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The influence of axial pressure on relaxor properties of $BaBi_2Nb_2O_9$ ceramics

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Abstract

On the basis of our studies it results that dielectric properties of $BaBi_2Nb_2O_9$ ceramics are sensitive to axial pressure applied. The pressure causes an increase of dispersion in the real part of dielectric permittivity $\varepsilon'(T,f)$ and a rise in the temperature T_m at which the maximum in $\varepsilon'(T,f)$ dependence occurs. The applied pressure induces in the $\varepsilon'(T)$ dependence an additional step-like anomaly, which appears at the temperature $T_A < T_m$. The applied pressure shifts both T_m and T_A at the same rate, i.e. $dT_A/dX = dT_m/dX = +14$ °C/kbar at high axial pressure range, above the threshold pressure X_{thresh}. The Vogel–Fulcher relationship is employed to determine the axial pressure influence on relaxor properties of BBN ceramics. The simulated order parameter q takes non-zero values below Burn's temperature T_B, where the polar clusters appear on cooling. For pressures higher than 0.8 kbar, the T_B changes at the rate $dT_B/dX = -200$ °C/kbar. The decrease in the difference between Burn's T_B and the freezing T_f temperatures induced by the applied axial pressure is observed. This could be ascribed to the narrowing of temperature range of relaxor behavior.

Keywords: C. Dielectric properties; Axial pressure; Ceramics; Relaxor ferroelectrics

1. Introduction

Extensive experimental and theoretical studies on ferroelectric relaxors have been carried out. They are prospective materials for multiple applications owing to their exceptional dielectric properties. They can be applied in multilayer ceramic capacitors, electro-optic devices, ultrasonic and medical imagining devices [1–3]. Unfortunately, majority of them are PbO containing materials and therefore toxic and environmentally unfriendly. At present, the investigation of lead free materials is in progress. From this point of view, the $BaBi_2Nb_2O_9$, (BBN), seems to be promising.

The materials, which belong to the so-called Bi–layered structure family, were sintered for the first time by Aurivillius [4]. These ceramics have tetragonal structure with *I*4/*mmm* space group [5,6] and exhibit a behavior characteristic for ferroelectric relaxors, e.g. a marked frequency dispersion in the vicinity of temperature (T_m) where permittivity shows its maximum value ε'_{max} and a significant shift of this temperature with frequency (f) [7,8]. Analysis of the real $\varepsilon'(T,f)$ and imaginary $\varepsilon''(T,f)$ part of permittivity allows us to determine the values of Burn's temperature (T_B) and the freezing temperature (T_f), which characterize the relaxor ferroelectrics. Technological investigations showed influence of sintering conditions, in particular the affect of the sintering temperature, not only on the grain structure but also on relaxor properties of these ceramics [9,10]. The validity of hydrostatic pressure application in studies of relaxor systems was demonstrated and widely discussed by Samara [11,12]. Moreover, the pressure studies have a practical significance for the engineering of electronic devices since the compressive stress effects can significantly modify the properties of relaxor films [13].

In the previous paper [14] it has been shown that the $BaBi_2Nb_2O_9$ ceramics exhibit relaxor like behavior, namely they show dielectric anomalies of highly dispersive nature with small broadening of relaxation spectrum on cooling [7,8]. This behavior was attributed to the smaller size of polar regions and the weak interaction between them [8]. On the other hand, several properties of the BBN compound differ from those reported for conventional relaxors. The BBN ceramics have a

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low value of dielectric permittivity. However, other ceramics, which belong to the group of layered perovskites, i.e. $SrBi_2Nb_2O_9$ [15], $K_{0.5}La_{0.5}Bi_2Ta_2O_9$ [16], and $BaBi_2Nb_2O_9$ [8] also exhibit such a low value of ε'.

In the present work, the study of dielectric response under applied axial pressure is presented for the $BaBi_2Nb_2O_9$ ceramics in order to determine the pressure influence on its electric features.

2. Experimental

The BBN ceramics were prepared as described in the previous paper [14], using the conventional mixed-oxides processing technique. The stoichiometric mixture of $BaCO_3$, Bi_2O_3 and Nb_2O_5 reagents was mixed for 12 h. The calcination of the pressed pellets was carried out at 950 °C for 2 h. Then the material was crushed, milled, and sieved, then it was pressed again to form cylindrical pellets and sintered at 1100 °C for 6 h and finally cooled to room temperature for 12 h. The obtained ceramics were semitransparent and dense. The Archimedes displacement method with distilled water was employed to evaluate the sample density. The bulk density of BBN ceramics was equal to 7.07 g/cm^3.

The samples for dielectric measurements were cut to form parallelepipeds of the size 0.4 mm × 1 mm × 1.8 mm and polished. Then the electrodes were painted with Ag paste. The axial compression X was applied to the samples in the direction perpendicularly to the electrode surface (see inset in Fig. 1) with a lever and a weight, within the range of 0.1–1.4 kbar. Accuracy of the pressure was estimated as $\Delta X = \pm 0.05$ bar.

The dielectric permittivity measurement of the parallel circuit of capacitance C_p and of the conductance G of the parallel circuit mode were carried out with use of an impedance analyzer HP 4192A at frequencies in the 700 Hz to 1000 kHz range. The measuring field was equal to $E = U/d = 1.3$ V/mm. Prior to the measurements, the sample was several times subjected to the heating–cooling cycle, within the range 300–723 K, to remove residual stresses.

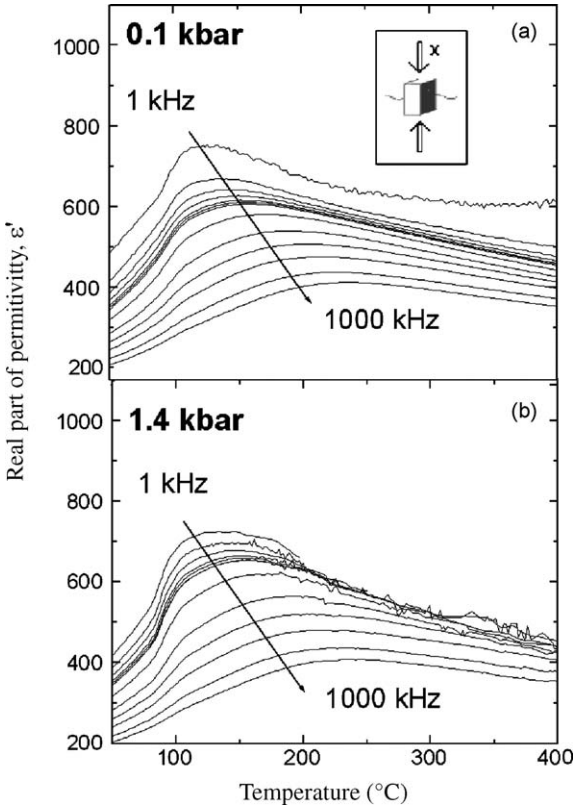

Fig. 1. Real part of permittivity (ε') vs. temperature plots measured at several frequencies of measuring field obtained for axial pressure applied to the sample: (a) 0.1 kbar, and (b) 1.4 kbar. Inset shows configuration of applied axial compression X with respect to the electrode.

3. Results and discussion

In the previous paper [14] it was shown, that the BBN ceramics exhibit a frequency dependent broad anomaly. With increasing frequency the temperature T_m of permittivity maximum shifts towards higher values. Moreover, the maximum value of permittivity ε'_{max} decreases with frequency. Such features are typical for relaxors materials. However, this anomaly occurs in a markedly wider temperature range than in classical or conventional relaxors, e.g. $Pb(Mg_{1/3}Nb_{2/3})O_3$ [17,18], and $(Pb_{0.94}La_{0.06})(Zr_{0.65}Ti_{0.35})O_3$ [19]. The $\varepsilon'(T,f)$ plots measured at various frequencies of the measuring field, in the case of the minimum (0.1 kbar), and the maximum (1.4 kbar) of the applied axial pressure, are shown in Fig. 1.

The applied axial pressure modifies the dielectric properties of the studied BNN ceramics. It should be noted that the dispersion in both of ε'_{max} and T_m values rises with increasing pressure (see Fig. 1). The degree of frequency dispersion can be described by evaluating the pressure dependence of ΔT_m value, defined as the difference between T_m measured at 0.7 and 1000 kHz, respectively (Fig. 2). The measurement of $\Delta\varepsilon'_{max}$ dispersion can be defined in a similar manner. The frequency dispersion $\Delta\varepsilon'_{max}$ changed from 435 to 485 when the applied pressure increased from 0.1 to 1.4 kbar. The pressure dependence of ΔT_m is shown in Fig. 2. For low pressure values, the ΔT_m parameter fluctuates and above the threshold pressure $X_{thresh} \approx 0.70 \pm 0.05$ kbar, the ΔT_m increases linearly at a rate of 40 ± 1 °C/kbar. The $\varepsilon'(T)$ plots measured at

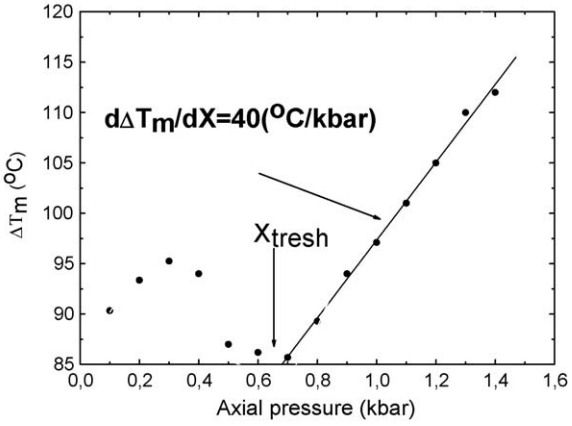

Fig. 2. The shift of ΔT_m, obtained from the maximum in the $\varepsilon'(T)$ plot, as the measure of dispersion, $\Delta T_m = T_m$ (1000 kHz) − T_m (0.7 kHz) vs. axial pressure.

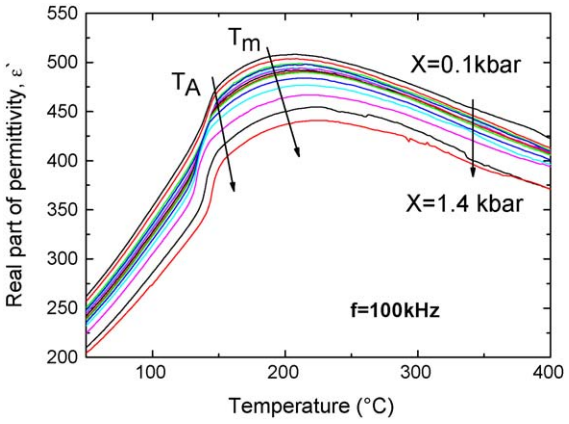

Fig. 3. Real part of permittivity ε' vs. temperature, measured at $f = 100$ kHz for and axial pressure applied subsequently from $X = 0.1$ bar up to 1.4 kbar.

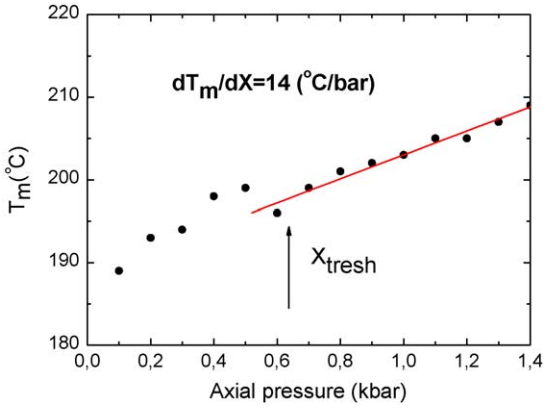

Fig. 4. Pressure dependence of temperature T_m, at which dielectric permittivity $\varepsilon'(T)$ of BBN ceramics shows maximum value. Frequency of measuring field was equal to 100 kHz.

$f = 100$ kHz, for the subsequent pressures applied, are shown in Fig. 3. Pressure induces shift in the T_m temperature. Moreover, an additional, step-like anomaly emerges at lower temperature, called here T_A (see Figs. 1 and 3).

The application of axial pressure causes a shift of the whole dielectric anomaly towards a higher temperature together with a decrease in the permittivity value, as can be seen in Fig. 3. The change of T_m shows linear dependence above the threshold pressure $X_{thresh,m} \approx 0.60 \pm 0.05$ kbar (Fig. 4). The shift of T_m, evaluated from $\varepsilon'(T)$ dependences, when measured above the X_{thresh}, at $f = 100$ kHz, is equal to $dT_m/dT = 14 \pm 1$ °C/kbar. Moreover, compression causes a decrease of the $\varepsilon'(T)$ maximum value at the T_m (see Fig. 3).

The other marked effect of the compression is a step-like anomaly at a temperature denoted T_A, which appears below temperature T_m. This step in the $\varepsilon'(T,f)$ anomaly dependence gradually increases with pressure and its shift towards higher temperatures is also observed (see Fig. 3). To obtain a more accurate value of T_A, the derivative $\partial\varepsilon'(T,f,X)/\partial T$ was calculated. Above the threshold pressure $X_{thresh} \approx 0.60 \pm 0.05$ kbar, the T_A value increases linearly at a rate of $dT_A/dX = 14 \pm 4$ °C/kbar (Fig. 5). The value of T_A is frequency independent, i.e. its value at this rate is the same for all frequencies (see Fig. 1).

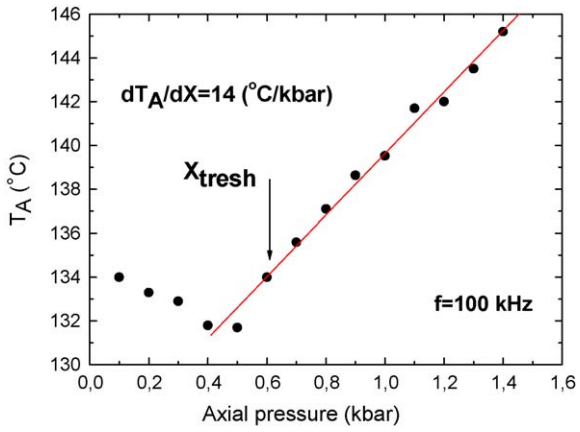

Fig. 5. The pressure dependence of temperature T_A obtained from the $\varepsilon'(T,f)$ plots.

The Vogel–Fulcher relation was employed to present the dielectric data in order to determine the influence of pressure on the relaxor properties of BBN ceramics. We assumed that, for each pressure value, the frequency $f(T_m)$ dependence is described by the Vogel–Fulcher equation:

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

where E_a is the activation energy, T_f is the freezing temperature of polarization fluctuation, k is the Boltzmann constant, and f_0 denotes the pre-exponential factor. The pressure dependences of the evaluated activation energy and freezing temperature are shown in Fig. 6. It is noteworthy that $T_f(X)$ and $E_a(X)$ dependences reach the extreme value at the pressure equal to 0.6 kbar. This coincides with the value of the threshold pressure X_{thresh} obtained from $T_m(X)$ and $T_A(X)$ dependences. However, both $T_f(X)$, and $E_a(X)$ values change rapidly above the threshold pressure $X_{thresh,m}$ which is equal to 0.8 kbar.

Within the framework of spin glass model, adapted for ferroelectric relaxors by Viehland et al. [20], the description of the $\varepsilon'(T)$ dependence in the range of the paraelectric phase modified by Sherrington and Kirkpatrick [21], the Curie–Weiss

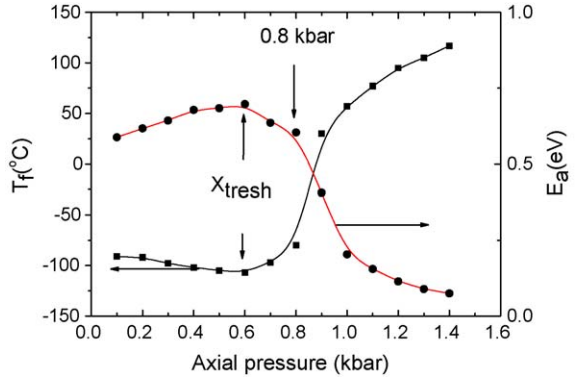

Fig. 6. The changes of activation energy E_a and freezing temperature T_f evaluated by fitting Eq. (1) to experimental $\varepsilon'(T)$ data obtained for different pressures.

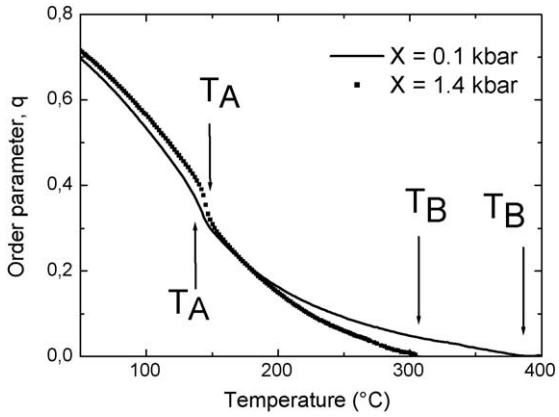

Fig. 7. The local order parameter q vs. temperature plot obtained for BBN ceramics in the case of measurements carried out under axial pressure equal to 0.1 and 1.4 kbar.

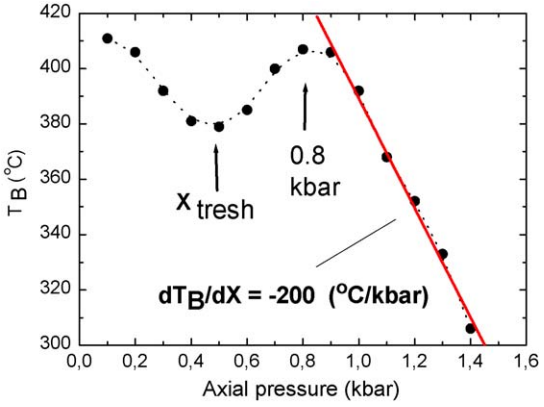

Fig. 8. The Burn's temperature T_B vs. axial pressure.

formula:

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

can be employed, where C is the Curie–Weiss constant, Θ is the Curie–Weiss temperature, q is the local order parameter. The order parameter q takes non-zero values below Burn's temperature T_B, where the polar clusters appear on cooling.

The subsequent fitting procedure carried out for the $\varepsilon'(T)$ dependences, enabled us to obtain the temperature changes of local order parameter $q(T,X)$ in the whole temperature range. Moreover the variations which occurred for the lowest and the highest applied axial pressure were compared (Fig. 7).

The pressure dependence of the estimated Burn's temperature T_B is shown in Fig. 8. The applied pressure decreases temperature T_B from about 410 °C to 300 °C. For pressures higher than 0.8 kbar, T_B varies linearly at the rate of $dT_B/dX = -200 \pm 25$ °C/kbar.

4. Discussion

The results of dielectric measurements described in a number of papers [7,8,14] indicated that BBN ceramics show relaxor like properties, which are strongly dependent on the technological conditions [9,10]. The results presented in the previous section show that external axial pressure also has a strong influence on relaxor behavior observed for the BBN ceramics. As can be seen in Fig. 3, the applied pressure causes a decrease of the value of the maximum of dielectric permittivity and shifts the temperature T_m towards a higher value. Above the threshold pressure X_{thresh} equal to about 0.60 ± 0.05 kbar, the $T_m(X)$ shows a linear dependence at a rate equal to 14 ± 1 °C/kbar. This value is comparable to the ones reported for several other perovskite ferroelectrics [11,22].

In the dielectric permittivity temperature dependences an additional anomaly appears at temperature denoted here as T_A. This anomaly is clearly manifested at higher values of the axial pressure (Figs. 1 and 3). Such an anomaly was previously reported for instance for $Pb(Sc_{0.5}Nb_{0.5})O_3$ [19,22], PLZT6/65/35 [11] and was ascribed to a spontaneous transition from the relaxor to the normal ferroelectric phase. However, in the case of BBN, this anomaly in the dielectric permittivity temperature dependence is related to the structural transition between the low temperature phase (*I*4*mm* space group symmetry) and the high temperature phase (*I*4/*mmm* space group symmetry) [23]. Moreover, it has been pointed out that the dielectric behavior of the BBN should be considered in relation to the combined effects of classical softening of polar phonons and the dielectric relaxation caused by cation disorder [23].

The pressure dependence of T_A is linear above the threshold pressure X_{thresh}, at a rate $dT_A/dX = 14 \pm 4$ °C/kbar (Fig. 5). It is noteworthy that within experimental accuracy both dT_A/dX and dT_m/dX dependences change at the same rate in the high axial pressure range, above the threshold pressure $X_{thresh} \approx 0.60 \pm 0.05$ kbar.

A similar effect of the $T_A(X)$ and $T_m(X)$ dependence was observed in other perovskite ferroelectric relaxors, e.g. for PLZT 12/40/60 [23], and $Pb(Sc_{0.5}Nb_{0.5})O_3$ [24,25]. However, in the case of those materials both discussed temperatures (T_m and T_A) decreased with hydrostatic pressure.

Moreover, dielectric measurements carried out on BBN samples under axial compression show the occurrence of the threshold pressure X_{thresh}. It has been found that the parameters related to the relaxor-like properties fluctuate below X_{thresh} and exhibit linear dependences above it. We interpret such an effect in the BBN ceramics as the manifestation of the clamping pressures, which can be overcome by external pressure higher than X_{thresh}. It has been shown in literature [26,27] that the clamping pressures may occur either due to defect dipole reorientation or due to drift of free charge carriers. The clamping pressure may appear at the ferroelectric domain walls, at grain boundaries or at local imperfections like dislocations, where point defects group during ageing and consecutively accumulate mechanical stresses. The quite high value of the threshold pressure $X_{thresh} \approx 60$ MPa obtained for the BBN ceramics indicates that the drift and accommodation of charge carriers is responsible for its occurrence. Such a conclusion can be drawn from the comparison of the threshold pressure X_{thresh} with the clamping pressure p_{clamp} estimated for $BaTiO_3$ containing various concentrations of defects. The

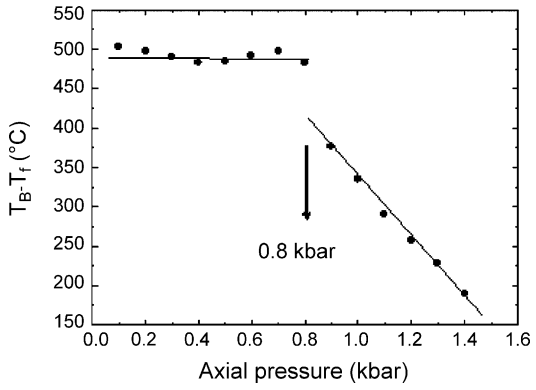

Fig. 9. The difference between Burn's T_B and freezing T_f temperatures vs. axial pressure.

reported values were as follows: p_{clamp} = 49 MPa and 97 MPa for the drift mechanism and only 39 and 4 MPa for the dipole-reorientation process [26].

The effects of pressure on relaxor behavior, shown in Figs. 1–8, can be described in terms of polar nano-regions and their mutual interaction. In general, polar nano-domains appear below temperature T_B where the commonly accepted onset of relaxor behavior occurs. Hence, the domains grow and the Coulombic interactions increase below T_B. This behavior corresponds to the increased value of the local-order parameter q.

The applied pressure shifts the T_B temperature to a lower value (Fig. 8). This indicates that it is more difficult for nano-regions to appear and grow in compressed samples. Moreover, the decrease with pressure of the order parameter q within the T_B–T_A range of temperature (Fig. 7) indicates that the applied pressure also blocks the correlations between polar nano-regions. On the other hand, for temperatures lower than T_A, the increase in value of q induced by the applied pressure indicates the growth of correlations and, presumably, the increase in size of the polar nano-regions [22]. This effect corresponds to the observed narrowing in the temperature range of the relaxor behavior that can be ascribed to the difference between temperatures T_B and T_f. The width of the temperature range of the relaxor behavior is shown in Fig. 9.

Moreover, the decreasing value of the activation energy with pressure, according to Veturini et al. [22], corresponds to the decrease in size of the polar nano-regions. Therefore the value of E_a is proportional to the volume. Moreover since smaller polar domains are easier to reorient, the estimated lower value of E_a is reasonable. This is also consistent with our result according to which axial pressure hampers the growth of the polar regions. The value of T_f fluctuated for low pressure values, but when the axial pressure exceeded the value equal to $X_{thresh,m}$ = 0.8 kbar, the value of T_f rapidly decreased (see Fig. 6). The same behavior of the freezing temperature T_f was observed for $Pb(Sc_{1/2}Nb_{1/2})O_3$ ceramics [15].

So far to the authors' knowledge no reports concerning the influence of pressure on BBN electric properties have been published. According to our findings T_m and T_A increase with hydrostatic pressure which is in contradistinction to the common tendency observed for perovskite relaxor materials. However, the other relaxor parameters, e.g. E_a, T_f, T_B, dependences on pressure remain in agreement with the dependences reported in literature.

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