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# Effect of mechanical activation on the internal structure and macroresponses of a lead-free multicomponent material based on alkali metal niobates

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The paper reports on the patterns of influence of mechanically activating procedures on the internal structure (crystalline, grain) and electrophysical properties of compositions based on alkali metal niobates of the type $(Na_aK_bLi_c)(Nb_dTa_mSb_n)O_3$ with the participation of a combined modifier $(Bi_2O_3+Fe_2O_3)$ and a non-isostructural compound $CuNb_2O_6$. It was determined, based on the results obtained, that the optimal conditions for the preparation of high-density, virtually impurity-free ceramics are mechanical activation for (10−15) min. It is evident that these technological conditions have the capacity to reduce dielectric losses and increase the values of macroresponses of the ceramics under investigation.

**Keywords:** alkali metal niobates, technology, mechanical activation, internal structure, microstructure, macroresponses.

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## Introduction

Greening of industrial production as one of the main technical-technological trends of our time necessitates implementation of environmental safety to newly created functional electronics materials. It is especially relevant for compositions used in piezoelectric engineering, since in most applications they are based on complex-oxide solid solutions (SS) that contain in their composition extremely toxic lead in quite big quantities [1].

Development of the field of lead-free materials science is characterized by several subsequent stages.

I — from 1980 to 2002 — formation of physical-technological basics for searching and designing compositions not containing toxic elements (first of all, lead).

II — from 2002 to 2007 — manufacturing binary systems with niobates of alkaline/alkaline earth metals, including, with a various type of dopants. In most cases, the main studied system was $(Na,K)NbO_3$, which has electrophysical parameters close to the solid solution LZT $(Pb(Ti,Zr)O_3)$.

III — from 2007 to 2018 — transition to multi-component systems (MS) that are clean and modified, with improved characteristics. Attempts to reach target properties that are optimal for each specific application of the solid solution, to improve their processability and to extend a „range" of functional capabilities by MS construction are described in the paper [2–6]. It is noted that the most promising MS in terms of implementation of high piezoactivity that is comparable with LZT compositions is the MS of the type $(Na_aK_bLi_c)(Nb_dTa_mSb_n)O_3$ [7–9] without additives and with introduced dopants (both simple and combined) [10,11]. For the latter case, the study [12] has shown that the most effective were the solid solutions of the said system that are modified simultaneously by oxides of bismuth and iron $(Bi_2O_3+Fe_2O_3)$. But, nevertheless, despite actions done by the technologists, the said MS was still much dependent on preparation conditions. The papers [13–16] could avoid it by introducing Cu-containing additives into the solid solution that enabled sharply reducing the sintering temperature of objects, maintaining stoichiometry of their defined composition and increasing the density of the samples. In this regard, it was suggested that simultaneous introduction of bismuth and iron oxides as well as a precursor (pre-synthesized) $CuNb_2O_6$ into the system $(Na,K,Li)(Nb,Ta,Sb)O_3$ would ensure production of ceramics that were not contaminated with ballast phases and had the density close to the theoretical one [14].

IV — from 2018 — up to now — further complication of the multi-component systems that are produced either using new technological approaches or improved known methods. This is explained by critical dependence of the properties of the lead-free ceramics (LC) on their thermodynamic history, which is confirmed in a number of the papers [17–20] that state that the number of technological difficulties related to lead-free ceramics specifics limit their wide application in practice [21–23].

In regard of the above-said, many research groups publish studies [24–27], which describe ways of solving this task, including by introducing an operation of mechanical processing of the compositions (at the selected stages of their production) into a technological process of creation of lead-free MS-based ceramics. At the same time, it is stated that it is advantageous of using mechanical activation (MA), especially during industrial production of electronics materials. [26]. We have also shown in the study [28] that activation before sintering of the synthesized powders of the materials based on niobates of alkaline/alkaline earth metals by mechanical processing in a ball planetary mill can substantially intensify the heterogeneous processes and, as a consequence, sharply reduce the sintering temperature $T_{sint.}$ of the objects as well as improve their electrophysical characteristics due to reduction of dielectric losses.

The present study was aimed at establishing physical mechanisms of mechanical activation effect on the internal structure (a crystal grain one) and macro-responses (dielectric, piezoelectric, ferroelastic, mechanical) of the solid solution of the multicomponent system based on $NaNbO_3$, $KNbO_3$, $LiSbO_3$ with involvement of a combined modifier ($Bi_2O_3$+$Fe_2O_3$) and a non-isostructural compound $CuNb_2O_6$ of the columbite type.

## 1. Objects, methods for obtaining and studying them

The object of investigation was the solid solution of the type $K_{0.432}Na_{0.508}Li_{0.06}Nb_{0.846}Ta_{0.094}Sb_{0.06}O_3$, modified by 1.5 mass% ($Bi_2O_3$+$Fe_2O_3$) and $CuNb_2O_6$, wherein the quantitative-quantitative composition thereof is selected to be optimal from a series of samples with variations of quantities of basic components and modifiers [29]. The solid solution was produced by double solid-phase synthesis ($T_1 = 1000\,^\circ$C, $T_2 = 1100\,^\circ$C, $\tau_1 = \tau_2 = 6$ h) with subsequent sintering by the common ceramics technology ($T_{sint.} = 1200\,^\circ$C, $\tau_{sint.} = 2$ h) with raw components being oxides of niobium, tantalum, iron, bismuth, copper and qualified as „chemically pure“ (chem. pure.) and hydrocarbonates of alkali metals qualified as „pure for analysis“ (analytically pure).

The synthesized (after synthesis at the temperature $T_2$) powders were mechanically activated in a ball planetary mill for high-energy milling AGO-2 manufactured by the Novits company (Novosibirsk) [30,31]. The prepared powder was poured into drums of the internal diameter of 63 mm together with the balls made of $ZrO_2$ and having the diameter of 8 mm with the total weight of 200 g. The drum with the mixture was placed into the planetary mill AGO-2. It was ground in an alcohol medium during 15 min, whereas the drub rotational speed was 1800 rpm.

The ceramics samples for subsequent diagnostics of the crystal and grain structures, of the experimental density $\rho_{\exp}$ were produced as discs $\varnothing 10\,\text{mm} \times (0.5 - 1.0)\,\text{mm}$. The piezoelectric properties were investigated by polarizing the samples with applied silver electrodes in the field of strength of 50–60 kV/cm for 15–20 min at the temperature of 150 °C.

The parameters of the investigated solid solution were characterized by methods of X-ray imaging [32], microstructure analysis [33,34], certification of the electrophysical properties [35]. The following equipment was used for this: diffractometer DRON-3 (Co$K_\alpha$-radiation, Bragg–Brentano focusing). The content of the impurity phases was evaluated by a relative intensity of their strong line: $I/I_1 \cdot 100\,\%$, where $I$ — the intensity of the strong line of the impurity phase, $I_1$ — the intensity of the strong line of the main phase (perovskite). The microstructure of the sintered ceramics was evaluated on a sample cleavage by means of the scanning electron microscope JSM-6390L (Japan) using the energy-dispersive microanalyzer manufactured by Oxford Instruments (Great Britain). The images are obtained in the secondary electrons, the accelerating voltage ranges from 0.5 kV to 30 kV; the impedance measurer Agilent E 4980A and the temperature regulator Varta TP 703.

The dielectric, piezoelectric and ferroelastic parameters included relative permittivities of the polarized, $\varepsilon_{33}^T/\varepsilon_0$, and the nonpolarized, $\varepsilon/\varepsilon_0$, samples; the low-field dielectric losses (the dielectric loss angle tangent), $\operatorname{tg}\delta$, the piezoelectric constants, $|d_{31}|$, $d_{33}$; the electromechanical coupling coefficient of the planar oscillation mode, $K_p$; the mechanical Q factor, $Q_M$; the speed of sound, $V_1^E$.

The relative errors of determinating the parameters were
$\Delta a = \Delta b = \Delta c = \pm 0.05\,\text{Å}$;
$\Delta a = \Delta\beta = \pm 0.05\,\text{deg}$; $\Delta V = \pm 0.05\,\text{Å}^3$;
$\Delta\varepsilon_{33}^T/\varepsilon_0 \le \pm 1.5\,\%$; $\Delta\operatorname{tg}\delta \le \pm 5\,\%$, $\Delta K_p \le \pm 2.0\,\%$;
$\Delta|d_{31}| = \Delta d_{33} \le \pm 4.0\,\%$; $\Delta Q_M \le \pm 12.0\,\%$;
$\Delta V_1^E \le \pm 0.3\,\%$.

The depth of frequency dispersion of permittivity was evaluated by the formula

$$\Delta\varepsilon'_m = \left(\frac{\varepsilon'_{mf1} - \varepsilon'_{mf2}}{\varepsilon'_{mf1}}\right) \times 100\,\%,$$

where $\varepsilon'_{mf1}$ — the maximum value of $\varepsilon'/\varepsilon_0$ at the lowest frequency, $\varepsilon'_{mf2}$ — the maximum value of $\varepsilon'/\varepsilon_0$ at the highest frequency.

## 2. Experimental results, discussion

The X-ray diffraction analysis and the precision X-ray diffraction investigation of phase formation processes of the studied solid solution that is produced using the mechanical activation procedures for 5 – 20 min, and without them, showed that all the samples contained the impurity ballast phase of the composition $Li_2K_3Ta_5O_{15}$ (the X-ray peaks are marked by the dots on Fig. 1) in the quantity of below 8 % of the main phase. Its largest quantity is contained in the non-mechanically-activated solid solution (8 %), while its least quantity is contained in the solid solution with time of activation of 10 min (3 %). At this, all the samples have a tetragonally-distorted structure of the perovskite type that is

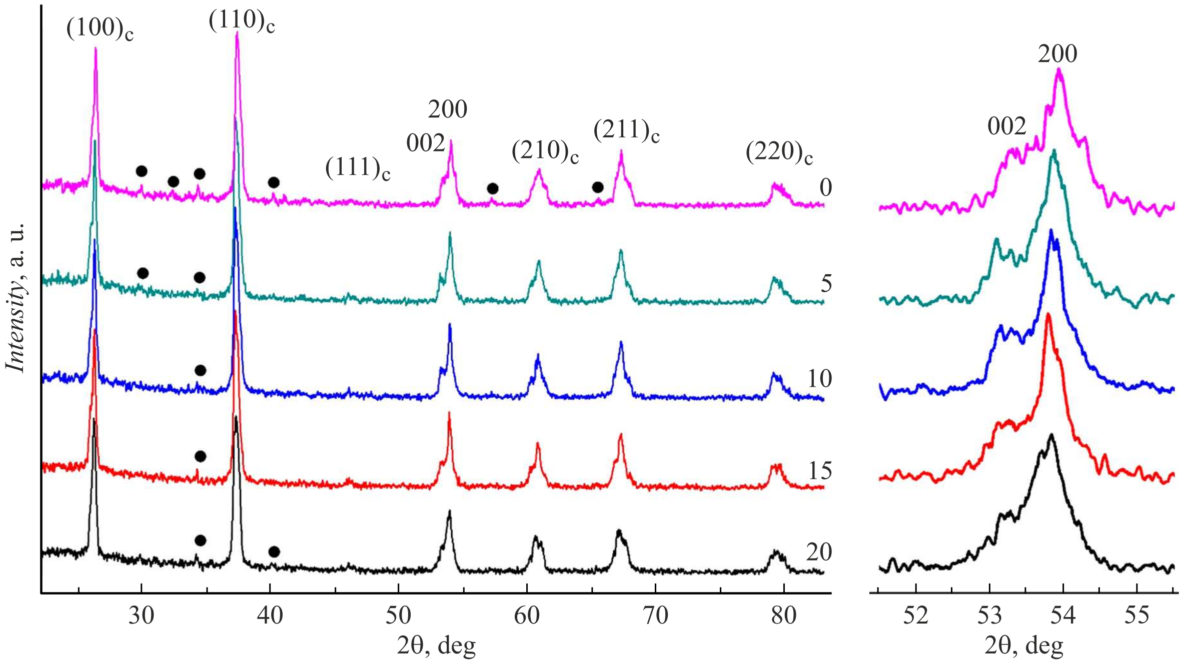

**Figure 1.** X-ray diffraction patterns of the solid solution $K_{0.4324}Na_{0.5076}Li_{0.06}Nb_{0.846}Ta_{0.094}Sb_{0.06}O_3$, mechanically activated for 0, 5, 10, 15 and 20 min and the diffraction peaks (002) and (200) in an enlarged scale.

quite heterogeneous, which is indicated by the diffraction peaks 002 and 200 shown on Fig. 1 in an enlarged scale. As it is seen on Fig. 2, with increase of duration of mechanical activation, the degree of distortion of the lattice cell $(c/a)$ decreases on the background of the increasing density of the solid solution ceramics. The highest $\rho_{\text{exp}}$ is typical for the solid solution that is mechanically activated for 15 min, which correlates with the nature of a grain landscape of these samples with many assemblies of closely-packed crystallites (they are shown by a dashed line on Fig. 3).

Note that the grains are crystallized in the form of regular geometric figures — parallelepipeds. As we noted in our papers [36,37], it was observed in cases when recrystallization sintering occurs with involvement of the liquid phase (LP). In our experiment, its source may be unreacted initial reagents or low-melting eutectics in blends of niobates and tantalates of sodium, potassium, lithium with the melting temperatures, $T_{\text{melt}}$, below 1000 °C: $K_2O$ with $T_{\text{melt}} = 740\,^\circ$C; $Sb_2O_5$ with $T_{\text{melt}} = 350\,^\circ$C; $Bi_2O_3$ with $T_{\text{melt}} = 817\,^\circ$C; $Na_2CO_3$ with $T_{\text{melt}} = 854\,^\circ$C; $K_2CO_3$ with $T_{\text{melt}} = 891\,^\circ$C; $Li_2CO_3$ with $T_{\text{melt}} = 732\,^\circ$C; NaOH with $T_{\text{melt}} = 323\,^\circ$C; KOH with $T_{\text{melt}} = 405\,^\circ$C; LiOH with $T_{\text{melt}} = 462\,^\circ$C [38].

The spectroscopic studies of the dielectric properties of the analyzed solid solution have shown that the dependences $\varepsilon/\varepsilon_0(T)$ within the wide range of alternate electric field frequencies (Fig. 4) have a form that is typical for the ferroelectrics with smeared phase transition: the frequency-independent peak $\varepsilon/\varepsilon_0$, increase of its smearness and reduction of the value of the maximum of $\varepsilon/\varepsilon_0$ with increase of the frequency. Strong dispersion of $\varepsilon/\varepsilon_0$ is noticeable in the vicinity of a ferro-paraelectric transition, so is its growth above the Curie temperature. Most likely, it

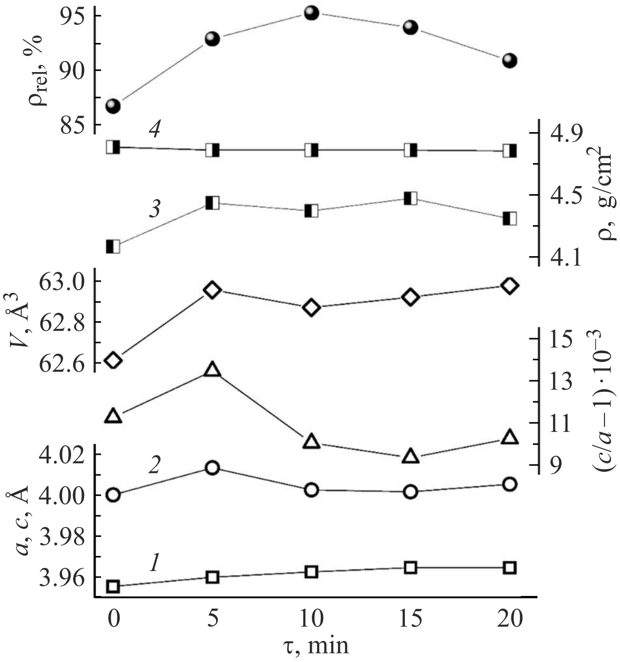

**Figure 2.** Dependences of the parameters $a$ (*1*), $c$ (*2*) of the tetragonality degree $(c/a-1)\cdot 10^{-3}$, the value, $V$, the tetragonal cell, the ceramics density: the experimental one, $\rho_{\text{exp.}}$, (*3*), the X-ray one, $\rho_{\text{XR}}$, (*4*) and the relative one, $\rho_{\text{rel.}}$, on the time of mechanical activation of the studied solid solution.

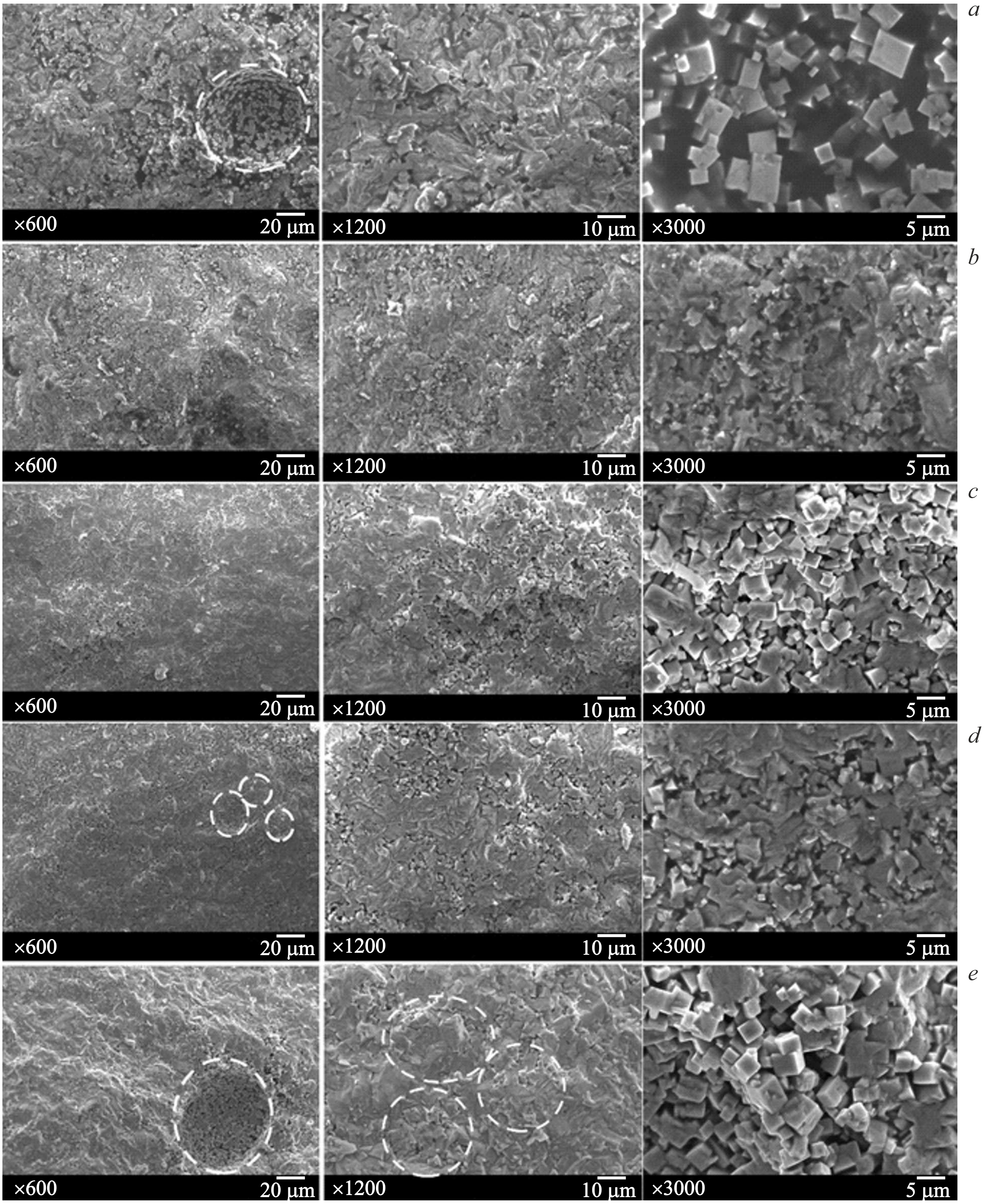

**Figure 3.** Fragments of the microstructures of the ceramics of the studied solid solution produced using mechanical activation for 0 (*a*), 5 (*b*), 10 (*c*), 15 (*d*), 20 min (*e*).

is due to oxidation-reduction processes in the solid solution at the high temperatures, when the oxidation degree of the mixed-valent ions ($Nb^{5+} \leftrightarrow Nb^{4+}$) [39] is changed and oxygen vacancies are generated [40], whose motion under impact of the applied electric field causes increase of electric conductivity of the solid solution. With increase of duration of mechanical activation, the temperature of a start of this process decreases.

Fig. 5 shows the dependence of the depth of the frequency dispersion of permittivity in the vicinity of

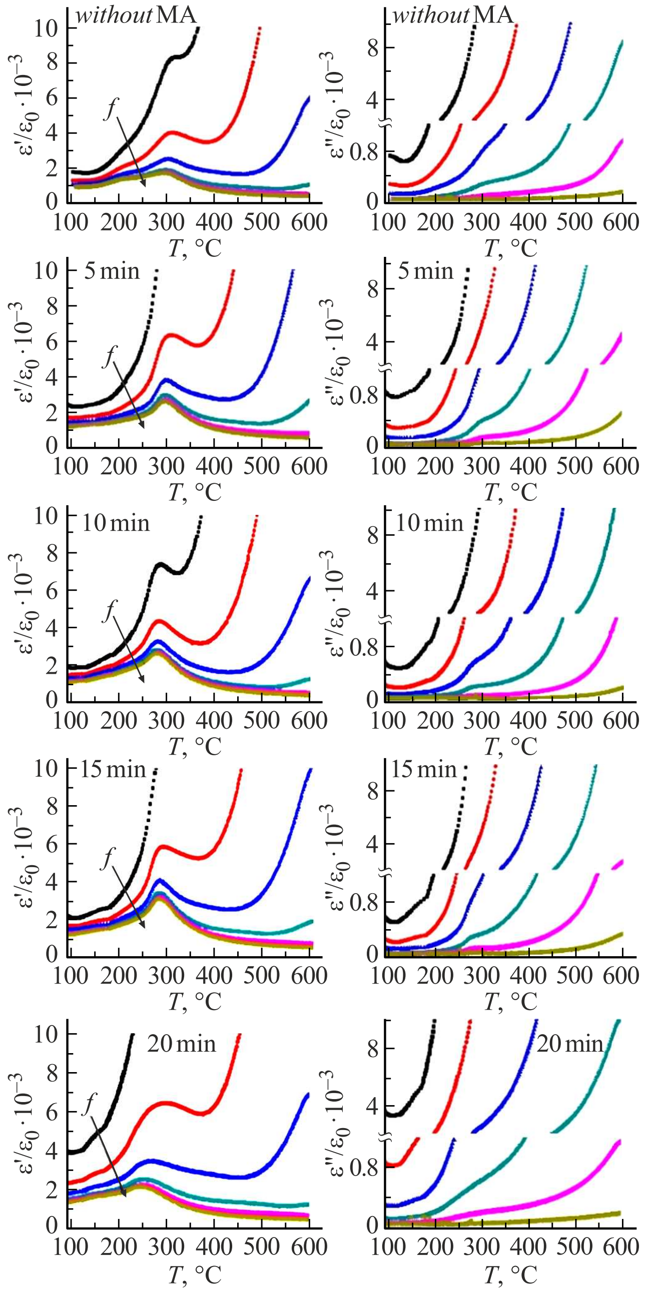

**Figure 4.** Dependences of the real $\varepsilon'/\varepsilon_0$ and the imaginary $\varepsilon''/\varepsilon_0$ parts of relative complex permittivity on the temperature in the solid solutions produced using mechanical activation for 0–20 min ($f$ — the electric field frequency, the arrow points a direction of increase of the frequency from 1 Hz to 100 kHz).

the Curie temperature, $\Delta\varepsilon_m$, on duration of impact by mechanical activation. It is clear that at the initial stage (up to 5 min) $\Delta\varepsilon_m$ is almost unchanged as compared to the non-mechanically-activated sample. With increase of the time of mechanical activation (up to 10 min.), $\Delta\varepsilon_m$ decreases with lengthening of the mode of mechanical processing of the composition, and then (up to 15 min) $\Delta\varepsilon_m$ insignificantly increases, while with long-term mechanical activation (20 min and more) it sharply increases. Thus, the most stable is the structure of the solid solution after its mechanical activation for 10–15 min, which we can see on Fig. 6, which shows dependences of the electrophysical characteristics of the solid solution on duration of mechanical activation with extremums of the magnitudes at such modes

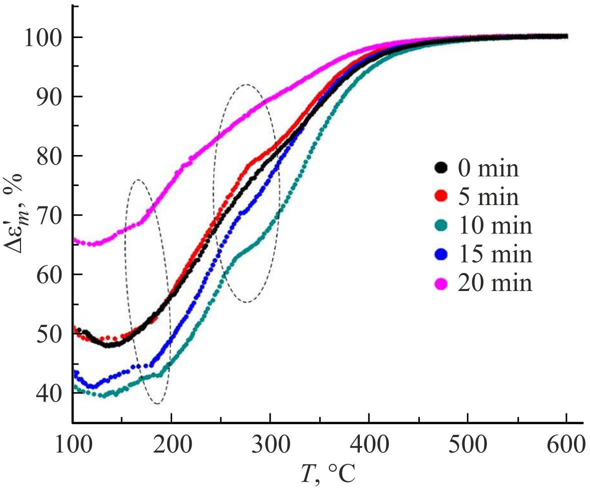

**Figure 5.** Dependences of the depth of the frequency dispersion, $\Delta\varepsilon'_m$, on the temperature in the studied solid solution that is mechanically activated for 0–20 min.

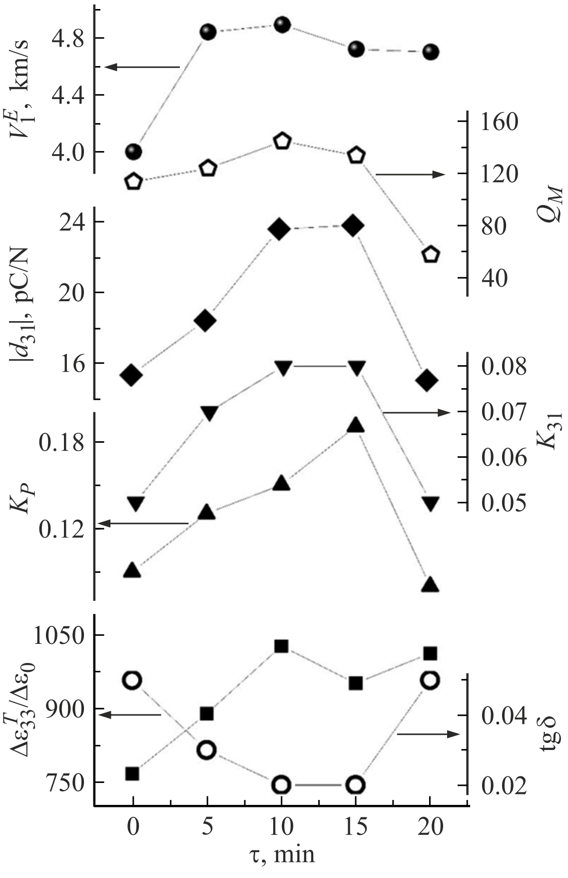

**Figure 6.** Dependences of the electrophysical parameters of the studied solid solution on the time of mechanical activation.

of mechanical activation. Returning to Fig. 5, we note that the dependences $\Delta\varepsilon_m = f(\tau)$ exhibit two anomalies at $T = 170\,^\circ\mathrm{C}-190\,^\circ\mathrm{C}$ and $250\,^\circ\mathrm{C}-300\,^\circ\mathrm{C}$, which are probably attributed to transitions from one ferroelectric phase into another as well as to a transition „cubic phase-tetragonal phase" [1,41].

All the above-said confirms the known correlation "the composition-the structure-the properties" in these solid solutions. The above-described state of the internal structure of the solid solution (the crystal and grains structures) as well as their high density and practical non-porosity that are implemented at certain technological conditions ensure two-time reduction of the dielectric losses and, as a consequence, a high level of the macro-responses. But it is worth noting another factor. As we state above, the synthesis and sintering of our object is characterized by liquid phases in the process of these technological operations, which can contribute to generation of a inter-crystalline intermediate layer (Fig. 2) that is favorable for reduction of internal friction and, as a result, improvement of transmission of a electromechanical signal. With a transition to the long-term modes of mechanical activation (20 min and more), there is high probability of conglomeration of the smallest particles, formation of their assemblies and, as a result, reduction of an interparticle specific surface. This significantly complicates the phase generation processes and results in attenuation of the macro-responses, as we see in practice (Fig. 6).

## Conclusion

Thus, the study has established the optimal conditions for preparing the high-dense, almost undoped solid solution of the type $K_{0.432}Na_{0.508}Li_{0.06}Nb_{0.846}Ta_{0.094}Sb_{0.06}O_3$, modified by 1.5 mass% ($Bi_2O_3$+$Fe_2O_3$) and $CuNb_2O_6$. It is demonstrated that the most stable structure of the solid solution with the least quantity of the impurity phase and of the largest density is generated after mechanical activation for 10−15 min. The said technological conditions ensure two-time reduction of the dielectric losses in the material as well as improvement of the electromechanical properties due to involvement of the liquid phase in sintering, that contributes to generation of the intercrystalline intermediate layer that is favorable for reduction of internal friction.

The obtained results shall be preferably used for designing of similar materials and devices based on these materials.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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