

Article

Barium Titanate Synthesis in Water Vapor: From Mechanism to Ceramics Properties

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Abstract: A facile and environmentally benign method for single-phase barium titanate synthesis in a water vapor medium was studied to reveal the mechanism of phase transformation of the initial simple oxide mixture and estimate the capability of the product to be used as a raw material for low-frequency dielectric ceramics. The composition and structure of the reactants’ mixture, treated in vapor at 130–150 °C as well as at 230 °C for various time periods, were investigated by means of XRD, SEM, TEM, EDX, and FTIR methods. The kinetics of the occurring phase transformation can be described using the Johnson–Mehl–Avrami–Erofeev equation. The reaction between the initial oxides was considered as a topochemical process with an apparent activation energy of 75–80 kJ mol^{−1}. A crucial role in this process belonged to the water vapor medium, which facilitated the generation of the reaction zone and the spreading inward of the solid particles. The synthesized tetragonal barium titanate powder (mean particle size of 135 nm) was sintered using a conventional technique at 1250 °C to obtain ceramics with grains of about 2 μm. Capacitance measurements identified a permittivity and dielectric loss factor of the ceramics that reached 3879 and 6.7×10^{-3} , respectively, at 1 kHz and room temperature.

Keywords: barium titanate; synthesis in water vapor; topochemical reaction; solid-state reaction; low-frequency dielectric ceramics; conventional ceramics technique; dielectric properties



Citation: Kholodkova, A.A.; Ivakin, Y.D.; Danchevskaya, M.N.; Muravieva, G.P.; Egorov, A.V.; Smirnov, A.D.; Khrustalev, A.N.; Arbanas, L.A.; Bazarova, V.E.; Smirnov, A.V. Barium Titanate Synthesis in Water Vapor: From Mechanism to Ceramics Properties. *Inorganics* **2024**, *12*, 76. <https://doi.org/10.3390/inorganics12030076>

Academic Editor: Kenneth J.D. MacKenzie

Received: 30 December 2023

Revised: 23 February 2024

Accepted: 24 February 2024

Published: 29 February 2024



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1. Introduction

Barium titanate is a highly in-demand material for a wide area of applications, including the production of ferro- and piezoelectric ceramics [1,2] and composites [3,4], as well as optoelectronic devices [5], thermistors [6], semiconductors [7], transducers [8], photocatalysts [9,10], coatings [11], and products for biomedicine [12,13]. A key feature of such a versatile application of BaTiO₃ is the ability of its crystals to perform spontaneous polarization in a temperature range below 120 °C, which is known as its Curie point. BaTiO₃ possesses a typical perovskite structure with a sequence of phase transitions: cubic to tetragonal (120–130 °C), tetragonal to orthorhombic (about 5 °C), orthorhombic to rhombohedral (about −90 °C) [14]. Besides cubic modification, the mentioned phases demonstrate ferroelectric properties due to their spontaneous polarization, among which the most prominent are reported for the tetragonal BaTiO₃. A vivid example of this was reported in [15] for BaTiO₃ ceramics produced by spark plasma sintering, with a room-temperature permittivity of up to 60,000 and a low dielectric loss factor of about 0.07.

The methods of BaTiO₃ powder production are mostly focused on the needs of the multilayer ceramic capacitor (MLCC) industry, as it remains the largest consumer of barium titanate. A wide variety of approaches in solid-state as well as wet chemistry have been developed to produce highly pure single-phase BaTiO₃ powders with a narrow size distribution and smooth particle shape [16–18]. The groups of solid-state [19,20], mechanochemical [21–23], complexation [24–28], co-precipitation [29,30], sol-gel [31], and hydrothermal [32–34] techniques for obtaining BaTiO₃ took their rightful place in laboratories as well as in industries of various scales. Besides the properties of the final product, there are different factors to consider when choosing strategies for BaTiO₃ powder production, such as energy consumption, the availability and cost of the initial substances, the complexity of the equipment and its servicing, and the environmental impact of the process. In this regard, a method of complex oxide synthesis in a medium of water vapor, as previously reported for several compositions [35,36] including BaTiO₃ [37–40], appears attractive as it is performed with widely available simple oxides as starting compounds and requires fairly mild conditions for the reaction (a temperature below 350 °C and autogenous vapor pressure). Compared to a technically relative hydrothermal method, this one does not involve the use of aggressive media with hard-to-remove auxiliary substances (NaOH and KOH). Unlike hydrothermal reactions, which are realized by the mechanism of the reactants' dissolution, followed by homogenous nucleation and the precipitation of the product [41–43], the synthesis of BaTiO₃ in water vapor was assumed to occur via solid-state transformation [39,40]. However, there is a lack of available detailed studies of the mechanism for this transformation. In addition, the properties of ceramics formed from BaTiO₃ powder synthesized in water vapor were poorly investigated, as well as a technology for their production not being properly developed [38,39]. The current work comprised a detailed study of the processes underlying BaTiO₃ formation from the initial barium and titanium oxides in a medium of water vapor, including the kinetics and microstructural evolution of the reaction system. For the first time, a stabilizing effect of acidic additives on the reactants' transformation was revealed and the activation energy of the process was assessed. To estimate the technological capability of the synthesized powder as a raw material for dielectric ceramics, its sintering behavior, as well as the properties of the derived ceramics, were investigated in comparison with the recent data.

2. Results

2.1. Study of Barium Titanate Formation in a Water Vapor Medium

2.1.1. Composition of the Reaction Mixture

The conversion of initial equimolar mixtures of BaO and TiO₂ with rutile modification was observed during isothermal treatment at 130 °C in a vapor atmosphere with an autogenous pressure of 0.27 MPa. The values of the conversion calculated from the X-ray diffraction (XRD) patterns of the obtained products are shown in Figure 1a. After less than 100 min of isothermal treatment, the obtained samples contained no BaTiO₃ phase, according to XRD. Further changes in the composition of the initial oxide mixture demonstrated an abrupt and non-monotonic character and had poor reproducibility (for 110, 120, and 130 min, groups of 3 samples (shown as 1, 2, and 3) were synthesized simultaneously).

The introduction of some additives to the reaction mixture appeared to have a stabilizing effect on its transformation into BaTiO₃. Figure 1b shows the initial parts of the kinetic curves representing BaTiO₃ formation from the BaO and TiO₂ mixture with the addition of iodine, as well as 1.2 wt. % of citric acid. Due to the presence of these additives, the observed part of the kinetic curves exhibited monotonic growth following the induction period, which took about 30 min. Citric acid, which was introduced by simple weighting and dry mixing, allowed for easier control of its amount in the reaction mixture, compared to iodine deposited through its sublimation. For this reason, citric acid was selected as an additive in further experiments. Table 1 presents the values of conversion corresponding to the mixtures of starting oxides with different amounts of citric acid, which have been

treated in water vapor for equal periods of time. A three-fold difference in the amounts of citric acid did not significantly affect the degree of the reagents' conversion. For subsequent experiments on BaTiO₃ formation kinetics, 1.2 wt. % of citric acid was introduced to the reaction mixture.

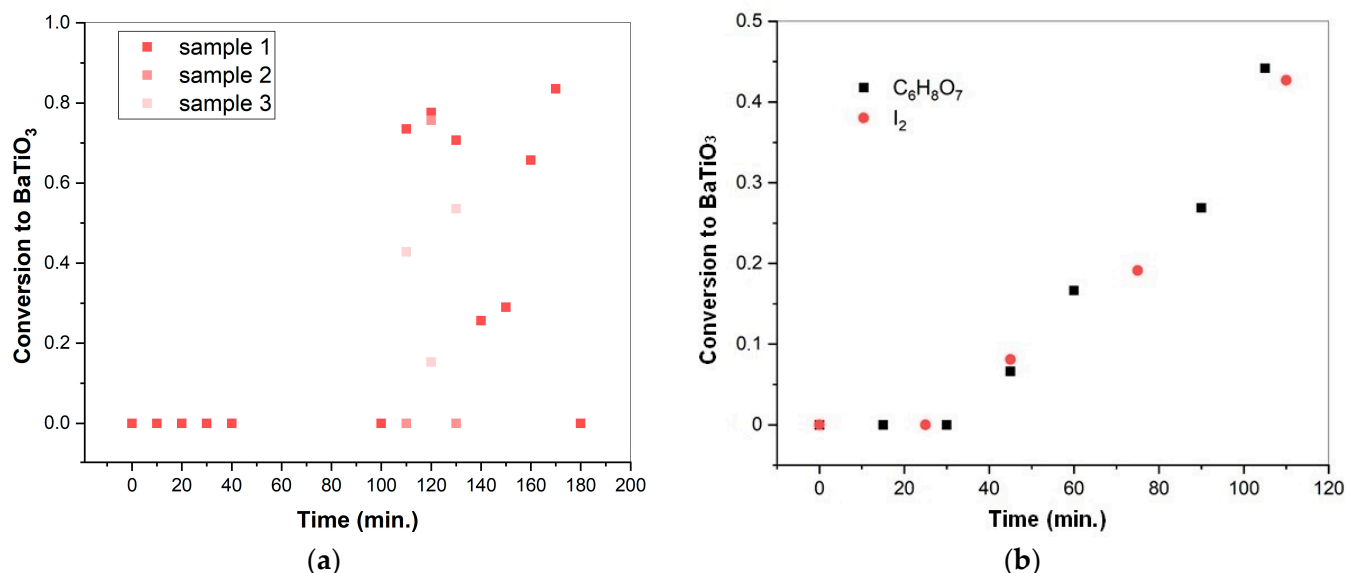


Figure 1. Conversion of an equimolar mixture of BaO and TiO₂ in a pure state (a) and with the additive of iodine and 1.2 wt. % of citric acid (b) in water vapor at 130 °C and 0.27 MPa. The standard uncertainties of the obtained points did not exceed 0.046.

Table 1. Conversion of the equimolar mixture of BaO and TiO₂ with the addition of citric acid after treatment in water vapor at 130 °C and 0.27 MPa for 105 min. The standard uncertainty of the conversion measurements is indicated as $u(\alpha)$.

Duration of Treatment (min)	Amount of Citric Acid (wt. %)	Conversion to BaTiO ₃ (%)	$u(\alpha)$ (%)
105	0.6	42.9	3.1
	1.2	44.2	2.4
	2.4	45.0	3.8

The thermal behavior of citric acid has been extensively studied in a few works [44–46]. When heated in air, anhydrous citric acid was reported to melt above 153 °C and then transform sequentially into aconitic acid at about 175 °C and into methyl maleic anhydride at 223 °C. From these data, it could be supposed that citric acid preserved its chemical composition in a temperature range of 130–150 °C used in the further study of BaTiO₃ formation.

2.1.2. Formal Kinetic Analysis of BaTiO₃ Formation

Figure 2a demonstrates the degree of conversion in the initial mixture of BaO and TiO₂ versus the duration of its treatment in a water vapor medium in the presence of citric acid. For each of the temperatures, there are two curves, calculated based on the amounts of BaO and TiO₂, respectively, remaining after the reaction. The kinetic curves possess a sigmoidal shape peculiar to the topochemical process. When processed at 130 as well as at 140 °C, the reaction system passed the induction period, which is associated with the formation and spreading of the reaction zone. The kinetic curve corresponding to 150 °C shows no induction period because this could occur during the heating process. After about 150 min of treatment at 150 °C, the conversion in the oxide mixture reached a plateau corresponding to 86% of the BaTiO₃ having been formed. Similarly, at 130 and 140 °C, the conversion of reagents did not exceed 83–84%, with a plateau reached after 225 and 210 min of processing, respectively.

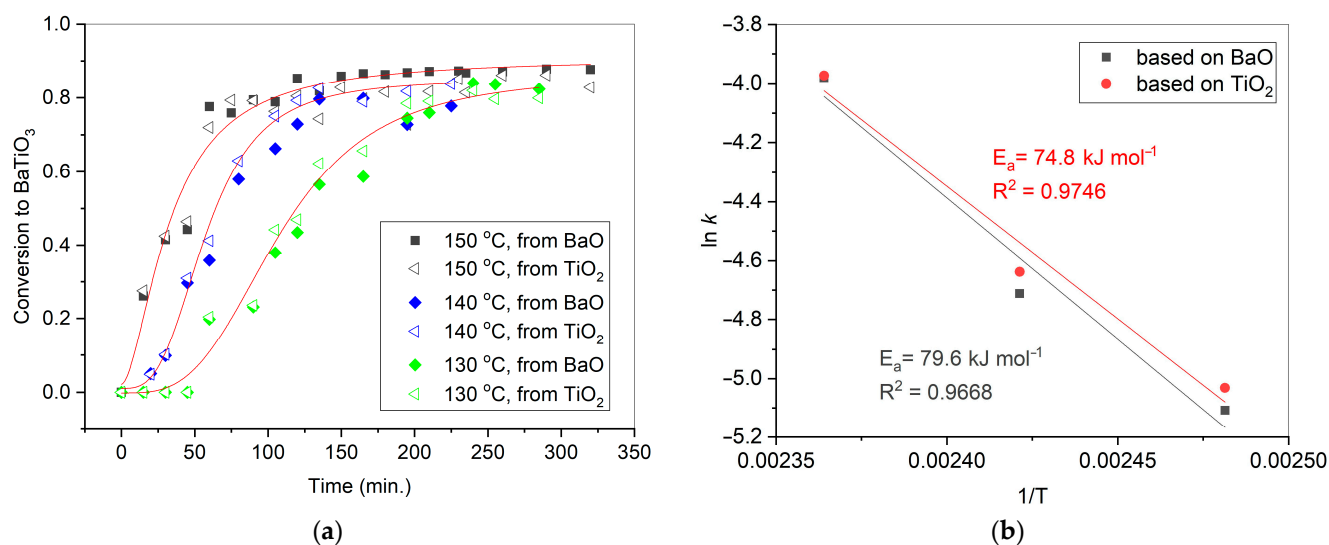


Figure 2. Conversion of BaO and TiO₂ equimolar mixtures with 1.2 wt. % of citric acid in water vapor at 130–150 °C, calculated from the amounts of BaCO₃ as well as TiO₂ in the products (a); the Arrhenius plots derived from the kinetic curves (b). The standard uncertainties of the obtained points in (a) did not exceed 0.037.

The analysis of the kinetic curves was conducted using the Johnson–Mehl–Avrami–Erofeev equation, often applied to processes in the solid state [47]:

$$\ln \ln \frac{1}{1 - \alpha} = m \ln k + m \ln t \quad (1)$$

where α is the conversion, k is the rate constant, t is time, and m is a parameter. The results of the kinetic curve linearization are presented in Figure A1 in the Appendix A, while the calculated $\ln k$ and the parameter m are shown in Table 2.

Table 2. Kinetic parameters for BaTiO₃ formation in water vapor medium from a mixture of BaO and TiO₂, with the addition of 1.2 wt. % of citric acid. The data was calculated from the amounts of BaO (BaCO₃) and TiO₂ remaining in the product. Standard uncertainties are indicated as $u(m)$ and $u(\ln k)$.

Temperature (°C)	Parameters Based on BaO Amount				Parameters Based on TiO ₂ Amount			
	m	$u(m)$	$\ln k$	$u(\ln k)$	m	$u(m)$	$\ln k$	$u(\ln k)$
130	1.59	0.12	−5.11	0.38	1.39	0.14	−5.03	0.50
140	1.52	0.27	−4.71	0.80	1.55	0.32	−4.64	0.91
150	1.01	0.21	−3.98	1.00	0.98	0.17	−3.97	0.64

According to Hancock and Sharp [48], some specific values of the parameter m could be used to determine the limiting stage of the solid-state reaction. Particularly when $m = 1.0$ – 1.24 , the reaction is limited by processes occurring at the phase boundary. This could be applied to the considered reaction between BaO and TiO₂ at 150 °C as the parameter was about unity in that case. At lower temperatures, the approach used by Hancock and Sharp is not applicable, indicating that neither diffusion ($m = 0.54$ – 0.62) nor nucleation ($m = 2.0$ – 3.0) are the only limiting factors.

An Arrhenius plot was used to extract the apparent activation energy from the collected kinetic data (Figure 2b). Its values were calculated based on the fractions of barium and titanium oxides remaining in the mixture after each iteration of treatment; they were rather close and reached 74.8 and 79.6 kJ mol⁻¹, respectively. The corresponding standard uncertainties of the activation energy measurements were 1.2 and 1.5 kJ mol⁻¹.

2.1.3. Microstructural Study of BaTiO₃ Formation

At a temperature of 130 °C, the reaction between BaO and TiO₂ in water vapor occurred the most slowly among the considered conditions, which allowed a detailed observation of BaTiO₃ formation by varying the time of treatment. In the sample obtained after 30 min of processing and then drastically cooled, two main kinds of particle shapes were observed by means of transmission electron microscopy (TEM) (Figure 3a). Local energy-dispersive X-ray spectroscopy (EDX) (Figure 3b) revealed that the rounded shapes belonged to the TiO₂ phase (probe II in Figure 3), while the elongated particles contained Ba, C, and O atoms among the detectable elements (probe I in Figure 3).

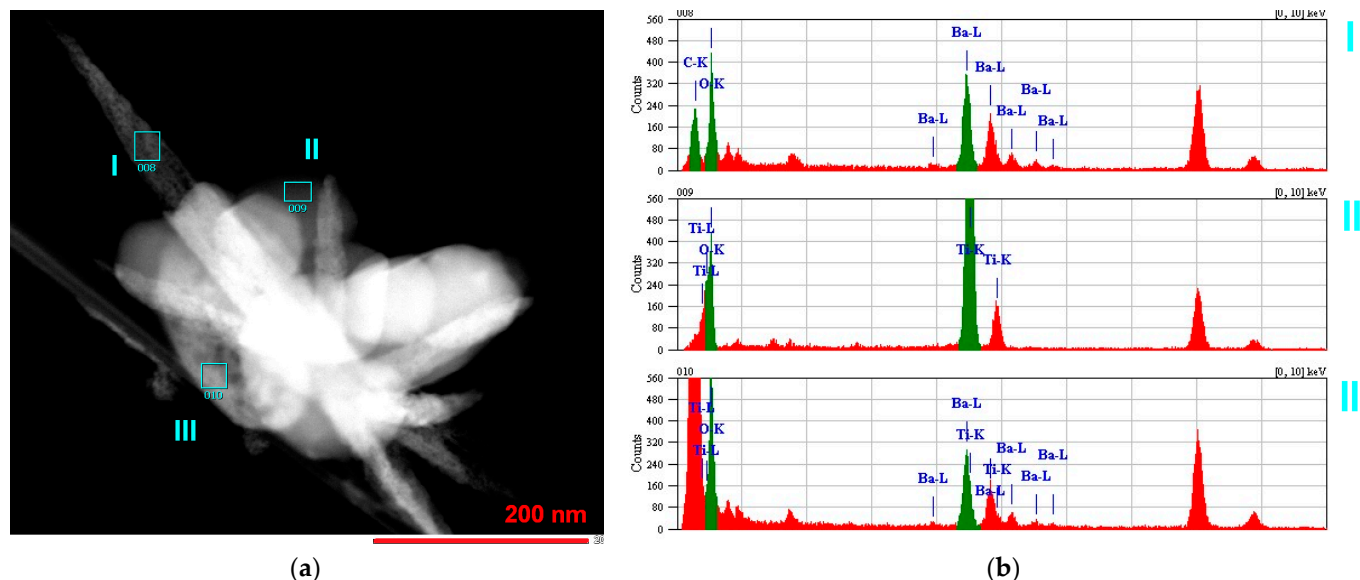


Figure 3. TEM (a) and EDX (b) studies of a sample prepared from the BaO and TiO₂ equimolar mixtures with 1.2 wt. % of citric acid in water vapor at 130 °C for 30 min.

XRD analysis of this sample showed that it consisted of BaCO₃ and TiO₂ in rutile modification (Figure 4). The presence of BaCO₃ could be explained by the intensive interaction between Ba-containing species, formed from BaO in the water vapor and CO₂ from the air, to which the sample was exposed after synthesis. In addition, probe III contained both types of metal ions (Ba, Ti) as well as oxygen and was likely to represent the early stage of BaTiO₃ formation. The composition of the studied sample corresponded to the termination of the induction period of the reaction (Figure 2a). A longer reaction time at 130 °C resulted in the accumulation of the newly formed BaTiO₃ phase, which can be observed in the XRD patterns (Figure 4).

Figure 5a shows the particles of TiO₂ in contact with the elongated particles of BaO derivative in the sample treated for 30 min at 130 °C. Surface diffusion of the reagents led to the formation of a neck between their particles. In this area, indicated as a reaction zone in Figure 5a, BaTiO₃ nucleation was expected to occur and to be followed by the formation of the product layer. Similar processes occurred in the agglomerate, as shown at the bottom of Figure 5b, where one can see rounded TiO₂ crystals that are partially covered with the mass of another reagent. Also in Figure 5b,c, elongated particles of Ba-containing reagent possessing a dendrite morphology are clearly visible, which points to their formation from a melt [49]. EDX analysis of the particles is presented in Figure 5d. The origin of the melt is probably connected to the initial BaO hydroxylation and hydration in water vapor, followed by its melting. Upon drastic cooling of the reaction system, this melt solidified in the shape of dendrites. When in contact with air, the hydroxylated barium oxide formed BaCO₃, which was identified by XRD and EDX. Another image of the dendrite structures is shown in Figure A2 in the Appendix B.

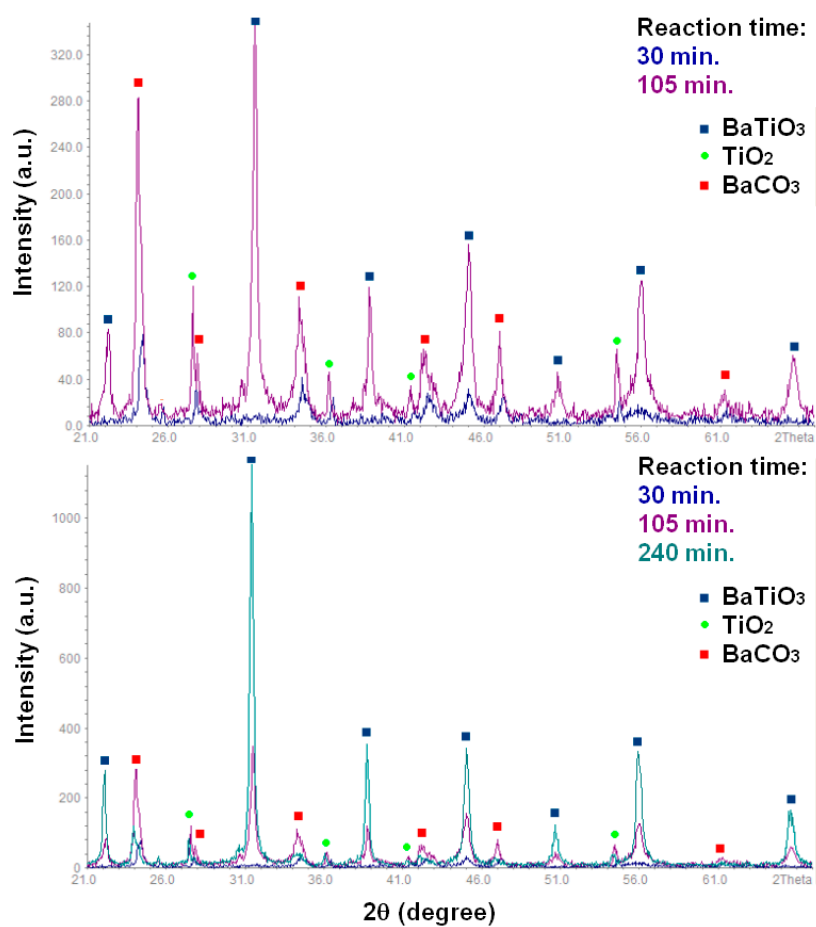


Figure 4. XRD patterns of the samples obtained from the BaO and TiO₂ equimolar mixtures with 1.2 wt. % of citric acid in water vapor at 130 °C for 30–240 min.

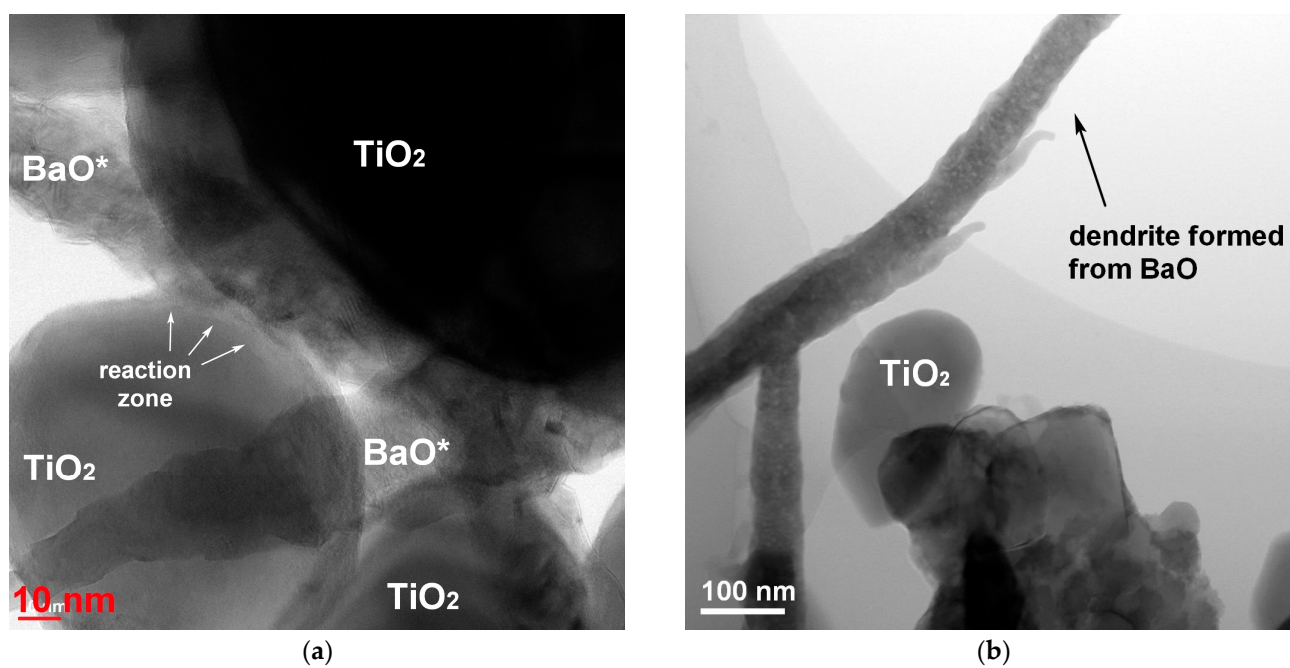


Figure 5. Cont.

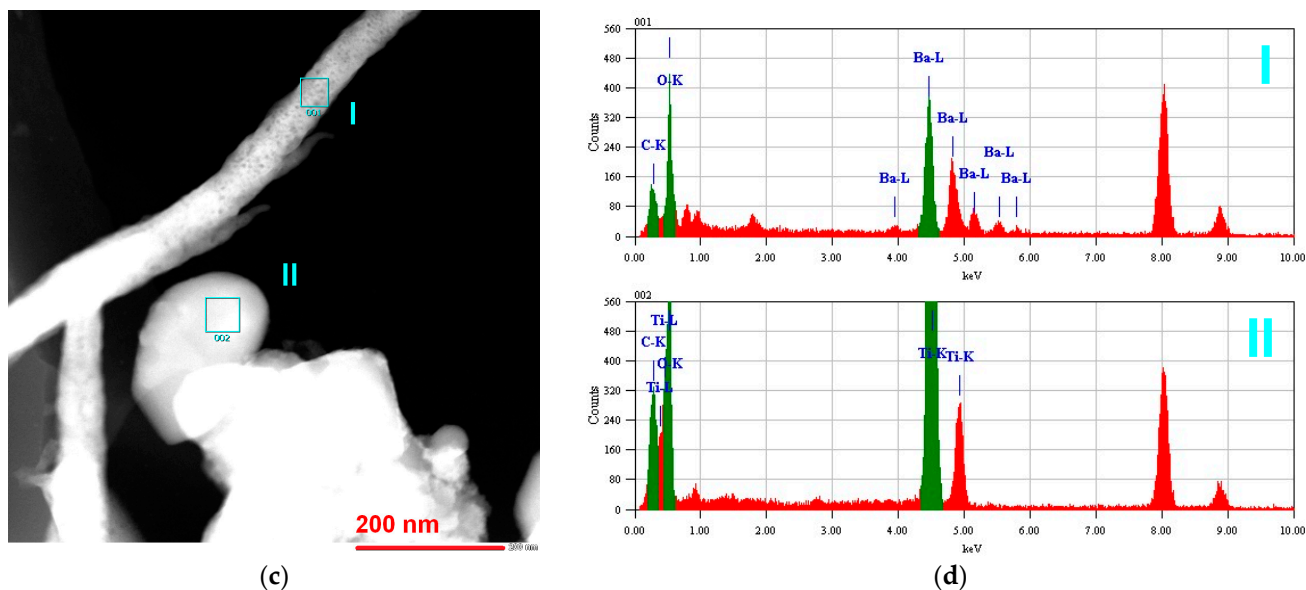


Figure 5. TEM images (a–c) and EDX analysis (d) of the sample prepared from BaO and TiO₂ equimolar mixtures with 1.2 wt. % of citric acid in water vapor, performed after 30 min. BaO* indicates the phase formed from the initial BaO component after treatment in vapor and subsequent storage in air.

2.1.4. FTIR Study of BaTiO₃ Formation

Figure 6 shows fragments of Fourier-transform infrared reflectance (FTIR) spectra of the powders obtained at 130 °C by treatment of the BaO and TiO₂ equimolar mixture in vapor for 15–285 min. The whole spectra in the range of 4000–350 cm^{−1} are shown in Figure A3. Valence vibration bands of Ti–O and Ba–O bonds [37,50] were detected at about 400 and 500 cm^{−1} in every studied sample except for the spectra corresponding to samples taken after 15 and 30 min of treatment. The latter band was asymmetrically broadened toward higher wavenumbers. This band broadening pointed to a weakening of Ti–O–Ti bonds and matched the induction period in the corresponding kinetic curve (Figure 2a). Further narrowing of the mentioned band during treatment reflected the saturation of the titanium coordination sphere, which naturally accompanied the formation of a new phase of BaTiO₃. There were bands between 1100 and 900 cm^{−1} (1095, 1025, 948, and 928 cm^{−1}) that gradually appeared in the spectra corresponding to 30 to 285 min of treatment and might be considered overtones of structural vibration in the range of 600–350 cm^{−1}. On the one hand, this points to an increase in metal–oxide bonding with the time spent on reactant conversion in BaTiO₃. On the other hand, the multiplicity of these overtones highlights the imperfect structure of the solid and the presence of similar bonds of different energies, which can be attributed to the solid-state transformation.

Wide bands observed in the range of 3500–3400 cm^{−1}, as well as narrower bands at 1753 and 1060 cm^{−1}, were related to the presence of the adsorbed water molecules and structural hydroxyl groups [51]. Noticeably, the band detected at about 3400 cm^{−1} and originating from the OH-stretching vibrations in the samples treated for 15 and 30 min changed its shape in those samples synthesized for 90 or 285 min. The mentioned band splits into a broader band that moved to slightly lower frequencies, along with a sharper band at 3500 cm^{−1}. Such an evolution of the FTIR spectrum indicates the involvement of water in the reactants' transformation. Band splitting in the mentioned wavelength region was studied with respect to metal oxides exposed to water vapor and can be explained by the different nature of OH groups [52]. The sharp band corresponded to the vibrations in hydroxyls connected with metal ions from the lattice, while the broad band corresponded to OH groups formed by structural oxygen protonation. The resolution of the bands was found to depend on the morphology of the solid, as well as on the nature of the

crystallographic planes with which the hydroxyls were bonded. The currently observed transition from a single broad band to a split one pointed to structural changes in the solid phase, caused by the failure of the parent TiO_2 structure and the formation of new crystallographic planes of BaTiO_3 .

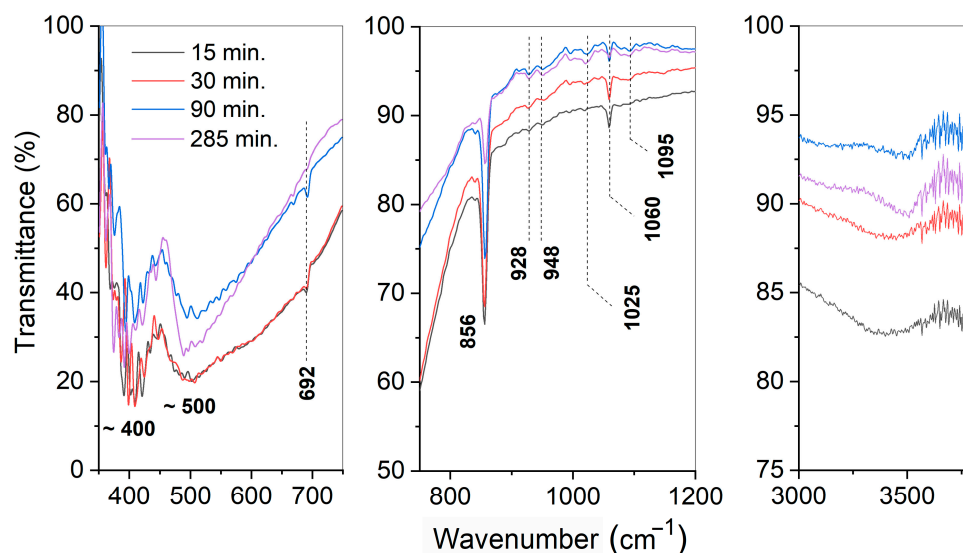


Figure 6. Fragments of the FTIR spectra of the samples prepared from BaO and TiO_2 equimolar mixtures with 1.2 wt. % of citric acid in water vapor after different periods of treatment.

The spectra shown in Figures 6 and A3 in the Appendix B demonstrate the presence of BaCO_3 in the studied samples, as identified by its characteristic bands found at 2445, 2361, 1415, 856, and 692 cm^{-1} .

2.2. Properties of Barium Titanate Ceramics Sintered from Powder Synthesized in a Water Vapor Medium

2.2.1. Characterization of the Synthesized Powder

In the kinetics and mechanism study of BaTiO_3 formation in water vapor at $130\text{--}150\text{ }^\circ\text{C}$, as described above, no single-phase powder was obtained. A plateau in the BaTiO_3 formation curve corresponding to $150\text{ }^\circ\text{C}$ was observed when the reagents' conversion approached 86%. In a previous study, it was shown that the reaction in an equimolar BaO and TiO_2 mixture in a vapor medium had not finished, even after an isothermal period at $230\text{ }^\circ\text{C}$ for 20 h [37]. The results of the reactants' conversion after longer exposure to the vapor conditions are shown in Figure 7a. At $230\text{ }^\circ\text{C}$ and 2.94 MPa of vapor pressure, an equimolar mixture of BaO and TiO_2 had transformed completely into BaTiO_3 after 48 h of treatment (Figure 7b). At lower temperatures and the corresponding pressures of vapor, the accumulation of BaTiO_3 in the mixture occurred more slowly, and the reagents had not reached 100% conversion, even after 96 h of treatment. The observed behavior of the system can be explained by the diffusion limitations caused by the growing product layer. The rise of temperature up to $230\text{ }^\circ\text{C}$ was accompanied naturally by an increase in the diffusion coefficient of barium ions on the solid oxide matrix. In addition, the higher corresponding autogenous pressure (2.94 MPa at $230\text{ }^\circ\text{C}$, compared to 0.48 MPa at $150\text{ }^\circ\text{C}$) favored the hydroxylation of the initial TiO_2 as well as the forming of BaTiO_3 , thus contributing to the diffusion processes.

When the Ba/Ti molar ratio was increased to 1.10–1.14, a single-phase BaTiO_3 was successfully obtained within a shorter treatment period in vapor [39,40], which can be explained by a higher gradient of barium ion concentrations in the reaction zone. In the current study, the initial Ba/Ti molar ratio was designed so as to obtain single-phase BaTiO_3 in vapor within a reasonable time.

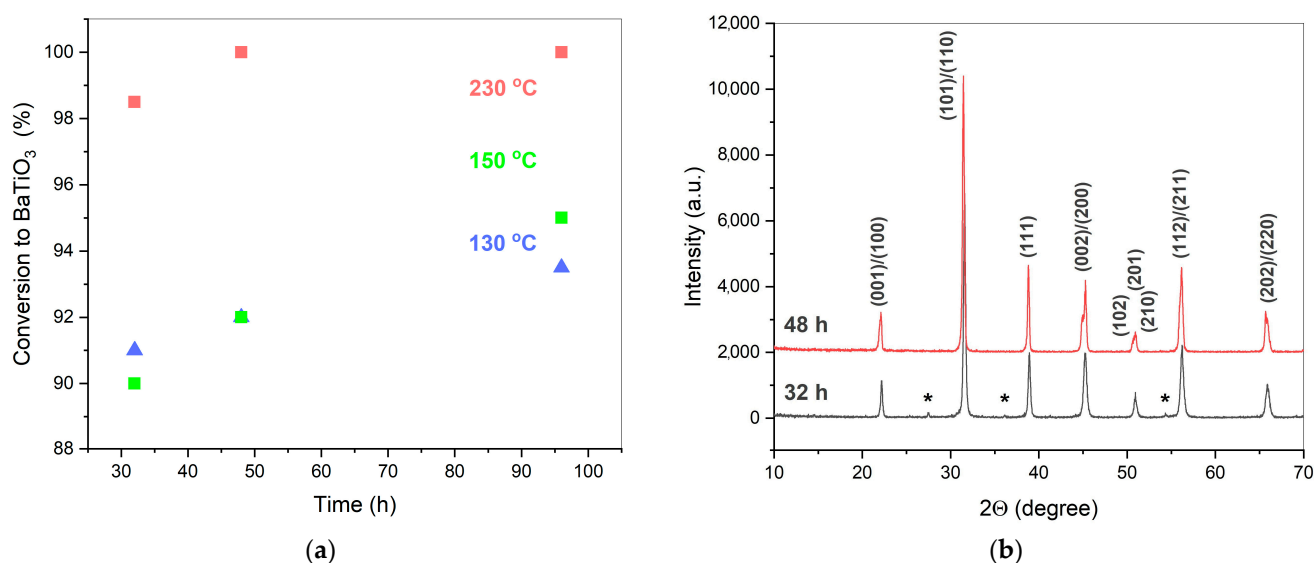


Figure 7. Conversion vs. time graphs for the synthesis of BaTiO₃ from the BaO and TiO₂ mixtures in water vapor at 130–230 °C and under autogenous pressure for 32–96 h (a); XRD patterns of the samples synthesized at 230 °C and 2.94 MPa for 32 and 48 h (b). The samples were preliminarily washed of the residual Ba²⁺ ions. * indicates the TiO₂ phase (rutile, PDF2 # 021-1276). The Miller indices correspond to the BaTiO₃ phase (PDF2 # 075-2117). Standard uncertainties of the obtained points in (a) did not exceed 0.049.

Figure 8 shows the results of XRD analysis of the samples that were synthesized from the initial oxide mixture by treatment in vapor at 230 °C for 20 h. In accordance with an earlier study [37], an equimolar mixture of the reactants led to the formation of BaTiO₃ with an admixture of TiO₂. Table 3 presents the calculated amounts of TiO₂ remaining in the prepared powders. One can see that the increase in the Ba/Ti ratio to 1.3 gradually continued until full consumption of the initial TiO₂ and the formation of single-phase BaTiO₃ powder.

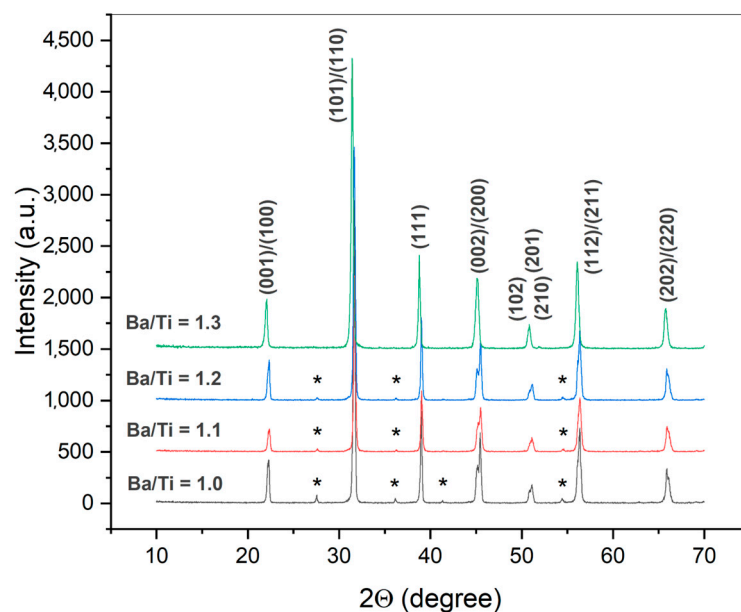


Figure 8. XRD patterns of the samples synthesized from BaO and TiO₂ mixtures with different Ba/Ti molar ratios in water vapor at 230 °C and 2.94 MPa for 20 h. The samples were preliminarily washed of the residual Ba²⁺ ions. * indicates the TiO₂ phase (rutile, PDF2 # 021-1276). The Miller indices correspond to the BaTiO₃ phase (PDF2 # 075-2117).

Table 3. Residual TiO₂ amounts and tetragonality (c/a) in BaTiO₃ samples synthesized in water vapor at 230 °C and 2.94 MPa for 20 h, with different initial Ba/Ti molar ratios (u(c/a) is the standard uncertainty of c/a measurement).

Ba/Ti Ratio	TiO ₂ Amount (wt. %)	c/a	u(c/a)
1.0	5.8	1.0073	0.0003
1.1	4.1	1.0071	0.0006
1.2	3.1	1.0068	0.0003
1.3	0	1.0057	0.0004

The XRD patterns of the synthesized powders corresponded to BaTiO₃ in a tetragonal modification. It was noticeable that the growth of barium excess in the reaction system resulted in the disappearance of the characteristic splitting of (002)/(200) peaks. As was calculated from the XRD data, the approach of the reaction system to the full transformation of TiO₂ into the product was accompanied by a decrease in BaTiO₃ tetragonality (c/a cell parameter ratio) (Table 3). This could be connected to the formation of a core-shell structure of BaTiO₃ particles [53,54]. This phenomenon has been described for the nanosized particles and grains of BaTiO₃. The tetragonal phase, which is known to be stable below the Curie point of BaTiO₃ (~130 °C), has been reported to deteriorate due to a high concentration of structural defects near the surface of the particle [55]. For this reason, the phase partially transforms into pseudocubic modification, which leads to a composite structure in the particle: a pseudocubic shell and a tetragonal core. The pseudocubic phase possesses the same XRD profile as in the high-temperature cubic modification of BaTiO₃. The coexistence of the mentioned BaTiO₃ modifications and the changes in their fractions between synthesized powders with different Ba/Ti ratios resulted in different tetragonality, which was calculated as an average value for each sample's volume. When BaTiO₃ was synthesized in a vapor atmosphere without the use of citric acid, a similar core-shell structure of its particles was assumed from XRD and Raman studies [37].

The morphologies of the initial TiO₂ powder and the resulting single-phase BaTiO₃ are shown in Figure 9. From an analysis of the scanning electron microscopy (SEM) images, it is evident that the BaTiO₃ powder consisted of micron-sized agglomerates of round-shaped particles in the range of 90 to 220 nm, with a mean value of 135 nm (Figure 9b). The observed agglomerates were likely to be formed directly from the particles of TiO₂ (Figure 9a). A similar inheritance of the starting TiO₂ morphologies by BaTiO₃ during synthesis in water vapor is described elsewhere [40]. Previously, in [37], particles obtained by a similar method to the current route but without the addition of citric acid were found to consist of agglomerated crystals, which were 101-nm-sized on average and showed a narrow size distribution. In the current research, a larger mean size pointed to faster nuclei growth in the presence of citric acid. Noticeably, the agglomerates visually differed in their density and neighbored almost-dispersed particles (Figure 9b). This pointed to the gradual deagglomeration of BaTiO₃ during the treatment in vapor, which would naturally be accompanied by an increase in the powder's surface area. Such an increase in surface area could be considered a factor governing the decrease in the powder's tetragonality when approaching the reaction's termination (Table 3).

The single-phase BaTiO₃ powder synthesized from the BaO and TiO₂ mixture with Ba/Ti = 1.3 was selected as a raw material for ceramics manufacturing via a conventional route, including room-temperature pressing followed by high-temperature sintering. To estimate its sintering behavior, a dilatometric analysis was conducted (Figure 10). From 40 to 1025 °C, only thermal expansion at a constant rate was detected. In the interval at 1025–1080 °C, a first stage of shrinkage associated with the particles' reorientation occurred and was followed by an interval of sintering, accompanied by pore elimination. The highest rate of shrinkage was found between 1252 and 1270 °C. Above 1295 °C, the real sintering was expected to end and change into grain growth.

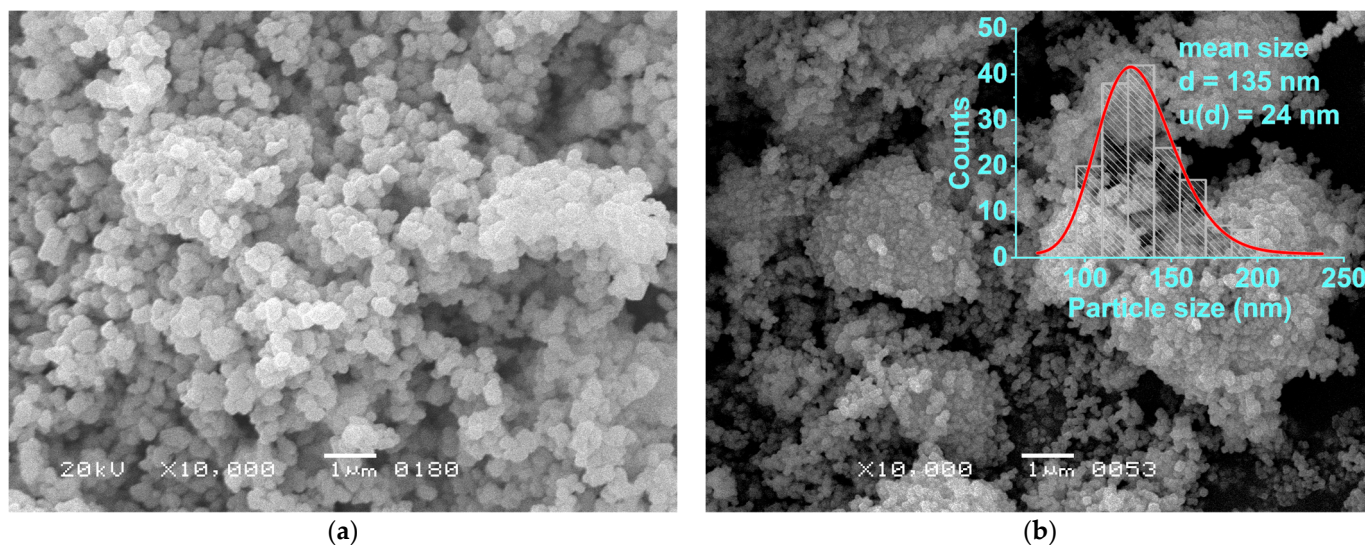


Figure 9. SEM images of the initial TiO_2 powder (a) and the BaTiO_3 synthesized from it in water vapor at 230 °C and 2.94 MPa after 20 h, with a molar ratio of Ba/Ti = 1.3 in the reaction system (d is the mean particle size, calculated from the measurements of 160 particles; $u(d)$ is the uncertainty of the measurement) (b).

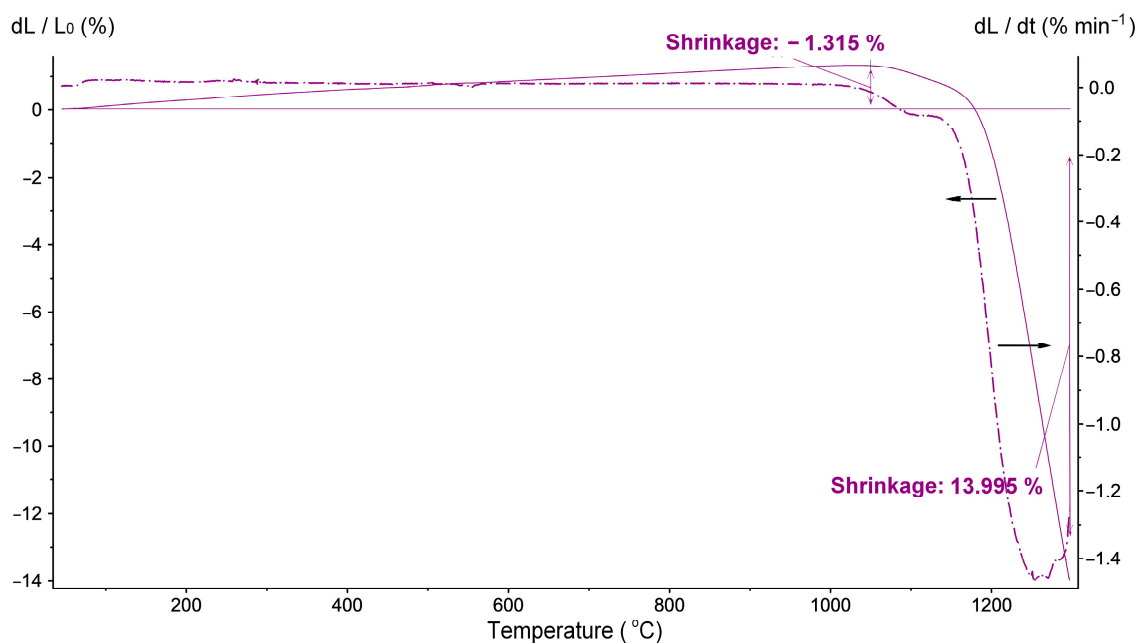


Figure 10. Shrinkage curve of the BaTiO_3 powder synthesized in water vapor at 230 °C and 2.94 MPa after 20 h, with a molar ratio of Ba/Ti = 1.3.

2.2.2. Properties of the Sintered Ceramics

Starting from the results of the dilatometric investigation of the synthesized BaTiO_3 powder, its sintering was carried out in a temperature range of 1250–1350 °C. According to the XRD analysis of the prepared ceramics, single-phase tetragonal BaTiO_3 was obtained at each of the sintering temperatures (Figure 11). Material consolidation and elimination of the structural defects during the ceramics processing halted any spontaneous polarization, which led to tetragonality enhancement compared to the raw powder ($c/a = 1.0057$) (Table 4). In addition, the tetragonality slightly increased with the sintering temperature.

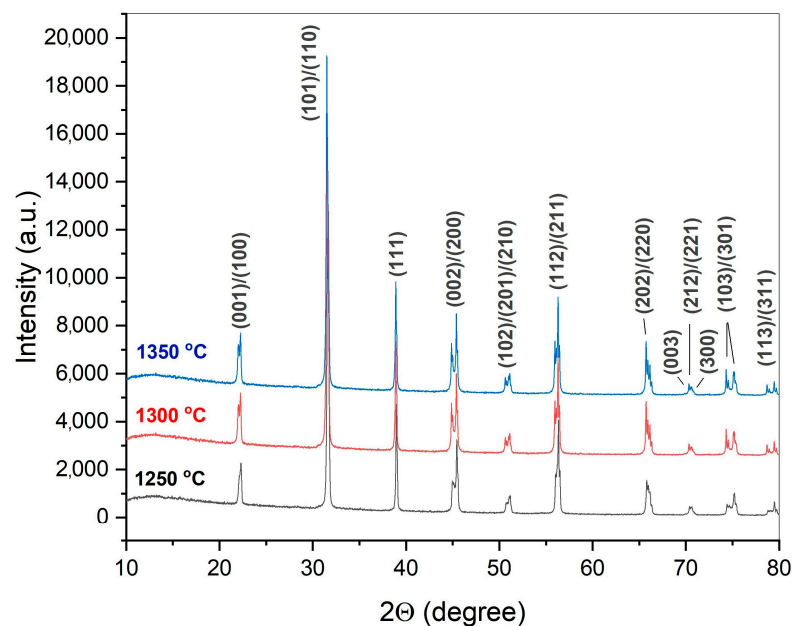


Figure 11. XRD patterns of crushed BaTiO₃ ceramics manufactured from the synthesized powder by uniaxial pressing at 150 MPa, followed by 1 h of sintering at 1250–1350 °C. The Miller indices indicate tetragonal BaTiO₃ modification.

Table 4. Structural and dielectric properties of the sintered BaTiO₃ ceramics (u is the standard uncertainty of measurement).

Sintering Temperature (°C)	Relative Density ρ (%)	Tetragonality c/a	Dielectric Properties				
			Frequency	ϵ	$u(\epsilon)$	$\text{tg } \delta \cdot 10^3$	$u(\text{tg } \delta) \cdot 10^3$
1250	94.3 $u(\rho) = 0.79$	1.0102 $u(c/a) = 0.0002$	1 kHz	3879	28	6.7	0.1
			100 kHz	3761	31	10.0	0.1
			1 MHz	3720	22	23.0	0.2
1300	95.6 $u(\rho) = 0.51$	1.0106 $u(c/a) = 0.0005$	1 kHz	3247	27	5.1	0.1
			100 kHz	3205	24	8.0	0.1
			1 MHz	3183	26	17.0	0.2
1350	96.0 $u(\rho) = 0.48$	1.0111 $u(c/a) = 0.0003$	1 kHz	1822	19	5.3	0.1
			100 kHz	1794	15	4.1	0.1
			1 MHz	1798	16	3.8	0.1

SEM study of the prepared ceramics revealed a formation of rather dense microstructures (Figure 12). When sintered at 1250 °C, the material consisted of micron-sized grains (mean size of 2.09 μm ; uncertainty of the measurement, 0.44 μm) partially separated by open pore spaces (Figure 12a,b). Its relative density exceeded 94% (Table 4), which could be considered high for conventional ceramic technology.

The material sintered at 1300 °C exhibited slightly higher density but its microstructure was less homogenous, demonstrating micron-grained areas (Figure 12c,d) neighboring the regions with round-shaped pores. The latter probably originated from discontinuous grain growth [56] in a fine-grained matrix. The presence of these large grains lowered the concentration of paraelectric grain boundaries [57,58], thus contributing to the increase in tetragonality. In addition, the large grains demonstrated a striped 90°-domain structure [59], which agrees with the stabilization of tetragonal modification. At 1350 °C, the sintering process occurred with the involvement of a liquid phase, which was reflected in the formation of large grains with spherical pores inside the material (Figure 12e,f). Liquid phase formation was caused by possible peritectoid and eutectoid processes, as reported for nearly stoichiometric barium titanate compositions at 1250–1320 °C [60,61]. The relative

density of the corresponding sample reached 96% and its tetragonality increased as well. However, the grain boundaries nearly disappeared, which, together with the darkening of the sample, proved the vicinity of the overburnt state.

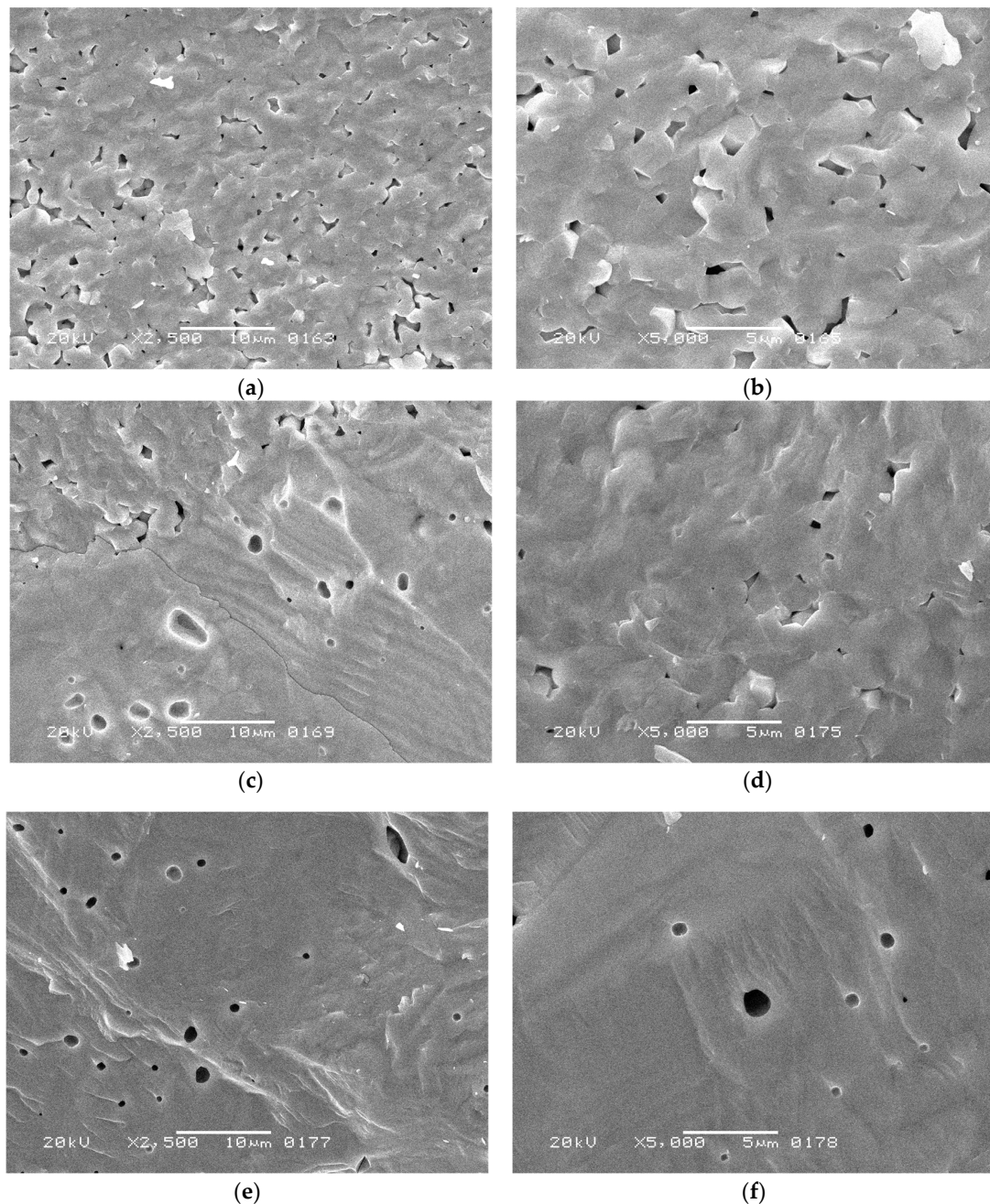
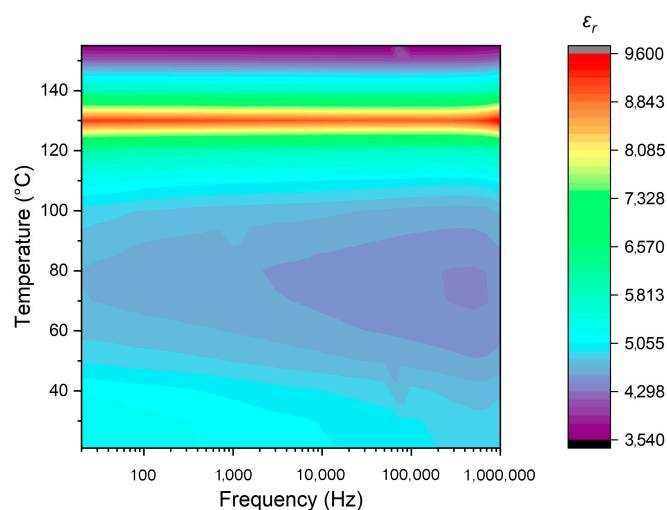


Figure 12. SEM images of the fracture surfaces of BaTiO₃ ceramics manufactured from synthesized powder by uniaxial pressing at 150 MPa, followed by 1 h of sintering at: (a,b) 1250 °C; (c,d) 1300 °C; (e,f) 1350 °C.

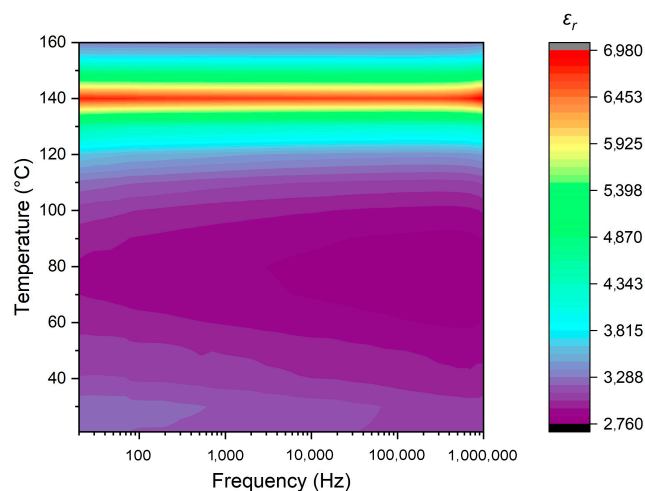
Despite an enhancement in the relative density and tetragonality of BaTiO₃ ceramics caused by the increase in the sintering temperature, their dielectric properties at room temperature demonstrated high sensitivity to the microstructure (Table 4). The highest permittivity was determined for the fine-grained material sintered at 1250 °C. Structural inhomogeneities in the sample sintered at 1300 °C led to a comparative decrease in the permittivity, while approaching a burnout at 1350 °C caused a drastic decrease in this characteristic. The dielectric loss factor exhibited sensitivity to the type of pore space. It

was higher in the sample with open intergranular porosity (in ceramics sintered at 1250 °C) than in those with combined inter- and intragranular pores (sintered at 1300 °C) or just closed porosity (sintered at 1350 °C). Open pores were prone to adsorbing water molecules from the atmosphere, which caused extra conductivity.

The thermal behavior of the dielectric permittivity observed in the prepared ceramic samples in a range from room temperature to above 140 °C and at frequencies between 20 Hz and 1 MHz is shown in Figure 13. The increase in the sintering temperature from 1250 to 1350 °C resulted in a significant fall in room-temperature dielectric permittivity, as well as in its value in a range up to 120 °C. Below 110 °C, the ceramics sintered at 1250 and 1300 °C demonstrated a decrease in permittivity with the rise in frequency, which can be explained by the reducing number of realized polarization mechanisms (Figure 13a,b). However, the sample sintered at 1350 °C was less sensitive to frequency (Figure 13c). The highest permittivity in the Curie point was exhibited by the sample prepared at 1250 °C, while the lowest value was observed for the one sintered at 1300 °C. Probably, this was caused by inhomogeneities in the ceramics' microstructure formed at 1300 °C. The drifting of the Curie point to higher temperatures that was observed with an increase in the sintering temperature reflects the stabilization of the ferroelectric modification, as also indicated by the increase in tetragonality (Table 4).



(a)



(b)

Figure 13. *Cont.*

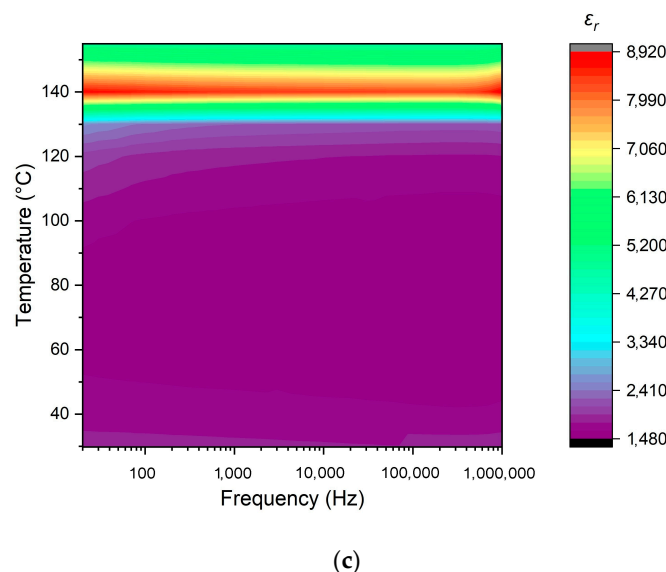


Figure 13. Temperature- and frequency-dependent behavior of the dielectric permittivity of BaTiO₃ ceramics manufactured at: (a) 1250 °C; (b) 1300 °C; (c) 1350 °C.

3. Discussion

Once subjected to water vapor, the particles of BaO and TiO₂ from the initial reaction mixture adsorbed water molecules and underwent surface hydroxylation. BaO is known to add water with the formation of a layer of amorphous hydroxide and further hydration into Ba(OH)₂·*x*H₂O [62–64]. For TiO₂, both the molecular and dissociative adsorption of water are typical [65]. Apparently, this resulted in the formation of similar charges on the particles' surfaces, which led to their mutual repulsion. The introduction of a foreign electrolyte locally changed the electrostatic conditions in the mixture and supported the formation of contacts between the reactants' particles. For this reason, the presence of small amounts of citric acid in the reaction mixture stabilized the initial stage of BaO and TiO₂ interaction. An additive of iodine reacted with water molecules to generate HI and HIO, which acted in a similar way as citric acid, making for stable growth of the reagents' conversion over time.

The observed reaction between the initial oxides possessed the features of a topochemical process [66]. The conversion vs. time curves for the BaO–TiO₂ system in water vapor demonstrated a sigmoidal shape, with an induction period imprinted at 130 and 140 °C. At this stage, hydration and hydroxylation of the reactants occurred and was accompanied by melting of the hydrated Ba(OH)₂, as was revealed by TEM. These processes allowed the formation and growth of a contact area between the reactants' particles. Due to their interaction with water molecules, the surfaces of the reactants became highly defective, which facilitated the appearance of a reaction zone. BaTiO₃ nucleation and its growth initiated the autolocalization of the process and moved the front of the reaction inward toward the TiO₂ particles. This autolocalization was accompanied and promoted by hydroxylation of the oxide structure, as shown by the FTIR analysis. The corresponding part of the kinetic curves exhibited an increase in the BaTiO₃ fraction. From our analysis of the kinetics, it appears that this complex process is likely to be controlled by phase transformations, rather than by diffusion. However, the collected data did not allow any unambiguous conclusion as to whether the process was limited by product nucleation or by the phase-boundary phenomena. Nevertheless, the final part of the kinetic curves, i.e., when reaching a plateau, could be caused by the diffusion limitations, which were overcome by enough of an excess of barium ions in the reaction medium.

The calculated apparent activation energy of the studied reaction (up to 80 kJ mol^{−1}) was close to the level reported for BaTiO₃ formation from TiO₂ in a concentrated Ba(OH)₂ solution (105 kJ mol^{−1}), which is recognized as a topochemical process as well [67]. A

conventional high-temperature solid-state synthesis of BaTiO₃ was characterized by a higher activation energy of 361 kJ mol^{−1}, while for the reaction between the same reactants (BaCO₃ and TiO₂) in water vapor at 700 °C, this was determined as 142 kJ mol^{−1} [68]. These results emphasized the key role of water in facilitating the studied topochemical reaction, due to defect generation on the surface of the reactants and further in their bulk. The current study proved the propositions and conclusions drawn in earlier works on the mechanism of BaTiO₃ formation from a mixture of simple oxides in water vapor [37,39,40].

In the current study, the BaTiO₃ powder synthesized in the water vapor exhibited fairly high capability in the manufacturing of ceramics for low-frequency applications. Table 5 shows some recent data on the structural and dielectric characteristics of pure BaTiO₃ ceramics obtained by the conventional technique. Most of these materials were produced from nanosized or nearly nanosized powders by pressing at different loadings (50–400 Pa), with subsequent sintering at a temperature in the range of 1050–1350 °C for several hours. It is known that the achievement of full density is quite difficult using the conventional route, so the reported materials possessed relative densities of 92–97% of the theoretical value (6.02 g cm^{−3}). However, density is not the deciding factor for the functional properties of BaTiO₃ ceramics. In the case of sufficient densification, the grain size is known to affect the dielectric properties of BaTiO₃. Among them, the highest permittivity was observed when the grain size of BaTiO₃ was about 1 µm. This effect can be seen in the data in Table 5 as well. The ceramics obtained in the current work exhibited worthwhile values of permittivity compared to the other mentioned results. In addition, its dielectric loss factor was maintained at the level of 0.02 up to 1 MHz, which is acceptable for this class of materials [69]. Nevertheless, the use of novel approaches that are different from conventional ceramics manufacturing, for instance, two-step sintering [70–72], the cold sintering process [73–76], etc., would open up possibilities for microstructural engineering and the effective application of BaTiO₃ powders synthesized in a water vapor medium.

Table 5. Structural and dielectric properties of the BaTiO₃ ceramics process using a conventional technique.

Ref.	Particle Size	Ceramics Processing Parameters				Ceramics Properties			
		p (MPa)	T (°C)	Time (h)	GS ** (µm)	ρ _{rel} *** (%)	E #	tg δ ##	f
[77]	20–40 nm	n/a *	1350	3	0.5–2.0	97	1223	0.0035	1 MHz
[78]	2 µm	200	1250–1350	2	5	90	2200	n/a	5 MHz
	40 nm	200	1250–1350	2	1	95	5000	n/a	
[79]	150 nm	n/a	1050	4	n/a	95.5	2200	n/a	1 kHz
[80]	20 nm	100	1300	3	n/a	92	1700	n/a	1 kHz
[69]	137 nm	400	1250	1	0.3–2.0	95.8	4200	0.0370	10 kHz
[81]	100 nm	150	1100	6	2	95	3300	0.0700	1 kHz
[82]	n/a	n/a	1300	3	5.53	data	2000	~0.0300	1 kHz
[83]	n/a	50	1350	2	1	n/a	3533	n/a	100 kHz
							3879	0.0067	1 kHz
This work	135 nm	150	1250	1	2	94.3	3761	0.0100	100 kHz
							3720	0.0230	1 MHz

* n/a—not available; ** GS—mean grain size; *** ρ_{rel}—relative density; # ε—permittivity at room temperature; ## tg δ—dielectric loss factor at room temperature.

4. Materials and Methods

Barium oxide (BaO, purity > 99.9%, GOST 10203-78, supplied by the LLC Laverna-Lab, Moscow, Russia), titanium dioxide in a rutile modification (TiO₂, purity > 99.9%, STP TU COMP 2-340-11, supplied by LLC Komponent-Reaktiv, Moscow, Russia), citric acid monohydrate (C₆H₈O₇·H₂O, purity > 99.9%, GOST 3652-69, supplied by JSC LenReaktiv, St Petersburg, Russia) and crystalline iodine (I₂, purity > 98%, GOST 4159-79, supplied by JSC LenReaktiv, St Petersburg, Russia) were used as the initial substances for the synthesis of BaTiO₃.

To prepare a reaction mixture, calculated amounts of BaO and TiO₂ with a Ba/Ti molar ratio of 1.0, 1.1, 1.2, or 1.3 were mixed together using an agate mortar and pestle and then

placed into PTFE containers. If it was required, a corresponding amount of citric acid monohydrate (0.6; 1.2 or 2.4 wt. % with respect to the mixture) was added to the reactants and underwent joint mixing. To introduce the iodine additive to the reactants, it was preliminarily applied to the surface of TiO_2 , as follows. An open crucible with 4 g of TiO_2 was placed into a glass vessel containing 1 g of I_2 . The buks was closed and stored at room temperature for 4 days. After that, the TiO_2 was removed and used for the preparation of a reaction mixture, as described above. The stabilizing additives to the reaction mixture were selected so that: (1) they generated protons in an aqueous medium and (2) they were solid at standard conditions, in order to prepare the mixture without it getting wet. The PTFE container with the reaction mixture was placed into a laboratory stainless-steel autoclave of 12–17 cm^3 in volume, which contained 2 mL of distilled water at the bottom. The autoclave was sealed and placed into a furnace to be heated up to 130–230 °C at a rate of 80 °C h^{-1} . The corresponding vapor pressure generated inside the autoclave was 0.27–2.94 MPa. The autoclave was stored in these conditions for 0 to 20 h, after which it was removed from the furnace and rapidly cooled by dipping its bottom in cold water (at about 14 °C). This method of cooling allowed water to condense on the bottom inside the autoclave, separately from the container with the product. Afterward, the autoclave was opened and the product was removed from it and dried in air at a temperature of 70–80 °C for 12 h. If it was required, the product was washed in 5 wt. % acetic acid solution and distilled water to remove the excess barium ions.

Ceramics processing was carried out with the use of 5 wt. % of polyvinyl alcohol aqueous solution as a temporary binder. Green pellets were prepared by uniaxial pressing at 150 MPa and were then sintered at 1250, 1300, or 1350 °C for 1 h in air. The density of the obtained ceramic samples was determined by the Archimedes method using kerosene. The processing procedure, as well as metallization, have been described in detail elsewhere [84].

XRD analysis of the synthesized powders and crushed ceramic samples was conducted with the use of the following diffractometers: the STOE STADI P with $\text{CuK}\alpha$ radiation (STOE & Cie GmbH, Darmstadt, Germany), the Rigaku D/Max-2500 with $\text{CuK}\alpha$ radiation (Rigaku Corp. Tokyo, Japan), and the PowDiX 600 with $\text{CuK}\alpha + \beta$ radiation (CJSC Linev Adani, Minsk, Belarus). The patterns were recorded in the range of $10^\circ < 2\theta < 80^\circ$, with a step of 0.02° . The ICDD PDF2 database was used for the phase analysis [85]. Whole diffraction pattern profile fitting was carried out using the Le Bail method by means of GSAS (version Win32) [86] and FullProf (version January 2012) [87] software. The structural models of BaTiO_3 (tetragonal), TiO_2 (rutile), and BaCO_3 (witherite) were found in the Crystallography Open Database [88]. Quantitative analysis of the samples, as well as cell parameter refinement, was performed using the Rietveld method [89].

Scanning electron microscopy of the powders and the ceramic fracture surfaces was performed with a Jeol JSM 6380 (Jeol Ltd., Tokyo, Japan). Transmission electron microscopy, combined with an EDX study, was conducted using a Jeol JEM-2100 F (Jeol Ltd., Tokyo, Japan).

FTIR study of the synthesized powders was conducted with a WQF-530A spectrometer (Beijing Beifen-Ruili Analytical Instrument (Group) Co., Ltd., Beijing, China) in a wavenumber range of $4000\text{--}350\text{ cm}^{-1}$ by the attenuated total reflectance method.

The permittivity and dielectric loss factor of the sintered ceramic disks with metalized-plane parallel sides were calculated using the capacitance measurements carried out with a GW Instek LCR-78210 meter (Good Will Instrument Co., Ltd., Xinbei, Taiwan).

5. Conclusions

For this paper, we have studied in detail the process of BaTiO_3 formation from a mixture of solid oxides of barium and titanium in a medium of water vapor, this being in equilibrium with the liquid at 130–230 °C and at 0.27–2.94 MPa. This process was revealed to occur as a topochemical reaction, which could be divided into an induction period and the subsequent periods of rapid conversion and deceleration. The initial reactants first underwent surface hydration and then further hydroxylation, which facilitated the autolocalization of the process. Barium oxide was found to transform into a melt when

exposed to the conditions of synthesis in water vapor. The apparent activation energy of BaTiO₃ formation in water vapor was estimated as 75–80 kJ mol^{−1}. To obtain a single-phase BaTiO₃ in these conditions, an excess of barium ions was required, corresponding to a Ba/Ti molar ratio equal to 1.3 in the initial mixture. At 230 °C and at a vapor pressure of 2.94 MPa, a tetragonal BaTiO₃ powder with a mean particle size of 135 ± 24 nm was obtained. Based on this powder, a conventional ceramics technique allowed the preparation of single-phase tetragonal BaTiO₃ ceramics with a grain size of about 2 µm, a room-temperature permittivity of 3820–3791, depending on the frequency, and a dielectric loss factor of less than 0.02. The synthesis of BaTiO₃ in water vapor was proved as an effective and environmentally benign route to producing high-performance dielectric ceramics.

Author Contributions: Conceptualization, A.A.K., Y.D.I. and M.N.D.; methodology, A.A.K., Y.D.I., M.N.D. and A.V.S.; validation, A.A.K., Y.D.I. and M.N.D.; formal analysis, A.A.K., A.N.K. and L.A.A.; investigation, A.A.K., G.P.M., A.V.E., A.D.S., A.N.K., L.A.A. and V.E.B.; resources, M.N.D. and A.V.S.; data curation, A.A.K.; writing—original draft preparation, A.A.K.; writing—review and editing, A.V.S.; visualization, A.A.K.; supervision, Y.D.I., M.N.D. and A.V.S.; project administration, A.V.S.; funding acquisition, A.V.S. All authors have read and agreed to the published version of the manuscript.

Funding: The article was written as part of the implementation of indicators for projects funded from the state budget or other external sources, namely, the National Project “Science and Universities”, to achieve the resulting “Creation of new laboratories, including under the guidance of young promising researchers (growing result)” FSFZ-2022-0003.

Data Availability Statement: The research data are available upon request.

Acknowledgments: The study was supported in part by the Lomonosov Moscow State University Program of Development. The authors are grateful to Nellya A. Popova from the Mendeleev University of Chemical Technology of Russia for her kind assistance in the dilatometric study. The authors would like to thank Igor A. Chmutin for his help with the study of the thermal behavior of the permittivity.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

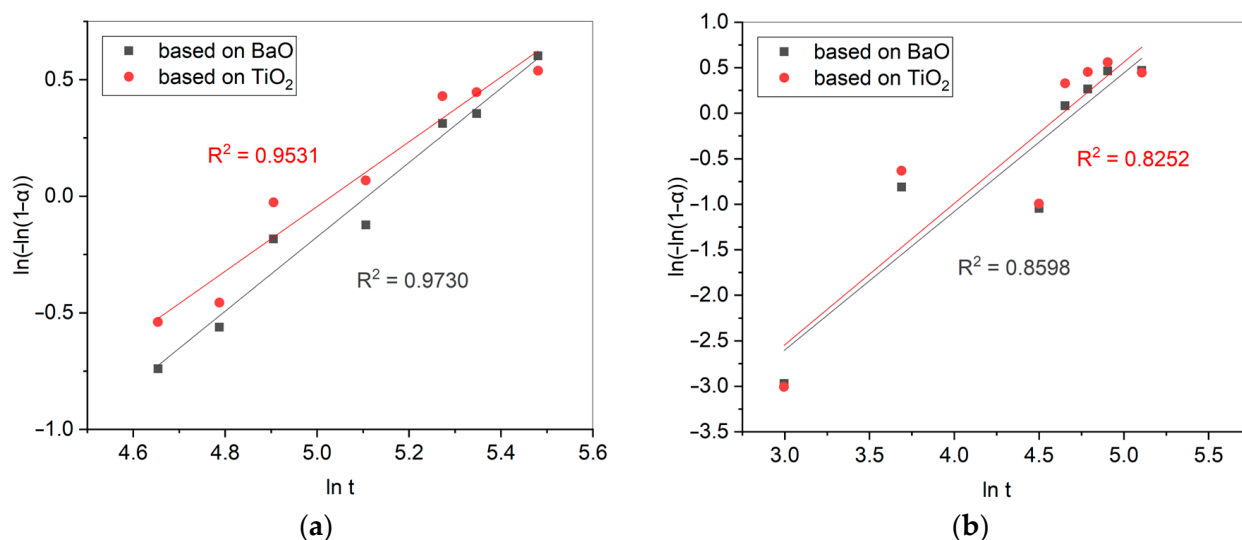


Figure A1. Cont.

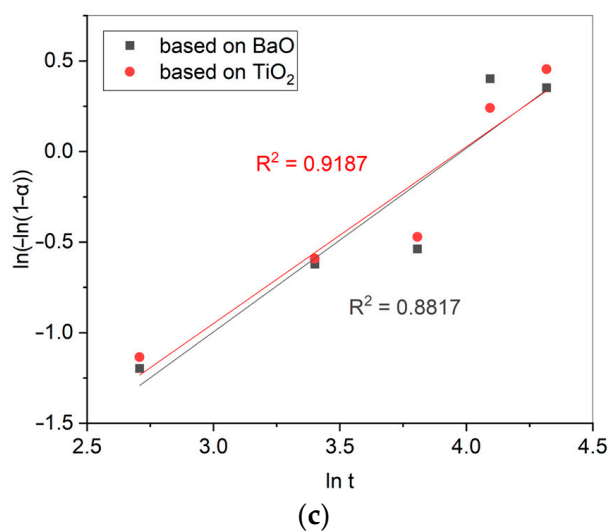


Figure A1. Johnson–Mehl–Avrami–Erofeev linearization of the kinetic curves of BaTiO₃ formation in a water vapor medium at different temperatures: (a) 130 °C; (b) 140 °C; (c) 150 °C. The data were obtained from the amounts of unreacted BaO and TiO₂ for each duration of the reaction.

Appendix B

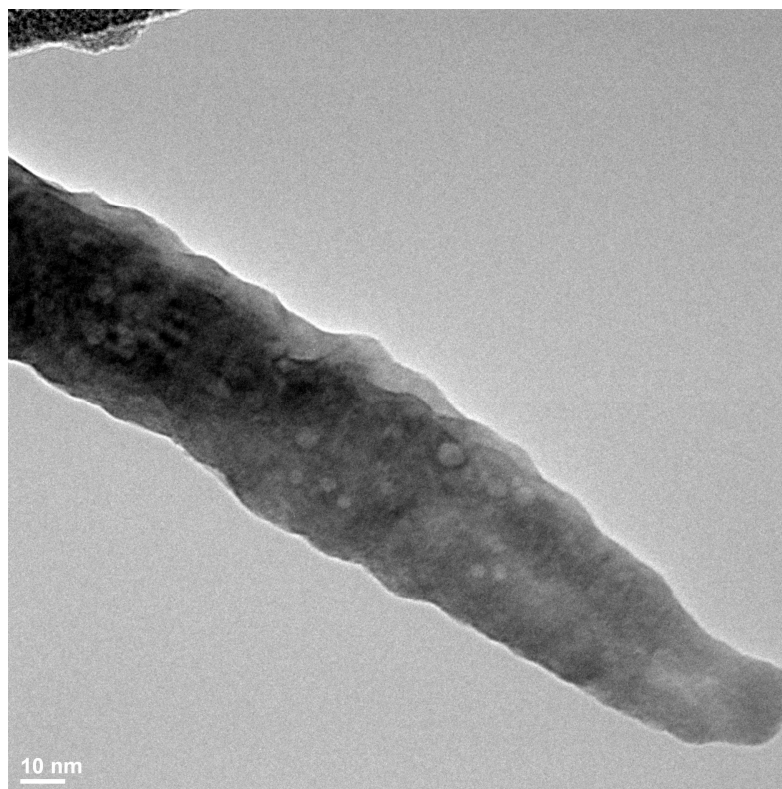


Figure A2. TEM image of a dendrite structure found in a sample prepared from BaO and TiO₂ equimolar mixtures with 1.2 wt. % of citric acid in water vapor at 130 °C for 30 min.

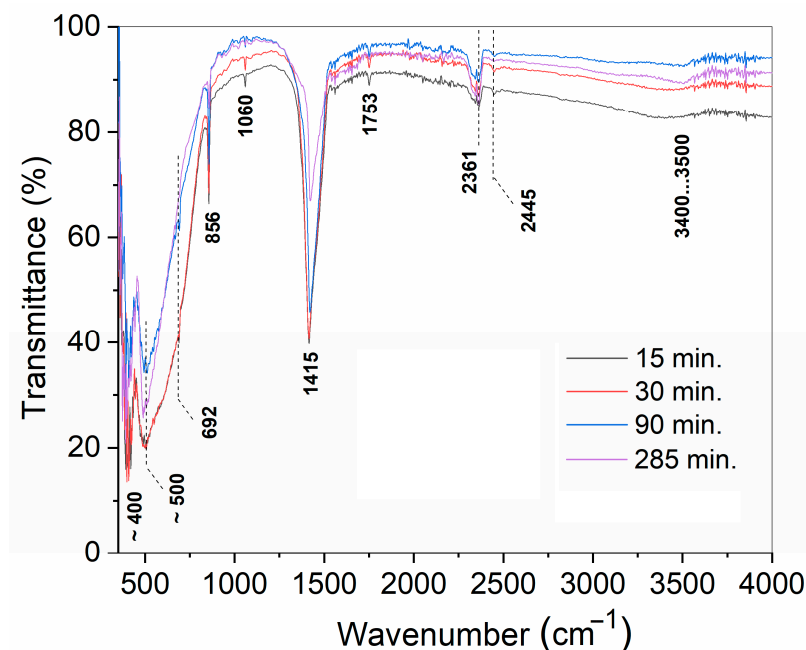


Figure A3. FTIR spectra of the samples prepared from BaO and TiO₂ equimolar mixtures with 1.2 wt. % of citric acid in water vapor, after different durations of treatment.

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