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**Title:** Study of phase transition in  $\text{Bi}_3\text{TiNbO}_9\text{-BaBi}_2\text{Nb}_2\text{O}_9$  ceramics

**Author:** Małgorzata Adamczyk, Joachim Kusz, W. Hofmeister, Maciej Zubko, Lucjan Kozielski, Michał Pilch, Dariusz Bochenek, Beata Wodecka-Duś

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STUDY OF PHASE TRANSITION IN  $\text{Bi}_3\text{TiNbO}_9$ - $\text{BaBi}_2\text{Nb}_2\text{O}_9$  CERAMICS

The subject of the paper is lead free bismuth layer structure oxides  $(1-x)\text{Bi}_3\text{TiNbO}_9$ - $x\text{BaBi}_2\text{Nb}_2\text{O}_9$  ( $x=0; 1; 2; 3$  mol). The influence of  $\text{Bi}_3\text{TiNbO}_9/\text{BaBi}_2\text{Nb}_2\text{O}_9$  ratio on dielectric and structural properties was studied in a wide range of temperatures. Change in the ratio causes a decrease in the maximum value of dielectric permittivity and shifts the temperature of  $\epsilon'_{\text{max}}$  to low values, leading to linear decreasing of average grain size and linear increasing of ceramics density. These results indicate an augment of the packing degree and the participation of pores are significantly decreased with the increase of  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  compound intake. Moreover, for  $0.7\text{Bi}_3\text{TiNbO}_9$ - $0.3\text{BaBi}_2\text{Nb}_2\text{O}_9$  ceramics the dielectric phase transition is broadened and the properties characteristic for the ferroelectric relaxor appear.

*Keywords:* Dielectric properties; X-ray methods; Grain size; Phase transition, Ceramics

## 1. Introduction

In the last few decades an enormous increase of ceramics components contributing to electronic devices has been seen. Slowly they have become an integral part of modern electronics. However the most used ceramics materials contain environmentally harmful lead. For this reason their use in devices has been continuously debated from the beginning of XXI century. As a consequence, directive 2002/95/EC was put into effect in July 2006, restricting the use of environmentally hazardous compounds in electrical and electronic equipment. The only exceptions to this rule are piezoelectric lead ceramics due to the fact that so far no one has managed to obtain alternative lead-free materials characterized by such high piezoelectric coefficients [1-3].

The search for such materials is the main purpose for investigations by a great deal of laboratories worldwide. The most promising candidates are the bismuth layer-type compounds. The subject of this paper is the fabrication and investigation of the temperature dependence of dielectric and structural properties of the  $(1-x)\text{Bi}_3\text{TiNbO}_9$  -  $x\text{BaBi}_2\text{Nb}_2\text{O}_9$  ((1-x)BTN-xBBN) solid solution [4]. The first member of the solid solution is the  $\text{Bi}_3\text{TiNbO}_9$  ceramics. This compound is a good prospect for high temperature piezoelectric sensors because of its highest Curie temperature in the family of bismuth oxide layered perovskites [5]. Most of the reported studies of BTN have concentrated on the crystal structure [6-8], the dielectric properties are often unsung. The second member of the discussed solid solution is the  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  ceramics characterized by the very interesting mechanism of ferroelectric relaxor behaviour, which is caused by the Ba-induced disorder. In the following papers [9-13] the problem

was widely discussed. The combination of the two compounds resulted in the increase of the piezoelectric properties observed in the x value between 0.1 and 0.3 [4], which make the materials very interesting, pointing to possible further applications.

In the present paper, the authors would like to discuss the temperature dependence of dielectric and structural properties of a solid solution with a particular emphasis on the problem of the BBN participation influence on the phase transition parameters. An additional advantage of the presented investigations is the correlation between dielectric and high-temperature structural studies

## 2. Experimental

At the beginning of the sample preparation the appropriate quantities of  $\text{BaCO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  were weighed according to the formula:  $(1-x)\text{Bi}_3\text{TiNbO}_9$ - $x\text{BaBi}_2\text{Nb}_2\text{O}_9$  ((1-x)BTN-xBBN). The concentration of BBN ceramics varied from  $x=0$  to  $x=0.3$ . The prepared reagents were mixed and pressed into cylindrical form. The thermal synthesis of both solutions was carried out at  $950^\circ\text{C}$  for 2 h. Then the obtained materials were crushed, milled and sieved and then again pressed into cylindrical pellets. The second sintering process was carried out at  $1150^\circ\text{C}$  for 6 h.

The microstructure and distribution of all elements throughout the grains of the materials were examined by the scanning electron microscope JSM – 5410 with an energy dispersive X-ray spectrometer (EDS). The grain size measurements were performed on the fractured surface of the ceramics. X-ray powder diffraction (XRD) experiments were performed on a Seifert XRD 3000 TT diffractometer with a high temperature device from Materials Research Instruments

\* INSTITUTE OF TECHNOLOGY AND MECHATRONICS, UNIVERSITY OF SILESIA, 12 ŻYTNA ST, 41-200 SOSNOWIEC, POLAND

\*\* INSTITUT FÜR GEOWISSENSCHAFTEN DER UNIVERSITÄT, JOHANNES GUTENBERG-UNIVERSITÄT, 55099 MAINZ, GERMANY

\*\*\* INSTITUTE OF MATERIALS SCIENCE, UNIVERSITY OF SILESIA, 12 BANKOWA ST, 40-007 KATOWICE, POLAND

\*\*\*\* INSTITUTE OF PHYSICS, UNIVERSITY OF SILESIA, 4 UNIWERSYTECKA ST, 40-700 KATOWICE POLAND

<sup>#</sup> Corresponding author: malgorzata.adamczyk-habrajska@us.edu.pl

(MRI). All measurements were carried out in air with  $\text{CuK}\alpha$  radiation at 45 kV and 30 mA ( $\lambda=1.5405 \text{ \AA}$ ). The lattice parameters were refined using full pattern refinement with the FullProf Program Suite [14]. In the first step the compounds were characterized without the high temperature attachment in the  $2\theta$ -range of  $5\text{--}100^\circ$  at room temperature on a zero diffraction plate made of silicon single crystal cut at special orientation. Such measurements confirmed the purity of all obtained ceramics. In the next step diffraction patterns were recorded using high temperature attachment at temperatures of: 100, 300, 500, 600, 700, 750, 800, 850, 900 and  $950^\circ\text{C}$  in the  $2\theta$ -range of  $27\text{--}57^\circ$  (steps of  $0.02^\circ$  in  $2\theta$ , 10 s/step).

The measurements of dielectric permittivity as a function of temperature were performed in the following range of frequencies: 1 kHz–1 MHz using a computerized automatic system based on the Agilent E4980A LCR meter.

### 3. Results

The bulk density of the discussed ceramics obtained by the Archimedes displacement method with distilled water increased linearly with the increasing of BBN content (Fig.1), which is connected with the significant changing of grain structure (Fig.2).

Namely a pure BTN sample exhibits a microstructure consisting of plate-like grains with anisotropic shape because of the anisotropic growth of BTN crystal: the grain growth rate is higher in the direction perpendicular to the  $c$ -axis of crystals [5-7]. Moreover grains are randomly oriented. Addition of the BBN compound caused a change in the shape of the grain. The shape transformed from plate-like to square

plate (Fig.2b-d), which is characteristic for pure  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  ceramics. The average size of grain measured along the longest dimension changes linearly from  $15.6 \mu\text{m}$  to  $5.1 \mu\text{m}$  for pure BTN ceramics and 0.7BTN-0.3BBN solid solution, respectively. An energy dispersion X-ray spectrometer was used to check the distribution of individual elements within the grains (Fig.3). The area of EDS investigations covered an area of a single grain. Tests were repeated for several randomly selected grains of all ceramics, discussed at hereby paper. The study took into account all the elements included in ceramics. The microanalysis was performed with ISIS-300 SEMQuant programme. The EDS analysis indicated a fairly homogenous distribution of all elements throughout the grains.

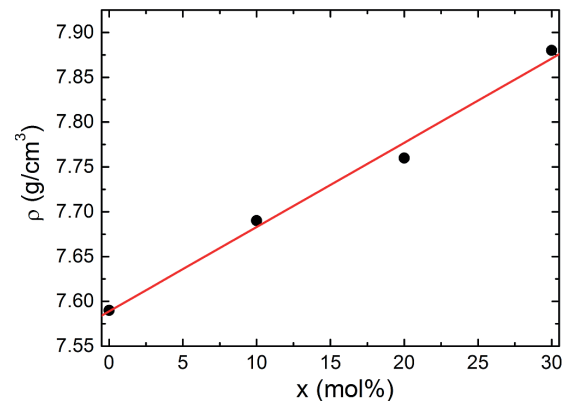


Fig. 1. The sample bulk densities for  $(1-x)\text{BTN}-x\text{BBN}$  ceramics

The pure  $\text{Bi}_3\text{TiNbO}_9$  ceramics crystallizes in orthorhombic crystal system. The lattice parameters determined by X-ray measurements at room temperature are as follows  $a=5.3943(2)$

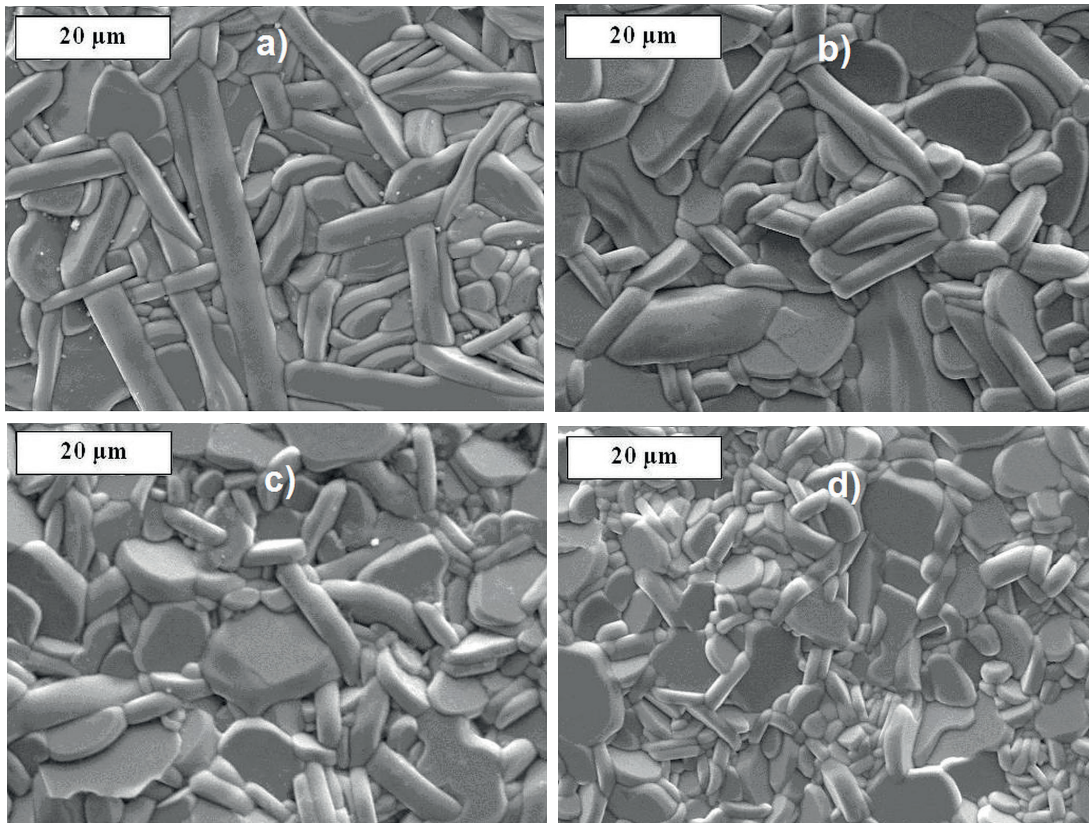


Fig. 2. Scanning electron microscope images of the fracture surface of  $(1-x)\text{BTN}-x\text{BBN}$  ceramics for a)  $x=0$ , b)  $x=0.1$ , c)  $x=0.2$  and d)  $x=0.3$



Å, b=5.4386(2) Å, c=25.1104(8) Å. The obtained results positively agreed with the results presented by R.W. Wolfe et al. [6 15-17].

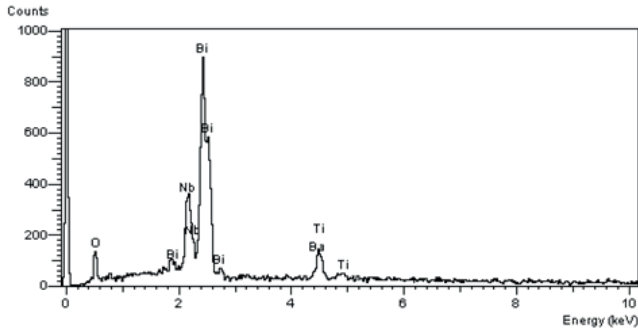


Fig. 3. The EDS analysis of 0.9BTN-0.1BBN solid solution

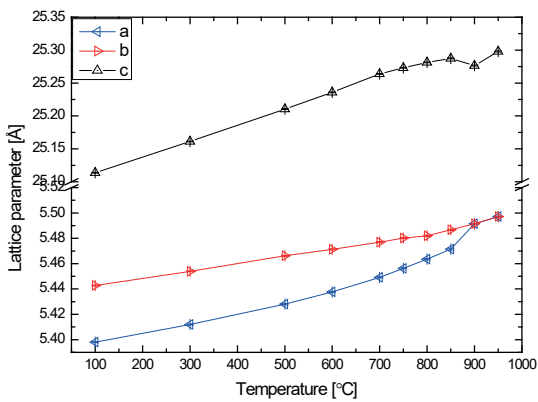


Fig. 4. Temperature dependence of lattice parameters of Bi<sub>3</sub>TiNbO<sub>9</sub> ceramics

Furthermore XRD measurements were performed as a function of temperature for Bi<sub>3</sub>TiNbO<sub>9</sub> ceramics over a wide temperature range, namely from room temperature up to 950°C. The obtained temperature characteristics of lattice parameters for pure Bi<sub>3</sub>TiNbO<sub>9</sub> ceramics indicated a presence at about 910°C of the phase transition from orthorhombic to tetragonal crystal system (Fig.4). At the mentioned temperature the lattice parameters are equal to a=b=5.4915(2) Å and c=25.2766(8) Å.

The above described procedure of XRD measurements was repeated for all discussed ceramics. The value of lattice parameters as well as volume of the unit cell obtained at room temperature for (1-x)BTN-xBBN solid solution gradually increased with increasing of BBN participation in materials (see Table 1).

TABLE 1  
The value of lattice parameters of the (1-x)BTN-xBBN solid solution

x BBN	a [Å]	b [Å]	c [Å]	V [Å <sup>3</sup> ]
0	5.3943(2)	5.4386(2)	25.1104(8)	736.67(5)
0.1	5.4437(1)	5.4047(1)	25.2059(3)	741.60(2)
0.2	5.4179(1)	5.4510(1)	25.2941(5)	747.01(3)
0.3	5.4305(1)	5.4583(1)	25.3646(6)	751.84(3)

The temperature dependencies of lattice parameters (Fig.5) indicated that the (1-x)BTN-xBBN solid solution also revealed the phase transition, which temperature decreased with the increasing participation of BBN compound. This can be clearly seen also on the temperature dependencies of parameter δ - the orthorhombic lattice distortion calculated as

$$\delta = \left( \frac{b}{a} - 1 \right) \text{ (Fig.6).}$$

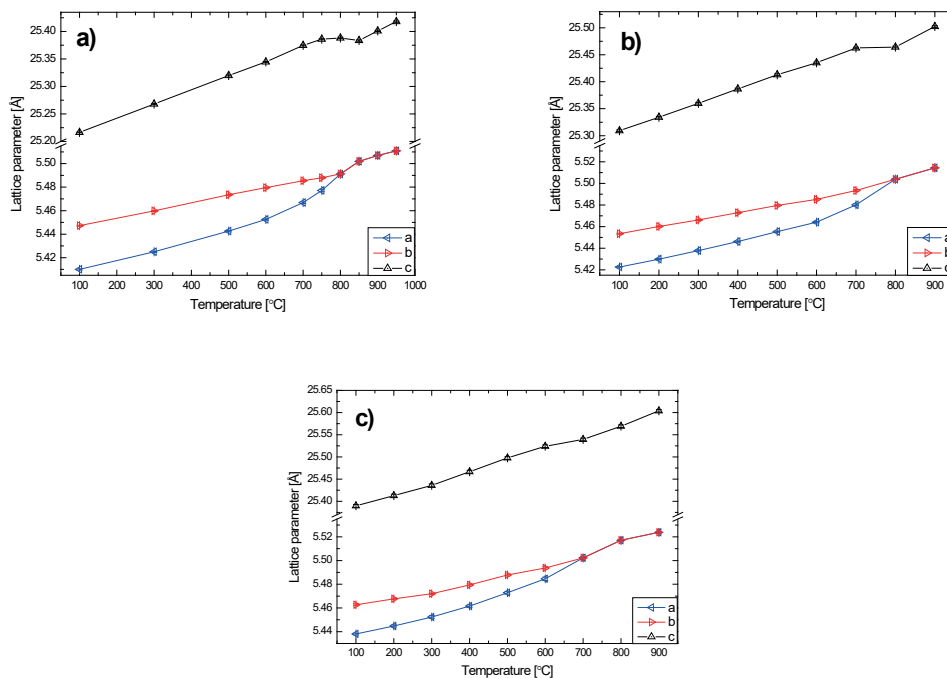


Fig. 5. Temperature changes of cell parameters obtained for (1-x)BTN-xBBN solid solution with a) x=0.1; b) x=0.2 and c) x=0.3 respectively

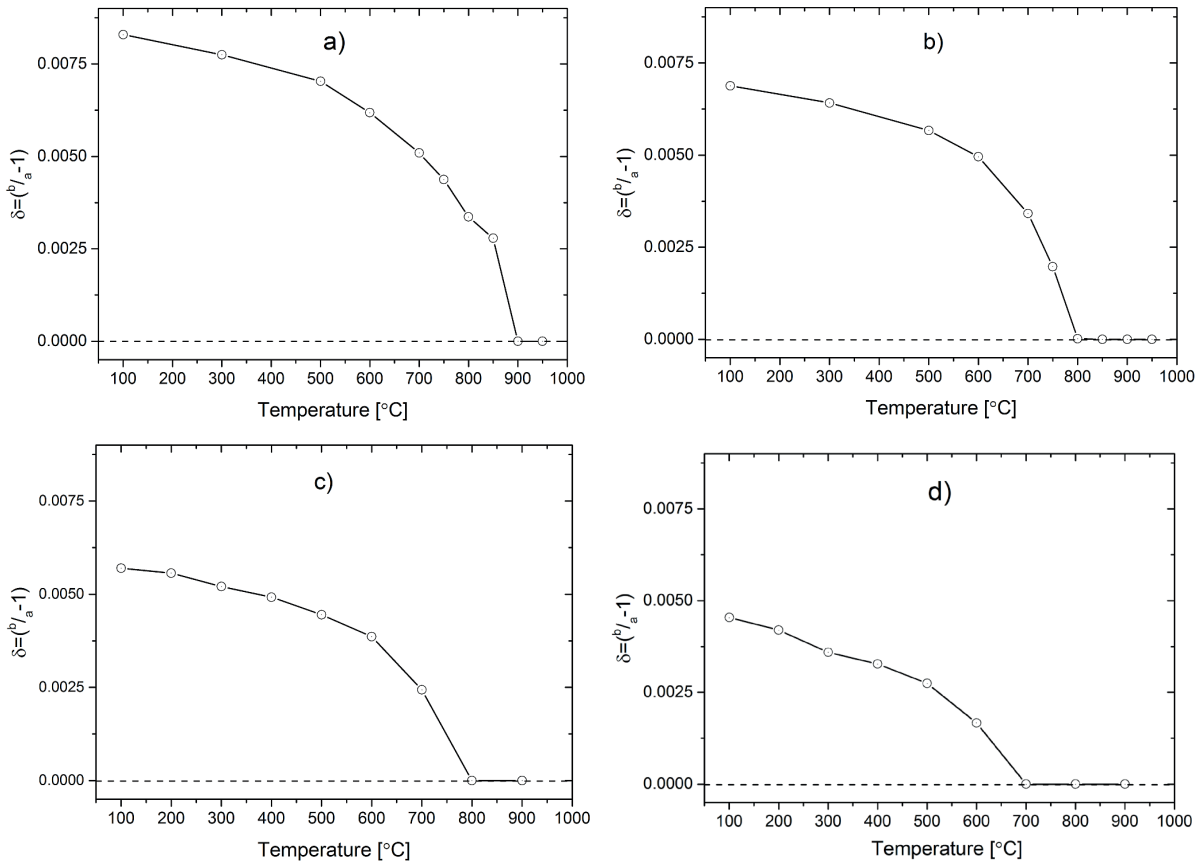


Fig.6 The temperature dependence of parameter  $\delta$  - the orthorhombic lattice distortion for studied ceramics

In the tetragonal symmetry (200) and (020) powder diffraction lines overlap. In the orthorhombic symmetry for  $a \approx b$  lattice parameters diffraction line (200) is a doublet composed of (200) and (020) Bragg peaks superimposed within the experimental resolution. Therefore above the phase transition widths of (200) line decrease monotonically with increasing temperature. These observations could be explained by the decrease of the orthorhombic distortion of the unit cell. In the vicinity of phase transitions the slope of overall FWHM(T) dependence of (200) diffraction line changes (Fig.7). In the case of pure  $\text{Bi}_3\text{TiNbO}_9$  as well as  $(1-x)\text{BTN}-x\text{BBN}$  with  $x=0.1$  mol and  $0.2$  mol the changes are more distinct. In the case of  $x=0.3$  mol the changes are not so sharp, which is probably connected with more significant influence of BBN compounds. The value of FWHM after phase transition for ceramic with  $x=0.3$  mol - further decrease with increasing temperature - indicating the diffuse character of phase transition and presence of the polar region in paraelectric matrix characteristic for the ferroelectric relaxor materials [18].

XRD measurements as a function of temperature were correlated with the dielectric measurements and shown that the successive structure change influences dielectric properties. Comparison of  $\epsilon(T)$  curves obtained in heating at the measuring field of frequency 100 kHz for pure  $\text{Bi}_3\text{TiNbO}_9$  ceramics as well as for  $(1-x)\text{BTN}-x\text{BBN}$  solid solution is given in Fig.8a.

In the range of low temperatures the value of dielectric permittivity is almost temperature independent for all discussed compounds. Above a temperature of 400°C the value dielectric permittivity begins to increase gradually. Next the increase of the dielectric permittivity value becomes steeper. The  $\epsilon(T)$  curve achieves the maximum in the vicinity of structural phase transition. The results indicate that it is the transition from ferroelectric to paraelectric phase. In the case of pure BTN ceramics as well as composites containing 0.1 and 0.2 mol of BBN compound the discussed maximum is very sharp whereas for ceramics with  $x=0.3$  mol the maximum stayed very broad so we could not talk about the Curie, but only about the average temperature of phase transition  $T_m$ . The maximum value of permittivity as well as the temperature of phase transition decreases almost linearly with the increase of BBN content (Fig.8b).

In case of the 0.7BTN-0.3BBN solid solution the distinct deviation from the Curie-Weiss law is observed in the range of the paraelectric phase (Fig.9).

The dependence  $\epsilon^{-1}(T)$  can be described by the parameter  $\gamma$  in the formula  $1/\epsilon' - 1/\epsilon'_{\max} = C/(T - T_{\max})^\gamma$  proposed by Martirena and Burfoot [19]. The value of  $\gamma$  ( $1 \leq \gamma \leq 2$ ) is the expression of the broadening degree of  $\epsilon'(T)$  dependence. In the case of 0.7BTN-0.3BBN ceramics the coefficient  $\gamma$  is equal to 1.6. The Curie-Weiss law ( $\gamma=1$ ) is observed only at temperatures much higher than  $T_m$ , which is in the case of the discussed sample equal to about 868°C.

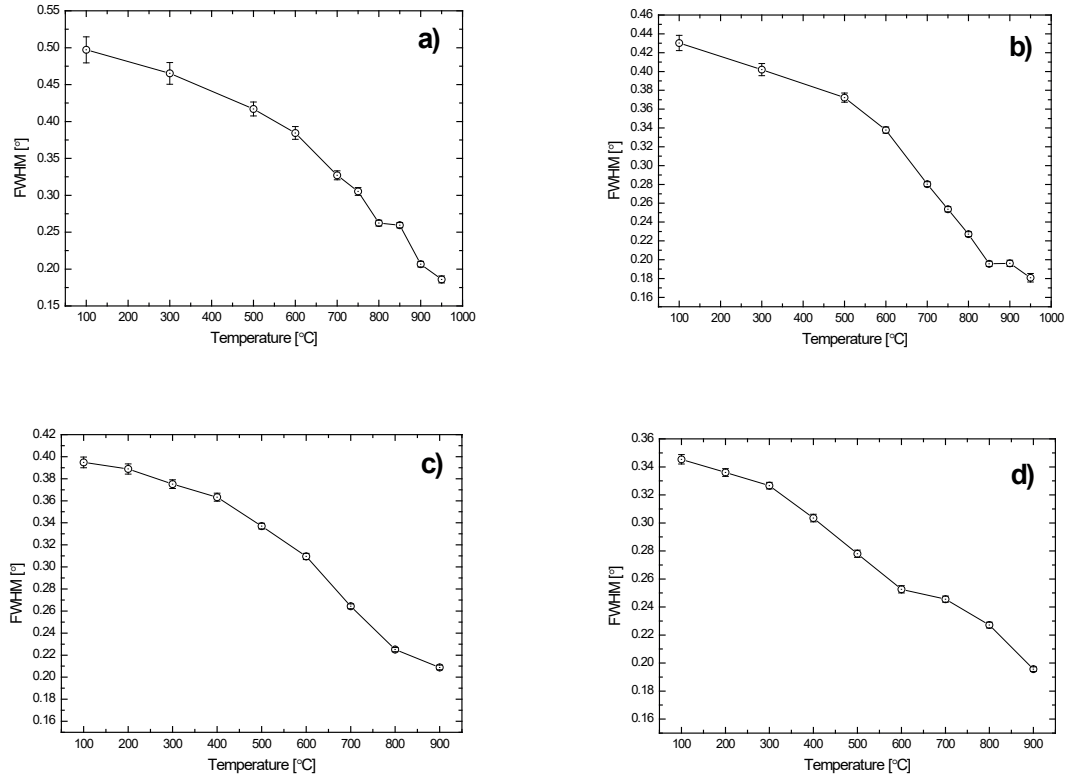


Fig.7 Temperature dependence of (200) diffraction line FWHM

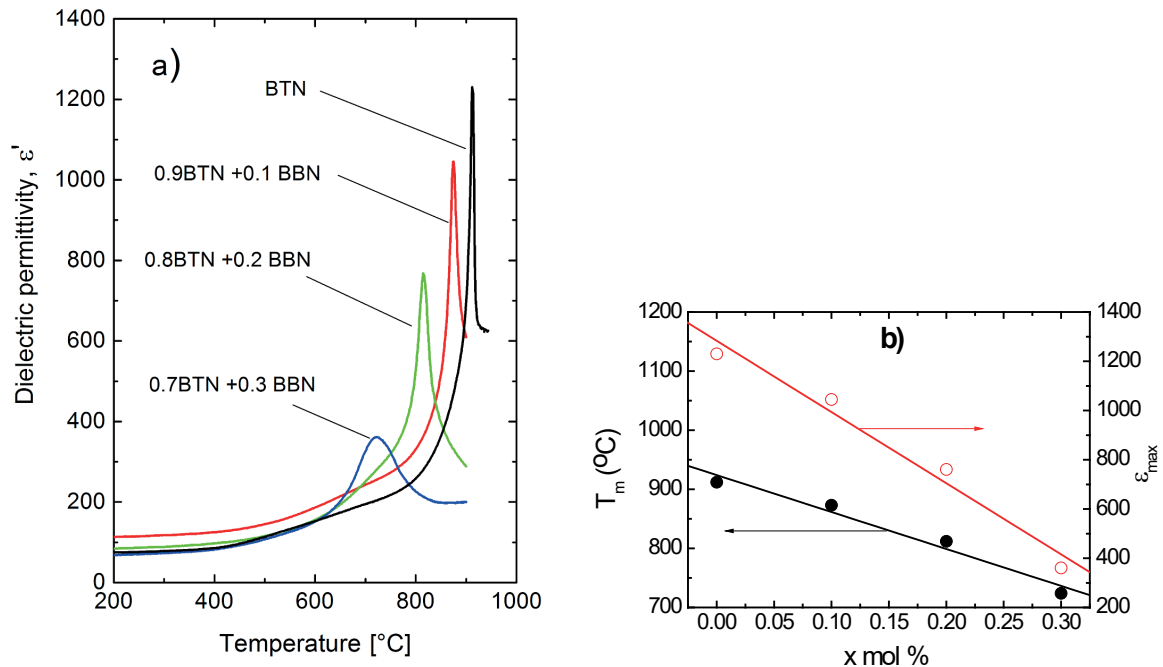


Fig.8. a) Dielectric permittivity as a function of temperature measured on heating at frequencies of measuring field equal to 100 kHz, for (1-x)BTN-xBBN ceramics x=0 mol, x=0.1 mol, x=0.2 mol and x=0.3 mol b) The temperature  $T_m$  and  $\epsilon_{max}$  vs. x mol of BBN content in the (1-x)BTN-xBBN solid solution

Temperature characteristics of  $\tan\delta$  measured at frequencies of a measuring field equal 100 kHz are shown in Fig.10a. In the case of pure BTN ceramics as well as the (1-x)BTN-xBBN solid solution with x=0.1 and 0.2 mol the function of  $\tan\delta(T)$  has a classic behaviour, i.e. the  $\tan\delta$  reaches the

minimum at Curie temperature and maximum slightly below the temperature.

The behaviour of the  $\tan\delta(T)$  completely changes for the 0.7BTN-0.3BBN solid solution (Fig.10b). Namely the local maximum and minimum  $\tan\delta$  disappear altogether.

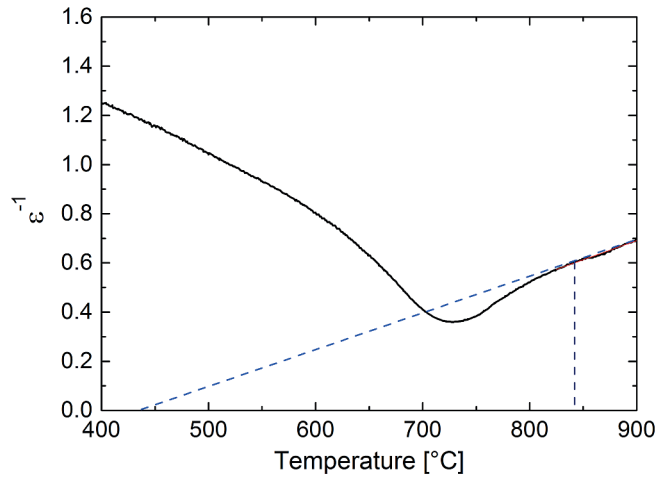


Fig.9. The inverse of the 100 kHz constant obtained for 0.7BTN-0.3BBN solid solution

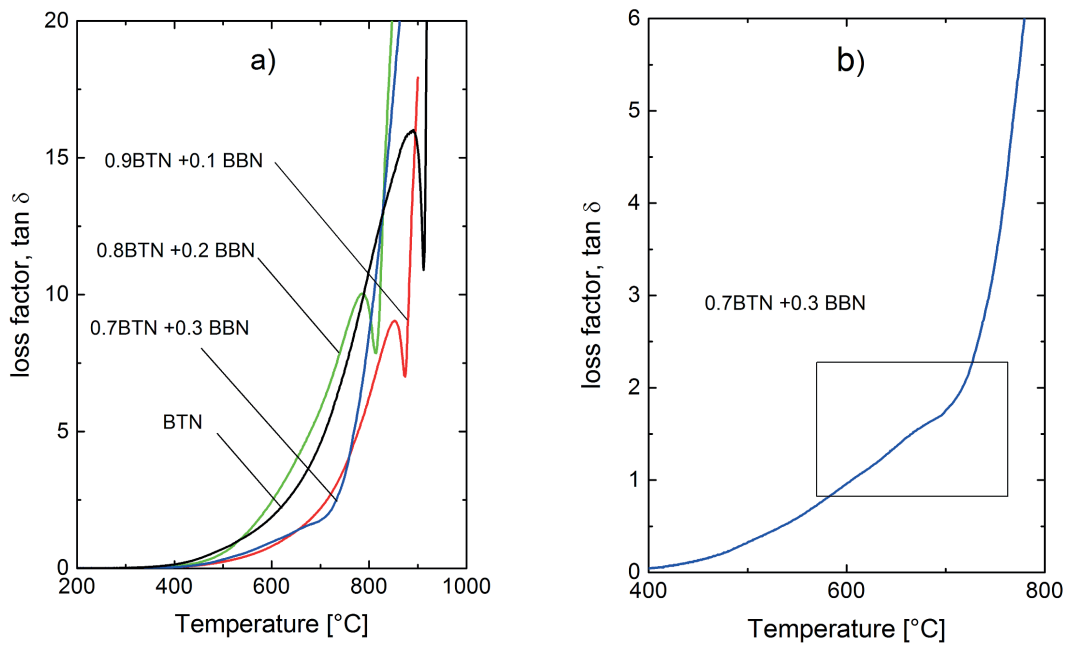


Fig.10. Loss factor as a function of temperature measured on heating at frequencies of measuring field equal to 100 kHz a) for all discussed ceramics, b) for 0.7BTN-0.3BBN

The loss factor monotonically increases with temperature. A more thorough analysis of the function revealed a small anomaly in the vicinity of structural phase transition, which is characteristic for ferroelectric-paraelectric diffuse phase transition.

Because BBN ceramics are characterized by a high frequency dispersion it was decided to measure the temperature dependence of dielectric permittivity in heating at two frequencies of the measuring field, namely 100 kHz and 1 MHz (Fig.11).

The frequency dispersion of the maximum value of dielectric permittivity is observed for all discussed ceramics, whereas  $T_m$  temperature moved insignificantly to a higher value with the increase of the measuring field frequency only for the 0.7BTN-0.3BBN solid solution (Fig.12). In the case of this material the degree of frequency dispersion of the  $T_m$  temperature, understood as the difference between the

$T_m$  value obtained for low and high frequencies ( $\Delta T_m = T_m(1 \text{ MHz}) - T_m(10 \text{ kHz})$ ), is equal to 12°C. It is suggested that the relaxor properties of BBN ceramics, widely described in the paper [10-12], started to play a crucial role. The obtained results support the assumption of the presence of polar nano-regions in paraelectric matrix up to temperatures significantly higher than  $T_m$ .

#### 4. Conclusions

The presented results indicate that the increase share of BBN compound in (1-x)BTN-xBBN solid solution causes:

- linear decreasing of average grain size and linear increasing of ceramics density - these results indicate that the packing degree augment and participations of pores significantly decrease with increase of BBN phase intake,

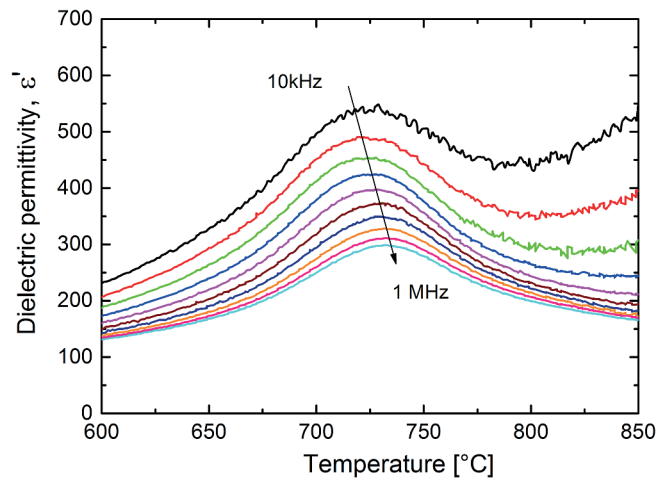


Fig.12. Dielectric permittivity as a function of temperature and frequency measured on heating for 0.7BTN-0.3BBN ceramics

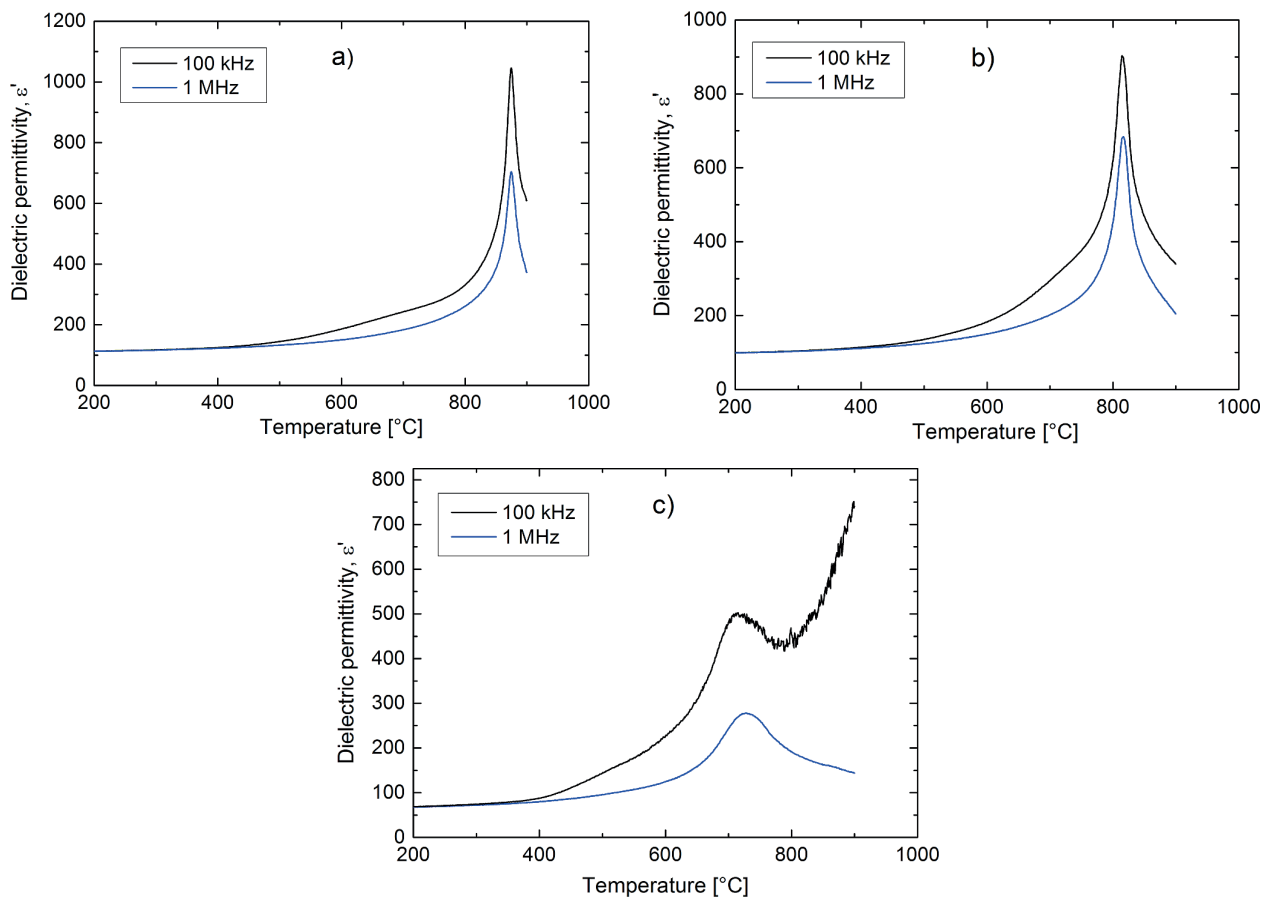


Fig.11 Dielectric permittivity as a function of temperature measured on heating at various frequencies of measuring filed, for (1-x)BTN-xBBN ceramics for a) x=0.1 b) x=0.2 and c) x=0.3

- increasing of the unit cell parameters and volume,
- decreasing of temperature of structural phase transition from orthorhombic to tetragonal system,
- decrease maximum of the value of dielectric permittivity and shift of the temperature of  $\epsilon'_{\max}$  to low value,
- broadening of dielectric phase transition and appearing characteristic for ferroelectric relaxor dispersion of temperature  $T_m$  for 0.7BTN-0.3BBN ceramics.

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