.65% Na, 14.19% F.

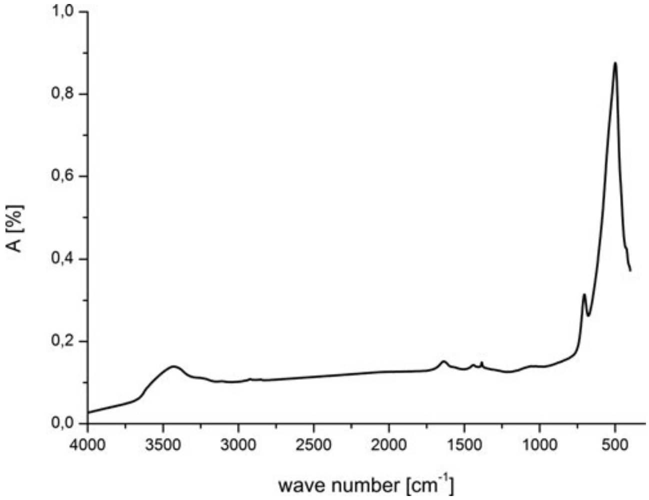

Figure 8. IR spectra of the new phase.

The new phase crystallizes regardless of which polymer (and in what concentration the process occurs) at the temperatures up to almost 200°C. In the case of crystallization in the PVA solution, some characteristic peaks originating from the monoclinic polymorph of zirconia appear in the XRD pattern (Fig. 5). The amount of zirconia in the sample increases with the crystallization temperature.

The obtained morphology of both new phase and zirconia are unusual (Fig. 6). In case of PVA, at 140°C, one can find two different types of morphology of the particles. First, the spherical agglomerates of small particles and second, the star-like assemblies of the brush-like smaller assemblies of the crystallites of the new phase. At 240°C, the new phase exists mainly in the form of large (several microns), hexagonal plates. However, the star-like assemblies presented in the SEM photograph are composed of–basing on EDX analysis–only from zirconium oxide, suggesting (basing on the XRD pattern) that these are assemblies of the crystallites of the monoclinic polymorph of zirconia. This is the first time ever such morphology of the zirconia is observed.

When the process occurs in the HPMC solution, at 140°C, randomly oriented aggregates of the plate-like crystallites of the new phase grown into each other were obtained. At higher temperatures, in this case it is 240°C, two types of morphology can be observed: randomly oriented agglomerates of the new phase crystals and the small amount of grains similar to the zirconia grain observed in the case of PVA. However, no zirconia was detected using the XRD technique. It is possible that the amount of such grains is so low that it cannot be detected using the XRD method.

When PEG was added as a polymer, at 140°C, another type of the grain morphology was observed: large, hedgehog-like aggregates of the thick plate-like crystals of the new phase. At the temperature of 240°C, two types of morphology are again observed. Small, randomly oriented plates of the new phase and, as in the case of HPMC, small amount of grains identical in morphology to the grains of zirconia detected in the powders obtained by using PVA as a polymer. However, in this case also zirconia cannot be found using the XRD technique, probably for the same reason as in case of HPMC.

TEM observations of the oriented aggregates of the new phase (Fig. 7) revealed, that those large, 1 micron or more in size plates, are composed of smaller, plate like crystallites of 50 nm to 100 nm in size. When one look closer on the SEM images of the self-assembled aggregates of the zirconia, one can notice that those aggregates have similar, hierarchical morphology. The fact one can observe such aggregates using TEM technique indicates that the durability of such structure is high–observed aggregate successfully survived the ultrasonification process in propan-2-ol, which is a typical step of preparation of powder samples in the TEM technique. Basing on the SEM and TEM observations, the following mechanism of the formation of such aggregates (Fig. 9) can be presented.

In the proposed mechanism, the crystallites are first assembled in the large plates. The origin of the shape of the plate remains unknown, however we presume it is dependent on the crystallites geometry and minimizes the energy of the system. In the middle of such assembled plate there is a nucleation spot, where either a new crystallite can grow or an already existing crystal can be joined, forming an object similar to a pin or a disc fragment in a middle of the disk. Then, the pin grows wider in the direction perpendicular to the plate by joining other crystallites. There is a possibility that sometimes, another plate, perpendicular to the both already existing plates, grows in the same manner as the second one. It can grow only on the one side of the assembly, or on the all sides.

The mechanism of the self-assembly of the singular crystallites (or even crystallization nuclei) is usually proposed as follows: the hydrophilic group of the polymer attach itself to the crystallite, while the other hydrophilic group attach itself to another crystallite. Attached

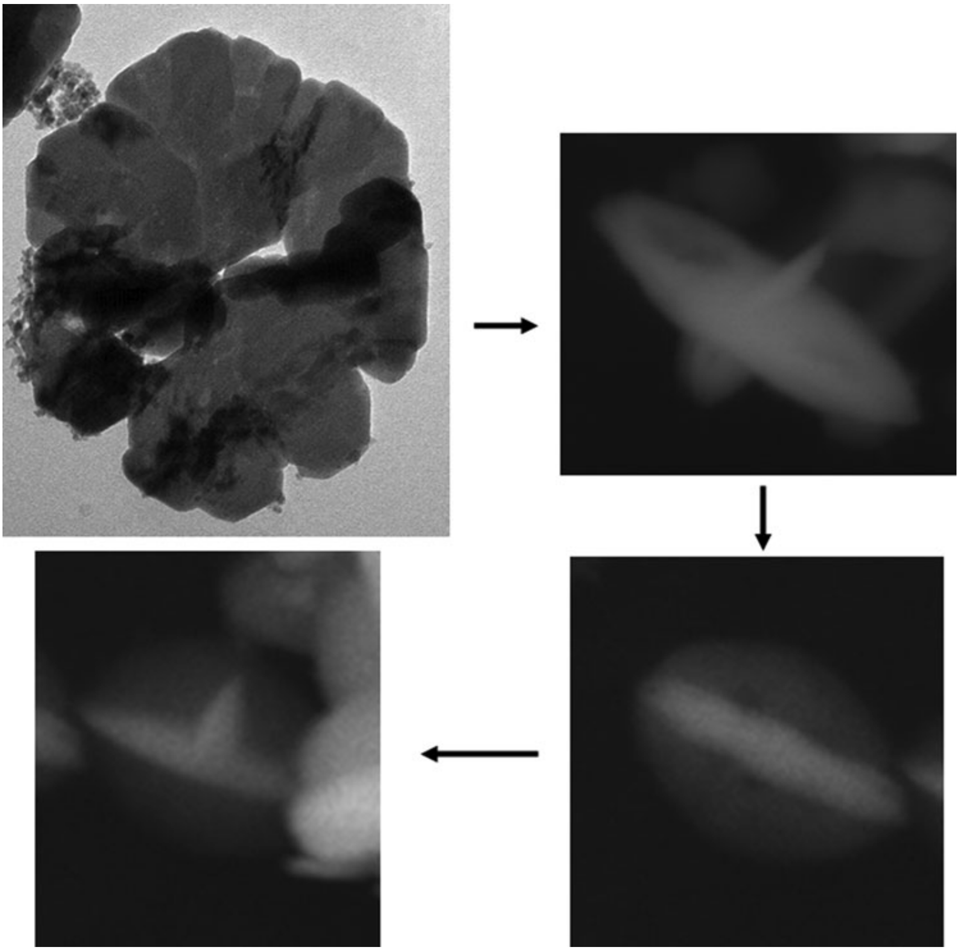

Figure 9. The proposed mechanism of the formation of the star-like, 3D assemblies.

polymer groups can influence nucleation, nanocrystal growth and aggregation [12, 13]. Crystallites with attached polymer have limited movement options and they aggregate in a manner ensuring maximization of the lowering of the system energy.

Conclusions

1. The choice of the inappropriate precursor can destroy the structure of the polymer used.
2. The choice of the mineralizer has a strong influence not only on the morphology of the resultant phase, but also on the phase composition.
3. The usage of NaF as a mineralizer in the nonclassical crystallization of zirconia leads to the new phase composed of zirconium, sodium, oxygen and fluorine, based on the structure of the zirconia. Further investigation is required to fully reveal the structure and the properties of this phase.

4. The new phase can be obtained using different hydrophilic polymers, at different crystallization temperatures. Increasing the temperature above about 200 °C can result in crystallization of the zirconia of the unusual, 3D, star-like morphology.
5. The new phase can exist in a number of morphologies, from randomly oriented crystals hundreds of nm in size, large, hedgehog-like assemblies of the thick plates of 1 micron in size or larger to the star-like assemblies of the brush-like assemblies.

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