# Investigation into the Formation of Phases with a Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-Type Structure in the BaO–TiO<sub>2</sub> and BaO–SrO–TiO<sub>2</sub> Systems

L. F. Grigor'eva, S. A. Petrov, O. Yu. Sinel'shchikova, I. A. Drozdova, and V. V. Gusarov

Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, ul. Odoevskogo 24/2, St. Petersburg, 199155 Russia

*e-mail:* s\_petrov9@mail.ru Received June 5, 2006

**Abstract**—The mechanism of formation of barium titanate  $Ba_2Ti_9O_{20}$  in the  $BaO-TiO_2$  and  $BaO-SrO-TiO_2$  systems is investigated using initial mixtures prepared by three methods, namely, mechanical grinding of the initial reactants, coprecipitation from aqueous solutions of salts, and the sol–gel technique. It is established that, irrespective of the preparation procedure, the formation of  $Ba_2Ti_9O_{20}$  proceeds through the formation of the intermediate phases  $BaTi_4O_9$  and  $BaTi_5O_{11}$ . The nature of the intermediate phases is determined by the homogeneity and dispersion of the initial mixture, as well as by the stability of the intermediate phase. The most optimum conditions for the synthesis of  $Ba_2Ti_9O_{20}$  are provided by the formation of  $BaTi_5O_{11}$  as an intermediate phase upon heat treatment of the coprecipitation products in the nanocrystalline state. The metastability and structural defects in the  $BaTi_5O_{11}$  intermediate phase encourage a decrease in the temperature of the final heat treatment by  $100-150^{\circ}C$  in the course of the preparation of  $Ba_2Ti_9O_{20}$  single-phase ceramics.

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### **INTRODUCTION**

Barium titanate Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> possesses unique dielectric properties in the microwave frequency range (permittivity  $\varepsilon \sim 40$ , temperature coefficient  $\tau = 4$  ppm/K, Q factor > 10000) [1-3]. However, these characteristics are very sensitive to the porosity of the material, as well as to the presence of impurity phases. In order to prepare a dense single-phase ceramic Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>, it is necessary either to perform long-term annealing at temperatures in the range 1250–1300°C or to introduce ZrO<sub>2</sub>, SnO<sub>2</sub>, and SrO (1–2 mol %) additives into initial mixtures. However, these procedures do not provide preparation of the material with completely reproducible dielectric parameters. Long-term annealings often lead to a partial decomposition of Ba2Ti9O20 with the formation of impurity phases. Cations of oxide dopants are isomorphously incorporated into the structure of the  $Ba_{2}Ti_{9}\bar{O}_{20}$  compound. This results in an improvement of the sinterability and in a decrease in the porosity but does not necessarily ensure the retention of good dielectric characteristics [4–6]. The solution of the problem associated with the preparation of  $Ba_2Ti_9O_{20}$ single-phase ceramics with stable dielectric characteristics calls for systematic investigation of both the phase formation processes occurring during the synthesis of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> from different precursors and the influence of these processes on the temperature-time conditions of crystallization and on the properties of the final product.

In this work, we experimentally investigated the processes of phase formation in the course of the synthesis of  $Ba_2Ti_9O_{20}$  in the  $BaO-TiO_2$  and  $BaO-SrO-TiO_2$  systems from initial mixtures prepared by three methods, namely, mechanical grinding of the initial reactants, coprecipitation from aqueous solutions of salts, and the sol-gel technique.

## SAMPLE PREPARATION, EXPERIMENTAL TECHNIQUE, AND RESULTS

The initial mixtures prepared by the three aforementioned methods and samples after heat treatment were studied using differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) (Paulik–Paulik– Erdey derivatograph), X-ray powder diffraction analysis (DRON-3 diffractometer,  $CuK_{\alpha}$  radiation), and transmission electron microscopy (EM-125 electron microscope; accelerating voltage, 75 kV).

Samples were prepared from  $BaCO_3$  (special-purity grade),  $SrCO_3$  (special-purity grade), and  $TiO_2$  (special-purity grade) initial components. The initial components taken in the stoichiometric ratio corresponding to the synthesized titanate were mixed and ground in a jasper mortar with a small amount of distilled water.



**Fig. 1.** Electron microscope images of the mixtures prepared by (a, b) mechanical grinding, (c, d) coprecipitation from aqueous solutions, and (e, f) the sol–gel technique: (a, c) initial mixtures and (b, d–f) mixtures after heat treatment at temperatures of (b) 1300, (d) 1150, (e) 500, and (f) 1300°C. Scale: 1 centimeter corresponds to 220 nanometers.

The time of mixing was 2 h per gram of the mixture. When synthesizing samples in the BaO–SrO–TiO<sub>2</sub> system, BaO (2 mol %) was replaced by SrO. As can be seen from the micrograph (Fig. 1a), the grain-size composition of this mixture is characterized by a large scatter in the particle sizes from 50 to 500 nm. The mean size of TiO<sub>2</sub> particles (150 nm) was calculated from the X-ray powder diffraction data according to the Scherrer

formula. The DTA curve of this mixture is characterized by an endothermal effect at a temperature of 850°C due to the decomposition of carbonates, which also manifests itself in the weight loss of the sample in the TGA curve (Fig. 2a). The exothermal peak observed at a temperature of 1250°C corresponds to the onset of the formation of  $Ba_2Ti_9O_{20}$ . According to these data, heat treatment of the batch was performed in the tempera-



Fig. 2. DTA and TGA curves for the initial mixtures prepared by (a) mechanical grinding, (b) coprecipitation from aqueous solutions, and (c) the sol-gel technique.



**Fig. 3.** X-ray powder diffraction patterns of the initial mixtures prepared by (a) mechanical grinding, (b) coprecipitation from aqueous solutions, and (c) the sol-gel technique in the (*I*) BaO–TiO<sub>2</sub> and (*II*) BaO–SrO–TiO<sub>2</sub> systems after heat treatment at specified temperatures for 1 h: (*I*) TiO<sub>2</sub>, (2) BaTi<sub>4</sub>O<sub>9</sub>, (3) BaTi<sub>5</sub>O<sub>11</sub>, and (4) Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>.

ture range 900–1000°C. Then, the cake was ground and heat treated at temperatures of 1250-1300°C for 1–7 h. It follows from analyzing the X-ray powder diffraction data (Fig. 3a, curve *I*) that, after heat treatment at

1000°C, the BaTi<sub>4</sub>O<sub>9</sub> compound (grain size, ~150 nm) is the main phase in the samples, which also contain unreacted titanium oxide. In the samples containing the SrO oxide, the (Ba,Sr)Ti<sub>4</sub>O<sub>9</sub> and (Ba,Sr)Ti<sub>5</sub>O<sub>11</sub> solid



**Fig. 4.** Schematic diagram illustrating the sequence of operations used for preparing the initial mixtures by (a) coprecipitation from aqueous solutions and (b) the sol–gel technique for subsequent solid-phase sintering.

solutions are formed after heat treatment at a temperature of 950°C (Fig. 3a, curve *II*). In order to prepare single-phase samples in the BaO–TiO<sub>2</sub> system, the final annealing should be performed at a temperature of 1300°C for 5 h. These samples contain the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> phase in the form of crystals with a mean size of 60– 80 nm (Fig. 1b). The Ba<sub>1.8</sub>Sr<sub>0.2</sub>Ti<sub>9</sub>O<sub>20</sub> single-phase samples were synthesized at a temperature of 1250°C (which is 50°C below the temperature required for the preparation of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>) for a somewhat shorter time.

An aqueous solution of TiCl<sub>4</sub> was prepared by diluting titanium tetrachloride with distilled water cooled to  $4^{\circ}$ C. The TiO<sub>2</sub> content in the solution was determined by the weighing method. Then, the solution was mixed with 0.1 *M* aqueous solutions of barium and strontium nitrates in the stoichiometric ratio corresponding to the synthesized titanate. The components were precipitated using a 0.1 *M* NH<sub>4</sub>HCO<sub>3</sub> solution. In this case, the pH of the solution was brought up to 9.5 by adding NH<sub>4</sub>OH. The sequence of operations used for preparing the initial mixture by the coprecipitation method is shown in Fig. 4a. The precursor thus obtained has the form of agglomerates composed of 10- to 12-nm particles (Fig. 1c). The DTA curve of this mixture is characterized by several thermal effects (Fig. 2b). The first (endothermal) effect accompanied by a considerable decrease in the weight of the sample is caused by the removal of water. This process is completed at a temperature of 550°C. Moreover, the DTA curve contains exothermal peaks at temperatures of 700, 800, and 1100–1150°C. In order to elucidate the origin of the observed effects, the samples were annealed for 1 h at temperatures corresponding to these peaks. After annealings at temperatures of 550 and 700°C, the samples remained X-ray amorphous. The heat treatment performed at 800°C leads to the formation of the phases  $BaTi_5O_{11}$  (the main phase) and  $BaTi_4O_9$  in the samples, which also contain unreacted titanium oxide (Fig. 3b, curve I). The BaTi<sub>5</sub>O<sub>11</sub> grain size calculated from the Scherrer formula is approximately equal to 75-80 nm. The  $Ba_2Ti_9O_{20}$  compound is formed at a temperature of 1100-1150°C. Annealing in the temperature range 1100–1150°C for 1 h is sufficient to prepare  $Ba_2Ti_9O_{20}$ single-phase ceramics with a mean particle size of ~60-80 nm. The introduction of  $Sr(NO_3)_2$  in amounts required to form the Ba<sub>1.8</sub>Sr<sub>0.2</sub>Ti<sub>9</sub>O<sub>20</sub> compound in the course of precipitation from an aqueous solution does not change the sequence of the phase formation of the

System	Procedure for preparing the initial mixture		
	mechanical grinding of oxides and carbonates	coprecipitation from aqueous solutions of salts	sol-gel technique
BaO–TiO <sub>2</sub>	$\xrightarrow{1000^{\circ}C} TiO_2 + BaTi_4O_9 \text{ (main phase)}$ $\xrightarrow{1300^{\circ}C} Ba_2Ti_9O_{20}$	$\frac{^{800^{\circ}\text{C}}}{(\text{main phase}) + \text{BaTi}_{4}\text{O}_{9}} \xrightarrow{\text{I150^{\circ}\text{C}}}{\text{Ba}_{2}\text{Ti}_{9}\text{O}_{20}}$	$\xrightarrow{>250^{\circ}C} \text{TiO}_2 + \text{BaTi}_4\text{O}_9 \text{ (main phase)}$ $\xrightarrow{1300^{\circ}C} \text{Ba}_2\text{Ti}_9\text{O}_{20}$
BaO–SrO–TiO <sub>2</sub>	$ \begin{array}{c} \xrightarrow{1000^{\circ}\text{C}} \text{ TiO}_2 \text{ (traces)} + \\ (\text{Ba,Sr})\text{Ti}_4\text{O}_9 \text{ (main phase)} + \\ (\text{Ba,Sr})\text{Ti}_5\text{O}_{11} \\ \xrightarrow{1250^{\circ}\text{C}} \text{ Ba}_{1.8}\text{Sr}_{0.2}\text{Ti}_9\text{O}_{20} \end{array} $	$ \begin{array}{c} \underbrace{^{800^\circ C}}_{(Ba,Sr)Ti_5O_{11}} (traces) + \\ (Ba,Sr)Ti_5O_{11} (main phase) + \\ (Ba,Sr)Ti_4O_9 (traces) \\ \underbrace{^{1150^\circ C}}_{(Ba_{1.8}Sr_{0.2}Ti_9O_{20})} \end{array} $	$\xrightarrow{>250^{\circ}C} TiO_2 (traces) + (Ba,Sr)Ti_4O_9 (main phase) + (Ba,Sr)Ti5O11 \xrightarrow{1250^{\circ}C} Ba_{1.8}Sr_{0.2}Ti_9O_{20}$

Phase compositions of the initial mixtures under investigation at different stages of heat treatment

final product in the mixture under investigation (Fig. 3b, curve *II*).

Furthermore, the initial mixture was also prepared by the sol-gel technique (Fig. 4) with the use of hydrated titanium dioxide, which was produced by the interaction of TiCl<sub>4</sub> with a dilute ammonium hydroxide NH<sub>4</sub>OH at pH 9.5. Soluble impurities were washed from a precipitate, and the necessary amount of hydrated titanium dioxide was dissolved in a 1.4 M solution of nitric acid. Aqueous solutions of barium and strontium nitrates and also citric acid in the ratio BaO(SrO): TiO<sub>2</sub>: C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> = 2 : 9 : 6 were introduced into the solution prepared. After complete dissolution of the citric acid, the pH of the mixture was brought up to 6 by adding the ammonium solution. This led to the formation of a sol, which, in the course of long-term heat treatment at a temperature of 80°C, transformed into a viscous yellowish gel. The sequence of operations used for preparing the initial mixture by the solgel technique is shown in Fig. 4b. The TGA curve of this gel is characterized by several thermal effects observed at temperatures of 120-140, 250, and ~400°C. As can be seen from the TGA curve (Fig. 2c), each exothermal effect is attended by a decrease in the weight of the sample. The largest weight loss is observed at a temperature of 250°C. In order to reveal the origin of the processes occurring during heat treatment of the gel, the samples were annealed at temperatures of 140-250, 500, and 700°C for 0.5-1.0 h. A decrease in the viscosity of the gel and the release of gases are observed at 140°C. The gel self-ignites at a temperature of 250°C. The combustion process proceeds rapidly for 5-10 s with the formation of a gravish highly porous bulk cake. In our opinion, the gray color of the sample is associated with the incomplete combustion of organic impurities. The removal of these impurities in the course of further heating is responsible for the appearance of the corresponding effects in the DTA and TGA curves at temperatures of 400-420°C. The X-ray powder diffraction pattern of the sample annealed at 250°C (Fig. 3c, curve I) indicates the presence of two phases, namely, BaTi<sub>4</sub>O<sub>9</sub> and unreacted titanium oxide. The heat treatment performed at temperatures of 500, 700, and 1250°C (for 1 h) does not bring about a change in the phase composition of the cakes. The  $Ba_2Ti_9O_{20}$  single-phase product was obtained from the gel subjected to sequential annealing at temperatures of 500 and 1250°C for 5 h. The analysis of the micrographs (Fig. 1e) demonstrates that, after annealing at a temperature of 500°C, the sample consists of BaTi<sub>4</sub>O<sub>9</sub> crystals with clearly defined faces. The particle sizes calculated from the Scherrer formula are approximately equal to 80 nm for the  $BaTi_4O_9$  phase and 150 nm for the  $TiO_2$  phase. After heat treatment at a temperature of 1300°C, the habit of other crystals somewhat changes (Fig. 1f) and becomes similar to that of crystals of the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> phase prepared according to the first two procedures (Fig. 1b). The mean size of particles in the Ba2Ti9O20 ceramics produced using the sol-gel technique is equal to 60-80 nm. Upon introduction of the aqueous solution of the  $Sr(NO_3)_2$  nitrate into the sol composition, the sample after the self-ignition of the gel contains the (Ba,Sr)Ti<sub>4</sub>O<sub>9</sub> solid solution, the  $(Ba,Sr)Ti_5O_{11}$  solid solution, and the TiO<sub>2</sub> phase (Fig. 3c, curve II). In order to prepare the Ba<sub>1.8</sub>Sr<sub>0.2</sub>Ti<sub>9</sub>O<sub>20</sub> single-phase samples from the initial mixture under investigation, it is necessary to perform heat treatment at a temperature of 1250°C for 4 h.

## DISCUSSION OF THE RESULTS

The results of the experimental investigation into the phase formation processes occurring during heat treatment of the initial mixtures prepared by three methods are presented in the table. It follows from these data that the phase formation during the synthesis of  $Ba_2Ti_9O_{20}$  and  $(Ba,Sr)_2Ti_9O_{20}$  is a multistage process proceeding through the formation of intermediate phases of different compositions. In the synthesis of  $Ba_2Ti_9O_{20}$ , the  $BaTi_4O_9$  compound is the main intermediate phase when the initial mixtures are prepared either by mechanical grinding of the initial components or by the sol–gel technique, whereas the  $BaTi_5O_{11}$  titanate appears to be the main intermediate phase in the case where the initial mixture is produced by coprecipitation from aqueous solutions.

A somewhat different situation is observed in the synthesis of the  $Ba_{1.8}Sr_{0.2}Ti_9O_{20}$  solid solution. At the intermediate stage of heat treatment of the initial mixtures prepared either by mechanical grinding of the initial reactants or by the sol–gel technique, the samples contain both the  $(Ba,Sr)Ti_4O_9$  and  $(Ba,Sr)Ti_5O_{11}$  solid solutions. Upon heat treatment of the coprecipitation products, the  $(Ba,Sr)Ti_5O_{11}$  solid solution is the main intermediate phase, even though there are traces of the  $(Ba,Sr)Ti_4O_9$  solid solution.

In a number of works [4, 7], it was noted that the presence of  $BaTi_5O_{11}$  in the reaction mixture at the intermediate stage of the phase formation leads to a decrease in the time and temperature of the final annealing in the synthesis of  $Ba_2Ti_9O_{20}$ . There is no agreement among researchers regarding the mechanism of the influence of BaTi<sub>5</sub>O<sub>11</sub> on the phase formation in the BaO(SrO)-TiO<sub>2</sub> system. It is known that the  $BaTi_5O_{11}$ phase is metastable and does not have a stability field in the phase diagram [8–10]. This titanate can be synthesized either by rapid quenching of the melt [11] or by the hydrothermal method from a mixture of aqueous solutions of the hydrated titanium dioxide  $H_2Ti_4O_9$ .  $1.2H_2O$  and the barium hydroxide  $Ba(OH)_2 \cdot 8H_2O$  [7]. The BaTi<sub>5</sub>O<sub>11</sub> metastable titanate decomposes upon heating to a temperature above 1100°C. The majority of the authors believe that the formation of this phase at the intermediate stage of the synthesis of the  $Ba_2Ti_9O_{20}$ titanate is favored by the high homogeneity of the components of the initial mixture [4, 7].

The BaTi<sub>4</sub>O<sub>9</sub>, BaTi<sub>5</sub>O<sub>11</sub>, and Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> compounds have related structures, which are based on the closest packing of titanium-oxygen octahedra joined together through vertices, edges, and faces. Holes in the octahedral framework are occupied by  $Ba^{2+}$  ions [11–14]. The structures of the BaTi<sub>5</sub>O<sub>11</sub> and Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> compounds are most similar to each other. The investigations of these compounds with the use of high-resolution electron microscopy and microdiffraction revealed that their structures contain a large number of defects due to local distortions of the stoichiometry and regularity in the arrangement of titanium-oxygen octahedra [15, 16]. The defects in these titanates are similar in character; however, a regular arrangement of defects is more frequently observed in the structure of the  $BaTi_5O_{11}$ metastable titanate and can lead to the formation of a new polytype. Thermodynamically, this phenomenon decreases the stability of the structure and brings about an increase in the reactivity of the BaTi<sub>5</sub>O<sub>11</sub> metastable phase.

Reasoning from structural considerations, the formation of the titanates under investigation in the course of solid-phase sintering should occur through diffusion of barium and oxygen atoms in the structure of the titanium oxide phase. This results in a transformation of the structure of the titanium oxide phase due to the change in the joining of titanium-oxygen octahedra and the breaking of a number of Ti-O bonds. The BaTi<sub>5</sub>O<sub>11</sub> compound should be formed first because the octahedral network of this titanate is most similar to the structure of the titanium oxide phase. Then, the process should be accompanied by the formation of  $Ba_2Ti_9O_{20}$ . The BaTi<sub>4</sub>O<sub>9</sub> compound is formed at the final stage of the phase formation. In actual fact, the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> compound is the final product in all the synthesis procedures. On this basis, Wu and Wang [4] made the inference that the structural similarity is not the main factor determining the sequence of the phase formation upon sintering of components in the BaO-TiO<sub>2</sub> system. In their opinion, the nucleation rate of the  $Ba_2Ti_9O_{20}$  phase is of crucial importance. This rate is limited by the high surface energy of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>. However, experimental data supporting the above hypothesis were not presented in [4].

The analysis of the temperature–time parameters of the formation of  $Ba_2Ti_9O_{20}$  through the  $BaTi_4O_9$  intermediate phase led the authors of [4] to the conclusion that the diffusion rates of barium and oxygen cannot be a limiting factor of the process. This process should be most rapidly developed in the temperature range 1100– 1200°C, whereas the  $Ba_2Ti_9O_{20}$  titanate is formed at temperatures of 1250–1300°C.

By generalizing the data available in the literature and our experimental results, we make the inference that the decisive role in the phase formation in the BaO-TiO<sub>2</sub> system is played by several factors, such as the homogeneity and dispersion of the components of the initial mixture, as well as the metastability of the BaTi<sub>5</sub>O<sub>11</sub> intermediate phase. The influence of the homogeneity can be clearly judged from a comparison of the phase formation processes occurring during heat treatment of the initial mixtures prepared by mechanical grinding of the reactants and those obtained by coprecipitation from the aqueous solutions. The characteristic feature of the former mixture is a large scatter in the particle size (50-500 nm). The heat treatment performed at temperatures in the range 1000-1050°C results in the formation of the BaTi<sub>4</sub>O<sub>9</sub> intermediate stable phase (grain size, ~150 nm). The interaction of this phase with titanium oxide leads to the formation of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> at temperatures of 1250–1300°C. The initial mixture prepared by coprecipitation from the aqueous solutions is characterized by the homogeneity and high dispersion (particle size,  $\sim 10-12$  nm). In this case, heat treatment at a temperature of 800°C results in crystallization of the  $BaTi_5O_{11}$  metastable phase (grain size, ~75–80 nm), whose structure have various defects. The high dispersion (nanocrystalline state) determines new surface properties of particles in the initial mixture. The metastability and defect structure of the  $BaTi_5O_{11}$  phase affect both the temperature–time parameters of the reaction resulting in the formation of the  $Ba_2Ti_9O_{20}$  phase and the nucleation rate of this phase. The  $Ba_2Ti_9O_{20}$  compound crystallizes from this mixture at temperatures of 1100–1150°C.

The use of the sol–gel technique must ensure a high homogeneity of the gel, which is the initial product for the synthesis of  $Ba_2Ti_9O_{20}$ . However, the self-ignition of the gel is observed even at a temperature of 250°C. The temperatures of the initial mixture during the combustion of the organic component depend on the heating rate and can be as high as 500–550°C. Most likely, the rapid combustion of the gel is accompanied by an increase in the temperature, so that it becomes sufficient for the formation of particles of the  $BaTi_4O_9$  intermediate phase (grain size, 80–150 nm). A further interaction proceeds according to the scheme identical to that described for the synthesis from the initial mixture prepared by mechanical grinding with a large scatter of grain sizes.

The introduction of 2 mol % SrO into the initial mixtures leads to the formation of solid solutions based on  $BaTi_4O_9$ ,  $BaTi_5O_{11}$ , and  $Ba_2Ti_9O_{20}$ , in which  $Ba^{2+}$  ions are partially replaced by  $Sr^{2+}$  ions with a smaller size. We believe that the incorporation of  $Sr^{2+}$  ions into the crystal lattice of  $BaTi_5O_{11}$  can stabilize this phase to some extent. Therefore, the  $(Ba,Sr)Ti_5O_{11}$  solid solution is formed as an intermediate phase at the first stage of heat treatment of the mixtures under investigation. The presence of this phase promotes the solid-phase reactions and leads to a decrease (by 50 K) in the temperature of the final stage of heat treatment required for synthesizing the  $(Ba,Sr)Ti_9O_{20}$  single-phase ceramic material from the initial mixtures prepared by mechanical grinding and the sol–gel process.

### CONCLUSIONS

Thus, the formation of  $Ba_2Ti_9O_{20}$  and  $(Ba,Sr)Ti_9O_{20}$ upon the solid-phase interaction in the BaO–TiO<sub>2</sub> and BaO–SrO–TiO<sub>2</sub> systems was investigated using the initial mixtures prepared by three different methods, namely, mechanical grinding of reactants, coprecipitation from aqueous solutions, and the sol–gel technique. It was demonstrated that these processes are the multistage reactions proceeding through the formation of the BaTi<sub>4</sub>O<sub>9</sub> and BaTi<sub>5</sub>O<sub>11</sub> intermediate phases.

The nature of the intermediate compounds is determined by the combined effect of a number of factors. The main factors are the homogeneity and dispersion of the initial mixture and the stability of the intermediate phases.

The most favorable conditions for the formation of  $Ba_2Ti_9O_{20}$  are provided by the formation of the  $BaTi_5O_{11}$  metastable compound as an intermediate phase.

The homogeneity of the initial mixture produced by coprecipitation from aqueous solutions favors a predominant formation of the  $BaTi_5O_{11}$  metastable titanate at the first stage of the heat treatment. The dispersion (nanocrystalline state) of this titanate is responsible for the new surface properties of particles of the initial mixture components and has a positive effect on the nucleation rate of the  $Ba_2Ti_9O_{20}$  phase. The defect structure of the  $BaTi_5O_{11}$  metastable phase (the presence of polytypes) reduces the thermodynamic stability of this compound, thus increasing the rate of the formation reaction of the  $Ba_2Ti_9O_{20}$  phase and the rate of its nucleation. This makes it possible to synthesize a single-phase ceramic material based on  $Ba_2Ti_9O_{20}$  at a temperature of 1150°C.

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