Effect of SrTiO3, KTaO$_3$, and LiTaO$_3$ modifier on the dielectric properties of Ca$_{0.3}$Ba$_{0.7}$Nb$_2$O$_6$ ceramics

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Using the method of solid-phase synthesis, we obtained ceramic samples with a structure like tetragonal tungsten bronzes, pure Ca$_{0.3}$Ba$_{0.7}$Nb$_2$O$_6$ (CBN30) and with modifying additives SrTiO$_3$, KTaO$_3$, or LiTaO$_3$. The dispersion of the permittivity in the frequency range from 1 Hz to 10 MHz, the temperature dependences of the permittivity (in the given frequency range) and the pyroelectric coefficient are studied. It is shown that if the introduction of the LiTaO$_3$ impurity into the composition of CBN30 destabilizes the dielectric characteristics at frequencies above 100 kHz, then the SrTiO$_3$ impurity increases both the permittivity and the pyroelectric coefficient, significantly reducing dielectric losses at low $(1-10\,\mathrm{Hz})$ frequencies. At the same time, both of these impurities (SrTiO$_3$ and LiTaO$_3$) lead to sample depolarization during heating above 150°C, while the KTaO$_3$ impurity, which slightly increases the permittivity and pyroelectric coefficient, does not affect the stability of the polarized state during heating up to higher temperatures.

Keywords: piezoelectric ceramics, barium-calcium niobate, lead-free materials, permittivity dispersion, pyroelectric effect.

1. Introduction

Alkali metal niobates and alkaline earth metal titanates, which have a perovskite type structure, are currently considered most widely as an alternative to PZT ceramics [1–6]. Structures such as tetragonal tungsten bronzes (TTB) have received much less attention. Apparently, this is due to the fact that ferroelectrics with a perovskite-type structure are multiaxial polar dielectrics (a classic example is barium titanate [7]) ferroelectrics, this, when obtaining a polycrystalline state (ceramics), makes it possible to achieve a sufficiently high value of spontaneous polarization in the samples. Whereas ferroelectrics with a structure like TTB (the most common example of this class of materials is barium-strontium niobate) are the uniaxial ferroelectrics [8], which, in theory, should make it difficult to obtain in ceramics based on them a spontaneous polarization value sufficient for practical application due to the chaotic orientation of the polar axis in single crystallites (grains).

At the same time, the materials with the TTB structure (whose general formula is A1$_2$A2$_4$C$_4$B$_{10}$O$_{30}$) have wide possibilities for obtaining various modifications of solid solutions [9,10]. Thus, positions A1 and A2 can be occupied by both alkaline earth and alkali metals (i.e. elements of the first and second groups of the table of chemical elements). Position C is most often vacant due to its small volume in the structure of the TTB crystal lattice. Position B can contain Nb, Ta, and Ti cations.

The barium strontium niobate (SBN) crystal is the most studied of this class of the materials; therefore, most works on ceramics based on TTB are also devoted to various modifications of the SBN material [10–13]. At the same time, one of the drawbacks for the practical application of SBN is its low phase transition temperature (less than 100°C). Replacing strontium with calcium (the material of barium–calcium niobate — CBN) significantly increases the phase transition temperature [14,15].

In the present work, the Ca$_{0.3}$Ba$_{0.7}$Nb$_2$O$_6$ (CBN30) material was chosen for the study, since, according to [16], Ca$_x$Ba$_{1-x}$Nb$_2$O$_6$ crystals exist in the crystalline phase only in the range $0.2 < x < 0.4$, and as we showed earlier [17], CBN30 ceramics have the most pronounced ferroelectric properties compared to CBN ceramics with other x values. Samples of unmodified CBN30 ceramics and CBN30 ceramics modified with SrTiO$_3$, KTaO$_3$, or LiTaO$_3$ (5 wt%) were obtained by solid-phase synthesis and studied. We chose modifying additives for the following reasons. Most industrial PZT compositions contain from 3 to 5% SrTiO$_3$. Li, due to its small ionic radius, is one of the few metals whose ions can occupy vacant C positions in the TTB structure. There is information about the possibility of replacing Ba ions with K ions [13]. The Nb, Ta, and Ti cations are interchangeable in the TTB structure [10]. Thus, it was of interest to check the effect of SrTiO$_3$, KTaO$_3$, or LiTaO$_3$ additions on the dielectric properties of CBN30 ceramics.

Characteristics of the modified CBN30 ceramics samples

	D, mm	ρ, g/cm^3	γ, 10^{-4} C/m$^2 \cdot$ K		$^*\varepsilon$	* tg δ
			$-P_s$	$+P_s$	($T = 30°$C)	
CBN30	9.50	4.7	0.05	0.18	152	0.063
CBN30 + 5% KTaO$_3$	9.30	4.7	0.33	0.27	115	0.059
CBN30 + 5% LiTaO$_3$	9.45	4.9	0.28	0.27	108	0.062
CBN30 + 5% SrTiO$_3$	9.50	4.2	0.55	0.35	211	0.058

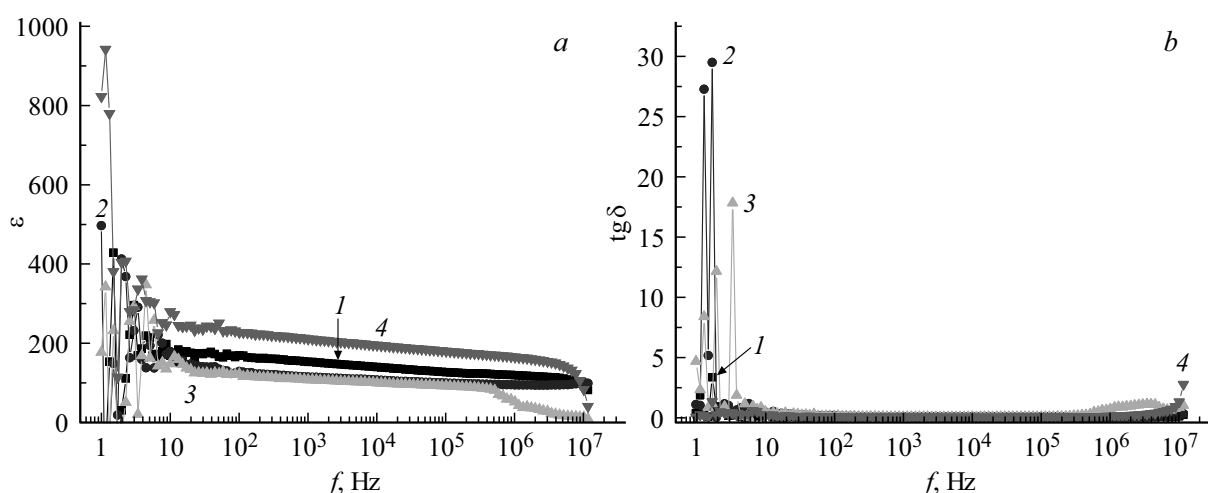* The measurements were carried out at a frequency of 1 kHz.

Figure 1. Frequency dependences of permittivity (*a*) and dielectric loss (*b*) of pure CBN30 ceramics (curve *1*) and modified with KTaO$_3$ (curve *2*), with LiTaO$_3$ (curve *3*), and with SrTiO$_3$ (curve *4*).

2. Sample preparation

If the raw materials for the synthesis of the PZT material consist only of metal oxides, which allow mixing of all components at the synthesis stage, then alkali and alkaline earth metal niobates are obtained as a result of solid-phase synthesis from niobium oxide and carbonates of the corresponding metals. Since [18] the decomposition temperature of carbonates strongly depends on the atomic mass of its metal, to obtain solid solutions with the TTB structure, all components, including modifying additives, must be synthesized separately. The mixing of the component powders in certain proportions is carried out only at the final stage, before pressing the pellet.

The solid-phase synthesis of the main compositions BaNb$_2$O$_6$ and CaNb$_2$O$_6$ was carried out at temperatures of 1300 and 700°C, correspondingly; the modifying additive SrTiO$_3$ — at a temperature of 1300°C, KTaO$_3$ and LiTaO$_3$ — at a temperature of 700°C. Mixing in certain proportions took place before pressing the samples (at a pressure of 5 atmospheres). The samples were sintered at $T = 1300°$C.

Although all pellets had a diameter (D) of 10.4 mm, after sintering, the size of the samples varied (see Table). The addition of both 5% KTaO$_3$ and 5% LiTaO$_3$ lead to a slight

reduction in size compared to pure CBN30. The change in density when 5% LiTaO$_3$ or 5% SrTiO$_3$ was added to CBN30 proved to be more significant. If the addition of 5% LiTaO$_3$ led to an increase in density by 4%, then the addition of 5% SrTiO$_3$ reduced the density by 10% (see Table).

3. Study of the physical properties

For the practical application of piezoelectric ceramics, not only dielectric properties are important, but also the possibility of obtaining a stable homogeneous polarized state in the samples. In this connection, we studied both the permittivity of the obtained samples and the pyroelectric coefficients.

The temperature dependence and dispersion of the permittivity was measured by the LCR method using the Frequency Response Analyzers PSM1735 with Impedance Analysis Interface (Newtons4th Ltd) in the temperature range from 30 to 330°C and in the frequency range from 1 Hz to 10 MHz.

The pyroelectric effect was studied by the dynamic pyroelectric method [19], which makes it possible not only to calculate the magnitude of the pyroelectric response, but
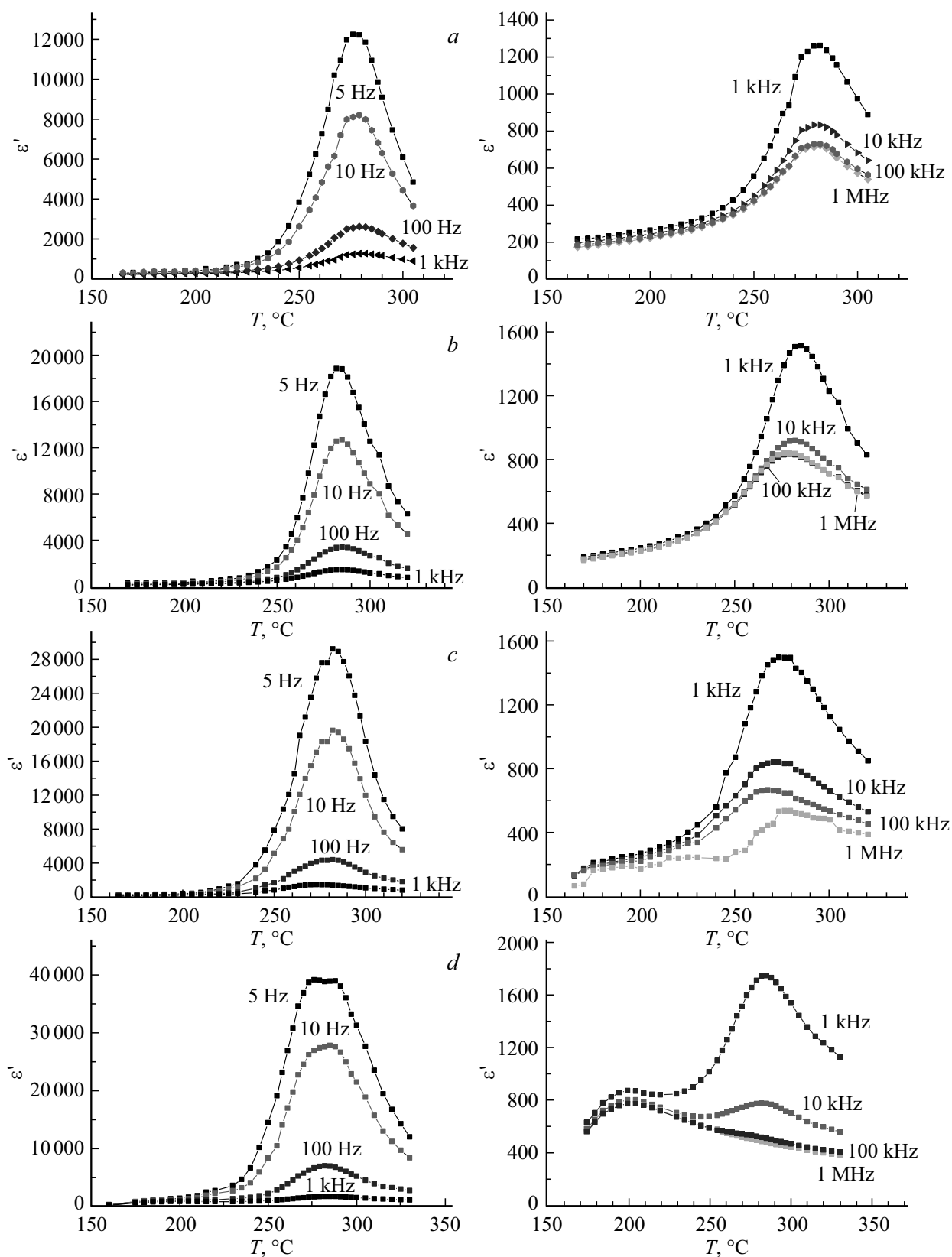
Figure 2. Temperature dependences of the permittivity of CBN30 ceramics (*a*) pure and (*b*) modified with KTaO₃, (*c*) with LiTaO₃, and (*d*) with SrTiO₃.

also to determine the direction of the polarization vector near the sample surface. Before measurements, the samples were polled in a DC electric field of 2 kV/mm.

3.1. Permittivity

Studies of the dispersion of the permittivity have shown that at room temperature at frequencies up to 10 Hz, all the samples under study have a strong spread in the values of the permittivity, which is proper to piezoelectric ceramics at low frequencies (Fig. 1, *a*). This behavior of the permittivity at low frequencies is usually associated with the migration of free charges along grain boundaries, which leads to significant dielectric losses. Indeed, the dielectric loss reaches more than 10 in this frequency range for all samples except for CBN30 modified with $SrTiO_3$ (Fig. 1, *b*).

For the CBN30 ceramic sample modified with $LiTaO_3$ at a frequency above 450 Hz, a sharp decrease in the permittivity and an increase in the dielectric loss are observed. This difference is apparently associated with the specificity of the Li ion, which, due to its small ionic radius, can occupy vacant *C* positions in the TTB structure [10].

The values of the permittivity and the dielectric loss for a measurement frequency of 1 kHz are presented in Table. As can be seen, the introduction of both 5% $KTaO_3$ and 5% $LiTaO_3$ led to a decrease in the dielectric constant by $25-30\%$, while the addition of 5% $SrTiO_3$ increases its value by 30% compared to pure CBN30.

In the frequency range from 10 Hz to 10 MHz, the behavior of the permittivity of all the studied samples, except for CBN30 modified with $LiTaO_3$, is stable and similar to the frequency dependences of PZT ceramics, but the permittivity values themselves are several times smaller.

The stability of the dielectric constant is maintained during heating to a temperature of $230°C$. Then, the values of the permittivity begin to increase, due to the approach to the temperature of the ferroelectric phase transition (Fig. 2). The value of the permittivity at the maximum strongly depends on the measurement frequency, decreasing with increasing frequency. At frequencies above 100 kHz, the behavior of the temperature dependence of the permittivity does not depend on the measurement frequency for all materials except CBN30 modified $LiTaO_3$ (Fig. 2, *c*).

Here, as before, the CBN30 material modified with $SrTiO_3$ stands out. If all compositions have a maximum at a temperature of $278°C$, which does not depend on either the measurement frequency or the type of additive, then the CBN30 sample modified with $SrTiO_3$ has an additional maximum at a temperature of $200°C$ (Fig. 2, *d*).

It should be noted that the Curie temperature of CBN30 ceramics is 60 degrees higher than that of a single crystal [14], for which it is $217°C$.

3.2. Pyroelectric effect

As expected, the value of the pyroelectric coefficient for the CBN30 ceramic turned out to be significantly lower (see Table) than for the single crystal [14], for which
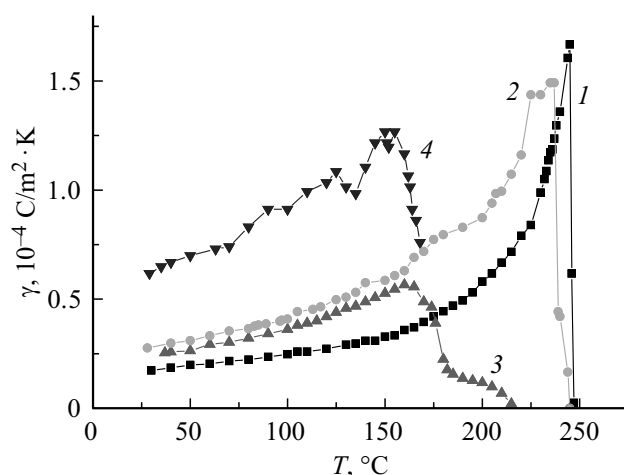
Figure 3. Temperature dependences of the pyroelectric coefficient of pure (curve *1*) and modified with $KTaO_3$ (curve *2*), with $LiTaO_3$ (curve *3*), and with $SrTiO_3$ (curve *4*) CBN30 ceramics.

it is $3.0-3.5 \cdot 10^{-4}\, C/m^2 K$. If the CBN30 single crystal has an uniform polarization across the thickness of the sample, while the CBN30 ceramic sample has a polarization gradient directed from the negative $(-P_s)$ to the positive $(+P_s)$ end of the polarization vector. The introduction of modifying additives $SrTiO_3$, $KTaO_3$, and $LiTaO_3$ led to an increase in the pyroelectric coefficient and a uniform state of polarization over the sample thickness. It is interesting to note that, as for the permittivity, among all the studied samples, CBN30 modified with 5% $SrTiO_3$ has the maximum value of the pyroelectric coefficient.

Despite the fact that for all the studied compositions the temperature of the maximum dielectric permittivity is the same, the maximum on the temperature dependence of the pyroelectric coefficient takes place at different temperatures (Fig. 3).

To explain this fact, it is necessary to take into account the following. The maximum on the temperature dependence of the permittivity uniquely determines the phase transition temperature. Whereas, the maximum on the temperature dependence of the pyroelectric current can exist at lower temperatures [20]. This is due to the fact that the pyroelectric effect is observed only in samples with macroscopic polarization. If the sample is depolarized during heating (i.e., there is the partition of the sample into ferroelectric domains), then the pyroelectric current decreases in the experiment. Apparently, this explains the position of the maximum of the pyroelectric current of CBN30 ceramics with 5% impurities of $SrTiO_3$ and $LiTaO_3$ at a temperature much lower than the Curie temperature (which is determined from the maximum of the permittivity).

4. Conclusion

The comparative studies of ceramics based on pure $Ca_{0.3}Ba_{0.7}Nb_2O_6$ and modified with 5% $SrTiO_3$, $KTaO_3$,

or LiTaO$_3$, carried out in this work, showed that the impurity of SrTiO$_3$ leads to an increase in the permittivity and pyroelectric coefficient, and a significant decrease in the dielectric loss at low frequencies, compared with pure CBN30 ceramics and other modified compositions. The LiTaO$_3$ impurity destabilizes the behavior of the dielectric characteristics at frequencies above 100 kHz. At the same time, despite the high value of the pyroelectric coefficient for CBN30 ceramic samples modified with SrTiO$_3$, its polarization, as well as for the CBN30 sample modified with LiTaO$_3$, disappears at temperatures above 150°C. This is confirmed by a sharp decrease in the pyro-response during the heating of the samples. For pure CBN30 ceramics and modified with KTaO$_3$, the pyroelectric current maximum is observed at 25 degrees below the maximum of the permittivity, while for the CBN30 crystal, a similar difference is 10 degrees [14].

In the structure of TTB, all metal ions are responsible for the occurrence of spontaneous polarization (for CBN, these are Ca, Ba, and Nb). Since the modifying additives were chosen based on the fact that their constituent ions can be included in the TTB structure, occupying the same positions as the CBN ions, the results obtained are interpreted as follows. Ta and Ti ions replace Nb at the oxygen octahedron center [10]. However, since the radius of the Ta ion is comparable to the ionic radius of Nb, while the ionic radius of Ti is smaller, its insertion changes the dipole moment of the unit cell more than the insertion of the Ta ion. The Li ion, due to its small radius [10], can occupy vacant triangular channels in the TTB structure, which should lead to additional vacancies in quadrangular and pentagonal channels. Since the anomalous behavior of the permittivity at frequencies above 100 kHz is observed only for CBN30 samples modified with LiTaO$_3$, Li ions are responsible for this behavior. According to [13], K occupies the positions of Ba in the TTB structure (pentagonal channels), while Sr can occupy both types of channels (quadrangular, occupied only by Ca in CBN, and pentagonal, occupied exclusively by Ba). Therefore, in the CBN30 samples modified with SrTiO$_3$, there should be local microscopic regions corresponding to the SBN composition, the Curie temperature of which is much lower than that of the CBN material. This fully explains the presence of an additional low-temperature maximum in the temperature dependence of the permittivity.

Conflict of interest

The authors declare that they have no conflict of interest.

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