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Effect of hot pressing on processing and properties of BBN ceramics

M. Adamczyk [a,*], L. Kozielski [b], M. Pawełczyk [a]

[a] Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland
[b] Department of Materials Science, University of Silesia, Śnieżna2, 41-200 Sosnowiec, Poland

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Abstract

BBN ($BaBi_2Nb_2O_9$) is very interesting and promising lead free material with relaxor properties in capacitors, sensors and actuators.

Results of investigations of fine-grained, weakly porous, BBN-type ceramics using hot-pressing method are presented. Based on a thermal deformation curve (i.e. a shrinkage curve) of a sample the method for optimisation of the hot-pressing sintering conditions has been proposed. Some advantages of hot-pressing method over the classical ceramic method used for BBN ceramics fabrication is shown. It has been found that the deficiency in bismuth causes a change of the space group of the perovskite phase crystalline structure of BBN and unit cell parameters. The influence of bismuth deficiency on dielectric properties materials and relaxor features is presented. The measurements of pyroelectric and thermally stimulated depolarization currents (TSDC) were carried out in order to better display unusual behaviour of dielectric characteristics.

Keywords: C. Dielectric properties; Relaxor ferroelectrics; Ceramics

1. Introduction

In recent years there has been increasing interest for the ferroelectric relaxors, mainly due to their widely technical applications, for example in multilayer capatitors, sensors and actuators. The most widespread representatives of these materials are $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and $Pb_{1-0.x}La_{0.x}Zr_{0.65}Ti_{0.35}$ (PLZT x/65/35 for $x > 5$) ceramics containing lead-oxide, but considering environmental interactions they are toxic. It is the main reason for exploration the lead free alternatives materials with relaxors properties. The very promising group of this ceramics seems to be Bi-layered perovskites, belonging to the Aurivillius family. The chemical formula of these compounds is expressed as $(Bi_2O_2)^{2+}(A_{x-1}B_xO_{3x+1})^{2-}$, where x indicates the number of perovskite building blocks between two $(Bi_2O_2)^{2+}$ layers and A and B represent the different cations of low and high valences [1]. The layered structure characterized by higher value of c-parameter in comparison with a and b in orthorhombic cell and consequently lead to high anisotropy of crystallographic structure. Such effect is directly connected with high anisotropy of electrical properties. The most known representatives of this family, which are currently investigated from point of view nonvolatile ferroelectric memories, are $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN) [2,3].

The BBN ($BaBi_2Nb_2O_9$) seems also to be very interesting and promising materials. These materials were widely described by Kholkin et al. [4] and Miranda et al. [5] and also in our previous article [6]. Materials samples were prepared using conventional mixed-oxide processing technique. It is commonly assumed that for relaxor behaviour the chemical disorder caused by Ba ions is responsible. They are entering not only in the perovskites blocks but also $(Bi_2O_2)^{2+}$ layers. It is resulting in inhomogeneous distribution of Ba ions and local charge imbalance in the layered structure [7]. Ismunadar et al. [8] showed, on the basis of XRD measurements that in BBN ceramics 15–20% of Ba^{2+} ions were located in the $(Bi_2O_2)^{2+}$layers.

A crucial question in the technology of ceramic ferroelectric materials is assuring the consistence in the stoichiometry between the obtained ceramics and the chemical composition described by a chemical formula. In case of ferroelectrics ceramics containing bismuth it is of great importance. The sintering temperature of these ceramics is higher than the bismuth sublimation temperature (860 °C). This is the main reason that the real ceramics of that type exhibit a disturbance in the stoichiometry. This disturbance is connected with the

* Corresponding author. Tel.: +48 32 2588211x1134; fax: +48 32 2588431.
E-mail address: madamczy@us.edu.pl (M. Adamczyk).

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creation of Bi vacancies in the BBN crystalline structure. It influences strongly the electrical properties (is leading to additional contributions to the intergrain impedance) and the structure parameters of elementary cell.

The experiments, described in this paper, were carried out in order to study the effect of the hot-pressing process on the relaxor behaviour of BBN ceramics. Based on a thermal deformation curve (i.e. a shrinkage curve) of a sample the method for optimisation of the hot-pressing sintering conditions was used in preparation of BBN ceramics. Optimal temperature of sintering (T_s) at a given pressure (p_s) and time of thermal processing (t_s) correspond with the point on the shrinkage curve, which shows the end of consolidation process of the sample. During the sintering under pressure there is an increase powder liquidity what leads to close defects and cracks and simultaneously a homogeneous microstructure with a density close to the theoretical one is obtained.

Some advantages of hot-pressing method over the classical ceramic method were used for ferroelectric oxides fabrication especially for materials containing elusive elements (La, Pb, $ZrTiO_3$) because this way of ceramics consolidation allow to decrease the sintering temperature of 100–200 °C [9].

In case of PLZT and PMN ceramics, the mentioned method significantly improved the quality of investigated ceramics [10].

2. Experimental procedure

Stoichiometric amounts of $BaCO_3$, Bi_2O_3, Nb_2O_5 were weighted and mixed. The sintering process was carried out by two-step sintering. In the first step the conventional sintering at 950 °C for 2 h was carried out. Then the materials were crushed, milled and sieved. The hot-pressing technological unit was used in the second step. Pressure was constant and equal to p_s = 20 MPa, time of sintering was t_s = 2 and 6 h and sintering temperature was T_s = 1060 °C.

The Archimedes displacement method with distilled water was employed for the evaluation of the samples density. XRD measurements were carried out on all ceramics samples, at room temperature, using a Huber diffractometer (Seemann–Bohlin geometry) with a monochromatic Cu $K\alpha_1$ radiation (30 kV, 30 mA). XRD patterns were made from 22° to 100° in 2θ with 0.02° steps and a 2 s counting time. The angle scale of received diffraction diagrams was scaled to 2θ (Bragg–Brentano geometry) by Au standard (JCPDS number 12-0403). The cut and polished 0.6 mm thick samples, coated with

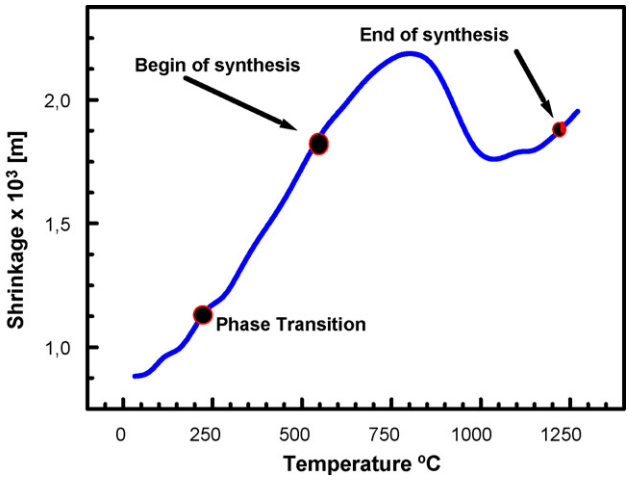

Fig. 1. Characteristic points on the shrinkage curve indicating the state of ceramics synthesis.

silver electrodes, were used for the measurements of the real (ε') and imaginary (ε'') parts of dielectric permittivity versus temperature. The measurements were carried out during heating by using an impedance analyzer HP4192A. The samples were heated at 723 K prior to measurement allowing the recombination and relaxation of part of the frozen defects, formed during the sintering.

3. Results and discussion

For fabrication of fine-grained, low porous, high density BBN-type ceramics the hot pressing was used. The method for optimisation of the hot-pressing sintering conditions based on a thermal deformation curve (i.e. a shrinkage curve) of a sample has been proposed. Optimal temperature of sintering (T_s) at a given pressure (p_s) and time of thermal processing (t_s) correspond with the point on the shrinkage curve, which shows the end of consolidation process of the sample (Fig. 1).

The characteristic points on the shrinkage curve indicates the temperature T_s = 1060 °C as optimal sintering temperature, in which the shrinkage of the sample finishes (Fig. 2a). Additional increasing in temperature (T_s = 1075 °C) leads to abnormal grain growth and to an increase of porosity.

The best chemical constitution and improvement of structure and microstructure (decrease in porosity, increase in density, decrease in grain size) is achieved at temperature T_s = 1060 °C (Fig. 2b).

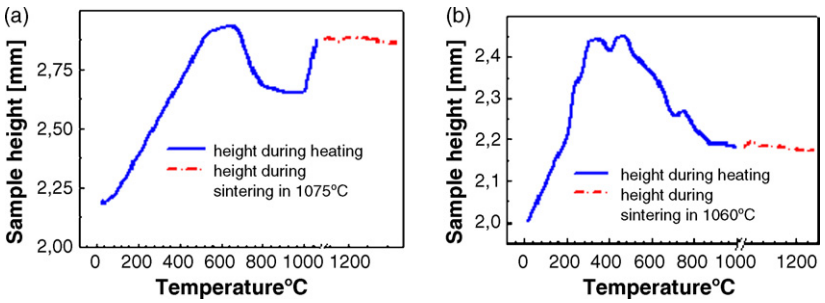

Fig. 2. Shrinkage curves of BBN ceramics in sintering temperature T_s = 1075 °C (a) and T_s = 1060 °C (b).

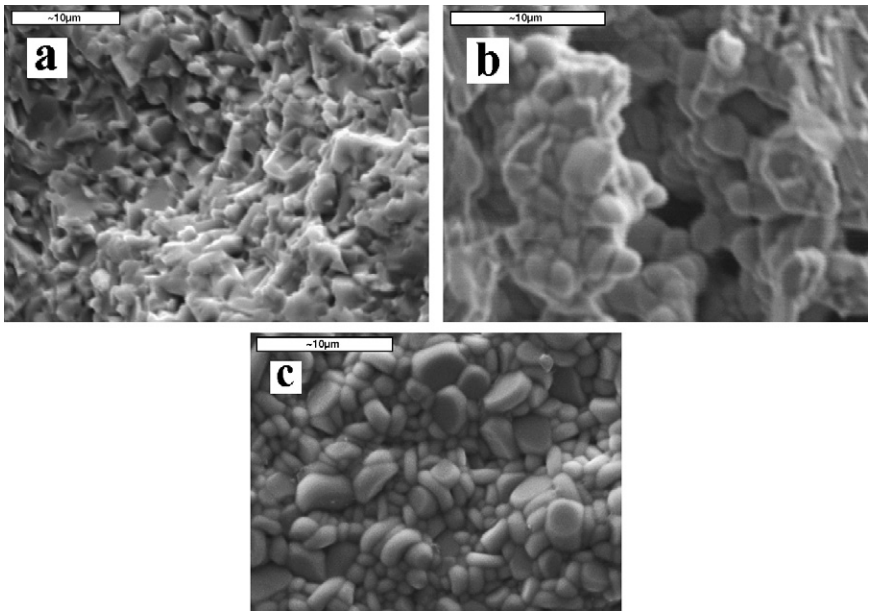

Fig. 3. SEM images of BBN ceramics obtained by hot-press sintering during 2 h (a), 6 h (b) and by conventional sintering during 6 h (c) at 1060 °C.

The density of hot-pressed BBN ceramics is higher than density of ceramics obtained by conventional method and is equal 6.92 g/cm^3 (95% theoretical density) whereas ceramics achieved by conventional method have a density of 6.9 g/cm^3 [11].

The microstructure and elemental analysis were examined by scanning electron microscope JSM-5410 with an energy dispersive X-ray spectrometer (EDS). The SEM micrographs of investigated ceramics are shown in Fig. 3.

When the time of sintering was increased, the microstructure changed significantly. The characterization of the microstructure for ceramics sintering only for 2 h (Fig. 3a) indicates the great number of small size weakly developed grains with high content of glassy phase. The main reason for the small size of grains is attributed to the too short time of sintering process [12]. For samples sintered for 6 h the grain size is large (Fig. 3b), with lower presence of pores in comparison with ceramics sintered by conventional method (Fig. 3c).

The X-ray quantitative microanalysis (EDS) reveals the percentage content of barium, bismuth and niobium within the grains (normalised to 100%) (Table 1). In the table are also shown results of EDS measurements performed for ceramics sintered by conventional method. The content of Ba and Bi depends on the processing technology. For samples prepared by a conventional method, the content of Ba as well as Bi is lower, then the results are not comparable to the theoretical stoichiometry of the ceramics and the location of Ba^{2+} in the $(Bi_2O_2)^{2+}$ layers is more probable. The hot-pressed method significantly prevented sublimation of Bi and content of those ions is greater than assumed by stoichiometry. The mentioned location of barium ions is more difficult. When the time of hot-pressing sintering become longer the amount of Bi insignificantly decreased.

Table 1
Ba, Nb, Bi content in BBN ceramics determined from EDS analysis

Method	Nb (%)	Ba (%)	Bi (%)
Conventional	43.15	17.92	38.93
Hot press 2 h	42.22	16.05	41.73
Hot press 6 h	43.38	16.02	40.60

XRD analysis of mentioned ceramics was carried out. The samples were investigated at room temperature using Huber diffractometer (focusing Seemana–Bohlina) with filtered Cu Kα radiation. XRD patterns presented in Fig. 4 were achieved from 22° to 100° in 2θ with 0.02° steps and a 2 s counting time. The X-ray diffraction patterns (XRD) of both discussed ceramics obtained at room temperature are shown in Fig. 4. The fitting by Gaussian (G), Lorenzian (L), modified Lorenzian (ML) and intermediate Lorenzian (IL) were made using the package of X-ray diffraction data DHN_PDS programs. IL profile showed the best agreement with experimental data and this profile was taken to fit all diffraction lines. The data received in this manner were used for the calculation of unit cell parameter. The BBN ceramics are characterized by a tetragonal structure with space group *I*4/*mmm* [13,14]. The lattice parameters obtained from X-ray patterns for both discussed samples are $a = b = 3.8204$ Å, $c = 24.5491$ Å and $a = b = 3.8809$ Å, $c = 25.0676$ Å, respectively for samples sintered during 2 and 6 h. These results are significantly different in comparison with samples obtained by conventional method ($a = b = 3.9406 \pm 0.0006$ Å, $c = 25.6378 \pm 0.0059$ Å), that indicates that applied pressure during the sintering process locks the grain growth.

We have designed the method of forming quasi-hydrostatic pressure, in our uniaxial hot-pressing unit. The measurements presented by Seo et al. [15] revealed that the grains in hot-pressed samples have tendency to orientate through the direction of the applied pressure. In our samples the intensity of the all XRD lines measured for perpendicular and parallel section to direction of applied pressure are comparable. This effect is connected with

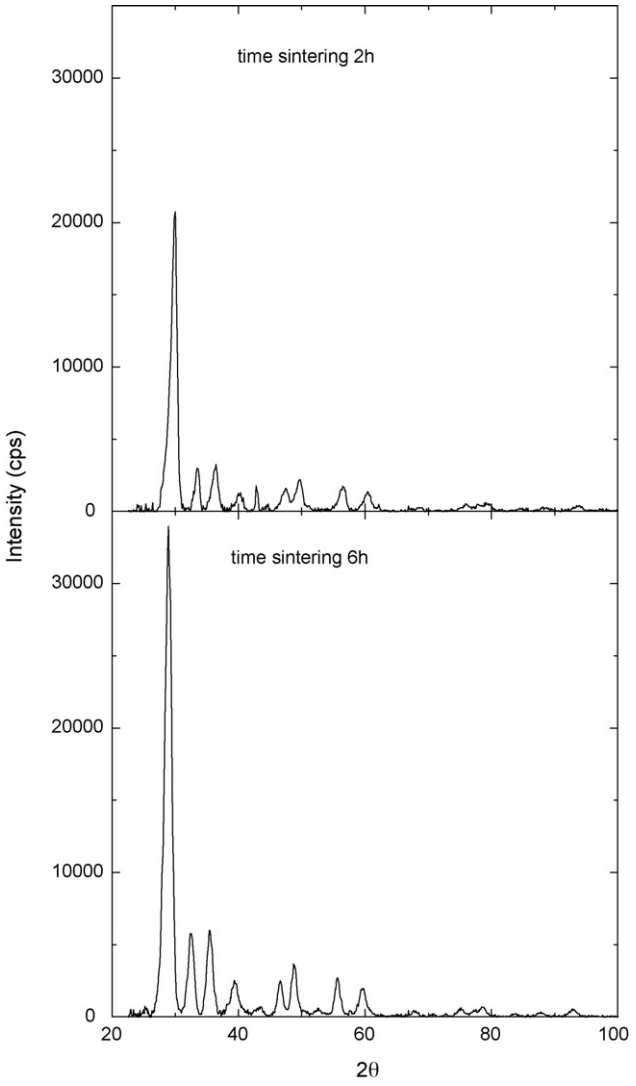

Fig. 4. XRD pattern of BBN ceramics obtained by hot pressing.

our improvement of using special sort of Al_2O_3 round shaped grains, which fulfil the hot-pressing matrix. The size of these grains were designed to create quasi-hydrostatic pressure on the sample sides during the sintering process.

Fig. 5 shows the variation of real (ε') and imaginary (ε'') parts of dielectric permittivity with temperature for several frequencies of measuring field. These characteristics reveal a strong diffuse character of phase transition for both investigated BBN ceramics. Moreover, deviations from Curie–Weiss law are observed in the range of the paraelectric phase and can be described by the formula $1/\varepsilon' - 1/\varepsilon'_{max} = C/(T - T_{max})^{\gamma}$. The origin of this behaviour is connected with inhomogeneous distribution of Ba ions and local charge imbalance in layered structure (what is widely described in our previously paper [11]).

The coefficient γ decreases really significantly with the time of sintering (from 1.23 to 1.32, respectively for samples sintering for 2 and 6 h). The value of γ for samples obtained by the hot-pressing method is smaller than for the conventional method ($\gamma = 1.81$), what could be connected with smaller

Table 2
The value of T_m, T_B, T_f, ΔT_m $\Delta\varepsilon_{max}$, E_a determined from measurements of $\varepsilon'(T)$ at $f = 100$ kHz

Method	ΔT (°C)	$\Delta\varepsilon_{max}$	T_f (K)	E_a (eV)	T_B (K)
Conventional	114	62	388	0.6	627
Hot press 2 h	108	47	406	0.56	684
Hot press 6 h	98	39	495	0.42	702

possibility of bismuth losses as results of sublimation and also better built Ba ions into the crystal lattice.

Strong frequency dispersion, characteristic feature of ferroelectric relaxors, was observed around the maximal real part of permittivity ε_{max}. With increasing frequency, decreased value of ε_{max} and the temperature of the maximal permittivity, T_m, shifts to higher temperatures. The shifts range ($\Delta T = T_m$ (1000 kHz) $- T_m$ (0.5 kHz)) and $\Delta\varepsilon_{max}$ (difference between ε_{max} measured at 0.5 and 1000 kHz) are given in Table 2. The discussed values for ceramics obtained by hot-pressing method (ΔT and $\Delta\varepsilon_{max)}$ decreased. For ceramics fabricated in conventional method these values are significantly higher (see Table 2). The imaginary part of permittivity is also frequency-dependent. Namely the maximum value of ε'' increased with increasing frequencies and the corresponding temperature shifted to higher value.

The frequency dependence of the temperature T_m could not be well described by the simple Debye relaxation and the Vogel–Fulcher (1) relationship was applied to fit the data:

$$f = f_0 \exp\left[\frac{-E_a}{k(T_m - T_f)}\right] \quad (1)$$

where E_a is the activation energy, T_f the freezing temperature of polarization fluctuation, and f_0 is the pre-exponential factor.

The Vogel–Fulcher plot relation T_m versus frequency, for BBN ceramics sintering during 6 h is shown in Fig. 6. The fit line (dotted line) represents a good agreement with the measured points, what allowed us to determine the values of E_a, T_f and f_0 (Table 2). The same procedure was repeated with good results for BBN ceramics sintering during 2 h.

The observed behaviour of $\varepsilon'(T)$ in the range of paraelectric phase can be also described by the Curie– Weiss formula modified by Kirkpartick and Sherrington [16]:

$$\varepsilon'(T) = \frac{C\{1 - q(T)\}}{T - \theta\{1 - q(T)\}} \quad (2)$$

where θ is the Curie–Weiss temperature, C the Curie–Weiss constant and $q(T)$ the temperature-dependent local order parameter, which is equal to zero at the temperature where the polar cluster begin to appear on cooling—Burns temperature (T_B). The value of T_B is given in Table 2. The temperature dependence of the local order parameter obtained from 100 kHz dielectric response for BBN ceramics sintering during 2 h is shown in Fig. 7.

In Fig. 5 it can be seen that the studied BBN ceramics demonstrated low frequency dispersion at high temperatures of the paraelectric phase. This additional dispersion is often found in ferroelectric ceramics of perovskite structure [17,18] and

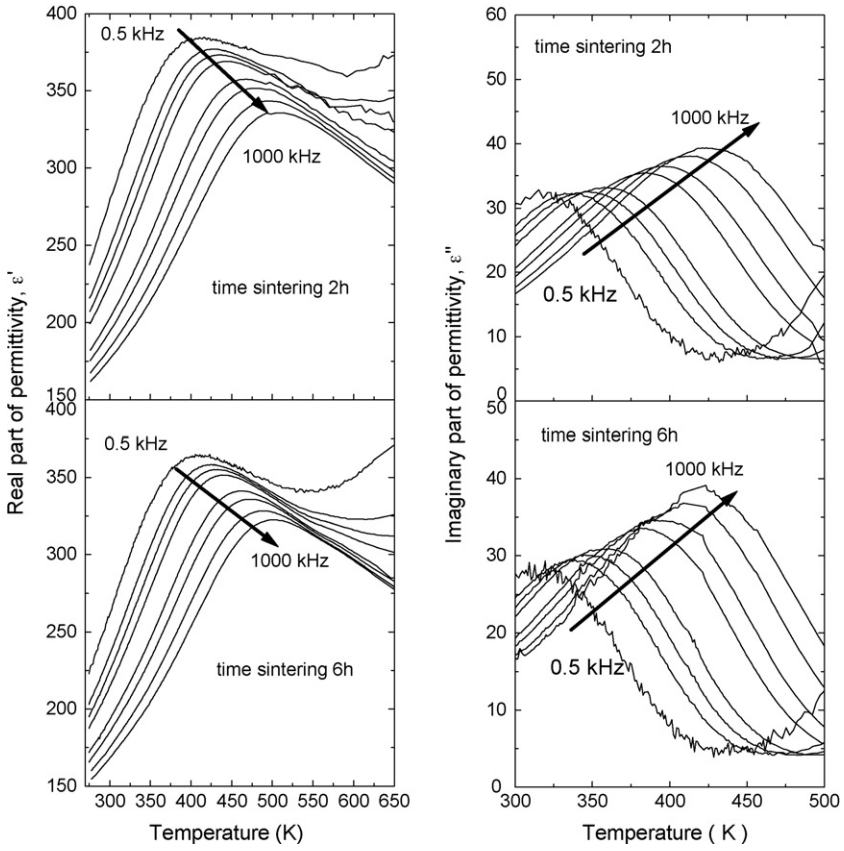

Fig. 5. Real and imaginary parts of permittivity as a function of temperature measured at various frequencies of the measuring field for BBN samples sintering during 2 and 6 h. The individual curves concern the following frequencies 0.5, 1, 10, 50, 100, 200, 500 and 1000 kHz.

originates from the non-homogeneous distribution of ion space charge participating in the screening process of polar regions [19]. It is generally worth to noticing that the considered dispersion is smaller for samples fabricated by hot-press method in comparison with samples sintered by conventional method.

In order to better understand the unusual behaviour of dielectric characteristics, shown above, the measurements of pyroelectric and thermally stimulated depolarization currents (TSDC) were carried out. The samples were polarized at dc field with a strength of 1 kV/cm applied for 10 min at temperature equal to 250 °C and then cooled with the field up to 0 °C and the field was switched off. The samples were heated with a constant rate of 5 °C/min up to the temperature 450 °C. The temperature changes of the observed TSDC are shown in Fig. 8. The maximum of TSDC is significantly greater for samples sintering by conventional method, what could be expected, because the participation of space charge in these ceramics is considerably dependent on easier sublimation of Bi ions.

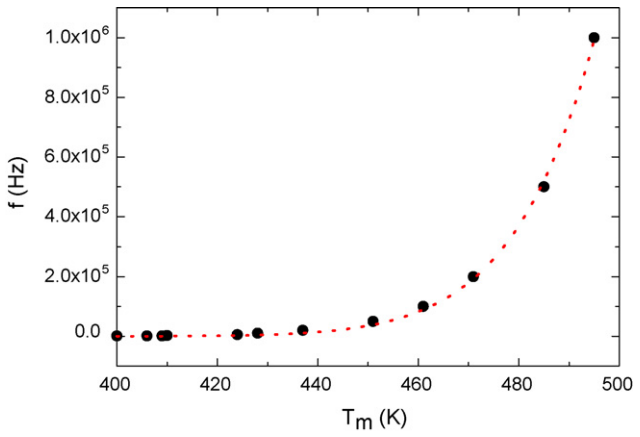

Fig. 6. Frequency as a function of temperature T_m. Points are experimental, the dotted line is the fitting of Vogel–Fulcher relationship for ceramics BBN sintering during 6 h.

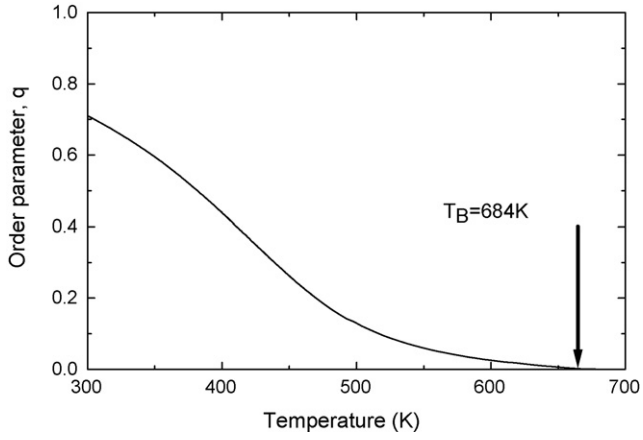

Fig. 7. Temperature dependence of the local order parameter calculated from data $\varepsilon'(T)$ measurements for the frequency 100 kHz.

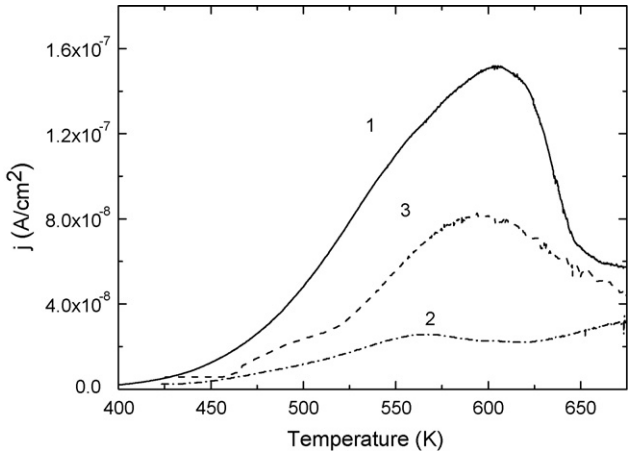

Fig. 8. Thermally stimulated depolarization currents vs. temperature for BBN ceramics (1, ceramics sintering by conventional method; 2 and 3, ceramics sintering by hot-press method for 2 and 6 h, respectively).

4. Conclusions

The BBN ceramics prepared by hot pressing have been investigated and compared to the samples obtained by conventional method. The results presented above lead to the following conclusions:

1. By means of sintering under pressure better stoichiometry was obtained. Using this method of sintering leads to a decrease of the number of the defects (concentration of Bi vacancies). The hot-pressing method prevents from sublimation of Bi ions.
2. The relaxor behaviour undergo deterioration which confirms our previously presumptions [20] that the concentration of defects is responsible for the properties.
3. Smaller concentration of defects was determined by measurements of thermally stimulated depolarization currents (TSDC). It was confirmed that the effect of increasing the synthesis time t_s (in hot-pressing method) leads to a decrease of Bi content (the maximum value of was TSDC current increased).

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