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REVIEW ARTICLE

Methods for the synthesis of barium titanate as a component of functional dielectric ceramics

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Abstract

Objectives. To examine the general principles and recent advances in the synthesis of high-purity and high-homogeneity barium titanate powders in the manufacture of electronic components.

Results. The main publications regarding the synthesis of barium titanate powder, including the works of recent years, were analyzed. The technological advantages and disadvantages of various synthesis methods were identified. Groups of methods based on solid-state interaction of reagents and methods of "wet chemistry" were also considered. The possibilities of producing barium titanate particles of non-isometric shapes for creating textured ceramics were discussed separately.

Conclusions. Barium titanate is a well-known ferroelectric with a high dielectric constant and low dielectric loss. It is used as a component in ceramic electronic products, for example, capacitors, memory devices, optoelectronic devices, and piezoelectric transducers. The possibilities of producing functional ceramics based on barium titanate powder largely depend on its state and morphological characteristics, determined during the synthesis stage. The most important factors affecting the functional characteristics of ceramics are the purity and morphology of the powder raw materials used.

Keywords

barium titanate, ferroelectrics, piezoceramics, perovskite-like oxide ferroelectrics, solid-state synthesis, sol–gel method, hydrothermal synthesis, supercritical water

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ОБЗОРНАЯ СТАТЬЯ

Методы синтеза титаната бария как компонента функциональной диэлектрической керамики

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Аннотация

Цели. Проанализировать общие принципы и последние достижения в области синтеза порошков титаната бария высокой чистоты и гомогенности для изготовления электронных компонентов.

Результаты. Рассмотрены основные публикации о синтезе порошка титаната бария, включая работы последних лет, отмечены достоинства и недостатки различных методов синтеза с технологической точки зрения. Проанализированы группы методов, основанные на твердофазном взаимодействии реагентов, и методы «мокрой химии». Отдельно обсуждены возможности получения частиц титаната бария неизометричной формы, предназначенные для создания текстурированной керамики.

Выводы. Титанат бария является широко известным сегнетоэлектриком с высокой диэлектрической проницаемостью и низким значением диэлектрических потерь и применяется в качестве компонента керамических изделий электроники, например, для конденсаторов, запоминающих устройств, оптоэлектронных устройств, пьезоэлектрических преобразователей. Возможности производства функциональной керамики на основе порошка титаната бария во многом зависят от его фазовых и морфологических характеристик, которые определяются на этапе синтеза. Одними из важнейших факторов, влияющих на функциональные характеристики керамики, выступают чистота и морфология используемого порошкового сырья.

Ключевые слова

титанат бария, сегнетоэлектрики, пьезокерамика,
перовскитоподобные оксидные сегнетоэлектрики, твердофазный синтез,
золь-гель метод, гидротермальный синтез, сверхкритический водный флюид

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INTRODUCTION

The synthesis of complex oxides can often be a challenging task in both laboratory and industrial practice. Along with oxygen, such compounds contain two or more other chemical elements. Depending on their quantitative ratio and the conditions of the synthesis process, stable compounds of various compositions can be obtained from the same components. Thus, the targeted synthesis of a single-state product with a strictly defined stoichiometry requires the use of certain technological approaches. Currently, several groups of methods for producing complex oxides have been developed in solid-state chemistry. They include high-temperature treatment of reagents, flow synthesis, melt synthesis, hydrothermal synthesis, and other methods using solutions, as well as their combinations. The article discusses the principles of the most important and popular methods.

METHODS FOR THE SYNTHESIS OF BARIUM TITANATE

At temperatures below 120°C, barium titanate has ferroelectric properties. The most important requirements for fine-crystalline $BaTiO_3$ powder are a high level of purity, uniformity of state composition, narrow size distribution of crystals, identical (usually round) shape, and a low degree of agglomeration [1]. To date, a large number of methods for the synthesis of $BaTiO_3$ powder have been developed. They can be attributed to one or another of the main groups of methods for the synthesis of complex oxides. There are also many hybrid methods (sol–gel hydrothermal process, sol–gel process in a supercritical medium, etc.).

High-temperature solid-state synthesis

In the solid-state synthesis of pure $BaTiO_3$, the reactants are typically $BaCO_3$ and TiO_2. They are mixed by grinding in a mill for 2 to 24 h in air or in an alcohol medium. The prepared mixture is then dried in air at a temperature of about 80°C. The synthesis is carried out at temperatures from 800 to 1400°C for up to 8 h [2–6]. The process of transforming the reactants into the final product, barium metatitanate, can be divided into three stages [2]. During heating of the reaction mixture, barium carbonate decomposes to form oxide, and barium ions diffuse into the structure of titanium dioxide. Pure $BaCO_3$ releases CO_2 at a temperature of 825°C [4], while in the presence of TiO_2, decomposition begins at a lower temperature. The removal of BaO from the decomposition reaction due to its interaction with TiO_2 accelerates the process at the initial stage. The formation of $BaTiO_3$ can be observed already at 650°C [7]. As a new $BaTiO_3$ state is formed on the TiO_2 surface, the reaction becomes diffusion-controlled and is hampered by the low solubility of BaO in metatitanate (less than 100 ppm). This leads to the formation of the orthotitanate Ba_2TiO_4 state [8]. The processes occurring in the solid-state reaction front can be expressed by the following equations:

$$BaO + TiO_2 = BaTiO_3 \tag{1}$$

$$BaTiO_3 + BaO = Ba_2TiO_4 \tag{2}$$

$$Ba_2TiO_4 + TiO_2 = 2BaTiO_3 \tag{3}$$

In practice, the reaction (3) does not always proceed completely, and the final product of the synthesis contains undesirable impurities of Ba_2TiO_4. The particle size of the initial $BaCO_3$ is usually of the order of 1 μm, and their interaction with TiO_2 requires fairly high temperatures (up to 1100°C). As a result, the product obtained consists of large agglomerates which require grinding.

The grinding procedure was carried out in one of three ways: once over a long period of time (12 h, 270 rpm) [2]; with the use of dispersants (ammonium polyacrylate) [7]; or repeatedly, alternating with heating the oxide mixture [6]. In some works, grinding was performed in liquid media such as water, alcohols, etc. [9, 10]. It was noted that, in this case, the surface of the reactants was found to be enriched with hydroxyl and/or alkoxy groups. This slowed down their solid-state interaction at the stage of heat treatment [10, 11]. At the same time, the reactivity of the components of the mixture increased, facilitating the diffusion of Ba^{2+} ions into the TiO_2 matrix. Grinding the reagents to a nanocrystalline state enabled the synthesis temperature to be reduced to 800°C. This also reduced the formation of Ba_2TiO_4, and eliminated the need to grind the final product. It was shown [12] that a similar effect persisted at grinding durations of up to 20 h, after which the particles reagglomerated. Due to the diffusion control of the process, the shape and size of the product particles in the absence of intensive agglomeration at low temperatures were close to the shape and size of the particles of the initial TiO_2 [7]. The morphology inheritance allowed for the characteristics of the final product to be controlled at the synthesis planning stage.

It was noted that by lowering the pressure of air or CO_2 over the oxides during the process, their reactivity increased due to easier release of CO_2 [7]. However, in this case, Ba_2TiO_4 is formed to a greater extent. Increasing the CO_2 pressure over the reaction mixture (up to 100 kPa), in turn, allows for the formation of orthotitanate to be completely suppressed. Pre-grinding of the reactants and control of CO_2 pressure create conditions for the synthesis of pure nanocrystalline $BaTiO_3$ by high-temperature solid-state transformation (Fig. 1).

Ultrasonic treatment is used as an alternative to grinding for preparing the reaction mixture for solid-state transformation [13–16]. Depending on the nature of the medium in which the reactants are placed, ultrasonic treatment has a dispersing effect (e.g., in ethanol [16]) and can also lead to chemical activation of the surface. $BaCO_3$ can partially dissolve in non-alkaline aqueous solutions. It was determined that ultrasonic radiation causes a rearrangement of barium ions on the surface of TiO_2 particles, which has a negative ζ potential [14]. As a result of these processes, the temperature required to transform the treated mixture of reactants into barium titanate is lower than in the case of grinding. The average particulate size of the product is also smaller.

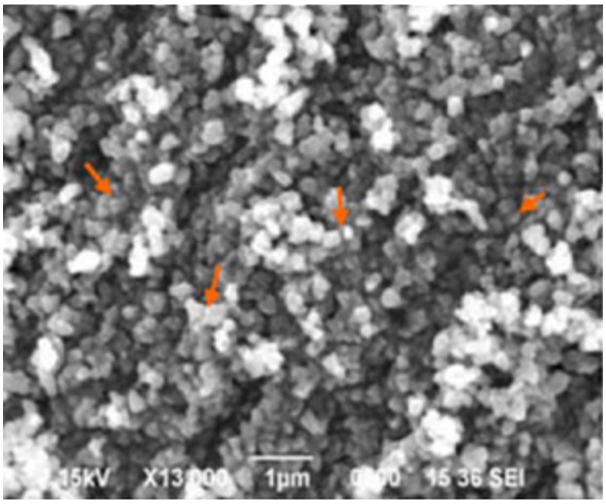

Fig. 1. Scanning electron microscope (SEM) image of a $BaTiO_3$ sample synthesized by high-temperature solid-state method at 800°C [6]

Mechanochemical synthesis

Mechanical treatment of the reactants in the solid-state production of $BaTiO_3$ is often a preparatory step before high-temperature heating. However, a number of studies have showed that the preparation of barium titanate can feasibly be achieved by entirely mechanochemical methods [17–21].

As in high-temperature synthesis, the source of titanium ions in such a process is TiO_2, and a more efficient source of barium ions is BaO or $Ba(OH)_2$[17]. It should be noted that these barium compounds tend to interact with carbon dioxide and water from the surrounding air. In order to estimate the amount of the reactant correctly, operations with BaO and $Ba(OH)_2$ must be carried out in an inert atmosphere. The path from the reactants to the final product passes through the formation of the intermediate compound Ba_2TiO_4 [22]. The near-room temperature at which mechanochemical synthesis is carried out is insufficient to decompose $BaCO_3$. As a result, the reaction is slow or inhibited. For the same reason, the reaction between barium and titanium oxides was performed without CO_2 access in a nitrogen atmosphere or in vacuum [22]. The medium in which the mechanical treatment of the reaction mixture is carried out significantly affects not only the completeness of the reaction, but also the size of the $BaTiO_3$ particles [23]. Replacing a gaseous medium with a liquid medium (e.g., toluene) allows a product to be obtained which consists of smaller crystals. The important role of mill design was also noted. For example, a ball mill enables a nearly 100% conversion of a mixture of BaO and TiO_2 into $BaTiO_3$ to be achieved in 4 h. When using an attritor, 12 min are sufficient for the complete reaction between TiO_2 and $BaCO_3$ [17, 19]. In order to increase the mechanical action intensity in the synthesis in a ball mill, a sufficiently high weight ratio of the balls and the reaction mixture was chosen: from 20 : 1 to 25 : 1 [17, 22, 23]. The range of energies imparted by the ball upon impact to ensure the transformation of a mixture of barium and titanium oxides into $BaTiO_3$ was established as 50–160 mJ [20]. Based on these values, efficient conditions for mechanochemical synthesis can be chosen.

Soft mechanochemical synthesis without thermal treatment of reactants can produce crystalline $BaTiO_3$ particles close in size to nanoparticles (Fig. 2). It is easy to perform, and has low energy consumption.

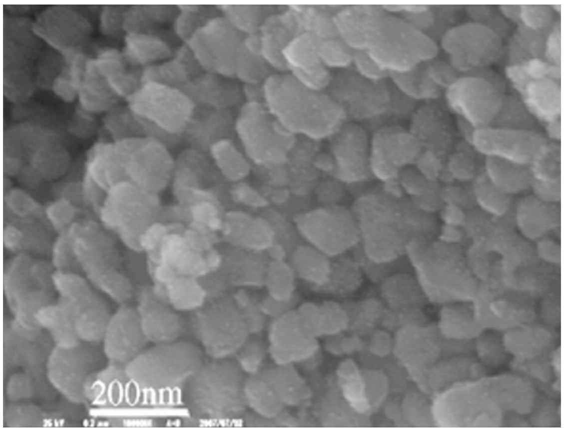

Fig. 2. SEM image of a $BaTiO_3$ sample obtained by mechanochemical synthesis [19]

Complexation methods

In complexation methods for the synthesis of crystalline $BaTiO_3$, the reactants are, as a rule, barium salts ($Ba(NO_3)_2$, $BaCO_3$, $BaCl_2$, $Ba(CH_3COO)_2$) and various titanium compounds (butoxide, isopropoxide, tetrachloride, dioxide). The chelating agent is citric or ethylenediaminetetraacetic (EDTA) acid. The auxiliary reagents can also be ethylene glycol, ammonium hydroxide, and nitric acid.

At the beginning of the citrate process, the titanium-containing reactant is hydrolyzed in the acidic medium of a complexing agent. A barium salt solution is also prepared (if the reactant is $BaCO_3$, it is also dissolved in the acidic medium). By mixing the prepared solutions, a solution of barium titanium citrate is obtained [24]. At this stage, it is important to control the acidity of the medium, since the composition of the mixed citrate depends on the pH. At a low pH value, a complex of the composition $BaTi(C_6H_6O_7)_3{\cdot}6H_2O$ with a molar ratio of cations of 1 : 1 is formed. By increasing pH, $Ba_2Ti(C_6H_5O_7)_2(C_6H_6O_7){\cdot}7H_2O$ with a Ba : Ti ratio of 2 : 1 is produced [25]. In order to maintain the stoichiometry of the final product ($BaTiO_3$) in the precursor, pH 5–6 is maintained in the reaction medium by adding the required amount of NH_4OH or HNO_3 [26, 27]. In some studies, citric acid was replaced with EDTA, which is a stronger complexing agent [27, 28]. The operations described herein are similar to those in the Pechini method, with the exception of the addition of ethylene glycol to the reaction system at one of the stages [29]. A simpler scheme was also proposed for preparing a precursor by dissolving $BaCl_2$ and TiO_2 in a solution of citric acid with heating and stirring until a viscous gel is formed [30].

Then, water is evaporated from the solutions (90°C, 1–2 h) and the precursor obtained is dried. In the Pechini method, the temperature is raised to 180°C for several hours, in order to esterify ethylene glycol and citric acid and form a polymer.

The final stage of synthesis in each of the methods is high-temperature heating of the precursor. At this stage, organic components are removed and $BaTiO_3$ crystallizes. Heating for up to 8 h is carried out in air at temperatures from 600 to 1000°C. The aim of the synthesis stages preceding heating is to achieve a high degree of reagent mixing. The heating conditions, in turn, determine the state purity and morphological features of $BaTiO_3$ crystals.

The literature presents two points of view on the mechanism of the process which occurs when the precursor is heated. According to one point of view, in the temperature range from 380 to 525°C, the precursor transforms into an intermediate compound of the composition $BaTi_2O_5CO_3$. This decomposes at a temperature of about 690°C to form the final barium titanate [31]. Other observations of the decomposition of the precursor establish that heating leads to only partial formation of an intermediate compound [32]. Most of the precursor decomposes into $BaCO_3$ and TiO_2 (X-ray amorphous) in the temperature range from 435 to 500°C which interact at a temperature of about 600°C [25, 26, 32]. The decomposition mechanism depends on the heating conditions [32]. A systematic study [33] showed that the formation of $BaCO_3$ can be avoided by removing organic components for a longer time up to 24 h at lower temperatures (about 300°C), at which no carbonate has yet been formed. Before further increasing the temperature, the precursor is ground. It is recommended to heat to the upper temperature at the maximum possible rate [27] and to apply a long holding time (about 8 h) [33]. Subject to such conditions, the purity of the product increases. It does not contain $BaCO_3$ impurities.

A significant conclusion which can be drawn from studies of the mechanism of precursor decomposition is the fact of the formation of $BaCO_3$ and TiO_2 in the form of separate states at temperatures lower than the temperature of the beginning of $BaTiO_3$ crystallization. This means that the mixing of cations at the atomic level, achieved by preparing complex compounds, is violated by heat treatment of the precursor. $BaTiO_3$ is formed by the solid-state reaction of $BaCO_3$ and TiO_2 [25]. An advantage of complexation over conventional solid-state synthesis is the smaller size of interacting particles (nanometers). This cannot be achieved by mechanical processing of coarser reactants. As a result, the crystals of the product are also micro- and nanosized (up to 130 nm). Under certain conditions, one can obtain samples consisting of crystals smaller than 50 nm in size with a narrow size distribution [29, 32, 34] (Fig. 3).

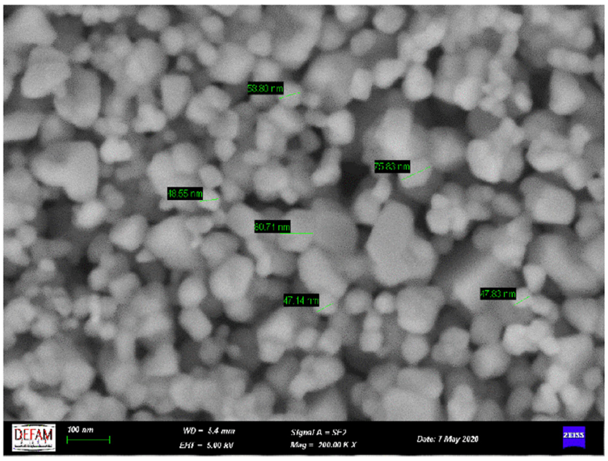

Fig. 3. SEM image of $BaTiO_3$ nanocrystals obtained by the Pechini method [29]

Another advantage of the technology under consideration is its high level of control over the stoichiometry of the product. This is due to the possibility of the formation of mixed complexes with a given Ba : Ti ratio in the solution [35]. However, nanocrystals are highly prone to agglomeration due to low ζ potential values at the pH of the solution above 1.5 [36]. Heat treatment at the final stage of the process reduces their size [34]. A high degree of powder agglomeration creates difficulties during the sintering of ceramics. This is because the behavior of the structure of workpieces containing agglomerates during firing has been insufficiently studied [35]. According to various data, $BaTiO_3$ nanocrystals obtained by complexation methods form agglomerates ranging in size from 0.2 to 2.0 μm [32, 37].

Sol–gel method

The sol–gel method is used to obtain crystalline $BaTiO_3$ powders, as well as thin films, coatings, and aerogels [38–43]. This method allows the stoichiometry of the final product to be easily adjusted, and facilitates the production of powders of various barium titanates ($BaTiO_3$, Ba_2TiO_4, $BaTi_2O_5$, $BaTi_4O_9$) by varying the molar ratio of the reactants [44, 45].

In the sol–gel synthesis of $BaTiO_3$, as in most other complex oxides, one of the reactants is a transition metal alkoxide (titanium isopropylate or titanium butoxide). This is due to its high activity in the hydrolysis and condensation reactions [46, 47]. Barium ions are introduced into the reaction mixture as an alcohol solution of hydroxide, acetate, acetylacetonate, or also alkoxides [44, 46, 48, 49]. The reactants are mixed in a dry inert atmosphere, in order to prevent them from interacting with water vapor or carbon dioxide [46, 48]. In this regard, the more suitable choice is acetylacetonate or barium acetate, since they are more moisture-resistant [46]. The mixing of the reactants leads to the rapid and complete alcoholysis of alkoxides and polycondensation, in order to form Ti–O–Ti and Ti–O–Ba^{2+} bonds [48]. In an acidic medium (pH 2.5–3.5), the acidity of which is provided by adding acetic acid, the mixture is converted into a sol by hydrolysis [46, 50]. In this case, water molecules contribute to the redistribution of fragments of the condensed system by the formation of hydrogen bonds [48]. With an increase in the pH, the hydrolysis of alkoxides leads to crystallization of metal hydroxides and oxides from the solution, rather than to the formation of a gel [51]. The hydrolysis rate decreases with the length of the carbon chain of alkoxides [46] and also depends on the presence of auxiliary reagents. The addition of chelating agents (e.g., acetylacetone) or surfactants to the reaction mixture enables the progress of condensation and polymer growth to be controlled by reducing the reaction rate [46, 52]. Gelation is often carried out at room temperature, in order to achieve a more uniform structure, since heating naturally accelerates the process [50]. The gel thus prepared is dried at temperatures from 50 to 110°C from several hours to several days. According to various observations, the structure of the gel and the precursor, as well as the temperature required for calcination, depends on the nature of the Ba-containing reactant. Heating the precursor to 200°C is accompanied by the evaporation of solvent residues, and then, with further heating to 400°C, organic fragments are pyrolyzed. When heated to 500°C, the powder has an amorphous structure. $BaTiO_3$ begins to crystallize at about 550°C in the case of synthesis from barium acetate or isopropylate [44, 49], at 600°C when synthesized from hydroxide [48], and at 620°C when using barium acetylacetonate [46]. The mechanism of crystallization of $BaTiO_3$ from gel has no unambiguous interpretation. Some studies reported the absence of any intermediate compounds and the direct formation of $BaTiO_3$ from the precursor [44, 48]. There is a point of view that, during the decomposition of the gel, barium titanate is preceded by oxycarbonate $Ba_2Ti_2O_5CO_3$ [49]. It is more likely that the gel will decompose to form $BaCO_3$ and TiO_2, which then enter into solid-state interaction [46, 49, 52], as in the complexation methods.

In most studies, calcination of the gel for up to 2 h is carried out at temperatures up to 900°C [44, 46, 49, 52]. It was noted the product is weakly crystallized [46] and contains small amounts of $BaCO_3$ [52–54]. The crystals in single-state $BaTiO_3$ powders obtained by the sol–gel method had a narrow size distribution in the range from 37 to 70 nm (Fig. 4) [49, 52, 55].

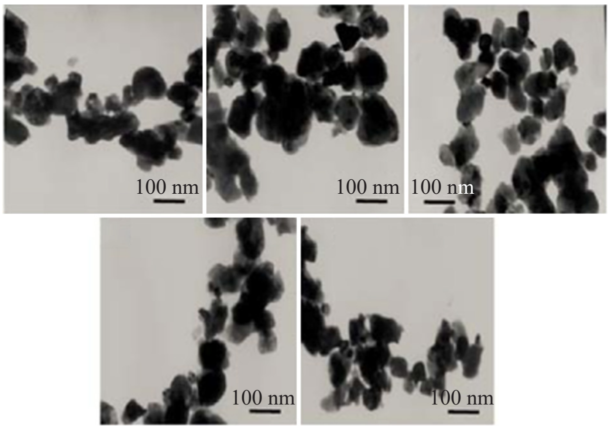

Fig. 4. Transmission electron microscope (TEM) images of $BaTiO_3$ crystals obtained by the sol–gel method [52]

Hydrothermal method

The hydrothermal method is one of the main methods used to obtain $BaTiO_3$. The reactants are typically barium salts ($BaCl_2$, $Ba(NO_3)_2$), or $Ba(OH)_2$ and titanium dioxide in the amorphous or crystalline state [56–58]. The reactivity of amorphous TiO_2 under hydrothermal conditions is higher than that of crystalline TiO_2 [59]. Therefore, it is often synthesized *in situ* using titanium alkoxides or chlorides as reactants which at the beginning of the process are hydrolyzed, in order to form $TiO_2 \cdot H_2O$ [57, 60, 61]. A mixture of reactants in an aqueous solution is placed in a closed reactor and maintained at a temperature from 130 to 250°C and at an equilibrium pressure [56–58, 61] for a time ranging from several hours [34, 56, 61] to several days [58, 62]. The product is cooled, washed with an acid solution and distilled water, in order to remove $BaCO_3$, and dried in air or vacuum [34, 56, 61, 62].

The literature shows two points of view on the mechanism of formation of $BaTiO_3$ under hydrothermal conditions. According to one of them, the transformation occurs by means of a solid-state mechanism without dissolving TiO_2 [63, 64]. In this case, the solution facilitates the transport of Ba^{2+} ions to the TiO_2 surface in comparison with high-temperature solid-state synthesis. The model of product formation remains the same: the formation of a $BaTiO_3$ layer on the TiO_2 surface and the gradual propagation of the reaction front into the initial particles. According to the other point of view, a dissolution–precipitation mechanism takes place in which the nucleation occurs homogeneously in the solution as a result of the reaction of Ba^{2+} and $Ti(OH)_n^{4-n}$ [58, 63–65]. This point of view garnered more experimental confirmations and is thus shared by most researchers.

An important advantage of hydrothermal synthesis is that $BaTiO_3$ is the only form of the complex oxide stable under these conditions. For the reaction system, thermodynamic parameters of ions in an equilibrium state were calculated. Taking solubility into account, diagrams were constructed to determine the conditions for obtaining a $BaTiO_3$ precipitate at different temperatures [68]. As an example, Fig. 5 shows such a diagram for 160°C. It can be seen that the $BaTiO_3$ precipitate forms at high pH values. However, the pH of the initial $Ba(OH)_2$ solution may be insufficiently high for the precipitate to form [69] (Fig. 6). Therefore, in order to maintain the required basicity of the medium, an excess of strong alkalis (KOH, NaOH) is initially added to the reaction mixture [56, 57, 60]. A study of the attenuation of X-ray radiation in samples of reaction mixtures and products of hydrothermal synthesis of barium titanate for 15–120 min at a temperature of 100–200°C revealed the presence of various polytitanates in the reaction medium [68]. The first product to form is the titanium dioxide-enriched state $BaTi_2O_5$. Metatitanate $BaTiO_3$ is formed in tandem with it. After further progress of the process, the third state, Ba_2TiO_4, is produced. At the final stage, the only remaining product is $BaTiO_3$. The formation of different states in a hydrothermal process may indicate that its mechanism is more complex than suggested by the dissolution–precipitation model and is complemented by the *in situ* model.

The problem in obtaining stoichiometric $BaTiO_3$ is the partial leaching of Ba^{2+} ions from the crystal surface, observed in both acidic and basic media [24, 66, 71, 72]. This process occurs least intensely at pH 7–11 [71].

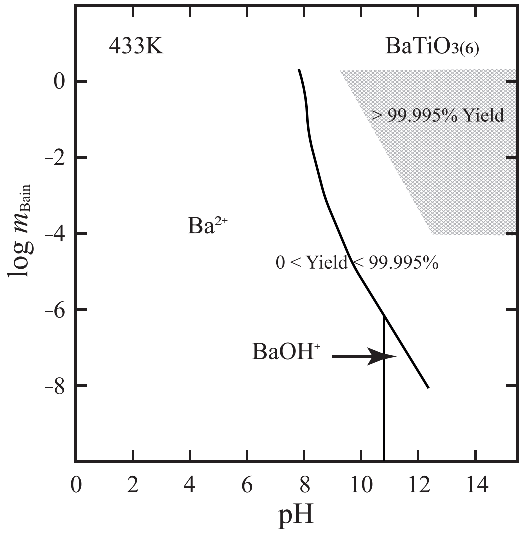

Fig. 5. Stable forms of barium ions in the Ba^{2+}–TiO_2 reaction system at 160°C and the yield of the product ($BaTiO_3$), depending on the pH and the input total molality of barium ions [68]

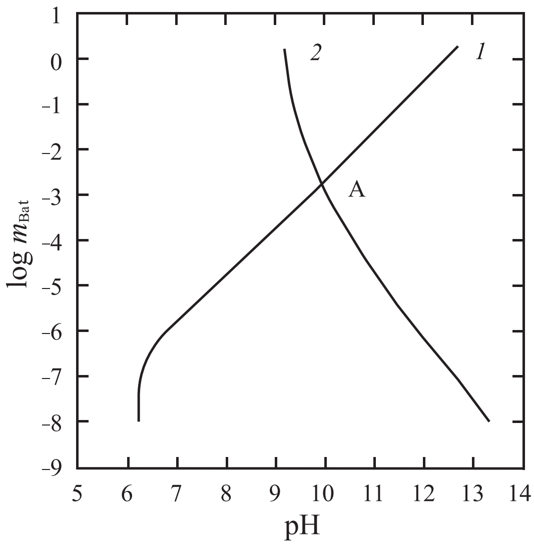

Fig. 6. Comparison of (*1*) the pH of an aqueous $Ba(OH)_2$ solution and (*2*) the pH required for crystallization of $BaTiO_3$ at various total molalities [69]

Hydrothermally produced $BaTiO_3$ crystals are usually round in shape and tend to form agglomerates. They can be characterized by narrow size distribution and an average size from 20 to 500 nm [32, 56, 58, 61, 62]. In some cases, it was possible to synthesize cubic-cut nanocrystals ranging in size from 5 to 15 nm [57] (Fig. 7).

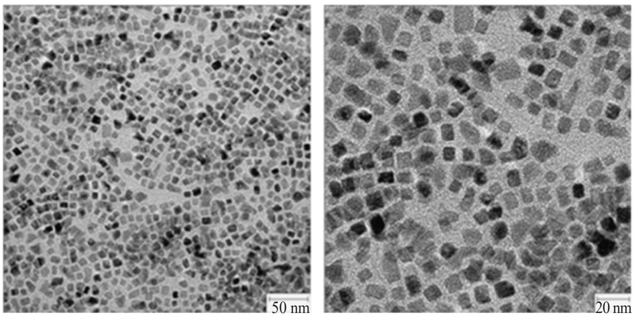

Fig. 7. TEM images of $BaTiO_3$ nanocrystals synthesized hydrothermally at 130°C in 16 h [57]

The different solubility of different forms of the initial TiO_2 makes it possible for small $BaTiO_3$ crystals (up to 110 nm) to be obtained from amorphous oxide and larger ones (from 200 to 700 nm) from sparingly soluble rutile [59]. Increasing the basicity of the medium accelerates the dissolution of TiO_2, resulting in the formation of smaller $BaTiO_3$ crystals [58]. The growth of larger crystals is promoted by an excess of Ba^{2+} in the reaction medium [62] and an increase in the temperature and duration of the process [58, 61].

Synthesis in a supercritical water medium

Under supercritical conditions, the synthesis of $BaTiO_3$ powder can be performed both in a flow reactor and in a batch reactor. The reactants are barium salts or hydroxide (oxide), and titanium dioxide or chloride. It is recommended to perform manipulations with BaO and $Ba(OH)_2$ for the preparation of the reaction mixture in an inert atmosphere. Under stationary conditions, the synthesis is carried out at 400°C and 26 MPa for 20 h [73]. The product of the reaction is pure crystalline $BaTiO_3$ powder consisting of round crystals with an average size of about 80 nm. Individual crystals reach 370 nm (Fig. 8) without the use of auxiliary reagents.

The results of the use of the flow conditions were presented for the synthesis at temperatures from 380 to 420°C and pressures from 25 to 40 MPa [74, 75]. The flow reactor was equipped with two mixers. One was supplied with solutions of reactants and auxiliary substances (e.g., alkali). In the other mixer, the reactant solution was combined with water preheated above the critical point. The mixture prepared in this way entered the reactor at a controlled flow rate and was then cooled in the downstream part of the reactor. The process took from a few milliseconds to 4 s. For the crystallization of $BaTiO_3$, the pH was maintained at 11–12 by adding a KOH solution to the reaction system or taking an excess amount of $Ba(OH)_2$. The suspension removed

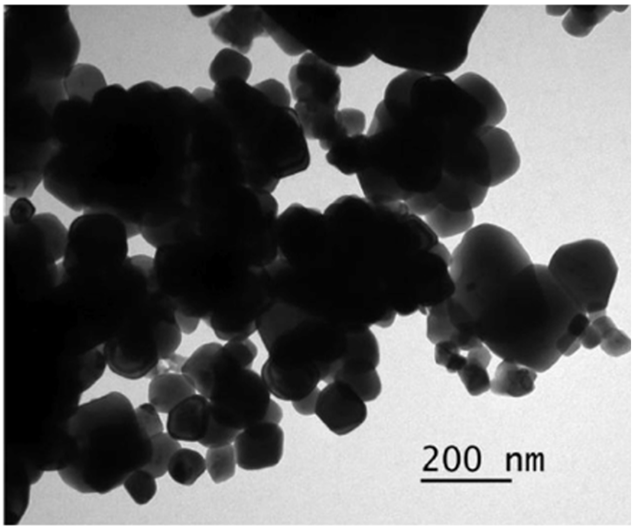

Fig. 8. TEM image of $BaTiO_3$ crystals synthesized in supercritical water at 400°C and 26 MPa in a batch reactor [73]

from the reactor was filtered. It was then successively washed with a solution of acetic acid and distilled water, and dried in air. Pure crystalline $BaTiO_3$ was obtained. The size of the crystals indicates its dependence on the duration of the process. Within 4 to 8 ms, nanocrystals (from 5 to 13 nm) were obtained [74], while at a duration of several seconds, the crystal size increased to 100 nm [75] (Fig. 9). Crystal growth was also observed with increasing process temperature and basicity of the medium. Due to the reduced surface tension of water in the supercritical state in comparison with the liquid state, the degree of particle aggregation in $BaTiO_3$ powders was found to be lower.

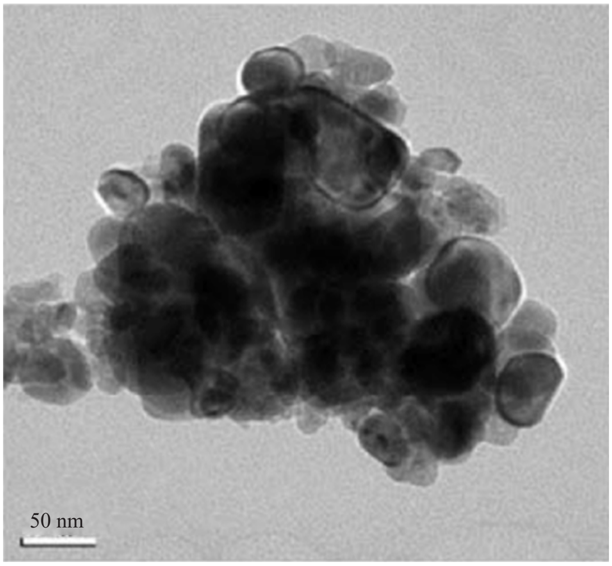

Fig. 9. TEM image of $BaTiO_3$ crystals synthesized in supercritical water at 400°C in a flow reactor [75]

SYNTHESIS OF CRYSTALINE BARIUM TITANATE OF DIFFERENT MORPHOLOGY

Effect of morphology on the properties of $BaTiO_3$ crystals

As noted earlier, the most important factor in the production of functional ceramics is to synthesize isometric submicron and nanosized $BaTiO_3$ crystals. At the same time, the ferroelectric properties of $BaTiO_3$ depend not only on temperature, but also on the size of its particles [76]. At temperatures below the Curie point, the thermodynamically stable tetragonal state is replaced by a metastable pseudocubic state in crystals the size of which is smaller than the critical size. The pseudocubic state is paraelectric, i.e., it does not possess ferroelectric properties. One explanation for this phenomenon is the lack of an external electric field capable of neutralizing the own field of polarized particles with a high specific surface area. A certain role is played by the excess surface energy of nanosized particles. Small particles are characterized by a noticeable increase in the effect of structural defects which have a charge disrupting spontaneous polarization. Moreover, spontaneous polarization is a bulk process based on long-range interactions which is difficult to achieve if the crystal volume is very small [77, 78]. Data on the critical size of $BaTiO_3$ crystals varies between different sources, indicating on average a value of several tens of nanometers [77, 79, 80].

The manifestation of ferroelectric properties depends on the size of the particles, as well as on their geometry [81]. In comparison with round submicron and nanoparticles, which can be considered 0-dimensional, 1- and 2-dimensional $BaTiO_3$ particles possess special properties. Interest in 1-dimensional particles (needles, bars, fibers, etc.) is caused by their ability to maintain spontaneous polarization when the thickness is reduced to several nanometers [82]. This is justified by the minimal effect of the depolarizing field on cylindrical particles [83]. Furthermore, for such particles, the emergence of a new type of dipole ordering was theoretically predicted [84]. Powders consisting of 2-dimensional crystals (plates) show advantages over isometric ones in the manufacture of ceramic materials. They facilitate control of the thickness of a sample of the material, increase surface hardness, and make it possible for the piezoelectric modulus to be increased due to a high degree of grain orientation [84, 85].

Anisotropic $BaTiO_3$ particles are difficult to obtain due to the isotropy of the perovskite structure [86]. Synthesis is carried out mainly by the hydrothermal method or in molten salt [81, 86]. Crystals of a given shape are often obtained using templates which can act as reactants or porous membranes subsequently removed by etching or calcination [81].

Control of the morphology of $BaTiO_3$ under hydrothermal conditions

One of the possibilities for controlling the shape of crystals during hydrothermal synthesis is to maintain a certain basicity of the medium. The layer-by-layer formation of the $BaTiO_3$ structure in an aqueous medium is accompanied by competition between the formation of Ti–O–Ba and Ti–OH bonds [84]. At a high pH, the formation of a Ti bond with the hydroxyl group is more likely and leads to inhibition of crystal growth. The faces corresponding to different crystallographic planes contain different specific numbers of Ti atoms. Therefore, the slowdown in their growth is not uniform. The (111) face is most susceptible to the effect of OH groups. Taking advantage of this, plate-like $BaTiO_3$ crystals (average thickness 5.8 nm, average diameter 27.1 nm) were obtained from $Ba(OH)_2$ and titanium isopropoxide at 225°C for 5 h with maintaining the pH of the solution around 13 [84].

The growth of certain $BaTiO_3$ faces can be inhibited by introducing additives into the reaction medium. For example, a synthesis was reported using polyacrylic acid, which is selectively adsorbed on the high-energy (111) face and impedes crystal growth in this direction [83]. As a result, plate-like crystals were also obtained.

Additives can promote the formation of extended structures. The introduction of ammonia into the reaction medium leads to the growth of fibrous $BaTiO_3$ crystals [81]. However, the mechanism of this effect has not yet been established.

A more complex, but also more efficient way of controlling the morphology of the product is to use a titanium-containing template reactant. Such templates are typically alkali metal polytitanates with a layered structure which are active in ion-exchange reactions ($Na_2Ti_3O_7$, $K_2Ti_4O_9$, etc.). The synthesis using such reactants requires preparation. Polytitanates can be obtained hydrothermally by treating TiO_2 in a medium of NaOH or KOH (K_2CO_3) [82]. $BaTiO_3$ is formed by the exchange of Na^+ or K^+ ions for Ba^{2+} ions and subsequent restructuring with a shift of the layers of TiO_6 octahedra relative to each other.

Under conditions of the dissolution–precipitation mechanism with the formation of nuclei of a new state in a liquid medium, the reaction produces isometric $BaTiO_3$ crystals, regardless of the morphology of the reactants. However, if the goal is to obtain a product with the preserved morphology of the reactant, reaction must take place by means of an alternative mechanism which excludes dissolution [87–90]. The shape of particles of the initial layered polytitanates can be best preserved at a relatively short reaction time, low temperature, low $Ba(OH)_2$ concentration, and the use of an alcohol additive [88, 90]. Lowering the temperature to 100°C reduces the solubility of polytitanates. Polytitanates are highly soluble in a highly alkaline medium. Therefore, decreasing the $Ba(OH)_2$ concentration also leads to the desired result. The introduction of ethyl alcohol reduces the solubility of $Ba(OH)_2$ and ensures saturation of the solution with Ba^{2+} ions with a smaller amount of this reagent. Using this information, the synthesis at temperatures from 100 to 150°C for 24 h yielded plate-like crystals and fibers of $BaTiO_3$ (Figs. 10, 11).

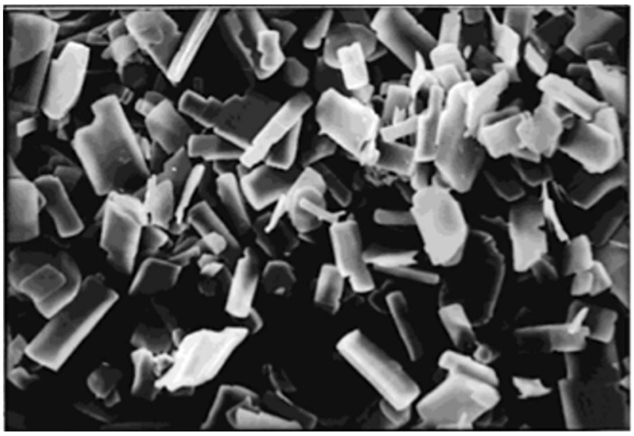

Fig. 10. SEM image of $BaTiO_3$ crystals obtained hydrothermally using plate-like $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ particles as a template [87]

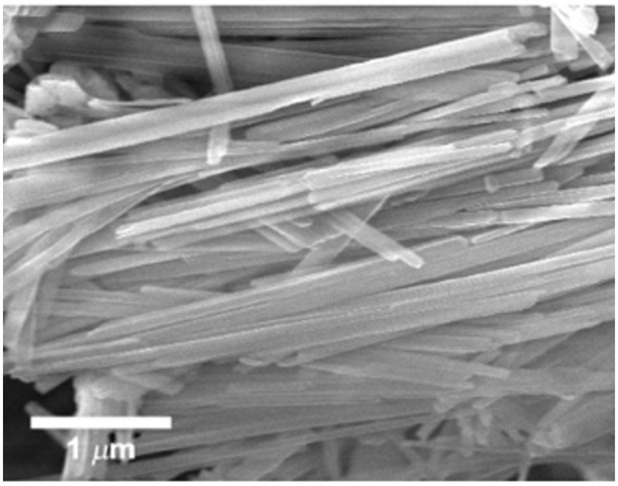

Fig. 11. SEM image of $BaTiO_3$ crystals obtained hydrothermally using bar $K_2Ti_4O_9$ particles as a template [88]

By varying the $Ba(OH)_2$ concentration, it is possible to direct the process along a path which combines both mechanisms of hydrothermal reaction. Depending on the contribution of one or the other mechanism, the shape of the product particles changes. Using extended $Na_2Ti_3O_7$ particles, $BaTiO_3$ crystals of various shapes were synthesized under hydrothermal conditions (Fig. 12) [91].

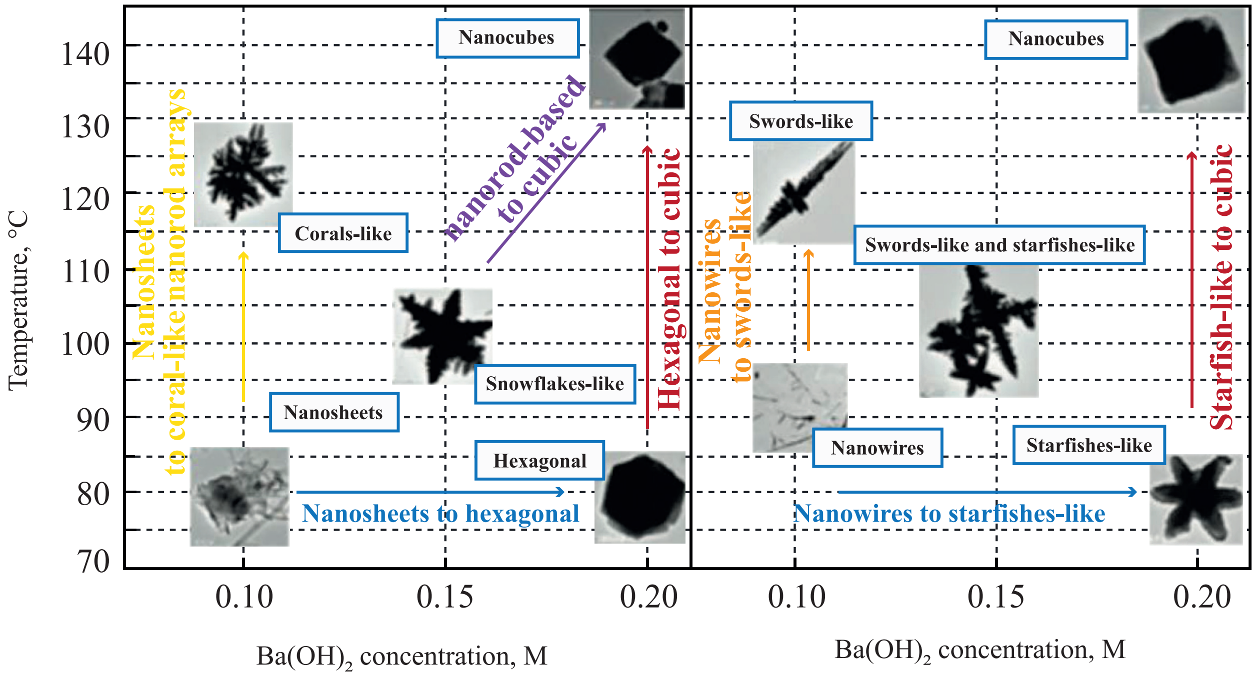

Fig. 12. Effect of the $Ba(OH)_2$ concentration and the hydrothermal process temperature on the morphology of $BaTiO_3$ synthesized using $Na_2Ti_3O_7$ particles as a template in the form of (a) nanotubes and (b) nanobars [91]

Control of the morphology of $BaTiO_3$ during molten salt synthesis

Due to features of the reaction medium, melt synthesis lacks many of the disadvantages of the previously discussed methods, but it also has its own. The melt is most often a eutectic mixture of alkali and alkaline earth metal halides, but salts with other anions, as well as hydroxides, are also used [92, 93]. The synthesis temperature ranges from 300 to 1000°C, depending on the nature of the melt and reactants. In the future, a decrease in temperature through the use of ionic liquids as a medium can be considered.

The process consists of grinding together calculated amounts of reactants and salts which will serve as a medium, then maintaining this mixture at a temperature above the melting point of the salts. $BaTiO_3$ is synthesized from TiO_2 and various barium compounds (BaO, $Ba(OH)_2$, $BaCO_3$, $Ba(NO_3)_2$) [86, 93–96]. The liquid medium facilitates the transport of ions, when compared with the conventional solid-state reaction and also slows down the growth and aggregation of $BaTiO_3$ crystals [95]. Upon completion of the high-temperature holding, the system is cooled and salts are removed by washing with water. In the synthesis of $BaTiO_3$, it is very important to control the molar ratio of the reactants, since polytitanates can be formed [94]. It was also noted that the use of amorphous TiO_2 as a reactant enables the purity of the product to be increased. The complete removal of salt ions from the final product is impossible, and $BaTiO_3$ inevitably contains impurities of other cations [94].

The principles of producing crystals with a given morphology are aimed at restraining the growth of certain crystal faces by choosing the composition of the salt mixture. A high molar ratio of salts and reactants inhibits the growth of high-energy faces. It was found that in a KCl–NaCl medium, the growth in the direction of the (101) and (001) planes is inhibited, resulting in cubic crystals. In a K_2SO_4–Na_2SO_4 medium, the growth of the (111) face slows down, and the product consists of plate-like crystals [93]. In molten salt, template reactants are also used. These can be layered polytitanates and TiO_2 with a required morphology [86, 96]. It is recommended that the source of Ba^{2+} ions be easily soluble compounds such as oxide or hydroxide, rather than salts [86]. It is important that the dissolution rate of the Ba-containing reactant should be higher than the dissolution rate of the Ti-containing reactant, and the reaction should occur by a solid-state mechanism by saturating TiO_2 with Ba^{2+} ions. Otherwise, the template morphology may be lost. Figure 13 presents an example of $BaTiO_3$ crystals synthesized from BaO and TiO_2 in a NaCl–KCl medium.

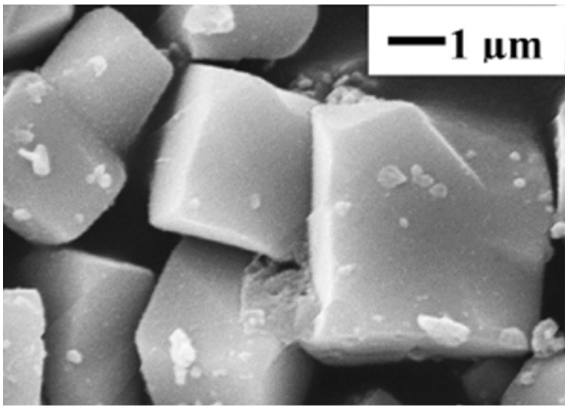

Fig. 13. SEM image of $BaTiO_3$ particles synthesized in a NaCl–KCl melt at 1080°C for 1 h [93]

CONCLUSIONS

The objective of this review was to analyze the literature data regarding for obtaining micro- and nanocrystals of $BaTiO_3$ of high purity and homogeneity, in order to find a method suitable for the synthesis of powder materials. The formation of various polytitanates in many cases complicates the production of pure $BaTiO_3$.

Experimental data on complexation methods and the sol–gel method, which were developed in order to achieve a high degree of mixing of reactants and to obtain a product of a given composition, does not always support the implementation of this idea. The data does not eliminate the formation of by-products such as carbonates and nonstoichiometric compounds. This was clearly confirmed by studies of synthesized powders by IR spectrometry and X-ray fluorescence analysis. The product typically contained traces of carbonates. Auxiliary reagents are often incompletely removed from the surface and from the bulk of the synthesized oxide. Despite the labor-intensive and expensive preparation of precursors, the temperature of their calcination can be comparable to the temperature of conventional solid-state synthesis.

The conventional solid-state synthesis method has some well-known disadvantages. It is inferior to wet chemistry methods in the homogeneity of the initial mixture of reactants and requires high temperatures to carry out the reaction. Thanks to the long-term development and improvement of this method, techniques have been found which make it possible to produce pure fine-crystalline oxides using this method (grinding the reactants and the product, repeated firing). Although the process of synthesizing complex oxides usually takes a long time, it is technically quite simple and does not require high costs for reagents and equipment.

The hydrothermal method uses mild conditions and also inexpensive reactants. Process planning requires careful monitoring of the solubility of the reactants. This method is suitable for the production of $BaTiO_3$ without impurities of polytitanates, even if the molar ratio of reactants is not 1 : 1. One general disadvantage of this method is the presence of adsorbed water on the surface of oxide crystals and OH groups as structural defects. Under hydrothermal conditions, the barium titanate particles are characterized by leaching of barium ions from the surface. The resulting local nonstoichiometry can manifest itself during further sintering of the ceramic as the undesirable growth of anomalous grains and a decrease in dielectric characteristics. The product of hydrothermal synthesis is often calcined before further use as a ceramic raw material. The hydrothermal method provides ample opportunities for controlling the shape of crystals of complex oxides.

The method for producing $BaTiO_3$ in supercritical water is promising. At the present time, the number of works on synthesis under these conditions is very limited. As such, they do not allow us to form an objective picture of the advantages and disadvantages of the method.

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Authors' contributions

A.A. Kholodkova, A.V. Reznichenko, A.A. Vasin – writing the text of the article, analysis and formulation of the results.

A.A. Kholodkova, A.V. Reznichenko, A.A. Vasin, A.V. Smirnov – conceptualization.

A.V. Smirnov – scientific editing, general management.

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