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*Research Article*

# Synthesis and Characterization of Low Loss Dielectric Ceramics Prepared from Composite of Titanate Nanosheets with Barium Ions

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We report a strategy for preparing barium titanate precursor, being the composite of titanate nanosheets (TN) with barium ions (Ba-TN), which subjected to step sintering allows obtaining $TiO_2$ rich barium titanate ceramics of stoichiometry $BaTi_4O_9$ or $Ba_2Ti_9O_{20}$. These compounds are important in modern electronics due to their required dielectric properties and grains' size that can be preserved in nanometric range. The morphology studies, structural characterization, and dielectric investigations were performed simultaneously in each step of Ba-TN calcinations in order to properly characterize type of obtained ceramic, its grains' morphology, and dielectric properties. The Ba-TN precursor can be sintered at given temperatures, so that its dielectric permittivity can be tuned between 25 and 42 with controlled temperature coefficients that change from negative 32 ppm/°C for Ba-TN sintered at 900°C up to positive 37 ppm/°C after calcination at 1300°C. XRD analysis and Raman investigations performed for the Ba-TN in the temperature range of 900 ÷ 1250°C showed that below 1100°C we obtained as a main phase $BaTi_4O_9$, whereas the higher calcinations temperature transformed Ba-TN into $Ba_2Ti_9O_{20}$. Taking into account trend of device miniaturization and nanoscopic size requirements, temperatures of 900°C and 1100°C seem to be an optimal condition for Ba-TN precursor calcinations that guarantee the satisfactory value of dielectric permittivity ($\varepsilon$ = 26 and 32) and ceramic grains with a mean size of ~180 nm and ~550 nm, respectively.

## 1. Introduction

Barium titanate ceramic materials have long history in electrotechnical applications. These dielectric oxide ceramics serve as microwave resonators and they are main components of many devices like cellular phones, global positioning system, and environmental monitoring systems on satellites [1]. The main aim of research in this area is to develop new materials or improve properties of already known systems (i.e., reducing dielectric loss and increasing dielectric permittivity). Recent revolutionary changes in wireless communication were achieved by reducing size and cost of components made from improved microwave ceramics. Wide variety of polytitanates has been synthesized and characterized up to now. Among them, particularly a $BaO$-$TiO_2$ system with Ti rich region is interesting because it exhibits eligible electrical properties like good electrical permittivity and low dielectric loss at radio frequencies. $BaTi_4O_9$, $BaTi_5O_{11}$, and $Ba_2Ti_9O_{20}$ are prominent low loss dielectric compounds in this group. $BaTi_4O_9$ as dielectric ceramic was for the first time reported by Masse et al. [2] at early 1970 and had a huge contribution to a breakthrough in dielectric resonators ceramic technology. Conventional method for the preparation of $BaTi_4O_9$ is the solid state ceramic route by ball milling of

stoichiometric amounts of $BaCO_3$ and $TiO_2$ for about 24 hours [3, 4] and sintering at about 1100°C. It is then again ball milled, pelletized, and sintered at about 1350°C to achieve densification of the ceramic body. Wet chemical methods, such as oxalate [5] and citrate route [6] as well as modified Pechini method [7], were also applied for $BaTi_4O_9$ powders preparation. Cernea et al. [5] obtained $BaTi_4O_9$ from oxalates and documented its stable dielectric properties: dielectric permittivity $\varepsilon = 38$, quality factor $Q = 3800 \div 4000$ at 6÷7 GHz, and temperature coefficient $\tau_f = 11$ ppm/°C. Pure $BaTi_4O_9$ suffers from relatively high values of temperature coefficient, so it is not very suitable as dielectric resonator. Hence the dielectric properties of $BaTi_4O_9$ phase are often modified by using different additives [8]. $BaTi_5O_{11}$ synthesis was for the first time described by Tillmanns, but it was not pure phase but mixed with rutile [9]. Single-phase $BaTi_5O_{11}$ was prepared by wet chemical methods like citrate route [10] or sol-gel [11]. This phase is stable under heating up to 1200°C, then, it decomposes into $TiO_2$, $Ba_2Ti_9O_{20}$, and/or $BaTi_4O_9$. $BaTi_5O_{11}$ phase has higher dielectric constant and quality factor compared to $BaTi_4O_9$; however the values of $\tau_f$ are also higher. Fukui et al. prepared $BaTi_5O_{11}$ by sol-gel method after heating at 1120°C for 48 hours. Obtained samples exhibited dielectric permittivity equal to 42, $Q \times f > 60{,}000$ GHz, and $\tau_f = 39$ ppm/°C [12]. $Ba_2Ti_9O_{20}$ can be conventionally synthesized by mixing $BaCO_3$ and $TiO_2$ in appropriate stoichiometry and calcined at about 1200°C, again milled, pelletized, and sintered at about 1400°C for 3 hours [13]. $Ba_2Ti_9O_{20}$ obtained by solid state synthesis usually coexists with $BaTi_4O_9$ phase as it is thermodynamically stable in the vicinity of the desired composition. However, pure phase synthesis was achieved by wet chemistry methods. Lu et al. [11] described synthesis based on mixing methanol solution of barium hydroxide with titania sol obtained from hydrolysis of titanium alkoxide. Obtained xerogel was stepwise heated up to 1100°C giving $BaTi_5O_{11}$ phase, while prolonged heating at 1200°C gave pure $Ba_2Ti_9O_{20}$. Fang et al. [14] prepared $Ba_2Ti_9O_{20}$ in reaction of $BaTi_4O_9$ with $TiO_2$ and sintering at 1390°C. Obtained sample showed grain size of about 2-3 micrometers and high sintered density of 99%. The dielectric permittivity was equal to 39, quality factor was 42000 GHz, and the temperature coefficient reached 5 ppm/°C. $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ have similar values of dielectric permittivity and quality factors. $BaTi_4O_9$ has temperature coefficient close to zero and is always positive, while reported values of $\tau_f$ for $Ba_2Ti_9O_{20}$ are close to zero as well as being negative in some reports [10].

The method of mixing of two low loss ceramic materials with positive and negative temperature coefficient has become well known [15]. This kind of approach is very convenient for preparation of new materials with desired properties by simple selection of proper components. However, very often it is difficult to obtain material with expected intermediate properties because it is impossible to retain individual character of components during sintering process. Thus, development of new precursors of barium titanates and study of their temperature transformation and dielectric properties are still very attractive.

The aim of this work was to develop a method for $TiO_2$ rich barium titanates synthesis by employing titanate nanosheets (TN). They have an orthorhombic layered structure that is composed of corrugated host layers of edge-shared octahedra and interlayer (tetramethyl)ammonium ions ($TMA^+$) compensating for the negative charge which arises from substitution of lower valence metal ions or vacancies of Ti [16]. These $TMA^+$ ions are exchangeable with a variety of inorganic and organic ions and in this way the TN is an ideal candidate for host-guest chemistry as well as ion exchange [17]. The ion exchangeability also provided the opportunity to prepare precursor of ceramics. For example, potassium hexatitanate ($K_2Ti_6O_{13}$) was prepared by ion exchange, followed by heat treatment at 600°C [18]. Taking this into consideration, in this work we applied TN in ion exchange process to immobilize barium ions from solution. The obtained by this way composite, under a thermal treatment in moderate temperature in air, transformed to $BaTi_4O_9$, $BaTi_5O_{11}$, and $Ba_2Ti_9O_{20}$ phases with desired dielectric properties.

## 2. Experimental Section

All reagents were used as received without further purification.

*Synthesis*. 250 ml aqueous solution of barium acetate monohydrate (5.45 g; 20 mol, purchased from Polish Chemical Reagents, POCH, Gliwice, Poland) was mixed with 250 ml aqueous colloidal solution of titanate nanosheets, TN (2.5 g; $R$ = 0,6). The details of preparation and characterization of TN have been reported elsewhere [19]. After mixing solutions, ion exchange reaction between (tetramethyl)ammonium ions from TN and barium cations from barium acetate in aqueous environment led to precipitation of the powder. The mixture was heated for 10 h at room temperature under stirring and next without stirring for 10 h at 90°C. After the reaction, the precipitate was separated by centrifugation, washed with water until pH 7, and dried under vacuum. The total yield of dried organic-inorganic powder was 2.3 g and it is labeled as Ba-TN or precursor of barium titanate. The Ba-TN powder after reaction was subjected to calcination at 500°C for 1 hour and pressed to get a pellet under pressure of 436 MPa for 10 min. Based on thermogravimetric measurement (data not shown) temperature of 500°C was chosen as an optimal one that allows a decomposition of the organic part of the precursor and the evaporation of volatile products from the sample. The higher temperatures allow for thermal diffusion of the reagents throughout the volume to facilitate the reaction that produces barium titanate ceramic. The pellet was sintered at 900°C for 4 hours and then subsequently at 950°C, 1000°C, 1050°C, 1100°C, 1150°C, 1200°C, 1250°C, and 1300°C for 2 h in each temperature. The time of sintering was chosen according to research of Pfaff who found that at temperature higher than 900°C a densification parameter of $BaTi_4O_9$ is constant after two hours of heat treatment [20]. During the applied step sintering procedure the mean particle diameter was investigated and pellets' green density calculated simultaneously with its phase transformation and dielectric properties studies.

## 3. Characterization

Raman investigations were performed using a Fourier Transform Raman spectrometer (Bruker). All spectra were recorded in the macrochamber light scattering mode; the Raman spectra were obtained at 20°C using the Nd:YAG laser wavelength $\lambda = 1064$ nm.

Room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer in the Bragg–Brentano reflection geometry. Copper $CuK_\alpha$ radiation was used from a sealed tube. Data were collected in the $2\theta$ range 5–90° with a step of 0.0167° and an exposure per step of 20 s. The samples were spun during data collection to minimize preferred orientation effects. For phase analysis, the PANalytical High Score Plus software package was used combined with the International Centre for Diffraction Data's (JCPDS) powder diffraction file (PDF-2 ver. 2009) database of standard reference materials.

Particle sizes of Ba-TN obtained in different step of calcination were estimated from SEM images that were collected using a Hitachi S3400N scanning electron microscope with accelerating voltage of 25000 V.

The dielectric properties of synthesized sample were investigated using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer equipped with Quatro Cryosystem in the frequency range of $10^{-1} \div 10^{6}$ Hz and in the temperature range of −140°C ÷ 200°C (in steps of 10°C). The obtained complex dielectric function ($\varepsilon^*$) was measured by

$$\varepsilon^* = \varepsilon' - i\varepsilon'', \quad (1)$$

where $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts, respectively.

Before electric measurement each pellet was additionally dried at 90°C under reduced pressure in order to exclude the influence of the humidity. To provide good contact between the sample and external electrodes during electrical investigations, 150 nm thick gold electrodes were deposited on both sites of the pellet. The densities of the samples sintered at different temperatures were evaluated based on the external dimensions and mass of the pellets. The relative density of pellets was estimated through comparison with theoretical crystallographic density of the major crystallographic phase defined from Raman and XRD investigations.

## 4. Results and Discussion

Raman spectra of the samples before and after the ion exchange are shown in Figure 1. For TN in Figure 1(a), the spectrum is essentially the same as the data reported for titanate nanosheets intercalated by $TMA^+$ ions [21]. According to the literature [21, 22] Raman bands observed at 275 $cm^{-1}$, 384 $cm^{-1}$, 448 $cm^{-1}$, 662 $cm^{-1}$, 883 $cm^{-1}$, and 899 $cm^{-1}$ can be attributed to the Ti-O lattice vibrations in the $TiO_6$ octahedral host layers and the strong peaks at 756 $cm^{-1}$ and 954 $cm^{-1}$ were related to (tetramethyl)ammonium ions ($TMA^+$). These two peaks just disappear after the exchange reaction-replacement (Figure 1(b)) of $TMA^+$ ions in TN by barium ions. The Raman vibration assigned to Ti-O still exists which is a convenient proof that 2D structure of TN

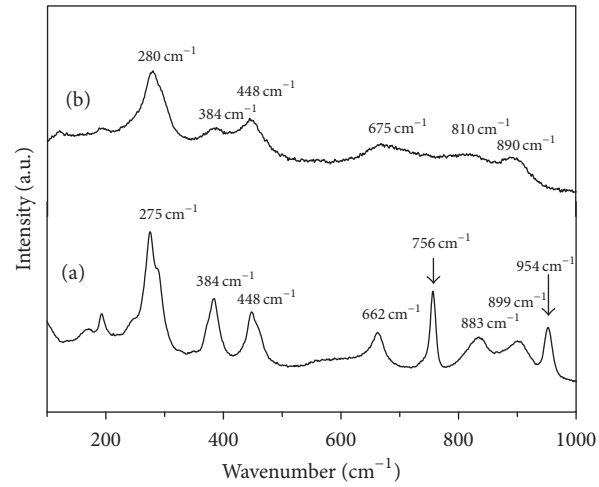


Figure 1: Raman spectra of dried (a) titanate nanosheets, TN, and (b) precipitate Ba-TN.

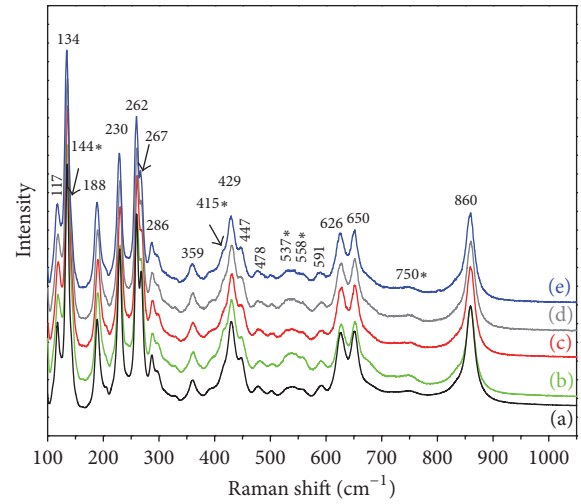


Figure 2: Raman spectra collected at room temperature for Ba-TN after sintering at (a) 900°C, (b) 950°C, (c) 1000°C, (d) 1050°C, and (e) 1100°C. Raman bands characteristic for $BaTi_5O_{11}$ are labeled by stars.

was preserved. However, peaks at 600–1000 $cm^{-1}$ spectral region shift to lower frequencies which could be affected by a presence of $Ba^{2+}$ ions in the interlayer of TN [23]. Obtained powder of Ba-TN could be considered as a precursor of $BaTi_4O_9$ since, after the thermal treatment at 900°C for 4 h, it gave the characteristic Raman spectrum for this compound (Figure 2(a)). One can observe bands located at 117 $cm^{-1}$, 134 $cm^{-1}$, 188 $cm^{-1}$, 230 $cm^{-1}$, 262 $cm^{-1}$, 267 $cm^{-1}$, 286 $cm^{-1}$, 359 $cm^{-1}$, 429 $cm^{-1}$, 447 $cm^{-1}$, 478 $cm^{-1}$, 591 $cm^{-1}$, 626 $cm^{-1}$, 650 $cm^{-1}$, and 860 $cm^{-1}$ that are characteristic for $BaTi_4O_9$ [24] according to work of Rössel et al. Further sintering at temperature range between 950°C and 1100°C, during 2 h at each temperature, gave the Raman spectra of the same intensity and identical Raman bands as observed for Ba-TN sintered at 900°C (see Figure 2(b–e)). These results allow for conclusion that there was not any phase transformation

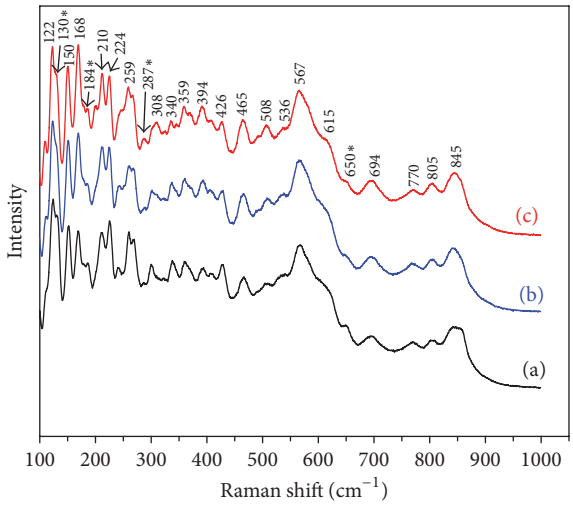


FIGURE 3: Raman spectra collected at room temperature for Ba-TN after sintering at (a) 1150°C, (b) 1200°C, and (c) 1250°C. Raman bands assigned to $BaTi_4O_9$ are marked by stars.

during the applied thermal treatment in the temperature range between 900°C and 1100°C. Moreover sharpness of Raman peaks denotes well crystallized structure that was independently revealed by X-ray diffraction studies. Detailed analysis of the recorded Raman spectra allowed observing bands of lower intensity which are located at 144 cm$^{-1}$, 415 cm$^{-1}$, 537 cm$^{-1}$, 558 cm$^{-1}$, and 750 cm$^{-1}$. They are marked by stars (in Figure 2) and their occurrence indicates the presence of barium titanate of stoichiometry $BaTi_5O_{11}$.

Figure 3 shows Raman spectra for Ba-TN precursor sintered for 2 h at (a) 1150°C, (b) 1200°C, and (c) 1250°C, on which one can observe a significant change of the spectra as compared to Raman spectrum of precursor sintered up to 1100°C. In Figure 3(a–c) there are Raman bands characteristic for $BaTi_4O_9$ phase that almost totally disappeared with exception of the bands located at 130 cm$^{-1}$, 184 cm$^{-1}$, 287 cm$^{-1}$, and 650 cm$^{-1}$. For the precursor sintered at the temperatures of 1150°C and higher, there are detected Raman bands located at 122 cm$^{-1}$, 150 cm$^{-1}$, 168 cm$^{-1}$, 210 cm$^{-1}$, 224 cm$^{-1}$, 259 cm$^{-1}$, 308 cm$^{-1}$, 340 cm$^{-1}$, 359 cm$^{-1}$, 394 cm$^{-1}$, 426 cm$^{-1}$, 465 cm$^{-1}$, 508 cm$^{-1}$, 536 cm$^{-1}$, 567 cm$^{-1}$, 615 cm$^{-1}$, 694 cm$^{-1}$, 770 cm$^{-1}$, 805 cm$^{-1}$, and 845 cm$^{-1}$ that can be assigned to barium titanate of stoichiometry $Ba_2Ti_9O_{20}$. Raman spectra shown in Figure 3(a–c) have a very good agreement with work of Javadpour and Eror [25], who detected by Raman spectroscopy $Ba_2Ti_9O_{20}$ phase after long treatment at 1200°C, as well as with work of Xu et al. [26].

The XRD diffraction patterns of the Ba-TN samples after sintering at 900°C–1250°C are shown in Figure 4. The XRD analysis revealed that below 1100°C we observed as a main phase orthorhombic $BaTi_4O_9$ (JCPDS number 34-0070) and the presence of $BaTi_5O_{11}$ (JCPDS number 35-0805) as secondary phase. The increase of the calcination temperature above 1100°C caused the phase transition and crystallization of $Ba_2Ti_9O_{20}$ (JCPDS number 40-0405), but the peaks attributed to $BaTi_4O_9$ were still visible. These results

TABLE 1: Phase composition [% w/w] of Ba-TN sintered at different temperatures estimated from XRD patterns.

| Phase | Temp. | | | | |
|---|---|---|---|---|---|
| | 900°C | 1100°C | 1150°C | 1200°C | 1250°C |
| $BaTi_4O_9$ | 66 | 42 | 8 | 6 | 6 |
| $BaTi_5O_{11}$ | 34 | 45 | — | — | — |
| $Ba_2Ti_9O_{20}$ | — | 13 | 92 | 94 | 94 |

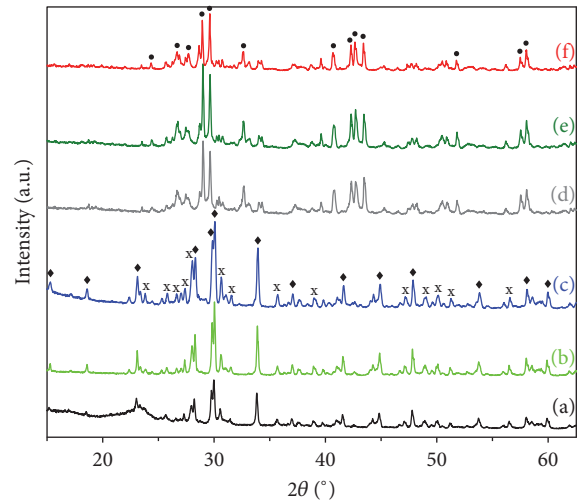


FIGURE 4: XRD patterns of Ba-TN after sintering at (a) 900°C, (b) 950°C, (c) 1100°C, (d) 1150°C, (e) 1200°C, and (f) 1250°C (◆: $BaTi_4O_9$; x: $BaTi_5O_{11}$; ●: $Ba_2Ti_9O_{20}$).

are in good agreement with Raman spectra, where phase transformation of $BaTi_4O_9$ into $Ba_2Ti_9O_{20}$ was also observed for Ba-TN sintered at temperature higher than 1100°C. The quantitative phases composition of the studied samples was estimated on the basis of XRD spectra using the reference intensity ratio (RIR) method [27] and the obtained data are gathered in Table 1. The RIR method involves comparing the intensity of one or more peaks of a phase with the intensity of a peak of a standard (usually the corundum 113 reflection) in a 50 : 50 mixture by weight. For the processing of diffraction data the PANalytical High Score Plus software package was used.

It was found that in the effect of sintering at 900°C the $BaTi_4O_9$ phase constituted 66% w/w and $BaTi_5O_{11}$ 34% w/w of the sample. An increase of the temperature to 1100°C induced certain changes in phase composition. A proportion of $BaTi_4O_9$ to $BaTi_5O_{11}$ phases slightly changed into ratio 42/45% w/w and a new phase showed up – $Ba_2Ti_9O_{20}$ with the content of 11% w/w. The rise of the temperature of only 50°C resulted in very significant changes in phase composition. $BaTi_5O_{11}$ phase disappeared completely and new phase, that is, $Ba_2Ti_9O_{20}$ with a content of 92% w/w and $BaTi_4O_9$ with a content of 8% w/w, was observed. Further increase of sintering temperature up to 1200°C and 1250°C did not influence significantly the phase composition. The $Ba_2Ti_9O_{20}/BaTi_4O_9$ weight ratio was estimated at 94/6% w/w for higher sintering temperatures. The observed changes

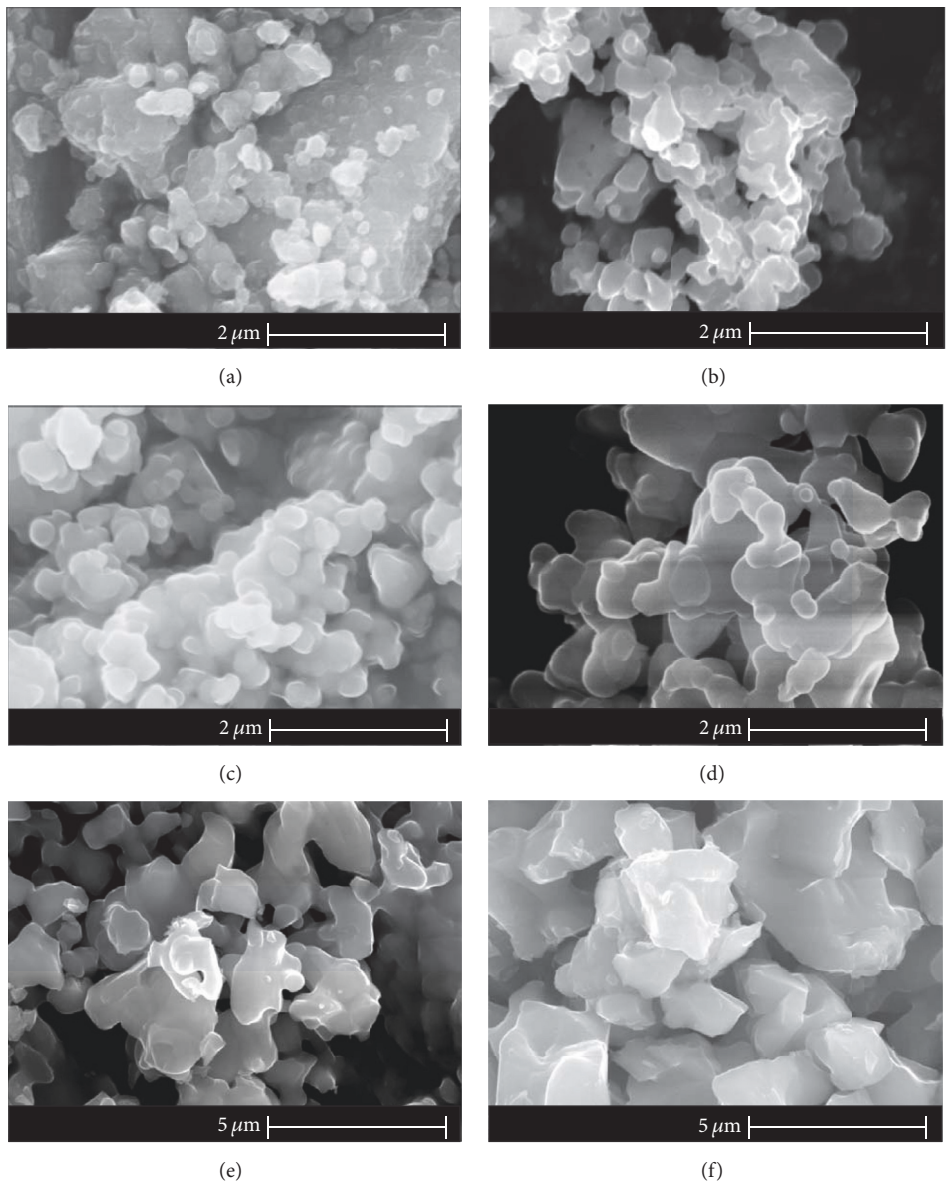


Figure 5: SEM images of Ba-TN subjected to step sintering at (a) 500°C, (b) 950°C, (c) 1050°C, (d) 1100°C (magnification 10k), (e) 1150°C, and (f) 1200°C (magnification 25k), collected with accelerating voltage 25 kV.

are in good agreement with observation made by Raman spectroscopy. However, the scattering intensities of $BaTi_5O_{11}$ and $Ba_2Ti_9O_{20}$ phases are markedly lower than $BaTi_4O_9$. Thus $Ba_2Ti_9O_{20}$ phase was not observed by Raman spectroscopy after the sample sintering at the temperature of 1100°C, but only after treatment at the temperature of 1150°C where the domination of this phase was reached.

Figure 5 illustrates SEM images of Ba-TN powder subjected to calcination at 500°C for 1 hour and sintering for 2 h at the temperature range from 950°C to 1200°C. Mean size of grains and standard deviation, evaluated on the basis of SEM images analysis, are presented in Figure 6, in relation to sintering temperature. The grain size of Ba-TN precursor annealed at 500°C and 950°C kept constant value below 200 nm.

After the sintering at the temperature of 1050°C the particles were still characterized by narrow size distribution and sphere-like grains morphology; however mean size increased to c.a. 400 nm and size distribution significantly widened. A shift of sintering temperature to 1100°C induced evident changes in morphology; partial coarsening of grains occurred. At the temperature of 1150°C and higher, the sphere-like morphology of grains disappeared and irregular agglomerates and large grains were mainly observed. The mean size of grains increases up to about 1.0 $\mu$m and 1.6 $\mu$m for the temperatures 1150°C and 1200°C, respectively. In the case of Ba-TN sintered at 1200°C irregular agglomerates of rounded shape transformed into sharp angular grains. A marked change in grains' size and morphology observed at the temperature above 1100°C coincides with the structural

Table 2: Pellets filling percentage and dielectric properties of the Ba-TN precursor sintered at different temperatures.

| Sintering temperature of Ba-TN precursor [°C] | Relative density [%] | Dielectric constant ($\varepsilon$) (at 1 MHz) | tan($\delta$) (at 1 MHz) | Quality factor ($Q$) at 1 MHz | Temperature coefficient ([c])ppm/°C |
|---|---|---|---|---|---|
| 900 | 64[a] | 25,7 | $4{,}2 * 10^{-4}$ | 2300 | −32 |
| 1100 | 78[a] | 32,4 | $8{,}7 * 10^{-5}$ | 11500 | −18 |
| 1200 | 85[b] | 35,1 | $7{,}7 * 10^{-5}$ | 13000 | 7 |
| 1250 | 88[b] | 37,6 | $7{,}5 * 10^{-5}$ | 13300 | 33 |
| 1300 | 98[b] | 42,0 | $1{,}5 * 10^{-5}$ | 66600 | 37 |

[a]Value calculated in regard to theoretical density of $BaTi_4O_9$; [b]value calculated in regard to theoretical density of $Ba_2Ti_9O_{20}$; [c]value calculated in a temperature range from −130°C to 100°C.

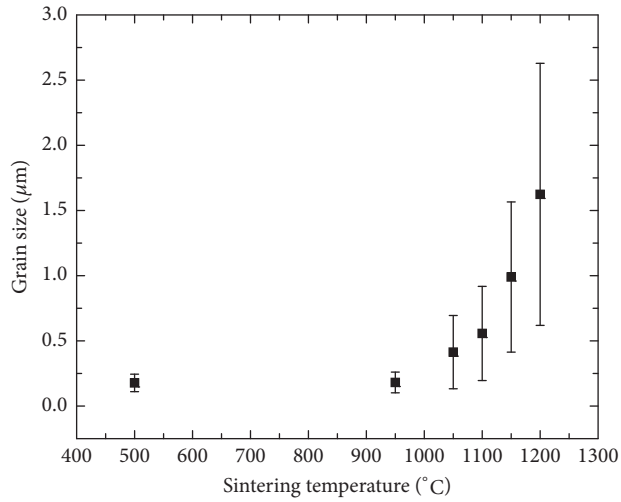


Figure 6: Grain size dependence as a function of calcination temperature.

transformation observed by Raman spectroscopy and XRD analysis.

The dielectric parameters of the sintered precursor are strictly dependent on densification behavior, that is, shrinkage of formed discs upon heating. From this reason the relative density and percentage of pellets' filling were investigated as a function of applied step sintering. It is well known that higher temperature of sintering rises these parameters; however in Figures 7(a) and 7(b) one can find some regimes that are distinguished by different behavior below and above temperature of 1050°C. Below this temperature the increase of relative density and percentage of pellets' filling is slow, whereas above 1050°C these parameters rise substantially. This caused a rapid pellet's contraction that can be connected with an acceleration of diffusion in solid state and initiation of neck formation between crystallites above this temperature, that is, in agreement with grains' morphology changes at 1100°C revealed by SEM investigations. Above this temperature there is a phase transformation of main ($BaTi_4O_9$) and secondary ($BaTi_5O_{11}$) phases into $Ba_2Ti_9O_{20}$ and concomitant further increase of pellets' relative density. The percentage of pellets' filling was calculated taking into account the theoretic density values of $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ that are equal 4,52 g/cm$^3$ (Pearson's Crystal Data, ICDD 04-007-2688) and 4,58 g/cm$^3$ (crystallographic data, reference code 00-035-0051), respectively. Finally after sintering at 1250°C calculated relative pellet's density was 4,01 g/cm$^3$ that corresponds to more than 85% of $Ba_2Ti_9O_{20}$ crystallographic density.

To characterize the dielectric properties of sintered at different temperatures Ba-TN pellets we applied broadband dielectric spectroscopy which allowed us to determine the following physical properties that are important for ceramic applications: dielectric permittivity ($\varepsilon$), quality factor ($Q$) defined as 1/tan ($\delta$), and temperature coefficient of resonant frequency ($\tau_\varepsilon$). Figure 8 shows three-dimensional graphs comprising the temperature-frequency representations of dielectric permittivity for Ba-TN sintered at 900°C (Figure 8(a)) and 1200°C (Figure 8(b)), respectively. The graphs clearly show that in very broad temperature and frequency ranges there is a lack of any relaxation process in the material. The increase in these variables at low frequencies and at high temperatures is connected with interfacial polarization or electrode polarization contribution that might be present under these conditions. These graphs are exemplary also for Ba-TN precursor sintered in other temperatures.

In Figure 9 the temperature dependence of dielectric permittivity of Ba-TN subjected to sintering at different temperatures is shown. All samples, in MHz frequencies, are characterized by very stable, flat response over broad range of temperatures (more than 230°C). One can observe an increase of $\varepsilon$ with sintering temperature that is connected to well known relationship between density of the sample and its dielectric properties, according to which higher density results in a higher dielectric permittivity and lower porosity, which improves also quality factor value $Q$. The relative density of ceramic pellets studied by us was varying from 64 to 96% (Table 2). It means that measured ceramics were partially porous and can be considered as capacitor composed of ceramic and air. Phase composition of measured sample (calculated from XRD, data gathered in Table 1) is another factor influencing dielectric permittivity. In the case of $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$, the maximum literature values of $\varepsilon$ were equal to 39 [5] and 52 [28], respectively. The Ba-TN subjected to step sintering in a range of temperatures from 900°C to 1300°C can be considered as a mixture of tetra- and nonatitanates; thus they are expected to possess intermediate dielectric properties. It can be concluded that Ba-TN precursor can be sintered at given temperatures, so that its dielectric permittivity can be tuned between 25 and

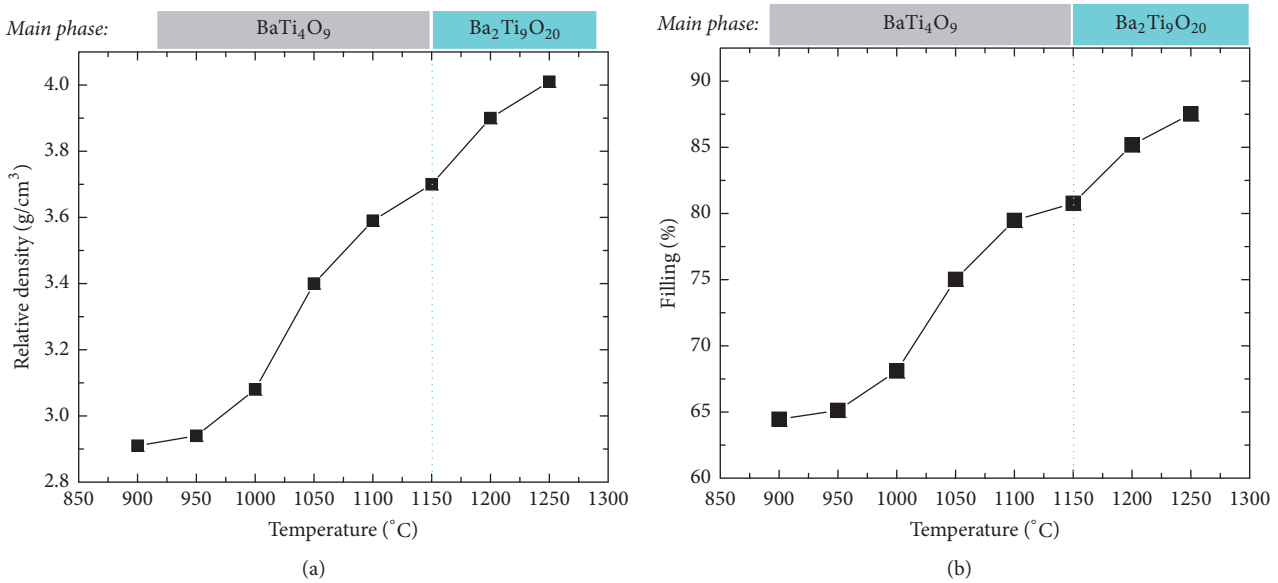


FIGURE 7: Dependence of pellet's relative density (a) and percentage of pellet's filling (b) on the Ba-TN sintering temperature.

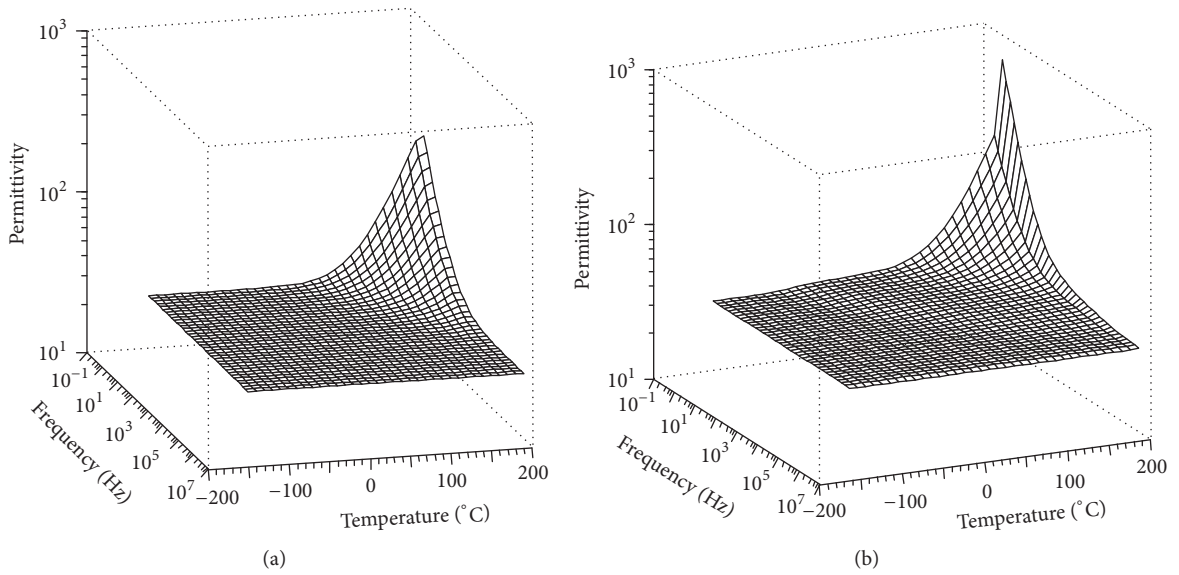


FIGURE 8: Temperature-frequency representation of dielectric permittivity Ba-TN sintered at (a) 900°C and (b) 1200°C.

42. Detected values of tan($\delta$), measured at 20°C for frequency 1 MHz, were also very interesting and vary from $4{,}2 * 10^{-4}$ (for Ba-TN sintered at 900°C) to $1{,}5 * 10^{-5}$ (for Ba-TN sintered at 1300°C). The lower value of loss tangent detected for samples sintered at higher temperatures can be connected to higher density of measured pellets. It can be noticed that $Q$ values arise with higher sintering temperature reaching a maximum value of 66,600 for sample sintered at 1300°C which exhibits the highest density equal to 4,42 g/cm$^3$, that is, 98% of $Ba_2Ti_9O_{20}$ theoretical density. This can be associated with a change of porosity, that is, higher density of pellets after treatment at higher temperature and it is in agreement with a statement according to which the porosity decreases the quality factor due to the presence of moisture in the pores.

From the representations given in Figure 5, the temperature coefficient ($\tau_\varepsilon$) was calculated as a function of temperature from −130°C to 100°C according to (2)

$$\tau_\varepsilon\Big|_{-130^\circ\mathrm{C}}^{100^\circ\mathrm{C}} = \frac{1}{\varepsilon_{(-130^\circ\mathrm{C})}}\left(\frac{\Delta\varepsilon}{\Delta T}\right) \text{ ppm/°C}. \quad (2)$$

It was observed that temperature coefficients changed from negative, for Ba-TN sintered up to 1100°C with $BaTi_4O_9$ as a main phase, to positive for Ba-TN sintered in a range of

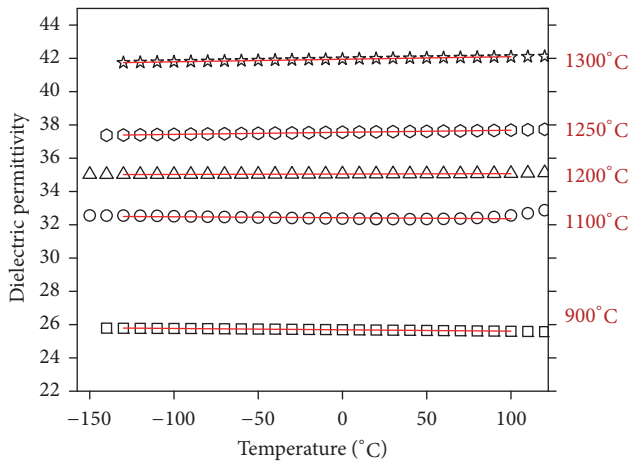


FIGURE 9: The temperature dependence of dielectric permittivity measured at 1.15 MHz of Ba-TN sintered at different temperatures. Red lines correspond to linear fits for calculation of temperature coefficients.

temperatures 1150 ÷ 1300°C with a main phase of $Ba_2Ti_9O_{20}$. This can be connected with phase transformation of $BaTi_4O_9$ into $Ba_2Ti_9O_{20}$ and low value of temperature coefficient for barium nonatitanate that was found equal to about 6 ppm/°C [28]. It should be emphasized that the dielectric properties of the investigated ceramics depend considerably on sintering temperature and their microstructures. According to this the temperature coefficient for $Ba_2Ti_9O_{20}$ may vary between −6 and 38 ppm/°C [10, 29]. Presented herein are dielectric results which are in agreement with results of Kumar et al. who obtained $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ ceramics by the wet chemical gel-carbonate method and found comparable dielectric permittivity, but there was no exact data concerning temperature coefficient values [28].

Obtained within this work are materials which are regarded as three important low loss dielectric ceramics. $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ are regarded as stable forms, whereas $BaTi_5O_{11}$ is a metastable one. The observed by us transformation is in agreement with phase diagram of $BaTiO_3$-$TiO_2$ system [30], where $BaTi_4O_9$ is located in the immediate vicinity of $Ba_2Ti_9O_{20}$ and both phases appear to be in equilibrium below 1420°C for compositions between 80 and 81,8 mol% $TiO_2$ in $BaTiO_3$-$TiO_2$.

## 5. Conclusion

Ba-TN precursor obtained from reaction of titanate nanosheets with barium ions was found as an interesting method to obtain barium titanates that exhibit elevated values of dielectric permittivity and low loss tangent in MHz frequencies. The dielectric properties of this composite can be tailored by suitably adjusting the sintering temperatures. According to this barium titanates of stoichiometry, $BaTi_4O_9$ being the predominant phase and $BaTi_5O_{11}$ as minor phase below 1150°C are present, whereas $Ba_2Ti_9O_{20}$ is formed at higher temperatures of sintering. The dielectric properties of these ceramics depend considerably on sintering temperature and their microstructures. From this reason structural studies as well as grain morphology and dielectric investigations were carried out simultaneously in each step of Ba-TN sintering. It was found that up to temperature of 1050°C barium titanate exhibits fine ceramics grain size. At higher temperature grain morphology radically changes simultaneously with crystallographic phase composition change revealed by XRD and Raman studies.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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