The influence of production conditions on the electrophysical parameters of piezoceramics for different applications

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Abstract. The conditions for the preparation of ceramic piezomaterials with low temperatures of synthesis and sintering have been studied. It is obtained that the materials based on the double system 0.2Pb(Nb2/3Zn1/3)O3-0.8Pb(Zr0.5Ti0.5)O3, alloyed with gallium and manganese ions and the triple system 0.41Pb(Ni1/3Nb2/3)O3-0.23PbZrO3-0.36PbTiO3, alloyed with zinc and copper ions can be used in multilayer devices. It is shown that the lead-free ceramic material of the composition (Na0.5Bi0.5)0.91Cd0.09TiO3 can be used in sensors and actuators.

1 Introduction

Piezoceramic materials, until now, occupy a significant place in the manufacture of various devices, allowing under conditions of intensive development of computerization to coordinate mechanical systems with electronic control and monitoring systems. Current requirements for energy saving, adaptability to computer control systems, miniaturization of individual assemblies and devices generally lead to the necessity of searching for new and improving already known piezoceramic materials [1-4].

In developing technologies for obtaining piezoelectric materials in the present-day realities, taking into account lower electricity consumption, cheaper products thanks to the use of cheaper raw materials, and a high degree of environmental friendliness of the industries, researchers are paying increased attention to studying methods of lowering the temperatures of synthesis and sintering of existing materials [5-9]. As well as to study the conditions for obtaining piezoceramics that do not contain lead in their compositions. The most probable alternative to lead-containing piezoceramics is materials based on the compound Na0.5Bi0.5TiO3 (NBT).

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The purpose of this work was to study the peculiarities of the conditions for producing piezoelectric materials with low synthesis and sintering temperatures, as well as lead-free ceramics based on (Na$_{0.5}$Bi$_{0.5}$)$_{(1-x)}$A$_x$TiO$_3$.

2 Methods

2.1 Experimental part

Ceramic materials for the study were obtained by two-stage technology [1] by solid-phase sintering.

To reduce the synthesis temperatures, the method of mechanochemical activation in a vibrating mill was used. The sintering temperatures were lowered by introducing before the sintering stage either ions, which were subsequently substitution defects, or by introducing a glass-forming component, which changes the sintering mechanism from solid-phase to liquid-phase. Table 1 shows the compositions based on which the studied piezoceramics were obtained.

| Composition | Synthesis, °C | Sintering, °C | Grain size, μm |
|-------------|---------------|---------------|----------------|
| 0.2Pb(Nb$_{2/3}$Zn$_{1/3}$)O$_3$-0.8Pb(Zr$_{0.5}$Ti$_{0.5}$)O$_3$ (0.2PNZ-0.8PZT) + 3 wt.% GaO + 1 wt.% MnO | 800-850 | 950-1100 | 1-3 |
| 0.41Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$-0.23PbZrO$_3$-0.36PbTiO$_3$ (PNN-PZT) + 3 wt.% ZnO + 1 wt.% CuO | 800-850 | 960-1000 | 2-4 |
| (Na$_{0.5}$Bi$_{0.5}$)$_{(1-x)}$C$_x$TiO$_3$ ((NB)$_{1-x}$Cd$_x$T) | 800-850 | 1120-1180 | 1-4 |

The phase composition of the samples after the synthesis and sintering processes was controlled by X-ray diffraction analysis. The Rietveld method (SGAS program) was used to clarify the crystal structure parameters.

The samples were microanalyzed using a Röntec Edwin microanalyzer (probing section diameter of 3 μm). Observation of surface morphology and determination of grain sizes of ceramic materials was carried out with a scanning electron microscope of LEO brand "Carl Zeiss."

The view of the grain structure of the investigated ceramics obtained at optimal temperatures of synthesis and sintering is shown in Figure 1.
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## Methods

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| Composition | Synthesis, °C | Sintering, °C | Grain size, μm |
|-------------|---------------|---------------|----------------|
| \(0.2\text{Pb(Nb}_{2/3}\text{Zn}_{1/3})\text{O}_3\) - \(0.8\text{Pb(Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3\) + 0.5% Ga + 0.5% Mn | 800-850 | 950-1100 | 1-3 |
| \(0.41\text{Pb(Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\) - \(0.23\text{PbZrO}_3\) - \(0.36\text{PbTiO}_3\) + 3 wt.% ZnO + 1 wt.% CuO | 800-850 | 960-1000 | 2-4 |
| \((\text{Na}_{0.5}\text{Bi}_{0.5})_{0.91}\text{Cd}_{0.09}\text{TiO}_3\) | 800 | 1120-1180 | 1-4 |

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The samples were microanalyzed using a Röntec Edwin microanalyzer (probing section diameter of 3 μm). Observation of surface morphology and determination of grain sizes of ceramic materials was carried out with a scanning electron microscope of LEO brand “Carl Zeiss.”

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### 3 Results and Discussion

To obtain piezoceramics with the perovskite crystal structure based on the composition of the double system 0.2PNZ-0.8PZT, which at the standard two-stage technology sintered at temperatures not below 1225 °C, was used method of mechanochemical activation before the synthesis process for 12–84 h, which allowed to synthesize a solid solution 0.2PZN-0.8PZT with perovskite structure at temperature 800 °C instead of 1000 °C. During the activation time of 40 h and more in the process of synthesis at 800 °C along with the phase with perovskite structure the phase with pyrochlore structure (Figure 2) is formed, the presence of which significantly worsens the physical properties of the ceramics obtained. The degree of defectiveness of powders after preliminary activation for 16 hours is optimal for obtaining the highest density ceramics after sintering.

![Fig. 1. Microstructure of ceramic compositions: a is 0.2Pb(Nb_{2/3}Zn_{1/3})O_3 - 0.8Pb(Zr_{0.5}Ti_{0.5})O_3 + 0.5% Ga + 0.5% Mn; b is 0.41Pb(Ni_{1/3}Nb_{2/3})O_3 - 0.23PbZrO_3 - 0.36PbTiO_3 + 3 wt.% ZnO + 1 wt.% CuO; c - (Na_{0.5}Bi_{0.5})_{0.91}Cd_{0.09}TiO_3](image)

![Fig. 2. X-ray diffractograms for solid solutions of 0.2PZN-0.8PZT composition (T_{synth} = 800°C) as a function of activation time](image)
At the sintering stage, to obtain ceramic materials, the compositions were alloyed with Ga$^{3+}$ ions having ionic radius close in value to that of zinc ion Zn$^{2+}$, which contributed additional charge +1. The charge increase led to an increase of dipole moment and, accordingly, to an increase of values of dielectric permittivity of ceramics (Figure 3), and values of piezo module $d_{31}$ (Tab. 2).

![Image of Figure 3](https://example.com/fig3.png)

**Fig. 3.** Temperature dependence of dielectric permittivity of alloyed ceramic compositions 0.2PZN-0.8PZT

When Mn$^{3+}$ ions are introduced to replace Nb$^{5+}$ ions, the charge is reduced by 2 units, which leads to a decrease in the dipole moment and, consequently, to a decrease in the temperature of the phase transition between segment electric and paraelectric (Figure 3). At the same time, the presence of Mn in the sintering process changes the mechanisms of substance transfer and, within a certain temperature range, the solid-phase mechanism sintering mechanism becomes liquid-phase, which made it possible to obtain high-density piezoceramics at low sintering temperatures (980°C). At the same time, the alloyed compositions have higher values of electromechanical coupling coefficient, piezo module, and quality factor (Table 2).

| Parameters          | 0%      | 0.5%Ga  | 0.5%Ga+0.5%Mn |
|---------------------|---------|---------|---------------|
| $\varepsilon$       | 1815    | 1850    | 1800          |
| $d_{31}$, $10^{-12}$ C/N | 167     | 170     | 176           |
| $k_p$               | 0.56    | 0.57    | 0.58          |
| $Q$                 | 95      | 90      | 300           |
| $tg\delta$          | 0.019   | 0.016   | 0.010         |
| $T_c$, °C           | 313     | 313     | 297           |

**Table 2.** Piezoelectric parameters of ceramics of composition 0.2PZN-0.8PZT ($T_{\text{synth}} = 800^\circ$C, $T_{\text{sint}} = 980^\circ$C)

After sintering, the ceramics had a structure with tetragonal (T, space group P4mm) and rhombohedral (R, group R3mR) crystal cells (Table 3). The peculiar structure of the ceramics was studied at the peaks: (002), (200) and (222). X-ray images were taken in the interval of angles $2\Theta = 43 - 46$ and $2 = 81 - 84$ with a step of 0.01 and exposure time of 10 s.
At the sintering stage, to obtain ceramic materials, the compositions were alloyed with Ga$^{+3}$ ions having ionic radius close in value to that of zinc ion Zn$^{+2}$, which contributed additional charge $+1$. The charge increase led to an increase of dipole moment and, accordingly, to an increase of values of dielectric permittivity of ceramics (Figure 3), and values of piezo module $d_{31}$ (Table 2).

![Graph showing temperature dependence of dielectric permittivity of alloyed ceramic compositions 0.2PZN-0.8PZT](image)

**Fig. 3.** Temperature dependence of dielectric permittivity of alloyed ceramic compositions 0.2PZN-0.8PZT when Mn$^{+3}$ ions are introduced to replace Nb $^{+5}$ ions, the charge is reduced by 2 units, which leads to a decrease in the dipole moment and, consequently, to a decrease in the temperature of the phase transition between segment electric and paraelectric (Figure 3). At the same time, the presence of Mn in the sintering process changes the mechanisms of substance transfer and, within a certain temperature range, the solid-phase sintering mechanism becomes liquid-phase, which made it possible to obtain high-density piezoceramics at low sintering temperatures (980°C). At the same time, the alloyed compositions have higher values of electromechanical coupling coefficient, piezo module, and quality factor (Table 2).

| Ions         | Phase ratio | Ratio of rhombohedral phase to tetragonal phase |
|--------------|-------------|-------------------------------------------------|
|              | rhombohedral., % | tetragonal., % |                                        |
| 0            | 52.3        | 47.7                                             | 1.096                                   |
| 0.5%Ga       | 53.7        | 46.3                                             | 1.16                                    |
| 0.5%Mn       | 63.7        | 36.3                                             | 1.75                                    |
| 0.5%Ga+5%Mn  | pseudocubic 53.0 | 47.0                                               | 1.13                                    |

**Table 3.** Ratio of rhombohedral and tetragonal phases for ceramics 0.2Pb $(\text{Nb}_{2/3}\text{Zn}_{1/3})\text{O}_3$–0.8Pb$(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$

X-ray reflexes (002) of the T-phase are strongly blurred and overlap with those of the R-phase (Figure 4). When Mn ions are introduced, the maximum R-phase content ~63-64% is observed at 0.5 wt%. At simultaneous presence in ceramics of 5 wt.% Mn and 0.5 wt.% Ga R-phase becomes pseudocubic.

![Graph showing shape of peaks (002) and (200) for samples of composition 0.2Pb(Nb2/3Zn1/3)O3-0.8Pb(Zr1/2Ti1/2)O3 depending on the type of microadditives in the range of angles 2$\Theta = (43 – 46)^\circ$](image)

**Fig. 4.** Shape of peaks (002) and (200) for samples of composition 0.2Pb(Nb2/3Zn1/3)O3–0.8Pb(Zr1/2Ti1/2)O3 depending on the type of microadditives in the range of angles $2\Theta = (43 – 46)^\circ$

The analysis of the received data testifies that decrease in the dissipation factor $\tan\delta$ and increase of values of mechanical quality factor $Q$ are connected with increase in the R-phase content in ceramic samples, increase in dielectric permittivity $\varepsilon$, coefficient of electromechanical coupling $k_\rho$, and piezo module $d_{31}$ with the increase in the T-phase content. Thus, the ratio of T- and R-phases in ceramics is the indicator for controlling the physical properties of the ceramics obtained.

At the same time, according to the data of Table 4, the change of ceramics is connected with the changes of both shortened and long titanium-oxygen bonds. The shorter the short bond and the longer the long titanium-oxygen bond, the higher values of relative dielectric permittivity the ceramic samples have.
Table 4. The main interatomic distances and angles for 0.2PNZ-0.8PZT ceramics: \(a\) is rhombohedral phase; \(b\) is tetragonal phase

| Distances, Å | Composition 0.2Pb(Nb\(_{2/3}\)Zn\(_{1/3}\))O\(_3\)-0.8Pb(Zr\(_{0.5}\)Ti\(_{0.5}\))O\(_3\) | 0 % | 0.5%Ga | 0.5%Ga+5%Mn |
|-------------|------------------------------------------------|------|--------|-------------|
| Pb-Nb, Zn, Zr, Ti | 3.3298 (12) | 3.4102 (8) | 3.2978 (8) |
| Pb-Nb, Zn, Zr, Ti | 3.4587(5) | 3.48779 (4) | 3.4564 (4) |
| Pb-Nb, Zn, Zr, Ti | 3.5967 (4) | 3.58379 (3) | 3.61987 (3) |
| Nb, Zn, Zr, Ti-O | 2.18866 (19) | 2.196 88(7) | 2.15750 (7) |
| Nb, Zn, Zr, Ti-O | 1.91408 (17) | 1.92038(1) | 2.02286(17) |
| Pb-O | 2.47413 (6) | 2.53282 (6) | 2.24382(21) |
| Pb-O | 2.9167(5) | 2.9150(4) | 2.96228(33) |

Angles, deg

| O-Pb-O | O-Nb,Zn, Zr, Ti-O | O-Nb, Zn, Zr, Ti-O | O-Nb, Zn, Zr, Ti-O | O-Nb, Zn, Zr, Ti-O | Pb-O-Nb, Zn, Zr, Ti | Pb-O-Nb, Zn, Zr, Ti |
|--------|--------------------|--------------------|--------------------|--------------------|---------------------|---------------------|
| 69.385(3) | 165.775 (3) | 100.012 (6) | 89.056 (2) | 80.090 (3) | 90.931 (11) | 103.293 (10) |
| 67.774 (6) | 165.765 (2) | 99.953 (0) | 89.128 (2) | 80.004 (5) | 91.999 (2) | 102.235 (1) |
| 68.043(17) | 154.863(3) | 106.403(8) | 88.209(12) | 71.577(3) | 97.038(21) | 108.099(2) |

When obtaining ceramics based on solid solutions of the ternary system Pb(Ni\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbZrO\(_3\)-PbTiO\(_3\) (PNN-PZ-PT), the fact that the best piezoelectric properties have ceramics with a pseudocubic structure with compositions near the morphotropic region was taken into account. The investigations were conducted on the compositions 0.41Pb(Ni\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-0.23PbZrO\(_3\)-0.36PbTiO\(_3\) which were alloyed with zinc and copper ions at the sintering stage. The experiments carried out to study the sintering process of 0.41PNN-0.23PZ-0.36PT ceramics made it possible to establish that to decrease sintering temperatures of ceramics of the ternary system PNN-PZ-PT whose compositions are close to the morphotropic area, it is more effective to introduce microadditives not in the form of ready-made glasses but in the form of initial components (oxides) on the basis of which they are prepared. These components were zinc oxides ZnO and copper oxides CuO, with copper oxide being the glass-forming component. The highest values of piezoelectric parameters had ceramics containing ZnO in quantity 3 wt.%. XRD data (Fig. 5) showed that piezomaterials based on PNN-PT-PZ solid solutions doped with zinc ions with the pseudocube structure could be obtained already at sintering temperatures of 1000°C and sintering time of 2 h.
The physical and piezoelectric properties of 0.41Pb(Ni\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-0.23PbZrO\(_3\)-0.36PbTiO\(_3\)+3wt.%ZnO+1wt.%CuO materials with pseudocubic structure obtained by solid-phase and liquid-phase sintering were studied on two types of ceramic samples: polarized (PNNZT-P) and unpolarized (PNNZT-NP). The piezoelectric constants of the polarized samples were determined by the resonance-anti-resonance method. During solid-phase sintering, the highest density (\(\rho = 8.15 \) g/cm\(^3\)) had ceramic samples at sintering temperatures of 1200 – 1220 °C and a duration of 2 – 4 h. The grain size of ceramics sintered by the liquid-phase mechanism varied from 1⋅10\(^{-6}\) m to 3⋅10\(^{-6}\) m, and the glass phase was distributed in the intergranular space. The grain size of ceramics sintered by the solid-phase mechanism was of the order of (4 – 6)⋅10\(^{-6}\) m.

Improvement of parameters of ceramic crystal structure conducted within Pm-3m spatial group at R-factor 5.5% showed that main interatomic distances for ceramic specimens with solid-phase sintering mechanism (without glass-forming additives) had values: Pb-(Ti, Zr, Ni, Nb) – 3.49992(6) Å, Pb-O – 2.85767(1) Å, Ti-O – 2.02068(4) Å. For samples sintered by the liquid-phase mechanism, a decrease in the parameter \(a\) of the unit crystal cell was observed. For samples containing 3 wt.% ZnO and 1 wt.% CuO and sintered at 1000 °C, the value of \(a = 4.03396\) Å. When liquid-phase sintering temperatures changed from 960 °C to 1100 °C, the lattice parameter changed within the range (4.03394 – 4.03398) Å. Compression of the unit crystal cell in the presence of the liquid phase leads to a decrease in the principal interatomic distances. The values of interatomic distances for samples obtained by the liquid-phase sintering mechanism are: Pb-(Ti, Zr, Ni, Nb) – 3.49351(3) Å, Pb-O – 2.85244(7) Å, Ti-O – 2.01698(2) Å.

Reduction of Ti-O length leads, in turn to the reduction of the dipole moment of the unit cell and, as a consequence, to decrease \(T_c\). In the experiment (Table 5, Figure 6), we observe not a decrease but an increase in the \(T_c\) values of the magnetoelectric-paraelectric transition temperature by 23 – 49°C for ceramics containing microadditives as compared to ceramics obtained by the solid-phase sintering mechanism.
Table 5. Segnetoelectric-paraelectric transition temperature and dielectric permittivity depending on conditions of ceramic samples production

| Composition | Curie temperature, T_c °C | Dielectric permittivity At 20°C | Dielectric permittivity At T_c |
|-------------|---------------------------|---------------------------------|-------------------------------|
| 0%CuO-0%ZnO 1200°C | 172 | 174 | 1664 | 1632 | 8198 | 8381 |
| 1%CuO-3%ZnO 1100°C | 221 | 217 | 1468 | 1370 | 9367 | 9082 |
| 1%CuO-3%ZnO 1060°C | 204 | 216 | 2158 | 2055 | 1147 | 1142 |
| 1%CuO-3%ZnO 1020°C | 201 | 212 | 2097 | 2113 | 1014 | 1012 |
| 1%CuO-3%ZnO 960°C | 195 | 204 | 1883 | 1814 | 9570 | 8703 |

Fig. 6. Temperature dependence of dielectric permittivity of ceramics during solid-phase (Tsint = 1200 °C) and liquid-phase (Tsint = 1060 °C) sintering

The explanation of the observed experimental behavior of the phase transition temperature of the obtained ceramics can be given on the basis of the relation $T_c = 0.5 \chi (\Delta Z)^2$, obtained in [4]. As it is clear from the given formula, the temperature of the magnetoelectric phase transition depends not only on the spontaneous displacement $\Delta Z$ of the magnetoactive cation relative to the centrosymmetric position, but also on some power constant $\chi$. The phase transition occurs when the energy of thermal motion becomes equal to the elastic energy of displacement of atoms by distance $\Delta Z$. Consequently, $T_c$ will depend on the local elastic stresses arising from the displacement of the magnetoactive cations. The presence of the glass phase in the intergranular space leads to an increase in local stresses, i.e., an increase in the rigidity of the domain structure relative to the translational displacements of the boundaries. At the same time, the process of domain structure destruction is energetically difficult and requires more energy, which is the reason for shifting the temperature $T_c$ towards higher temperatures.

Experimentally obtained data (Table 6) indicate that the samples of composition 0.41PNN-0.36PT-0.23PZ +1 wt.%CuO+3 wt.%ZnO with liquid-phase sintering mechanism...
have the highest piezoelectric parameters \( (d_{31} = 610 \text{ pC/N}; k_p = 0.86, g_{31} = 7.86 \times 10^{-7} \text{Vm/N}) \) at sintering temperature 1000 °C. The piezo sensitivity (Table 7) and electromechanical coupling coefficient of piezoelectric ceramics sintered at 960°C are of the same order as the samples obtained by solid-phase sintering. At the same time, the piezo module values of liquid-phase sintered ceramics at 960°C are higher than those of solid-phase sintered ceramics.

**Table 6.** Piezoelectric parameters of ceramics of composition 0.41PNN-0.36PT-0.23PZ depending on sintering temperatures and values of microadditives

| Composition                          | \( d_{33}, \text{ pKl/H} \) | \( d_{31}, \text{ pKl/H} \) | \( k_p \) | \( g_{31} \times 10^3, \text{ Bm/H} \) |
|--------------------------------------|-----------------------------|-----------------------------|----------|--------------------------------------|
| 0%CuO-0%ZnO, 1200°C                 | 790                         | 380                         | 0.69     | 6.8                                  |
| 1%CuO-3%ZnO, 1100 °C                | 1380                        | 660                         | 0.58     | 2.03                                 |
| 1%CuO-3%ZnO, 1060°C                 | 1200                        | 520                         | 0.70     | 5.17                                 |
| 1%CuO-3%ZnO, 1000°C                 | 1400                        | 610                         | 0.86     | 7.86                                 |
| 1%CuO-3%ZnO, 960 °C                 | 1020                        | 440                         | 0.66     | 6.45                                 |

Single-phase ceramic materials with a pseudocubic crystal structure obtained at the lowest sintering temperature of 960°C retain high values of piezoelectric parameters to be effectively used to manufacture multilayer devices with simultaneous deposition of silver electrodes, which have a melting point of about 970 °C.

Lead-free ceramic piezoelectric materials were obtained based on solid solutions \((Na_{0.5}Bi_{0.5})_{(1-x)}A_xTiO_3 ((NB)_{1-x}A_xT), \) where \( A=\text{Sr, Cd} \). Strontium ions \( \text{Sr}^{2+} \) and cadmium ions \( \text{Cd}^{2+} \) acting as substitution defects, are located in cationic A-positions.

To obtain the ceramics of composition \((Na_{0.5}Bi_{0.5})_{(1-x)}\text{Sr}_x\text{TiO}_3 \) firstly, the compounds \( \text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 \) and \( \text{Sr}_{0.7}\text{Bi}_{0.3}\text{TiO}_3 \) \( (\text{SBT}) \) were synthesized at temperatures of 800 – 850°C and 1050 – 1150°C respectively. Ceramics were sintered at temperatures of 1140 – 1200°C.

For oxide compounds with perovskite structure \([4]\), values of tolerance-factor \( t \) (stability criterion) act as an indicator of determination of their physical properties’ optimality. The data for the tolerance factor (Table 8) calculated by the formula

\[
 t = (Ra + Ro)\sqrt{2}/(Rb + Ro) \tag{1}
\]

where \( Ra, Rb, \) and \( Ro \) are ionic radii of cations and oxygen accordingly, have shown, that for ceramics \((Na_{0.5}Bi_{0.5})_{(1-x)}\text{Sr}_x\text{TiO}_3 \) the maximum possible dielectric and, hence, and piezoelectric parameters, according to \([4]\), will possess ceramics of compositions 0.7BNT-0.3BST, 0.65BNT-0.35BST and 0.6BNT-0.4BST \( (t \) values should be \( 0.990 < t < 0.993) \). The values of element radii are taken from \([3]\).

The ceramics obtained from the composition \((0.63-0.66)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-(0.37-0.34)\text{Sr}_{0.7}\text{Bi}_{0.3}\text{TiO}_3 \) had the following dielectric and piezoelectric parameters for polarized samples: \( \tan \delta = 0.013 – 0.009, \varepsilon_{r,20^\circ C} = (1200 – 1500), d_{31} = (370 – 400) \times 10^{-12} \text{C/N}, k_p = 0.4 – 0.58. \)

Table 7 presents the results of dielectric properties investigation for ceramics of \((Na_{0.5}Bi_{0.5})_{(1-x)}\text{Cd}_x\text{TiO}_3 \) composition \([5]\) at room temperature depending on sintering temperatures and cadmium ions content.

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**Table 5.** Composition of ceramics obtained by solid- and liquid-phase sintering mechanisms

| Composition | \( \rho \) (Ohm·m) | \( p \) (GPa) | \( m \) (kg/m³) |
|-------------|-----------------|--------------|----------------|
| 0%CuO-0%ZnO, 1200°C | 790 | 380 | 0.69 |
| 1%CuO-3%ZnO, 1100 °C | 1380 | 660 | 0.58 |
| 1%CuO-3%ZnO, 1060°C | 1200 | 520 | 0.70 |
| 1%CuO-3%ZnO, 1000°C | 1400 | 610 | 0.86 |
| 1%CuO-3%ZnO, 960 °C | 1020 | 440 | 0.66 |
Table 7. Values of the tolerance factor for ceramic compositions \((Na_{0.5}Bi_{0.5})(1-x)Sr_xTiO_3\)

| Composition          | \(t\) | Composition          | \(t\) |
|----------------------|-------|----------------------|-------|
| BNT                  | 0.986 | 0.5BNT-0.5BST        | 0.994 |
| 0.8BNT-0.2BST        | 0.989 | 0.4BNT-0.6BST        | 0.995 |
| 0.7BNT-0.3BST        | 0.990 | 0.3BNT-0.7BST        | 0.997 |
| 0.65BNT-0.35BST      | 0.991 | 0.2BNT-0.8BST        | 1.002 |
| 0.6BNT-0.4BST        | 0.992 |                      |       |

Analysis of the data in Table 8 showed that the optimal cadmium microaddition is 0.09, and the sintering temperature of the ceramics is 1160°C.

Temperature (Fig. 8) dielectric permittivity dependences show that in the presence of Cd ions in NBT compositions, there is a strong blurring and shift of maximums (T) towards low temperatures. At cadmium content of 6–9%, blurring of dielectric permittivity is observed in the region of room temperatures; the values of the tangent of dielectric losses lie within 0.5–1% at higher values of dielectric permittivity in comparison with samples NBT at room temperature.

Table 8. Values of dielectric parameters at 20°C for ceramics \((Na_{0.5}Bi_{0.5})(1-x)Cd_xTiO_3\) as a function of sintering temperatures

| Sintering temperature, °C | Cadmium content, x |
|---------------------------|--------------------|
| 0                         | 0.06               |
| 1120                      | \(\varepsilon=760\) |
|                           | \(tg\delta=0.18\)  |
| 1140                      | \(\varepsilon=1027\) |
|                           | \(tg\delta=0.025\) |
| 1160                      | \(\varepsilon=1100\) |
|                           | \(tg\delta=0.024\) |
| 1180                      | \(\varepsilon=1100\) |
|                           | \(tg\delta=0.013\) |
| 1120                      | 0.09               |
| 1140                      | \(\varepsilon=830\) |
|                           | \(tg\delta=0.033\) |
|                           | \(\varepsilon=1100\) |
|                           | \(tg\delta=0.031\) |
| 1160                      | \(\varepsilon=1150\) |
|                           | \(tg\delta=0.022\) |
| 1180                      | \(\varepsilon=1212\) |
|                           | \(tg\delta=0.01\)  |
| 1120                      | 0.12               |
|                           | \(\varepsilon=800\) |
|                           | \(tg\delta=0.026\) |
| 1140                      | \(\varepsilon=1212\) |
|                           | \(tg\delta=0.01\)  |
| 1160                      | \(\varepsilon=1660\) |
|                           | \(tg\delta=0.005\) |
| 1180                      | \(\varepsilon=1295\) |
|                           | \(tg\delta=0.012\) |
| 1120                      | 0.15               |
|                           | \(\varepsilon=800\) |
|                           | \(tg\delta=0.26\)  |
| 1140                      | \(\varepsilon=1295\) |
|                           | \(tg\delta=0.012\) |
| 1160                      | \(\varepsilon=1270\) |
|                           | \(tg\delta=0.05\)  |
| 1180                      | \(\varepsilon=1300\) |
|                           | \(tg\delta=0.012\) |
| 1120                      | \(\varepsilon=960\) |
|                           | \(tg\delta=0.01\)  |
| 1140                      | \(\varepsilon=1400\) |
|                           | \(tg\delta=0.009\) |

Fig. 8. Temperature dependences of dielectric permittivity of ceramics of composition \((Na_{0.5}Bi_{0.5})_{0.91}Cd_{0.09}TiO_3\)
Thus, the investigations of the ceramics have shown that the introduction of Sr\(^{2+}\) strontium ions into the Na\(_{0.5}\)Bi\(_{0.5}\)TiO\(_3\) compositions changes the ordering pattern in the Na\(^+\) and Bi\(^{3+}\) ion arrangement that leads to a narrowing of the domains of the rhombohedral, tetragonal, and cubic phases of the xNa\(_{0.5}\)Bi\(_{0.5}\)TiO\(_3\) – (1–x)Sr\(_{0.7}\)Bi\(_{0.2}\)TiO\(_3\) system. It was found that the highest values of dielectric and piezoelectric parameters, which are: tangent of dielectric losses 0.013 – 0.009, \(\varepsilon'=1500–2000\), \(d_{31}=(370–400) \times 10^{-12} \text{C/N}\), \(k_p=0.4–0.58\) have ceramics of composition (0.63-0.66)Na\(_{0.5}\)Bi\(_{0.5}\)TiO\(_3\) – (0.37-0.34)Sr\(_{0.7}\)Bi\(_{0.2}\)TiO\(_3\).

4 Conclusions

The study of the preparation of piezoceramics based on solid solutions of double and triple systems showed that the obtained piezomaterials have low synthesis and sintering temperatures. Ceramics of composition 0.2 Pb(Nb\(_{2/3}\)Zn\(_{1/3}\))O\(_3\)-0.8Pb(Zr\(_{0.5}\)Ti\(_{0.5}\))O\(_3\)+0.5\%Ga+0.5\% Mn and composition 0.41PNN-0.36PT-0.23PZ modified with copper and zinc oxides are obtained at a low sintering temperature (960 °C), retain high values of piezoelectric parameters, so they can be effectively used to manufacture multilayer devices with simultaneous deposition of silver electrodes, which have a melting point of about 970 °C.

Ceramic lead-free materials doped with cadmium and having the composition (Na\(_{0.5}\)Bi\(_{0.5}\))\(_{0.01}\)Cd\(_{0.09}\)TiO\(_3\) are the highest priority for practical applications as piezoceramics for sensors and actuators.

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