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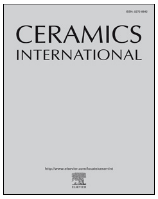

Properties of barium titanate ceramics based on powder synthesized in supercritical water

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ABSTRACT

Fine-crystalline barium titanate was synthesized by a new method using supercritical water and examined as a raw material for dielectric ceramics preparation by semidry pressing and further high-temperature sintering. The nature of temporary technological binder utilized at the stage of pressing significantly affected the structural, mechanical and electro-physical properties of $BaTiO_3$ ceramics. Ceramics prepared from $BaTiO_3$ powder synthesized in supercritical water possessed necessary applied characteristics: the dielectric permittivity as high as 2819 and loss tangent as low as 0.012.

1. Introduction

An activation effect of supercritical water on the process of solid state interaction was reported previously [1]. This phenomenon provided with opportunity of energy-saving and ecologically benign synthesis of widely used and industrially required powder materials. The activation effect became a basis for developing the technologies for fine-crystalline materials such as SiO_2, Al_2O_3, $Y_3Al_5O_{12}$, ZnS, $LiNbO_3$, $BaFe_{12}O_{19}$, $MgAl_2O_4$ and $BaTiO_3$ [2–7].

Production of dense fine-grained ceramics for microelectronics requires pure fine-crystalline raw materials with narrow size distribution [8]. One of the most important raw materials for multilayer ceramic capacitors is barium titanate, which composes up to 98 mass.% of a device depending on the MLCC model [9,10]. Methods for $BaTiO_3$ synthesis may be divided to those based on conventional solid-state process and to the approaches of wet chemistry [11–13]. However a large number of the proposed methods are not applied in industry for the reason of their complication and high cost. The exceptions are solid-state, hydrothermal and oxalate technologies mostly applied for $BaTiO_3$ preparation on modern plants [10]. Previously the authors proposed a method of fine-crystalline $BaTiO_3$ synthesis in supercritical water [7]. This method allowed obtaining of high-quality and industrially perspective product.

Currently a number of rather novel technologies such as hot pressing, spark plasma sintering, microwave sintering, and others find a use in production of different types of technical ceramics, in particular, microelectronic ceramics [8]. However a conventional method of semidry pressing with further high-temperature treatment still ranks high in industry of radio-technical devices due to operation simplicity and low cost. Pressing as a method is especially of interest in the production of thin microelectronic components [14]. The pressing of powder mass usually requires the use of temporary technological binders. Without an addition of temporary technological binder the densification of powder is less effective [15]. The applied pressure is spent in part to overcome the friction of particles. The purpose of temporary technological binder is to enhance the mobility of particles under pressure and to provide the mechanical strength of the green body sufficient for further operations [14]. Chemical purity and high density of ceramics are of importance for microelectronics because these characteristics significantly affect the electro-physical properties. In this connection ceramics processing mostly utilizes temporary binders of organic nature, which could be completely removed from the material during high-temperature treatment. It is also required that the binder wetted the surface of powder particles and possessed minimal adhesion to the details of the die. It is strongly undesirable to use toxic or high-cost substances as binders [14–16].

The most common kind of temporary technological binders used in case of semidry pressing is aqueous binder, for example, polyvinyl alcohol (PVA) [17–23] and sodium polymethacrylate [24]. A widespread use of PVA is caused by its low ash content, high binding strength, and consequently, high strength of the obtained green bodies [14]. However, aqueous temporary binders have some disadvantages. The

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prepared press-powder should be kept in a hermetically closed container to prevent water evaporation which leads to the loss of binding properties. In particular, the lowering of wet content in green bodies pressed with the addition of PVA was accompanied by weakening of bonding between particles and lowering of the strength of green bodies [25]. At the same time, availability of the use of nonaqueous binders such as paraffin was previously noted [15]. Paraffin provides high plasticity of press-powder and strength of green bodies, is non-volatile at room temperature, and does not loose binding properties in case of prolonged storage of press-powder.

The main goal of the present study was to examine the fine-crystalline $BaTiO_3$ powder synthesized in supercritical water as a raw material for ferroelectric ceramics processed by semidry pressing. Also the influence of the nature of temporary technological binder on the properties of ceramics was revealed and the most adequate binder was chosen for the processing.

2. Experimental

2.1. Materials

Fine-crystalline barium titanate was synthesized from an equimolar mixture of TiO_2 (STP TU KOMP 2-340-11, ≥ 99.5% purity) and BaO (TU 6-09-03-375-74, ≥ 98% purity) in a medium of supercritical water according to the technique described elsewhere [7]. The mixture of reagents was placed into a stainless steel container inside a laboratory autoclave. The amount of water required to generate pressure in supercritical conditions was poured at the bottom of the autoclave separately from dry reagents. The synthesis was carried out at the temperature of 400 °C and the pressure of 26.0 MPa during 20 h. The obtained product consisted of $BaTiO_3$ crystals in tetragonal modification with the mean size of 130 nm (Fig. 1).

Synthesized $BaTiO_3$ powder was used to prepare two types of press-powders: one with the use of an aqueous temporary technological binder (polyvinil alcohol (PVA) solution, 5 mass.%, Zschimmer & Schwarz (Germany)) and another with the use of non-aqueous temporary technological binder (paraffin). Binders of both types were added to the powder in amount of 5 mass. %.

Green bodies of $BaTiO_3$ were prepared by cold uniaxial pressing at three different values of pressure: 50, 100, or 150 MPa.

Sintering of the samples was carried out in air at temperature of 1250, 1300, or 1350 °C during 1 h. The temperature regimen of heating was chosen on the base of thermogravimetric analysis (TGA) of press-powders with the aim to ensure complete removal of temporary binders (see Fig. 3). At the first step the heating rate for green bodies with PVA was $200^\circ h^{-1}$. Green bodies with paraffin were heated with the rate of $100^\circ h^{-1}$. After reaching 300 °C the samples were held at this temperature for 0.5 h. Then the heating continued with the rate of $200^\circ h^{-1}$ for both types of green bodies until the temperature of sintering was reached.

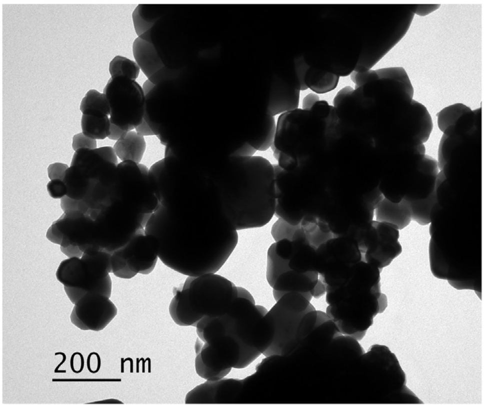

Fig. 1. TEM image of $BaTiO_3$ powder synthesized in supercritical water at 400 °C, 26.0 MPa.

2.2. Methods

The size and shape of the synthesized $BaTiO_3$ crystals were observed by means of transmission electron microscope JEOL JEM-1011 (JEOL Ltd., Japan).

Rheological properties of two types of press-powders based on synthesized $BaTiO_3$ powder with addition of PVA solution or paraffin as temporary technological binders were tested in accordance with standard procedures.

The apparent density of ceramic samples was estimated by the Archimedes method. The method of kerosene saturation was used to measure the porosity of the samples.

The surface of ceramic samples was prepared for the scanning electron microscopy studies by polishing and chemical etching. Mean grain size of each ceramic sample was calculated from SEM images on the base of 200 measurements.

Ultimate compression strength of ceramics was determined by means of electromechanical testing machine LFM-C (Walter + Bai AG, Switzerland).

Ceramic powders were characterized by X-ray diffraction (Rigaku D/Max-2500, Japan). The patterns were registered using CuKα radiation in a range of $20^\circ < 2\theta < 90^\circ$ with a step of 0.02°. Phase contents of samples were identified by comparison of experimental data with those from PDF-2 database. Jana2006 program was utilized for fitting of diffraction pattern profiles by Le Bail method and for refinement of unit cell parameters by Rietveld method [26].

To evaluate the dielectric properties of the manufactured $BaTiO_3$ ceramics, the disks of 11–13 mm diameter and 1.6–2.2 mm thickness were polished and silver electrodes were painted on their both parallel sides. DC resistivity of the samples was measured by means of Agilent 4339 B (Agilent Technologies, Japan) with the Agilent 16008 B measuring cell. Dielectric constant and loss tangent were calculated from the results of the capacitance measurements in a range of 20 Hz to 2 MHz carried out at Agilent E 4980A.

3. Results and discussion

3.1. Properties of $BaTiO_3$ press-powders prepared with different types of temporary binders

Rheological tests of two kinds of press-powder prepared from $BaTiO_3$ with addition of 5 mass% PVA solution or paraffin as temporary technological binders performed close values of the angle of repose and of the bulk density regardless the nature of the binder (Table 1).

Berezhnoy equation, which shows the dependence of density of a green body ρ on logarithm of applied pressure P from a range of 10–200 MPa, is used often to compare the compaction ability of press-powders [27,28]:

$$\rho = A + B\ \lg\ P. \tag{1}$$

The lower the ratio A/B the higher the compaction ability of a press-powder. The experimental data on the density of green bodies pressed

Table 1
Rheological properties of $BaTiO_3$ press-powders prepared with the addition of different types of temporary technological binders.

Property	Type of temporary technological binder	
	PVA (aq., 5%)	Paraffin
Angle of repose	60.6°	60.1°
Bulk density ($g\,cm^{-1}$)	1.14	1.16

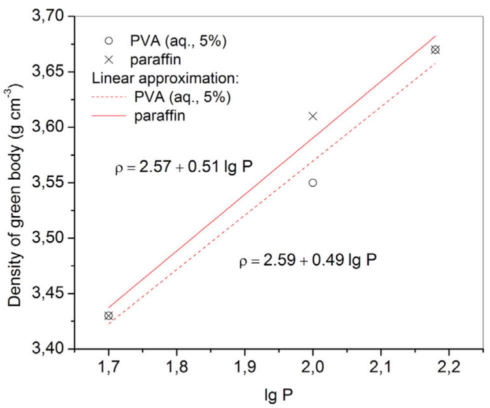

Fig. 2. Linear approximation of density of $BaTiO_3$ green bodies with addition of 5% aqueous PVA or paraffin *vs* compacting pressure.

from $BaTiO_3$ powders with addition of PVA or paraffin at 50–150 MPa and a linear approximation of these data according to the Eq. (1) are shown in Fig. 2. The ratio A/B takes close values though in case of paraffin it was slightly higher than when PVA was added (5.04 and 5.29, respectively).

The density of green bodies was 3.4–3.7 g cm^{-3} as in case of PVA, and in case of paraffin as a binder. This value corresponded to 56–61% of the theoretical density of $BaTiO_3$ ceramics (6.01 g cm^{-3}). It is known that low density of green bodies (40–45% of the theoretical value) does not allow production of dense ceramics. Higher green density (55–60%) provides better densification on sintering and shows a positive correlation with the density of final material [29]. The results showed that the both types of temporary technological binders provide compaction sufficient for subsequent sintering of dense ceramics.

From thermogravimetric analysis (TGA) of two types of press-powders, in both cases the weight loss was observed in a wide temperature range and mostly terminated by 500 °C (Fig. 3, a). It was reported that elimination of PVA might last while the sample was being heated up to 800 °C, elimination of paraffin from $BaTiO_3$ based body – up to 900 °C, but these processes could hardly be observed by TGA [30,31]. It should be noted that the weight loss of press-powders with PVA was only 3.57 mass.%, which was less than 5 mass.% added initially. This fact pointed to evaporation of water from this type of press-powder even during short-term storage in a closed storage tank.

Thermal effects observed by means of DSC showed the processes occurred to the technological binders on heating of press-powders (Fig. 3, b). Below 400 °C press-powder containing PVA evaporates water and emits acetic acid which is formed as a result of partial decomposition of the polymer [30]. Exothermic effects in this area were observed about 279 and 325 °C. Full decomposition of polyvinyl chains occurred above 400 °C and appeared as an exothermic effect at about 418 °C. Elimination of paraffin from $BaTiO_3$ press-powder began from its melting accompanying by an endothermic effect at 55 °C. Pyrolysis of paraffin as of hydrocarbon mixture occurred in several stages at temperature above 200 °C. An intensive exothermic effect at 254 °C and less pronounced peaks at 352 and 403 °C corresponded to this process.

3.2. Composition and properties of the sintered ceramics

$BaTiO_3$ crystals above 120–130 °C (Curie temperature for $BaTiO_3$) possess cubic symmetry and typical paraelectric properties. On cooling below this temperature barium titanate undergoes a phase transition to tetragonal modification which possesses practically important ferroelectric properties. Such a phase transition is usually difficult in nanosized crystals [32,33]. High defect concentration and high specific surface area impede spontaneous polarization. $BaTiO_3$ nanocrystals perform a size effect consisting in retention of metastable paraelectric modification until the room temperature. Previously it was shown by means of XRD and Raman spectroscopy that $BaTiO_3$ crystals synthesized in a medium of supercritical water were ferroelectric tetragonal at room temperature [7].

The absence of side phases such as polytitanates is essential for ferroelectric properties of $BaTiO_3$. Polytitanates do not possess high dielectric permittivity [11,34,35] and thus deteriorate functional properties of ceramics.

Fig. 4 shows XRD patterns of $BaTiO_3$ powder synthesized in supercritical water and of ceramics prepared from it with the use of PVA (a) or paraffin (b). The samples consisted of barium titanate (PDF-2 no. 00-075-0460). The increase in peak intensity and decrease in its width during the transition from powder to ceramics pointed to perfection of crystal structure on sintering. In case of using PVA this effect was observed for all the ceramic samples. In case of paraffin as a binder similar result was fixed for sintering at 1250–1300 °C. The sintering at 1350 °C led to broadening of peaks and decrease in their intensity. This might sign the changing in mechanism of sintering at high temperature, partial structure disorder, and formation of glass phase.

A transition from powder to ceramics was accompanied by an increase in unit cell tetragonality (c/a ratio) at room temperature. This value reached 1.0069 for the starting $BaTiO_3$ powder and increased after the sintering (Fig. 5). When ceramics were prepared with the addition of PVA and sintered at 1250–1300 °C, its tetragonality was 1.0083–1.0084 (Fig. 5, a). Processing of a similar green body at 1350 °C led to $c/a = 1.0086$. Ceramic samples produced with the use of paraffin as a binder possessed lower tetragonality (1.0076–1.0084), which reached maximum after sintering at 1300 °C (Fig. 5, b).

Microstructure of ceramic samples substantially depended on the type of temporary technological binder used for its preparation and on the temperature of sintering. Fig. 6 shows the microstructure of samples pressed at 150 MPa and processed at different temperatures. Ceramics sintered at 1250 °C consisted of rectangular and round-shaped grains

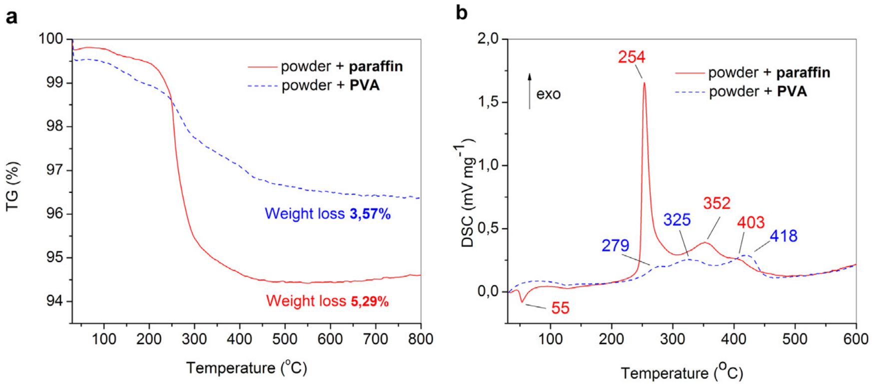

Fig. 3. TGA (a) and DSC (b) curves of $BaTiO_3$ press-powders containing 5 mass. % of temporary technological binders: 5% aqueous PVA or paraffin.

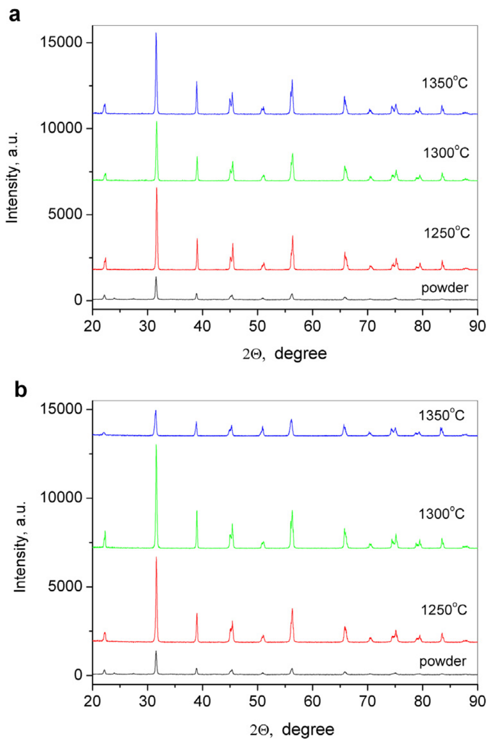

Fig. 4. XRD patterns of raw $BaTiO_3$ powder and ceramics produced by compaction at 150 MPa and sintering at 1250–1350 °C with the use of temporary technological binders: a – 5% aqueous PVA, b – paraffin.

separated by a large amount of intergranular pores (Fig. 6, a, d). Average grain size in the sample pressed with paraffin was $1.2 \pm 0.4\,\mu m$ (Fig. 6, d). The sample pressed with addition of PVA consisted of smaller grains, $0.8 \pm 0.2\,\mu m$ (Fig. 6, a). Increase in the temperature of sintering led to significant changes in microstructure of samples pressed with paraffin (Fig. 6, e). When processing temperature rose from 1250 to 1300 °C the growth of grain size from 1.2 to 4–5 μm and formation of facets were observed as well as the decrease in the amount of intergranular pores. Such changes were not found in case of sintering of green bodies with the addition of PVA at 1250–1300 °C (Fig. 6, a-b). Increase of temperature did not affect the size and arrangement of grains and led to formation of areas with different degree of compaction. A further increase in the sintering temperature to 1350 °C in the case of ceramics with a paraffin binder (Fig. 6, f) led to intensive growth of grains and the formation of rounded intracrystalline as well as elongated pores. In case of PVA, the structure of ceramics consists of continuous networks of solid matter and pores (Fig. 6, c).

$BaTiO_3$ ceramics are characterized by a solid-phase mechanism of sintering which occurs due to diffusion. Depending on the character of the diffusion, the sintering process can proceed predominantly in the direction of consolidation or coarsening of grains [29,36]. Analysis of the microstructure of the obtained samples showed that when paraffin was used as binder, bulk diffusion and diffusion along the grain boundaries occurred, accompanied by a change in the shape and size of the pores and a general decrease in porosity (Fig. 6, d-e). At 1350 °C the formation of a liquid phase also contributed the sintering process, as indicated by the presence of pores of an elongated shape (Fig. 6, f). In the case of using PVA as a binder, the green bodies showed lower sintering activity. The change in the microstructure observed at 1250–1350 °C was typical for the realization of surface diffusion, which facilitated the grain growth while maintaining intercrystalline porosity (Fig. 6, b, d, f).

Local microscopic study of ceramics was supplemented by studying its integral structural characteristics, such as density and porosity. Using a temporary technological binder on both aqueous and non-aqueous basis, an increase in the density of the sintered $BaTiO_3$ ceramics was observed with an increase in the compaction pressure from 50 to 150 MPa and a sintering temperature in the range 1250–1350 °C, but the character of this growth was different in the two cases (Fig. 7). Ceramics prepared with the use of paraffin (Fig. 7, b) possessed a relative density of 0.82 at the lowest values of applied pressure and firing temperature (50 MPa and 1250 °C) to 0.87 at the highest values of these parameters (150 MPa and 1350 °C). In the case of using PVA as a binder (Fig. 7, a), the relative density of the ceramics increased from 0.65 to 0.89 with a similar change in the parameters of sintering. Under the mildest operating conditions (50 MPa and 1250 °C), the density of the obtained ceramics slightly differed from that of a green body. However, this value increased rapidly with increasing sintering temperature. When using paraffin, a significant compaction was achieved already at 1250 °C. For both types of binders it was characteristic that an increase in temperature of sintering led to a more pronounced densification of the samples than an increase in the compacting pressure. After the sintering at the highest of the temperatures used, samples prepared under the same conditions had close density values, regardless of the nature of the temporary technological binder.

The increase in the compacting pressure and the sintering temperature led to a significant reduction in the open porosity of the ceramics when either PVA or paraffin were used as temporary binders (Fig. 8). In samples pressed with paraffin, the maximum value of open porosity reached 14.3%, the minimum value was 2.4%. For samples from another series (PVA), these values corresponded to 31.9% and 4.8%, respectively. For each pair of values of compacting pressure and sintering temperature, the value of open porosity of ceramics prepared using PVA was 2–3 times higher than its value for ceramics pressed with paraffin. Taking into account that the maximum density of ceramics obtained with two different binders had similar values, it can be concluded that in samples prepared using paraffin, the proportion of closed pores was much higher than for samples with PVA. This indicated a more intensive growth of grains in samples with paraffin additive

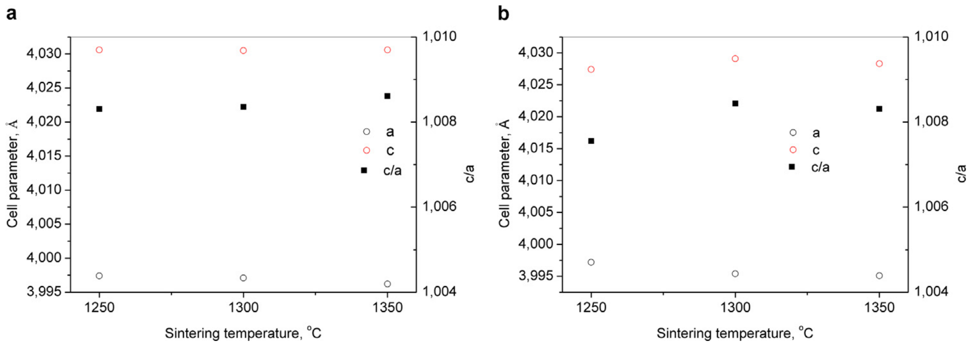

Fig. 5. Cell parameters and tetragonality *c/a* of $BaTiO_3$ ceramics produced by compaction at 150 MPa and sintering at 1250–1350 °C with the use of temporary technological binders: a – 5% aqueous PVA, b – paraffin.

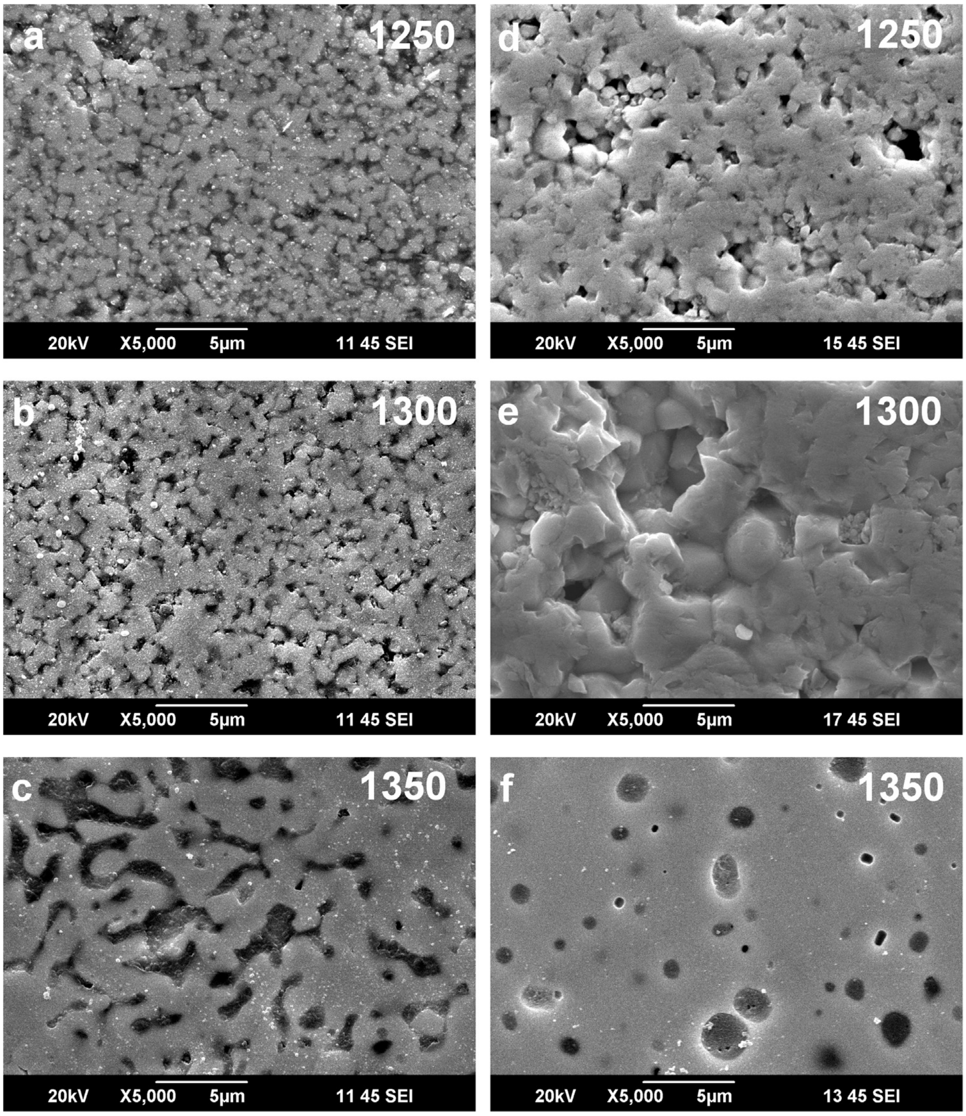

Fig. 6. SEM images of the surface of $BaTiO_3$ ceramics. Pressure of 150 MPa was applied for compaction of green bodies. The sintering temperature is indicated at each image. The temporary technological binders used: a, b, c – 5% aqueous PVA; d, e, f – paraffin.

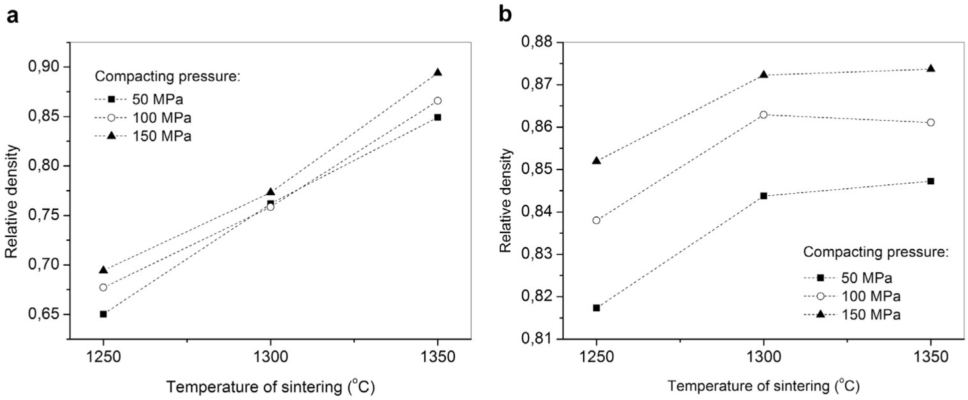

Fig. 7. Relative density of $BaTiO_3$ ceramics processed by compaction at 50–150 MPa and sintering at 1250–1350 °C with the use of temporary technological binders: a – 5% aqueous PVA, b – paraffin.

compared to samples originally containing PVA, and is consistent with the data of a microscopic study of the structure.

The type of temporary technological binder also had a significant effect on the compressive strength of ceramic samples (Fig. 9). On average $BaTiO_3$ ceramics have a compressive strength of about 300–450 MPa [37]. All the samples, prepared with the use of paraffin, possessed a higher compressive strength than samples from the series with PVA. In the case of PVA, a slight increase in the tensile strength

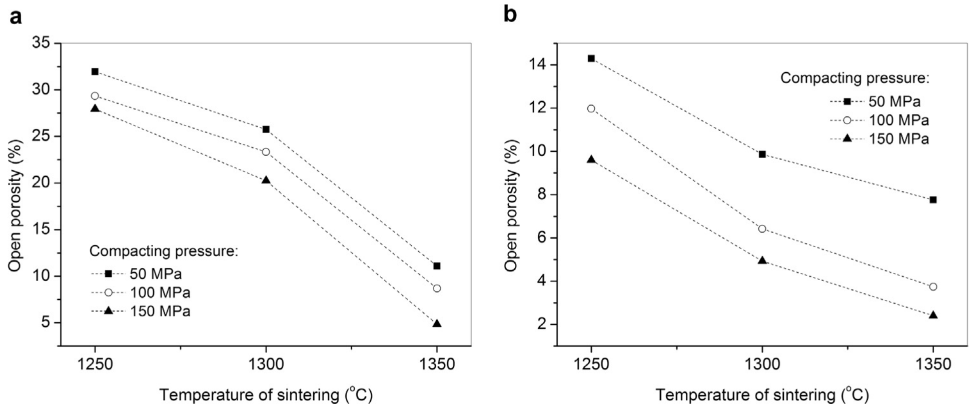

Fig. 8. Open porosity of $BaTiO_3$ ceramics processed by compaction at 50–150 MPa and sintering at 1250–1350 °C with the use of temporary technological binders: a – 5% aqueous PVA, b – paraffin.

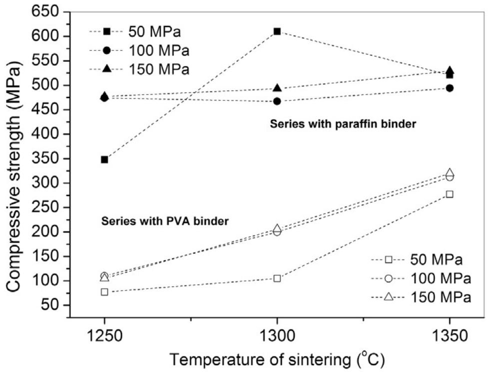

Fig. 9. Compressive strength of $BaTiO_3$ ceramics processed by compaction at 50–150 MPa and sintering at 1250–1350 °C with the use of 5% aqueous PVA or paraffin as temporary technological binders.

was observed with an increase in the compacting pressure and a more pronounced growth - with an increase in the sintering temperature. The ultimate strength as a whole increased from 77 to 320 MPa. With the use of paraffin as a binder, the increase in the tensile strength of samples with pressure and temperature was less significant (from 448 to 529 MPa). Thus, the samples of the series produced with addition of paraffin possessed an increased compressive strength.

As a result of pressing and sintering of press powders with two types of temporary technological binder (paraffin and aqueous PVA solution) having close rheological properties and the compacting ability, two series of samples of ceramics with different properties were obtained. Comparison of the structural characteristics of samples from two series showed that when using paraffin as a binder, the powder particles exhibited higher activity during sintering and subsequent grain growth than when using PVA. The essential difference in the properties of the obtained ceramics with two different types of binders was determined to a large extent by the process of their removal from bodies during heating. As it was shown above, paraffin removal began with its melting and outflow from the body and was accompanied by the action of pulling capillary forces on the powder particles, thereby promoting their mutual orientation and additional compaction [38]. The changes to which PVA underwent on heating occurred inside the body. In the initial stages, additional connection of molecular chains was possible with an increase in the degree of polymerization. As a result, agglomerates of $BaTiO_3$ particles were separated by polymer films. Later on, when the polymer burned out, the body underwent mechanical stress due to the pressure gradient caused by the flow of gases from the inside. Thus, when using PVA in the process of pressing, further compaction and rearrangement of the structure of the samples during sintering was difficult. The effect of compacting the body, accompanying the removal of paraffin, had a positive effect on the uniformity and mechanical strength of the resulting ceramics.

3.3. Electrophysical properties of $BaTiO_3$ ceramics

The most important characteristics of ceramic materials for capacitors are electrical conductivity, dielectric permittivity and dielectric losses. To estimate the electrical conductivity, the inverse of the conductivity is often used, the resistance. Fig. 10 shows the dependence of the specific volume resistance of $BaTiO_3$ ceramics on the conditions of its fabrication. With the increase in the sintering temperature, a pronounced increase in the resistivity of the ceramics prepared with the use of paraffin as a binder was observed (Fig. 10, b). This result

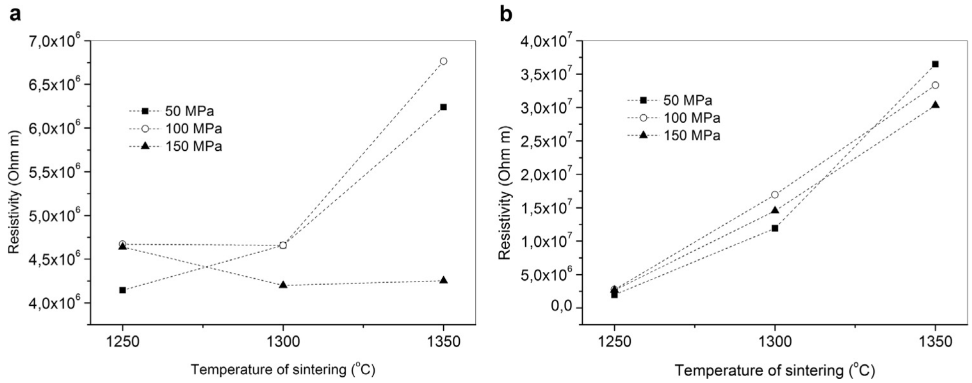

Fig. 10. Specific volume resistance of $BaTiO_3$ ceramics processed by compaction at 50–150 MPa and sintering at 1250–1350 °C with the use of temporary technological binders: a – 5% aqueous PVA, b – paraffin.

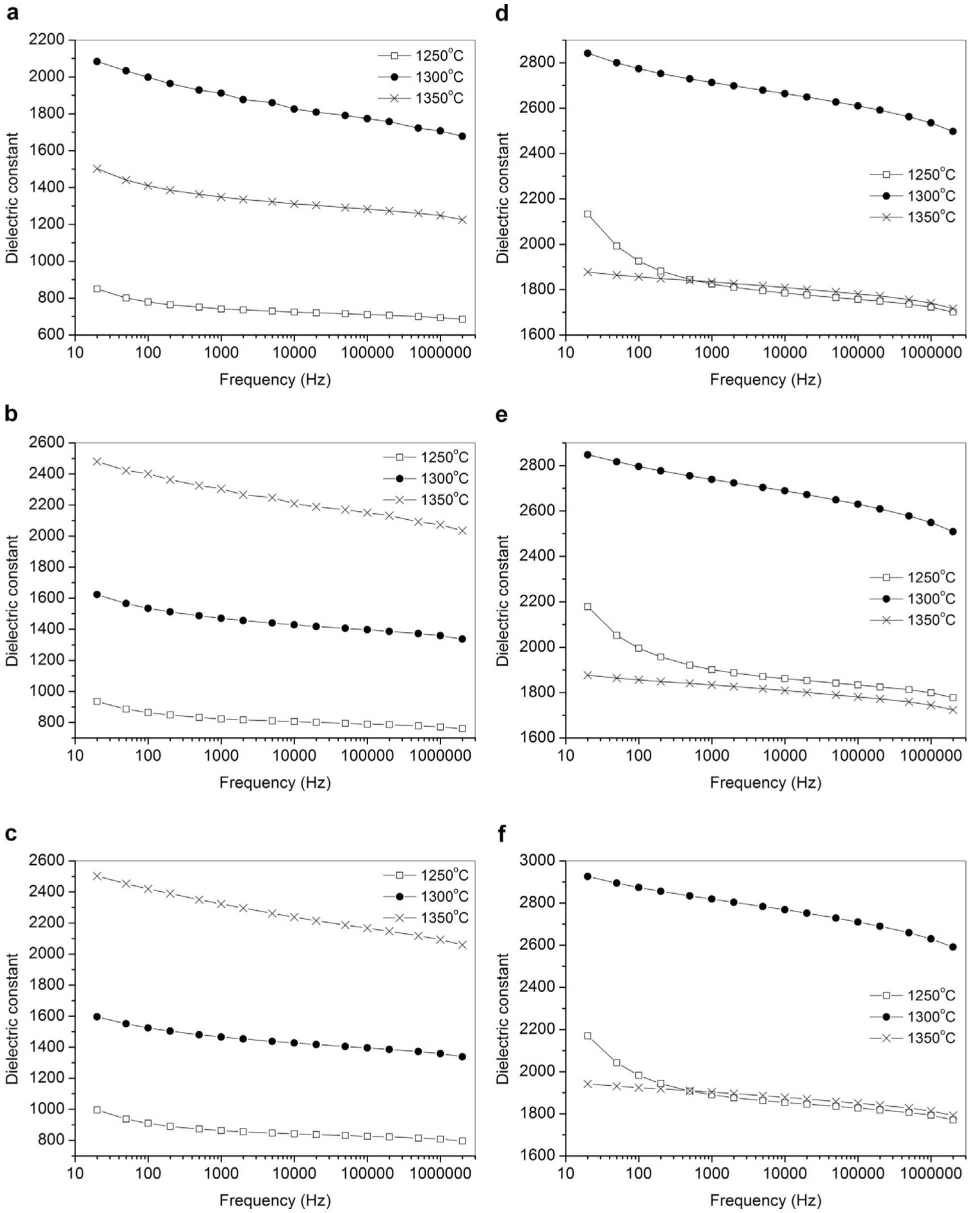

Fig. 11. Frequency dependence of dielectric permittivity of $BaTiO_3$ ceramics processed by compaction at 50–150 MPa and sintering at 1250–1350 °C with the use of temporary technological binders: a-c – 5% aqueous PVA, d-f – paraffin.

conformed to the data on the density and porosity of these samples. Moisture inevitably contained in open pores under experimental conditions increased the conductivity of the material and reduced its resistance [39]. Thus, the smallest values of resistivity corresponded to the most porous samples in this series. In a series of samples manufactured using PVA, the resistivity had lower values, and the dependence on the sintering temperature was less pronounced (Fig. 10, a).

Fig. 11 shows the frequency dependences of the dielectric permittivity of $BaTiO_3$ ceramics fabricated with the use of paraffin and PVA. Permittivity increased with decreasing frequency. In the low-frequency region, the dielectric was polarized due to the redistribution of free charges in its volume [28]. In the region of medium frequencies, this type of polarization contributed less to its overall value, and the dielectric constant of the samples reached the plateau. In a series of samples prepared using paraffin as a binder (Fig. 11, d-e), the highest permittivity values (2590–2700) were achieved after the sintering at temperature of 1300 °C. For ceramic samples prepared with addition of PVA, the maximum permittivity values (2050–2150) were recorded after the sintering at 1350 °C (Fig. 11, a-c). It should be noted that the nature of the changes in permittivity with the sintering temperature correlated with the changes in the tetragonality *c/a* in both series of samples (see Fig. 5). The ratio *c/a*, characterizing the degree of tetragonal distortion of the $BaTiO_3$ cell, is considered as an indirect estimate of the permittivity, since distortion is the main reason for the high permittivity of this material [40]. The microstructure features, such as porosity and the presence of an amorphous phase prevent spontaneous polarization and lead to a decrease in tetragonality *c/a* and dielectric permittivity. Along with this, an important role for the value of permittivity is played by the grain size and the effect of paraelectric grain boundaries [41]. George et al. [42] fabricated $BaTiO_3$ ceramics with a grain size of 0.5–2 µm and a relative density of about 97%, having a dielectric constant of 1223 at room temperature at a field frequency of 1 MHz. Bocquet et al. [43] reported for a similar ceramics $\varepsilon = 2000$. For ceramics $BaTiO_3$ with a grain size of 0.2–0.8 µm and a density of 98%, the value $\varepsilon = 2780$ is given in their work. Ávila et al. [44] reported a value of $\varepsilon = 1000–1100$ with a grain size of 0.2–0.8 µm, but a lower relative density of 83–90%.

The increase in the dielectric constant and the loss tangent at low

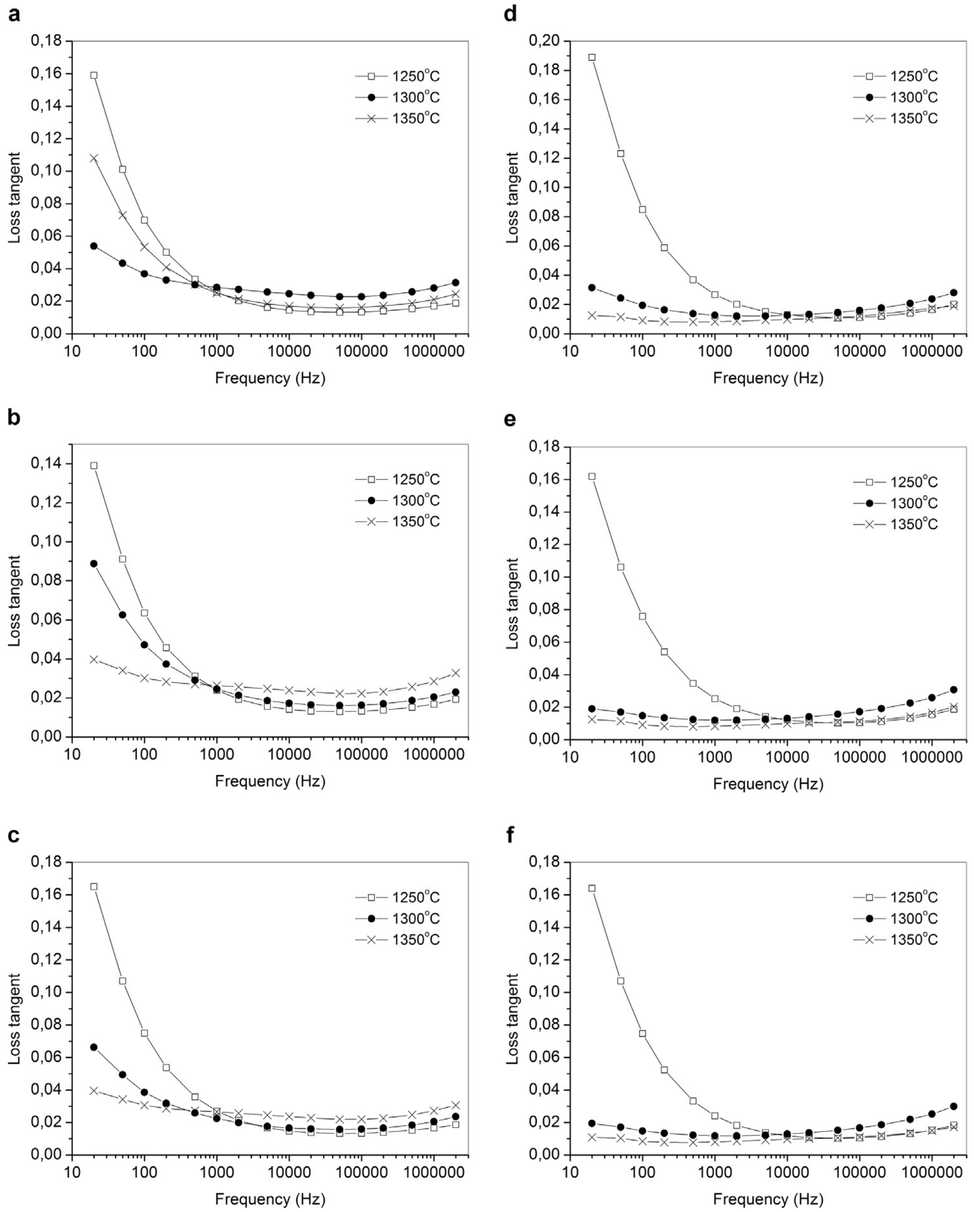

Fig. 12. Frequency dependence of loss tangent of $BaTiO_3$ ceramics processed by compaction at 50–150 MPa and sintering at 1250–1350 °C with the use of temporary technological binders: a-c – 5% aqueous PVA, d-f – paraffin.

frequencies depend to a large extent on the conditions of the sintering [28]. Fig. 12 showed that at a low compacting pressure (50 MPa) and low sintering temperature (1250 °C), the greatest increase in dielectric losses occurred in the considered frequency range, both in a series prepared with the use paraffin and in a series with PVA. Ceramics with the lowest dielectric losses (0.007–0.011) and the least pronounced its frequency dependence was obtained with the use of paraffin during sintering at 1300–1350 °C. One of the lowest values of $tg\delta = 0.0035$ for $BaTiO_3$ ceramics is given in [42]. High, but acceptable, values for such ceramics are the results of [45], which are 0.021–0.037. In ceramic materials, dielectric losses are usually made up of the energy expended on electrical conductivity, polarization, and ionization of gases contained in pores [46]. For ferroelectric materials, the largest contribution is made by losses to polarization.

A study of ceramics prepared from fine-crystalline $BaTiO_3$ synthesized in supercritical water showed the perspective of its use for the production of capacitor ceramics with high dielectric characteristics. Depending on the model of the capacitor and its application, the ceramic layer performs different permittivity (from 100 up to 18,000) and the loss tangent in a certain range of operating temperatures (−55…125 °C) [9,10]. The achievement of the required characteristics occurs, in particular, by chemical modification of barium titanate. According to research data and industrial report, the ceramics produced from pure barium titanate powder and recommended for production of capacitors were characterized by a permittivity of 1050–3000 and a loss tangent of the order of 10^{-2} at room temperature [47–49]. In the current work, comparable results were obtained on the dielectric constant of ceramics from pure barium titanate powder. When using the technology of semidry pressing with high-temperature sintering, the best functional properties were obtained for the $BaTiO_3$ material compacted with the use of paraffin as a temporary technological binder.

4. Conclusion

In the present work, the process of sintering of fine-crystalline $BaTiO_3$ synthesized in supercritical water in accordance with the previously developed technique was studied in detail. The structural, mechanical and electro-physical properties of the ceramics obtained from

$BaTiO_3$ powder were studied. The nature of the temporary technological binder and the mechanism of its removal during the sintering of ceramics had a significant influence on the microstructure and dielectric characteristics of the final $BaTiO_3$ material. Ceramics with homogeneous structure were obtained from the synthesized powder using paraffin as a temporary technological binder by pressing at 100–150 MPa and subsequent sintering at a temperature of 1300 °C. The dielectric constant of the prepared ceramics (88% of theoretical density) was 2819 at 1 kHz and 2630 at 1 MHz. Based on the obtained result, it can be concluded that $BaTiO_3$, synthesized in supercritical water medium, is a promising raw material for the production of capacitor ceramics.

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