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Switching processes in ceramics of solid solutions based on $Ca_{0.3}Ba_{0.7}Nb_2O_6$

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In this work, ceramic samples with a structure of the type of tetragonal tungsten bronzes, composition $Ca_{0.3}Ba_{0.7}Nb_2O_6$ (CBN30) pure and with modifying additives $SrTiO_3$, $KTaO_3$ or $LiTaO_3$ (5 mass%) were studied by the oscillographic method. It is shown that the introduction of modifying additives into $LiTaO_3$ ceramics leads to an increase in the reversal polarization and to a decrease in dielectric losses, both at room temperature and at high temperatures. The introduction of $SrTiO_3$ impurity into the CBN30 composition leads to the greatest increase in the reversal polarization. In contrast to ceramics based on lead zirconate titanate, which have a perovskite type structure, the introduction of SrTiO3 into CBN30 (having the structure of tetragonal tungsten bronzes) does not significantly improve the ferroelectric properties. It has been found that at temperatures above 100°C for pure CBN30 ceramics, above 165°C for CBN30 + 5% $SrTiO_3$ and CBN30 + 5% and above 200°C for CBN30 + 5% $LiTaO_3$, there is a strong increase in dielectric losses. The contribution of dielectric losses to switching processes makes it impossible to determine the temperature of the ferroelectric phase transition for solid solutions based on CBN30 from the temperature dependences of dielectric hysteresis loops.

Keywords: piezoelectric ceramics, barium-calcium niobate, lead-free materials, switching processes, dielectric hysteresis.

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1. Introduction

Significant efforts have been taken recently to investigate lead-free ceramic materials based on alkali and alkaline earth niobates and titanates [1–7]. There has been a progress in the improvement of properties of these materials, however, their temperature restrictions are one of the main disadvantages of these systems. Modified materials based on sodium-potassium niobate demonstrate a polymorphous phase transition between orthorhombic and tetragonal structure from 200°C to room temperature, thus, its temperature stability is still an important problem requiring solution. Materials based on bismuth-sodium titanate are depolarized below 130°C, while the phase transition temperature of materials based on barium titanate remains approximately below 120°C, thus, the polarized state cannot be maintained, when the devices made from such materials are operated at high temperatures.

Increasingly greater attention has been paid recently to compounds with the structure of tetragonal tungsten bronzes (TTB) [8–11], because their general formula written as: $A1_2A2_4C_4B_{10}O_{30}$, provides wide opportunities in changing the structure and improving the piezoelectric and pyroelectric properties. The majority of studies is devoted to ceramics based on barium–strontium niobate (SBN), because increasing concentration of strontium enhances the ferroelectric properties in this ceramics. At the same time, low phase transition temperature (below 100°C) is the main disadvantage for the practical application of SBN ceramics. Therefore, replacement of strontium ions in the TTB structure is of interest. Replacement of strontium with calcium (barium–calcium niobate material–CBN) is known to significantly increase the phase transition temperature in single-crystal solid solutions [12,13]. The first experiments with modified ceramics based on barium–calcium niobate (CBN) [14] have shown that material had ferroelectric properties. At the same time due to significant difference in the maximum permittivity (~ 280°C) and pyroelectric coefficient (~ 150°C) temperatures found by us before [14], investigations of temperature dependences of the dielectric hysteresis loops in solid solution samples based on CBN30 ceramics with addition of 5% $SrTiO_3$, $KTaO_3$ or $LiTaO_3$ were of interest. Formulation of such samples is described in detail in [14].

2. Investigation of dielectric hysteresis loops

Switching processes were studied by the oscillographic method of dielectric hysteresis loop investigation. The standard Sawyer–Tower circuit was used for observation of

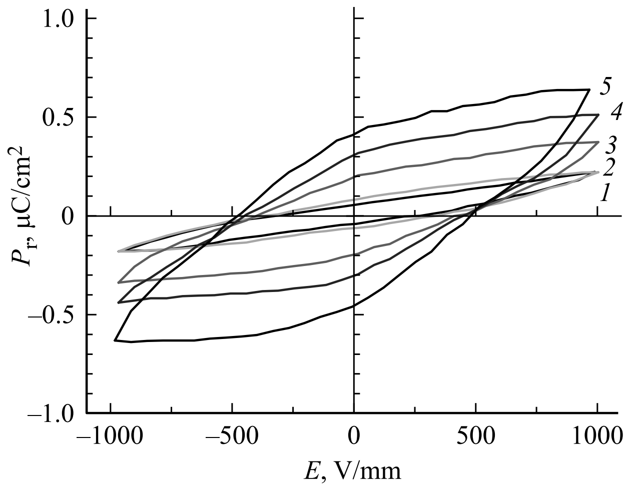

Figure 1. Dielectric hysteresis loops for the CBN30 ceramics: curve *1* — 27, *2* — 70, *3* — 110, *4* — 170 and *5* — 210°C.

the dielectric hysteresis loops [15]. G6-28 generator with voltage output up to 10 V and frequency from 0.001 Hz to 1 MHz was used a sinusoidal filed source. The generator was connected to TREK 677B high-voltage non-inverting power amplifier capable of amplifying the voltage applied to it with the fixed amplification factor of 200 V/V within the output voltage range from 0 to ±2 kV by AC voltage and output current peaks from 0 to ±5 mA. Temperature dependences of the dielectric hysteresis loops of the CBN30 ceramic samples were measured on nonpolarized samples in the 1 kV/mm field.

At room temperature on 50 Hz and 100 Hz, only local hysteresis loops were observed. Since [16] has shown that ferroelectric materials with strong coercive fields have hysteresis loops formed during self-heating (by domain switching) of the sample in an AC field with frequency higher than 100 Hz, we have carried out measurements within the frequency range up to 400 Hz. For temperature studies, a frequency of 300 Hz was chosen, because at this frequency dielectric hysteresis loops opening was observed for all studied compounds. For pure CBN30 at 200 Hz, dielectric hysteresis loop opening was partial, and at 400 Hz conductivity occurred during loop formation in the sample that was recorded as voltage drop on the sample. As a result, loop formation process was recorded during heating (Figure 1, 2). Error of the oscillographic method for dielectric hysteresis loop investigation according to [15] is equal to 20%, therefore we have shown confidence intervals on the temperature vs. switchable polarization (P_r) and vs. coercive field (E_c) curves (Figure 3).

For pure CBN30 ceramics, general expansion of the dielectric hysteresis loops was observed with the increase in temperature (Figure 1) up to the temperature above the maximum permittivity temperature [14]. Since the loop broadening was followed by the coercive field growth (Figure 3, *a*), it would appear reasonable that we observed only local dielectric hysteresis loops, i. e. 1 kV/mm field is insufficient for full opening of the loops for the polycrystalline (ceramic) CBN30 sample, unlike the CBN30 single-crystal [13]. Addition of 5% $SrTiO_3$, $KTaO_3$ or $LiTaO_3$ as modifiers to the CBN30 ceramics resulted in dielectric hysteresis loop opening with the temperature increase above 100°C (Figure 2).

Several fundamental distinctions were found between the CBN30 ceramics (i. e. polycrystalline state) and single-crystal in the temperature behavior of parameters, that are defined by the dielectric hysteresis loops and characterize the switching processes, such as switchable polarization and coercive field. Thus, during loop formation followed by the increase in the switchable polarization (Figure 1, 2, 3, *a*), all compounds exhibited the growth of the coercive field at the initial stage (Figure 1, 2, 3, *b*), then the modified compound exhibited the decrease of the coercive field. For the CBN single-crystal [13], growth of the switchable polarization during heating was immediately followed by the decrease of the coercive field and much faster growth of the switchable polarization. At the same time, the temperature (∼ 100°C) at which the switchable polarization starts growing coincides with the corresponding temperature for the CBN30 single-crystal.

It should be noted that above 210°C (the Curie temperature of the CBN30 single-crystal as specified in [13], ∼ 217°C), „rounding“ of the dielectric hysteresis loop started for all compounds that may be attributable to fast growth of dielectric loss in the samples.

3. Analysis and discussion of findings

Since the dielectric loss may contribute considerably to the investigation of the dielectric hysteresis loops, curves of temperature vs. dielectric loss angle tangent for 300 Hz were plotted (Figure 4). For plotting, temperature dependences of complex permittivity were measure by the dielectric spectroscopy method using Vektor-175 (Newtons4th Ltd) phase-sensitive meter in the temperature range rom 30 to 330°C.

The investigations (Figure 4) have shown that the dielectric loss in the pure CBN30 ceramics even at low temperatures exceeds the dielectric loss in modified compounds and fast growth starts after 100°C. At the same time, in the CBN30 + 5% $SrTiO_3$ and CBN30 + 5% $KTaO_3$ samples, dielectric loss increases at temperatures above 160°C, and the CBN30 + 5% $LiTaO_3$ sample — above 200°C. Apparently, beginning from the corresponding temperatures, the dielectric hysteresis loops for all compounds are gradually transformed into dielectric loss ellipse. Therefore, the shape of the dielectric hysteresis loops cannot be used to determine the temperature at which spontaneous polarization disappears in the samples.

Switchable polarization in the CBN30 ceramics with the corresponding single-crystal [13] was compared for the temperatures at which contribution of the dielectric loss to the dielectric hysteresis is low. The switchable polarization obtained for the CBN30 ceramics is by an

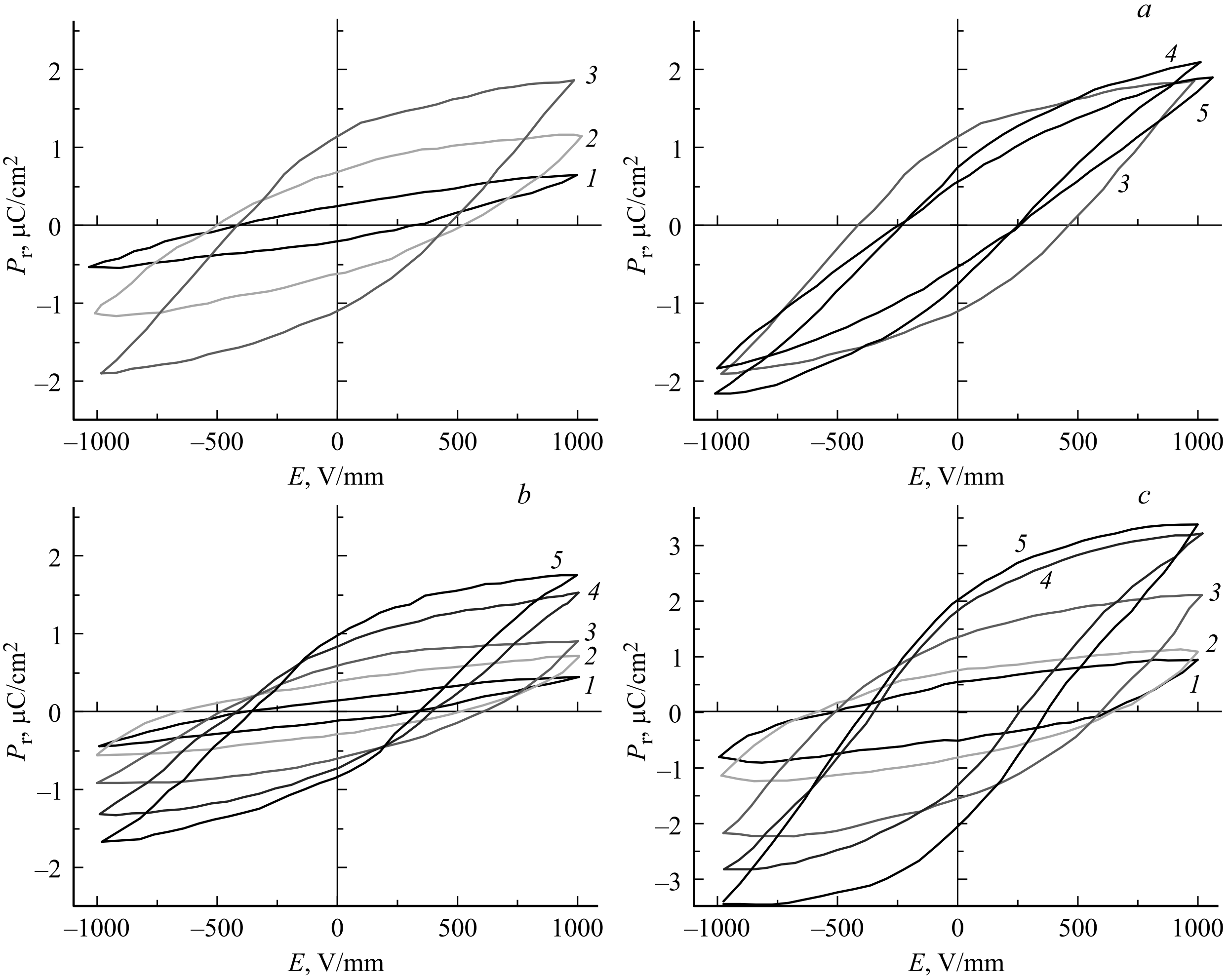

Figure 2. Dielectric hysteresis loops for $CBN30 + 5\%\,KTaO_3$ (*a*), $CBN30 + 5\%\,SrTiO_3$ (*b*) and $CBN30 + 5\%\,LiTaO_3$ (*c*) ceramics. Curve *1* — 27, *2* — 70, *3* — 110, *4* — 170 and *5* — 210°C.

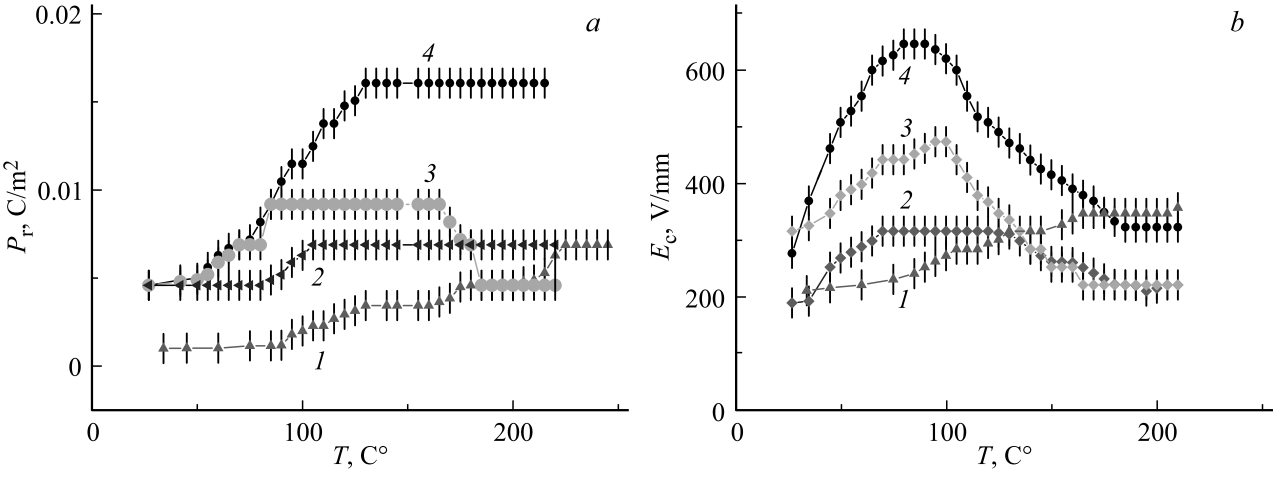

Figure 3. Temperature vs. residual polarization (*a*) and coercive field (*b*) for the CBN30 ceramic samples (curve *1*), $CBN30 + 5\%\,SrTiO_3$ (curve *2*), $CBN30 + 5\%\,KTaO_3$ (curve *3*) and $CBN30 + 5\%\,LiTaO_3$ (curve *4*).

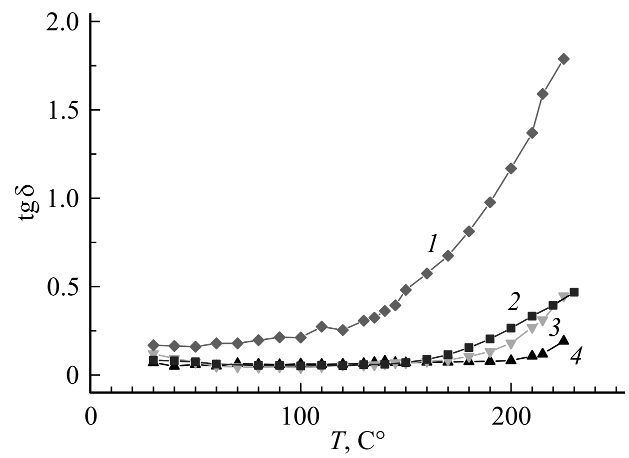

Figure 4. Temperature vs. dielectric loss angle tangent (measurement frequency 300 Hz) for the CBN30 ceramic samples (curve *1*), CBN30 + 5% $SrTiO_3$ (curve *2*), CBN30 + 5% $KTaO_3$ (curve *3*) and CBN30 + 5% CBN30 (curve *4*).

order of magnitude higher than that for the corresponding single-crystal ($0.015\,C/m^2$ [13]) (investigations were carried out at the same strength of the external sinusoidal electric field). CBN crystals are uniaxial ferroelectric materials, while ceramics is a polycrystalline material. Assuming that the polar crystal axis in each individual grain (single-crystallite) with equal probability may be oriented in any direction relative to the line perpendicular to the sample planes to which the external electric field is applied, then the reduction factor (k) for the total switchable polarization of the ceramics sample relative to the single-crystal can be calculated as follows

$$k = \frac{\iint\limits_{\substack{x^2+y^2+z^2=1\\ z\geq 0}} z\,ds}{\iint\limits_{\substack{x^2+y^2+z^2=1\\ z\geq 0}} ds}. \qquad (1)$$

Here, the Z axis is chosen as the direction of the applied electric field. Sum all possible directions of the polar axis by all crystallites. Integration is performed over hemisphere, because we suppose that, when a field is applied, spontaneous dipole moments will be re-oriented in a direction as slow as possible to the electric field direction. We suppose that this assumption is also true for the case when polar direction in a particular grain is directed at a wide angle to the field direction.

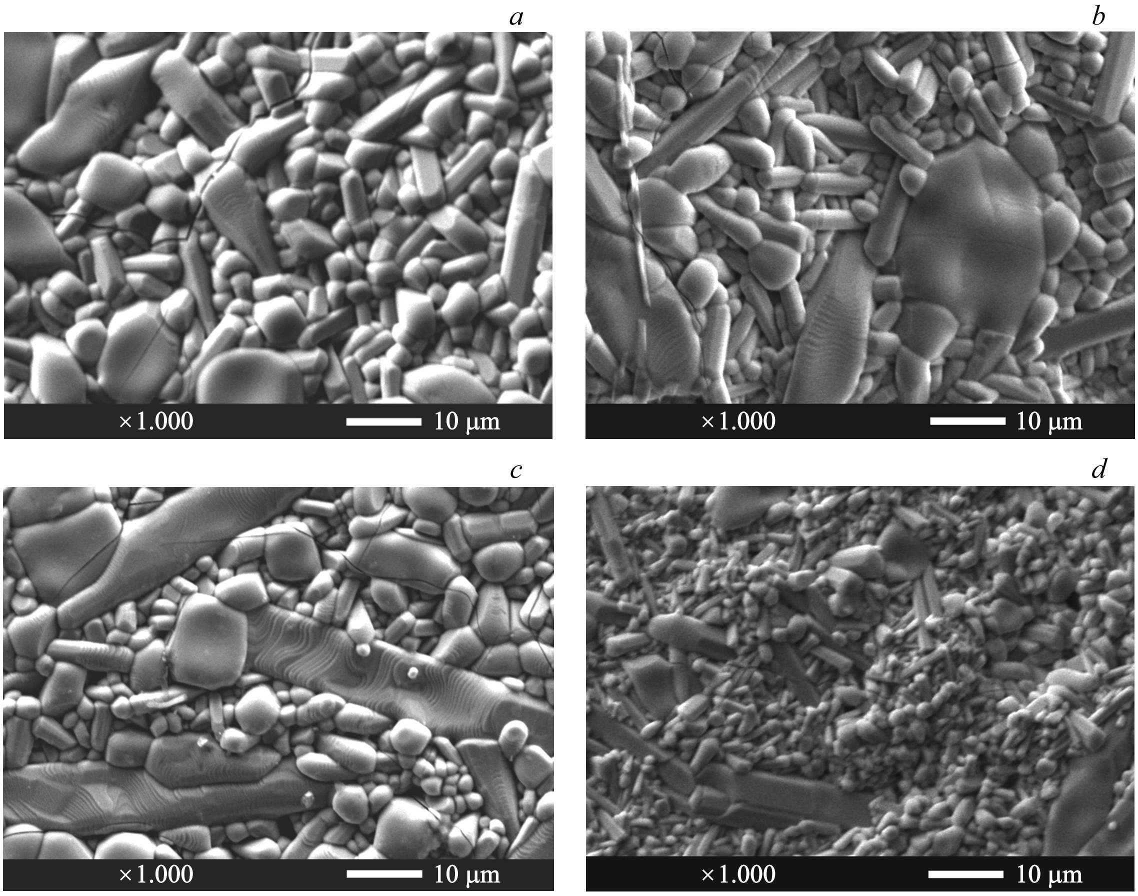

Figure 5. Grain structure images for the CBN30 (*a*), CBN30 + 5% $SrTiO_3$ (*b*), CBN30 + 5% $KTaO_3$ (*c*) and CBN30 + 5% $LiTaO_3$ (*d*) ceramics samples made using the scanning-electron microscope.

As a result, we have $k = \pi/4 \approx 0.785$. Then, according to the estimate, the ceramic sample shall have the switchable polarization $0.011\,C/m^2$. In real practice (Figure 3, *a* curve *1*), it is 10 times lower. The cause is probably as follows. CBN30 crystal habit is elongated along the polar axis, the CBN30 ceramic grains also have the same shape (Figure 5, *a*) and, therefore, the polar axis in grains is directed along their long axis. When such grains are arranged at a wide angle to normal to the sample surface, switching of the spontaneous polarization by the external AC field is hindered in them.

Let's find the grain orientation angle at which dipole switching takes place with coefficient k which is ten times lower than the calculated coefficient, i.e. $k = \pi/40$. To find the grain orientation angle, integration by equation (1) will be performed over a cone with vertex in the center of a sphere, rather than over a hemisphere. The angle between the cone generatrix and the normal to the cone base is in this case that very unknown variable to be found. As a result, the unknown variable id equal to ~ 4 degrees. Therefore, in practice, only the switching processes in few grains oriented at 86–90 degrees to the sample plane contribute to the macroscopic switchable polarization of the CBN30 ceramics.

CBN30 crystals, modified $CBN30 + 5\%\,SrTiO_3$, $CBN30 + 5\%\,KTaO_3$ or $CBN30 + 5\%\,LiTaO_3$ exhibit the switchable polarization at room temperature several times higher than that of the pure CBN30 (Figure 3, *a*). Since grains in modified CBN30-based solid solutions (Figure 5, *b–d*) have the same elongated shape (only in $CBN30 + 5\%\,LiTaO_3$, the grain size is several times smaller than that of other compounds) as that for the pure CBN30 ceramics, it would appear reasonable that the switchable polarization increases due to the increase in the dipole moment of the lattice cell, when ions of the modified additives (Li, K, Sr, Ti or Ta) are introduced.

4. Conclusion

Comparative investigations of the switching processes in ceramics based on $Ca_{0.3}Ba_{0.7}Nb_2O_6$ pure and modified 5% $SrTiO_3$, $KTaO_3$ or $LiTaO_3$ performed herein have shown that introduction of substitution ions into the TTB structure results in the increasing switchable polarization as well as in the increasing coercive field in the modified CBN30 samples compared with undoped samples. For the pure polycrystalline CBN30 material, compared with the single-crystal, full opening of the dielectric hysteresis loops (with the same AC electric field strength $\sim 1\,kV/mm$) was not observed, which is probably attributable both to the increase in the coercive field and rather fast growth of dielectric loss at room temperature above 100°C.

At room temperature, for local dielectric hysteresis loops for all modified CBN30-based solid solution, switchable polarization ($\sim 0.0045\,C/m^2$) is several times higher than that of the pure CBN30 ceramics ($\sim 0.001\,C/m^2$). Then, during temperature increase beginning from 70°C, $CBN30 + 5\%\,KTaO_3$ and $CBN30 + 5\%\,LiTaO_3$ compounds exhibit fast growth: $CBN30 + 5\%\,KTaO_3$ sample — by 2 time ($\sim$ up to $0.009\,C/m^2$), and $CBN30 + 5\%\,LiTaO_3$ sample — by 4 times ($\sim$ up to $0.018\,C/m^2$). At the same time, $CBN30 + 5\%\,SrTiO_3$ compound exhibit the growth of the switchable polarization beginning from $\sim 90°C$, with the increase itself being not so considerable. Such behavior is probably indicative of various contribution of the substitution ions to the dipole moment in the TTB structure. Thus, Ta ions substituting, as specified in [8], the Nb ions in the center of the oxygen octahedron give a more significant contribution to the spontaneous dipole moment of the lattice cell than Ti ions that also substitute Nb ions. It cannot be ruled out here that introduction of Sr ions into the TTB structure, that can occupy both types of channels (tetragonal channels occupied only by Ca in CBN and pentagonal channels occupied only by Ba), increase the spontaneous polarization [9]. Thus, the growth of the switchable polarization of the $CBN30 + 5\%\,SrTiO_3$ material compared with the switchable polarization of the pure CBN30 may be caused by the contribution of Sr ions, rather than Ti ions.

The difference in the switchable polarization values with the increasing temperature in $CBN30 + 5\%\,KTaO_3$ and $CBN30 + 5\%\,LiTaO_3$ may be explained as follows. According to [10], K ions occupy Ba ion positions in the TTB structure and their contribution to the additional (compared with the undoped CBN30 ceramics) dipole moment is low. Li ion, owing to its short radius, may occupy the vacant triangular channels in the TTB structure [8], that probably results in additional shift of charge states in the lattice cell and, therefore, in the increase in macroscopic switchable polarization.

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Conflict of interest

The authors declare that they have no conflict of interest.

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