Multi-element ferroactive materials based on KNN-PZT compositions with fundamentally different physical properties

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ABSTRACT

Quasibinary section solid solutions of a four-component system of the (1-x)(Na0.5K0.5)NbO3-xPb(Ti0.5Zr0.5)O3 composition, based on compositions with fundamentally different physical responses (Na, K)NbO3 (KNN), Pb(Ti, Zr)O3 (PZT), have been produced by two-step solid-phase synthesis followed by sintering using conventional ceramic technology. The features of their structural formation have been revealed, a phase diagram of equilibria has been constructed, correlation relationships composition – structure – microstructure – macroproperties have been established. Based on the measured X-ray fluorescence intensities, the concentrations of chemical elements, included in the surface composition of the samples of piezoceramic materials, have been determined. Statistical characteristics and variations in the chemical composition of the structure-forming chemical elements of the ferroactive composite materials were researched. Micro-XRF combined with methods of mathematical statistics provides to characterize a degree of chemical homogeneity and statistically compare the average concentrations of the chemical elements. Changes in atomic concentrations were revealed as result of varying technological conditions of synthesis. We have carried out the X-ray quantitative analysis for the thickness of surface layer corresponding to the chemical elements at the depth yield of X-ray fluorescence. Three groups of solid solutions – the foundations of intelligent materials have been identified: with high $K_p$, $\varepsilon_33$, low $V_{33}$ (near PZT) – promising for low-frequency applications; with low $\varepsilon_33$, high $V_{33}$ (near KNN) – for high-frequency use; with intermediate values of the piezoelectric parameters (near SS1–SS2 – transition), intended for operation in combined equipment complexes.

1. Introduction

The desire for the universality of high-tech products leads to the necessity for the combination of several heterogeneous functions in one chemical composition, which, due to various fundamental physical limitations, can complicate the implementation of the operation principles of many devices. Besides, it becomes obvious that the possibilities of creating new functional materials have been exhausted due to the almost full use of existing chemical bases and methods for their preparation, and a variety of options cannot be achieved within the framework of mono-
hexavalent cations; B'-monovalent, divalent and trivalent cations; α = 1/2; 1/3; 1/4 – depending on valencies B', B''. More than 100 copyright certificates and patents have been obtained for the piezoceramic materials of many of these systems [1].

It should be noted, that with an increase in the number of components, the composition regions with characteristics optimal for various applications expand, the variety of options for solid solutions (SS) grows, and the most important electrophysical parameters increase. All this indicates the significant advantages of MS over their simpler components [1], which, moreover, may have fundamentally different properties. Recently, the attention of researchers, including us, has been riveted to them in connection with the possibility of the formation of a new set of parameters combining the heterogeneous functionality of the macroresponses of basic compositions [1].

Among other systems, MS based on industrially developed PZT and SS of alkali metal niobates (AMN) are also promising and are characterized, respectively, either by high dielectric permittivities and piezoelectric coefficients (Pb-containing compositions), or low dielectric permittivities and high sound speeds against a background of more than half the specific gravity (lead-free ceramics). Above mentioned ensures the applicability of the former in low-frequency devices, the latter in microwave technology, as well as in devices where weight characteristics are decisive. The combination of these basic foundations (PZT and AMN) can ensure their applicability in combined hardware complexes operating in a fairly wide operational frequency ranges.

The present work is a continuation and development of the comprehensive studies of four-component systems undertaken by us in [2] based on binary SS of the PZT-KNN (Na, K)NbO3 [3,4] composition.

In the general case, during studying the MS, the main task is to search for the morphotropic region (MR) (the region of the concentration symmetric phase transition), in the vicinity of which the SS properties are extreme [5]. The MR search method consists in preliminary approximation of its boundary surfaces by planes, further refinement of the shape and length, and in identification of zones of optimal combinations of parameters [5]. Moreover, the approximation more reliably reflects the position of the MR in the MS, the more informative the information on the components of the MS of the initial simpler systems are Taking into account the absence of such data in many of them and, as a consequence, the uncertainty of the localization of the MR in the indicated MS based on PZT and AMN, in both cases we preliminary studied the SS of only one beam connecting SS with extreme properties – (Na0.875Li0.125)NbO3, (Na0.5K0.5)NbO3, Pb(Ti0.5Zr0.5)O3 in the tetrahedra of the compositions [1, 5, 6]. This way of studying MS in this case seems to be the most reasonable because of the possibility of characterizing the system with a minimum number of experiments. But it is necessary to consider the following.

The main problem in the manufacture of multicomponent ferroceramics, which include lead and niobium, is the formation at the stages of sintering during subsequent heat treatments, and also during the process of sintering at temperatures that ensure high-density of the samples. One of the reasons for this may be the mismatch between the sizes of the cations included in the SS and the conditions of isomorphism: the difference in ionic radii (ΔR) should not exceed 15% relative to a smaller value and the difference in electronegativity (ΔEN) should not exceed 0.4 according to Pauling [6]. If these conditions are violated, only limited solubility or even microisomorphism are possible, such as in the (Na0.5Li2)NbO3 system, in which Li dissolves only up to x = 0.14 even when using hot pressing (ΔR(Na–Li)~44%, ΔEN(Na–Li) = 0.09). In the (Na0.5K)NbO3 system these values, respectively, are ~36% and 0.11, and in PZT-SS: 28% and 0.14. In the latter case, this exceeds the “softer” threshold value calculated in [2]. In the named four-component systems, these indicators are as follows: (Na0.5K0.5)NbO3 – Pb: ~33%; 1.4; (Na0.5K0.5) – Pb: ~9%; 1.46; (Ti0.5Zr0.5) – Nb: ~9%; 0.13. We have been able to achieve the complete solubility of the components in these quasi-binary MS sections only by choosing the right ceramic preparation conditions, including through the use of applied pressure from the outside during sintering, the use of mechanically activating procedures and other technological methods ensuring the purity of the samples.

The objective of this work was to establish correlation relationships between the composition (and the degree of its homogeneity) – phase equilibrium diagrams - grained landscape - electrophysical responses of ferroceramics of the system, the extreme components of which fundamentally differ in properties. Moreover, in contrast to the previously undertaken “panoramic” experiments [2], in the present study, the number of the analyzed samples has been expanded both by narrowing the concentration “step” (Δx = 0.025 ± 0.05), and by increasing their number in each batch, which is while of meticulous step-by-step optimization of the conditions for the preparation of the objects, provides greater reliability and authenticity of the obtained results.

2. Materials and methods

2.1. Fabrication of samples

The objects of the study were SS of the (1-x)(Na0.5K0.5)NbO3 – xPbTiO3 (0 ≤ x ≤ 1.0; Δx = 0.025–0.05:1.0) composition of quasi-binary section of a four-component system of the (Na, K)NbO3 – PZT type. Figure 1 shows a tetrahedron of composition with an isolated quasi-binary section and experimental points plotted on it.

The samples were prepared by two-stage solid-phase synthesis followed by sintering using conventional ceramic technology in the optimized modes. NaHCO3 (“chemically pure”), KHCO3 and LiHCO3 (“pure for analysis”), PbO, Pb3O4 and ZrO2 (“pure”, TiO2 (“especially pure”) were used as the feedstock. The synthesis and sintering conditions were selected on a series of the samples based on the results of X-ray phase analysis, measurements of the experimental density and calculation of the relative density of the samples, analysis of the grain structure of ceramics and their electrophysical characteristics.

Sintered ceramic billets (in the shape of columns 12 mm × 20 mm in diameter) were subjected to mechanical processing (plane cutting, grinding over the entire surface and ends) in order to obtain measuring samples with a diameter of ø10 mm × 1 mm. In each composition of such samples there were (10...15) pieces. Before metallization, the samples were calcined at a temperature of Tcalc. = 770 K for 0.5 h to remove...
residues of organic substances and degreasers the surface in order to increase the adhesion of the metal coating with ceramics. The electrodes were deposited by double burning silver-containing paste at a temperature of 1070 K for 0.5 h. Polarization of the obtained samples was performed by the method of "hot" polarization. In this case, the samples were loaded into the chamber with PES-5 polyethylene siloxane liquid at ~300 K for 0.5 h, then temperature was smoothly risen to 423 K, which was accompanied by an increase of the created field from 0 to (3.0–4.0) kV/mm. Under these conditions, the samples were kept for (20–25) minutes, and then cooled under the field at temperatures up to ~300 K (room temperature).

2.2. X-ray diffraction studies of samples

X-ray diffraction studies were performed by powder diffraction using a DRON-3 (300K) diffractometer (CuKα radiation; Fe-filter, Bragg-Brentano focusing scheme). We studied bulk and ground ceramic objects, which allowed us to exclude the influence of surface effects, stresses and textures that arise in the process of obtaining ceramics. The structural parameters were calculated according to standard methods [9], the textures that arise in the process of obtaining ceramics. The structural parameters were calculated according to standard methods [9], the profiles of the diffraction lines were approximated by the Lorentz function. The uniform strain parameter, δ, was calculated using the formulas δ = cosa (for the Rh phase) and δ = 2/3(c/a-1) (for the Y phase). The measurement errors of the structural parameters were: Δω = Δb = Δc = ±0.003–0.005 Å, Δψ = ±0.05°, Δν = ±0.1–0.2 Å², where a, b, c, β = parameters, V – cell volume.

Ceramic density (ρexp) was determined by hydrostatic weighing; octane was used as a liquid medium.

2.3. Study of the microstructure of samples

To study the microstructure of cleaved samples, we used a JSM – 6390L scanning electron microscope (Japan) with a system of microanalyzers from Oxford Instruments (Great Britain).

2.4. Measurement of electrophysical parameters

The electrophysical parameters of SS at 300 K were measured using Agilent 4980A precision LCR meters by the resonance – antiresonance method [10], at the same time we determined the relative permittivities of unpolarized (ε/ε0) and polarized (ε'/ε0) samples, dielectric losses in a weak field (angle tangent of dielectric loss, tanδ), piezoelectric modules (d31, d32, d33), piezoelectric coefficients (piezoelectric sensitivity) (q10, q20, q33), electromechanical coupling coefficient of the planar vibration mode (Kp), mechanical Q factor (Qm), Young’s module (Y11), speed of sound (V11). The dependences of the real (ε'/ε0) and imaginary (ε''/ε0) parts of the relative complex permittivity on temperature in the range of T=(300–943) K were studied using a specially designed bench including the Agilent 4980A LCR meter (frequency range of (20÷10⁶) Hz), and using a computer program developed by one of the authors. The measurement errors of the electrophysical parameters are as follows: ε'/ε0 ε32/ε33 ≤ ±1.5%, Kp ≤ ±2.0 %, |d32| ≤ ± 4.0 %, |d34| ≤ ± 10 %, Qm ≤ ±12%; Y11 ≤ ±0.7%. The polarization measurements were performed at room temperature using Sawyer–Tower method at a frequency of 50 Hz. The piezoelectric module d33 and, the piezoelectric coefficient g33, respectively, were studied at room temperature by the quasistatic method using the Piezo d33 Test System (YE2730A d33 METER).

2.5. Statistical simulation

The influence of variations in the composition of the SS on the electrophysics parameters was studied and described in [11] on the base of the math statistics:

- standard deviation of the average value:

  \[ s_n = \sqrt{\frac{1}{n(n-1)} \sum_{i=1}^{n} (x_i - \bar{x})^2} \]  

- absolute deviation:

  \[ \Delta x = s_n t_c(n) \]  

- relative deviation:

  \[ \Delta x = \frac{\Delta x}{\bar{x}} \times 100\% \]  

where \( \bar{x} \) – the average value of the parameter, \( x_i \) – the current value of the parameter, \( n \) – the number of samples in the suite, \( t_c \) (n) – is the Student coefficient, the characteristics were estimated at a confidence level of 0.95.

To study chemical composition of the ferroceramic samples we used the micro-X-ray fluorescence analysis (micro-XRF). The X-ray microfluorescence quantitative analysis was carried out in the Multi-Point mode using X-ray spectrometer M4 TORNADO (Bruker).

To evaluate the measurement results obtained on the testing samples and to determine the degree of chemical homogeneity we performed a statistical comparison of the samples using the Fisher F-criterion, as well as the test on significance of differences of the average chemical concentrations on the base of t- Student criterion [12]. Twenty areas of 1 × 1.5 mm² were selected on the surface of each flat sample and in the each of these regions were measured of X-ray fluorescence on 100 points (uniformly distributed microfocus positions of the polycapillary lens). This corresponds to twenty local surface areas (regions) for which intensities were measured and their average values were calculated. The experimental data were divided into two equal groups: ten and ten. Since the average concentrations in each of the area were considered as unit measurements and the values of \( n_1 = n_2 = 10 \) correspond to each group. At the confidence level of \( P = 95\% \) the statistical comparison for chemical concentrations was made according to the Fisher F-criterion, as well as mathematical expectations based on the Student t-criterion too. In the calculations used the table values \( F_{tab} = 2.7; t_{tab} = 1.95 \) [13]. It is assumed that the independently measured intensities form two sets of random variables \( X_1 \) and \( X_2 \), are distributed according to the normal law – Gaussian distributions. For independent groups with amounts in the sets of \( n_1 \) and \( n_2 \) the sample variances \( S_1^2 \) and \( S_2^2 \) can be calculated. Using the calculated values of sample variances at a given statistical significance level “α” we can test a hypothesis of equality of these variances. Since the values of \( S_1^2 \) and \( S_2^2 \) present estimates of the corresponding variances without an offset, one can check whether the sample variances of two independent samples are equal to each other, because the numerical values of \( S_1^2 \) and \( S_2^2 \) usually are different. To test this hypothesis we used the ratio of the larger variance of \( S_2^2 \) to the smaller one \( S_1^2 \):

\[ F = S_2^2/S_1^2 \]

We compared the calculated (1) value of the Fisher distribution with the table value of Ftab. It was taken in account the degrees of freedom \( f_1 = n_1 - 1 \) and \( f_2 = n_2 - 1 \), where \( n_1 \) is the parameter for the set with larger variance; \( n_2 \) is the parameter for the set with smaller variance. If the inequality \( F_{tab} \geq F \) is satisfied then on the confidence probability of \( P = 1 - \alpha \) the difference in the values of two sample variances is considered statistically insignificant.

To test the hypothesis of equality of average values of \( \chi_1 \) and \( \chi_2 \), a weighted average estimate of two sample values should be calculated:
3. Results and discussion

3.1. Optimization of samples fabrication conditions

The extreme components of the studied system with the same perovskite type structure have different crystal lattice symmetries. (Na0.5K0.5)NbO3 (NKP0.00) SS has orthorhombic symmetry with a perovskite type structure having different crystal lattice symmetries.

\[
\overline{X} = \frac{(S_1(n_1 - 1) + S_2(n_2 - 1))}{(n_1 + n_2 - 2)}
\]

and random variable can be calculated too

\[
t = \left(\overline{X} - \overline{X_2}\right) / S \sqrt{n_1 n_2 / (n_1 + n_2)}
\]

The number of freedom degrees is \(f = f_1 + f_2 = n_1 + n_2 - 2\). This value used to find the table value of the Student criterion then can be assumed insignificant differences of \(X_i\) and \(X_2\) at the given level of confidence level.

For the studied samples the values of confidence intervals \(X ± \Delta X\) of the average concentrations of chemical elements are satisfied to the condition of \(X - \Delta X < \mu < X + \Delta X\). It is assumed that the statistical measured values of the concentrations correspond to the Gaussian distribution:

\[
X ± \Delta X = X ± t(P_f) S / \sqrt{n}
\]

Here \(S\) is the estimation of the mean square deviation, \(n\) is the number of measurements, \(t(P_f)\) is the table value of the \(t\)-criterion at a given level of confidence probability.

The extreme components of the studied system with the same perovskite type structure have different crystal lattice symmetries. (Na0.5K0.5)NbO3 (NKP0.00) SS has orthorhombic symmetry with a monoclinic subcell, the parameters of which are: \(a = 4.001\) Å, \(b = 3.944\) Å, \(\beta = 90.3\)°, \(V = 63.15\) Å\(^3\), phase designation is O. The symmetry of Pb(Zr0.5Ti0.5)O3 (NKP1.00) SS is tetragonal with the cell parameters: \(a = 4.025\) Å, \(c = 4.141\) Å, \(c/a = 1.029\), \(V = 67.08\) Å\(^3\), phase designation is T. Obtained in this study, the cell parameters NKP0.00 and NKP1.00 are close to the data given for them in [14]. The small discrepancy is explained by the significant influence of the thermodynamic history on the phase composition of samples belonging to near the morphotropic region. The synthesis of SS of the 4-component system, as noted above, is not an ordinary task, since their formation is hindered by the large difference in ionic radii (AR) and electronegativity (ΔEN) for some interchangeable ions. For illustration Figure 2 shows the X-ray diffraction patterns of NKP0.00 (a), NKP0.30 (b) and NKP0.70 (c) SS after the second synthesis and after sintering at different temperatures.

It is seen in Figure 2a that NKP0.00 has been formed without impurity phases after the second synthesis, it is well structured, and has rhomboic symmetry with a monocrinally distorted perovskite cell. The X-ray diffraction pattern (1273 K) shows the diffraction peak indices corresponding to the monoclinic cell in the perovskite axes. After sintering at 1398 K, the diffraction peaks broadened, and a weak maximum of the second phase, the content of which increased after sintering at \(T_{sinter} = 1473\) K, appeared between the peaks 200 and 020. The diffraction peaks of the second phase (shown by arrows) are indicated in tetragonal symmetry. As far as is known, Na0.5K0.5NbO3 SS transits from the O phase to the T phase at about 473 K [15]. In [16], it was shown that in Na0.5K0.5NbO3 the O → T transition occurs through the MR, in which both these phases coexist, the width of the MR is 38 K (460–500 K). The authors of [16] also found that the introduction of only 0.5 mol % of Bi0.5Na0.5TiO3 into Na0.5K0.5NbO3 expands the MR in the latter from 38 K to 90 K and shifts the O → (O + T) boundary by 30 K towards lower temperatures. This suggests that the crystal lattice of sodium-potassium niobate is metastable, it has regions with different directions of polarization, therefore, the realization of a two-phase state in Na0.5K0.5NbO3 at room temperature under certain technological conditions is quite possible.

It can be seen in Figure 2b that the formation of NKP0.30 proceeds according to the scheme which is characteristic of compositions containing PbTiO\(_3\), PbZrO\(_2\) and niobium containing components. First, SS are formed on the basis of lead titinate, lead zirconate, SS based on sodium potassium niobates, and then SS with stoichiometric composition. According to this, the profile of the diffraction peak of (200) \(\Delta\) NKP0.30 after the second synthesis is a superposition of the peaks of successively formed phases. During sintering, as the temperature rises, the phase ratio changes and at \(T_{sinter} = 1523\) K, NKP0.30 becomes almost single-phase. Single diffraction peaks correspond to cubic symmetry, but the asymmetry of their profiles can be a consequence of the concentration of diffuse scattering near the main reflection and/or very small cell distortion; therefore, the symmetry NKP0.30 at \(T_{sinter} = 1523\) K is designated as pseudocubic. The extinction of diffraction reflection 100 indicates the formation of NKP0.30 SS with a statistical distribution of atoms along the A and B positions of the perovskite structure. Only in this case, the scattering factors of the average atoms in these positions are almost equal. In this case, the crystal lattice becomes almost body-centered, and the structural factor for the (100) planes is \(F_{100} = 0\).

NKP0.70 SS (Figure 2c) is two-phase after the second synthesis and sintering at 1473 K SS; it contains Psc and T phases with close cell parameters. It is impossible to determine the symmetry of the Psc phase due to the superposition of x-ray peaks of two phases. At \(T_{sinter} = 1523\) and 1573 K, a part of ZrO\(_2\) precipitates; in this case, the stoichiometry of NKP0.70 is violated towards an increase of the concentration of niobium; therefore, as expected, the transition to the T phase does not occur.

NKP1.00 SS (Figure 2d) after the second synthesis has a perovskite-type structure that does not contain impurity compounds.
and is a mixture of two phases, one of which is tetragonal, while the second phase can be rhombohedral or monoclinic. Due to the heterogeneity of the SS and the ambiguity in determining the symmetry of the second phase, it is designated as pseudocubic. After sintering at a temperature of 1373 K, NKP1.00 became more homogeneous, but traces of the second phase were still preserved and the relative density of ceramics was only 80%. The most homogeneous and high-density NKP1.00 is formed at $T_{\text{sint}} = 1473$ K. At $T_{\text{sint}} = 1523$ K, it decomposes into a series of perovskite phases, ZrO$_2$ (JCPDS set 3, card 515), and a phase with a pyrochlore type structure Pb$_2$Ti$_2$O$_6$ (JCPDS set 26, card 142).

Table 1 shows the cell parameters and the density of ceramic samples shown in Figure 2. From the data of the table it is seen that after a double synthesis, the final formation of the phase composition and structure of SS does not occur. As a rule, in the absence of starting reagents and/or intermediates in the synthesized product, SS of stoichiometric composition are formed after double synthesis, while sintering only increases the uniformity and density of ceramics. In this system, the formation of the structure of stoichiometric SS continues during sintering, and an increase in $T_{\text{sint}}$ changes their phase composition, cell parameters and does not always lead to an increase in density. Based on the analysis of X-ray diffraction patterns and the data given in the table, it can be concluded

| $x$ | $T_{\text{sint}}, K$ | Symmetry | $a$, Å | $b/c$, Å | $\beta/c/\alpha$ | $V$, Å$^3$ | $\rho_{\text{exp}}, g/cm^3$ | $\rho_{\text{rel}}$, % |
|-----|-------------------|-----------|--------|-----------|-----------------|----------|----------------|----------------|
| 0.00 | $T_{\text{sint}} = 1223$ | O | 4.006 | 3.947 | 90.35 | 63.33 | 3.69 | 81.6 |
| 1398 | O | traces T | 4.002 | 3.943 | 90.23 | 63.14 |
| 1473 | O | T | 4.007 | 3.951 | 90.30 | 63.44 | 2.49 | 55.2 |
| 0.30 | $T_{\text{sint}} = 1248$ | T | 3.924 | 4.154 | 1.053 | 63.66 | 66.1 |
| 1373 | T | Psc | 3.930 | 4.081 | 1.045 | 63.04 | 3.97 | 70.1 |
| 1473 | T | Psc | 3.914 | 4.071 | 1.040 | 62.39 | 2.49 | 43.9 |
| 1523 | T | Psc | 4.015 | 64.74 | 5.11 | 91.51 |
| 0.70 | $T_{\text{sint}} = 1373$ | T | 4.029 | 4.066 | 1.009 | 66.01 | 66.24 |
| 1473 | T | Psc | 4.017 | 4.058 | 1.010 | 65.49 | 6.05 | 85.58 |
| 1523 | T | Psc (-ZrO$_2$) | 4.006 | 4.045 | 1.010 | 64.91 | 6.67 | 93.51 |
| 1573 | T | Psc (-ZrO$_2$) | 3.986 | 4.038 | 1.013 | 64.17 | 5.88 | 82.22 |
| 1.00 | $T_{\text{sint}} = 1273$ | T | 4.023 | 4.138 | 1.029 | 66.96 | 68.38 |
| 1373 | T | Psc | 4.013 | 4.140 | 1.032 | 66.66 | 6.51 | 80.59 |
| 1473 | T | Psc | 4.026 | 4.141 | 1.029 | 67.11 | 7.64 | 94.6 |
| 1523 | T | Psc (-ZrO$_2$-Pyr.) pyr | 4.027 | 4.127 | 1.025 | 66.94 | 7.44 | 92.08 |

Figure 3. X-ray diffraction patterns of (1-x)(Na$_{0.5}$K$_{0.5}$)NbO$_3$-xPb(Ti$_{0.5}$Zr$_{0.5}$)O$_3$ solid solutions: $\alpha$-rhombic, $b$-pseudocubic, $c$-tetragonal regions of the phase diagram, the numbers to the right of the X-ray diffraction patterns show the value of $x$, the asterisk indicates the ZrO$_2$ line.
that the SS structure of the studied (1-x) (Na0.5K0.5)NbO3-xPb(Ti0.5Zr0.5)O3 system, regardless of x, is labile and critically dependent on technological conditions. The maximum density of ceramics, providing the best electrophysical parameters, can be obtained only after careful selection of the conditions of synthesis and sintering. Such work was done for all the studied TRs, after which the samples with the highest density were selected for constructing a phase diagram of the system and measuring electrophysical parameters.

Figure 3 shows fragments of X-ray diffraction patterns of all SS in the angle range of 2θ = 20-58° (d = 4.69-1.84 Å), in which diffraction lines (100)c, (110)c, (111), and (200)c, characterizing the symmetry of the perovskite cell, are located. In the region of larger angles 2θ, the number of diffraction peaks in the multiplet increases, and with the nonuniformity of SS and the proximity of the parameters of the phase cell, it is impossible to unambiguously characterize each phase. Figure 3a shows X-ray diffraction patterns of SS adjacent to NKP0.00 (rhombic region). It is seen that the diffraction pattern sharply changes in the range of 0.20 < x < 0.25, at x \leq 0.20 the samples are two-phase: O and Psc phases with close cell parameters, and the phase ratio varies nonmonotonically with x. At x > 0.20 the main phase is Psc, but the diffuse halo from the side of larger angles \( \theta \) indicates that the O phase is still present in the form of clusters that periodically violate the matrix structure. In the range of 0.35 < x < 0.60 (Figure 3b, Psc region), there is only the Psc phase with a very small cell distortion. The exception is NKP0.50 SS, which is cubic, as evidenced by narrow and symmetric diffraction peaks. The profile of the (200)c diffraction peak NKP0.60 SS corresponds to a mixture of Psc and T phases.

X-ray diffraction patterns of SS adjacent to NKP1.00 are shown in Figure 3c (tetragonal region). It can be seen that NKP0.65 and NKP0.70, like NKP0.60, are a mixture of Psc and T phases; at x ≥ 0.75 SS become tetragonal.

Thus, in the (1-x)(Na0.5K0.5)NbO3-xPb(Ti0.5Zr0.5)O3 system, between the O and T regions of the phase diagram, an intermediate Psc phase with a very slightly distorted perovskite cell was revealed. This phase is not a wide MR, but itself forms a MR with O and T phases.

3.2. Phase diagram of the system state (Na, K) NbO3-PZT

Figure 4 shows the dependences of the parameters and cell volume on x. In the rhombic region, for convenience of comparison, in the interval 0.00 < x < 0.20 the dependence of the average cell parameter, equal to, is given. The nature of the dependences fully confirms the conclusion made on the basis of the analysis of X-ray diffraction patterns, namely, two regions of constancy of the V cell (invar effect) are located in the intervals 0.05 < x < 0.20 and 0.60 < x < 0.70, in which the O and Psc phases (MR1) coexist and T and Psc phases (MR2), respectively. In the Psc phase, in the interval 0.20 < x < 0.60 the dependences \( a(x) \) and \( V(x) \) pass through a maximum \( (x = 0.35) \) and a minimum \( (x = 0.45) \). We have shown that the invar effect takes place in the region of coexistence of phases in binary systems based on NaNbO3 [14] and PZT [6] both with a change in concentration and temperature. To explain the behavior of \( a(x) \) and \( V(x) \) in the monophasic Psc region, it is necessary to consider the real (defective) structure of the extreme components of the quaternary system. As shown in [17], the real structure of NaNbO3 and SS based on it, inherits the block structure of Na2O5, formed by repeated crystallographic shift (CS) in two almost orthogonal directions. The SS structure of the PZT system in the tetragonal region is not block, it contains the CS planes perpendicular to the [001] direction. The number, length and direction of the CS planes varies depending on the number of oxygen

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**Figure 4.** Dependences of perovskite cell parameters of (1-x) (Na0.5K0.5)NbO3-xPb(Ti0.5Zr0.5)O3 solid solutions on x: rhombic region - 1-a, 2-V, pseudocubic region - 3-a, 4-V, tetragonal region - 5-a, 6-c, 7-(c/a-1)×10^5, 8-V.

**Figure 5.** Fragments of the microstructure of ceramics SS from different fragments of the phase diagram of the studied system: Tsint. = 1423K, CCT, x = 0.2 (a-c), Tsint. = 1458K, CCT, x = 0.4 (d-f).
vacancies arising from a change in the valence of transition metal ions $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$, $\text{Nb}^{5+} \rightarrow \text{Nb}^{4+}$. Since the structure is densified along the CS planes, the cell volume, due to the cooperative effect of x-ray radiation, decreases or increases in accordance with a change in the real (defective) structure.

Since the crystal lattices of $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ and $\text{Pb} (\text{Ti}_{0.5}\text{Zr}_{0.5})\text{O}_3$ are fundamentally different, a very complex rearrangement of the TP structure is required, which affects the nonmonotonic behavior of the structural parameters in the Psc phase with a “dip” at $x \sim 0.4 - 0.5$, that is, with an equal number of extreme components. The latter probably indicates the formation of two types of SS (SS1 and SS2) with a predominant influence, respectively, of $(\text{Na}_{0.3}\text{K}_{0.7})\text{NbO}_3$ and PZT, which differ in different mechanisms of defect structure formation. Therefore, the transition Psc phase occupies such a wide concentration interval. At the same time, a high degree of disorder created due to complex substitution in the A and B sublattices has led to the fact that the intermediate phase has almost cubic, and at $x = 0.50$ cubic symmetry.

Thus, on the basis of the constructed phase diagram of the studied 4-component system, it can be concluded that TP located in the vicinity of structural instabilities can have extreme electrophysical properties, which has been observed in practice (Figure 5), about which we will tell below.

### 3.3. Microstructure

It should be noted that an unstable pattern is observed in the grain structure of two-phase ceramics. Thus, SS from SS1 ($x = 0.2$) differ in the irreproducibility of the grain landscape in different areas of cleavages of the same sample (Figure 5 a-c). A fine-grained structure with chaotic, sometimes loose packing of grains in one section transforms into an even finer structure with single regions of radial-ring crystallite formation (indicated by dashed lines) (Figure 5b). In these cases, large pores are framed by a layer (or layers) of close-packed crystallites of slightly larger size than the bulk, often having a shape close to...
ideomorphic. And away from this group, smaller, loose-packed, less perfect grains grow. In the next section (Figure 5c) an even finer-grained structure crystallizes with columns of close-packed crystallites forming bizarre exotic figures (indicated by dashed lines). The same cannot be said for single-phase SS (x = 0.4), in which the grain structure is the same in different fields of observation (Figure 5d-f). Attention is also drawn to the fact of a catastrophically sharp transformation of the grain structure of SS that are close (almost at the boundary) to SS1 (x = 0.0) (Figure 6a-c) and inside it (x = 0.2) when mechanical activation (MA) is introduced into the technological process at the stage of obtaining press powder. In this case, due to the strong activation of the initial metastable structure, a rapid growth of grains to gigantic sizes is observed, which are the larger, the lower the Tsint (Figure 6a-c). The fact that in this case the grains are formed of almost regular geometric shape with distinct faces, indicates that they grow in the presence of a liquid phase. Moreover, ideomorphic grains crystallize first in the form of single polyhedra, forming a bimodal structure (Figure 6e) with individual crystallites framed by almost rectilinear boundaries, and then (at the higher Tsint) creating a landscape consisting entirely of giant grains of regular geometric shape. This type of crystallization is characteristic of heterogeneous, non-ideomorphic structures that are often found in AMN. In the case of a single-phase SS (x = 0.4), its polycrystalline structure practically does not respond to such an effect, remaining fine-grained (Figure 5d-f).

Figure 7 shows fragments of the microstructure of ceramics SS of the studied system obtained under optimal conditions, and Figure 8b – dependencies of Tsint,opt., average grain size, δ, and a uniform strain parameter, δ, on the concentration (x) of the PZT-component. All curves are nonmonotonic with extrema (maximums of Tsint and minimum δ) at x~0.4±0.6.

An increase in Tsint,opt. as the system is enriched with a Pb-containing component to a state where SS1 and SS2 are parity (in quantitative ratio), in our opinion, it is caused by a gradual transition from sintering with the participation of the liquid phase, characteristic of alkali metal niobates [18], to solid-state sintering, characteristic of PZT materials [19]. The subsequent decrease in Tsint,opt. at large x values, is probably the result of a less pronounced simultaneously occurring recrystallization process, generally speaking, complicating the formation of a dense ceramic frame. The dependence of (x) is known to be inversely proportional to δ(x), which is realized in our case and is quite explainable by the inhibition of grain growth in the presence of significant internal stresses in ceramics with high spontaneous deformation and, conversely, by the activation of recrystallization phenomena in media with lower values δ, favoring diffusion processes and mass transfer. Liquid-phase sintering, which was mentioned above, also facilitates the growth of grains in SS, similar in composition to AMN.

Another interesting fact related to the visualization of the microstructure of SS from different fragments of the x-T diagram of the system is noteworthy. Thus, in SS1, the grain boundaries are clearly visible, which suggests that the cleavage of samples passes precisely along them. In SS2, the intergranular boundaries are almost invisible, and the grain structure is practically “guessed” either in separate large surface pores or in individual grain conglomerates. This indicates the high strength of such boundaries and, as a consequence, the passage of cleavage through...
the body of the grains themselves. It would seem that the latter should have been realized in SS1, which were sintered with a liquid-phase. However, this does not occur due to the greater “ferro softness” of these SS and, as a consequence, the greater mobility of intercrystalline and domain walls here compared to SS2 with the predominant “ferro hard” T phase.

3.4. Electrophysical properties. Static analysis

As expected, the electrophysical characteristics of the studied SS turned out to be extreme near (and at the boundaries) the phase stability, mainly, in the vicinity of the Psc → T transition, which corresponds to the logic of their change in systems with MR (Figure 9). The exception was only two single-phase fields (Psc and T) inside which anomalies were noted both during structural and macrocharacteristics. In the first case, this is undoubtedly associated with the transition from SS1 to SS2, in the second (x~0.8), it is due to the following. The fulfillment of the correlation $\frac{\varepsilon_{33}}{\varepsilon_0} < \varepsilon/\varepsilon_0$ at x < 0.8 suggests that the main contribution to the polarization of these TRs is made by reorientations of domains other than 180-degree ones. At x > 0.8 the polarization is due to the reorientation of 180-degree domains, since $\frac{\varepsilon_{33}}{\varepsilon_0} < \varepsilon/\varepsilon_0$. At x≈ 0.8 ($\frac{\varepsilon_{33}}{\varepsilon_0} \approx \varepsilon/\varepsilon_0$) both polarization mechanisms are apparently equally probable. The statistical analysis of the macroscopic responses of single- and two-phase SS, performed by us, also showed a greater scatter of the main electrophysical characteristics in heterophase SS (Figure 10).

The observed is, undoubtedly, the result of a fluctuation in the compositions of SS, which are especially noticeable in single-phase regions. Thus, in MR, SS of which are characterized by a rapid change in characteristics even with small variations in the elemental composition, any violation of the given stoichiometry of the chemical composition leads to a very serious change in the phase state and structure and, as a result, to a significant spread in the electrophysical properties of SS. The observed, undoubtedly, is the result of a fluctuation in the compositions of SS, which are especially noticeable in single-phase regions. So, in MR, SS of which are characterized by a rapid change in characteristics even with small variations in the elemental composition, any violation of the

![Figure 10. Dependences of statistical characteristics $\varepsilon$, $\bar{\varepsilon}$, $S_{n, d_{33}}$, $\Delta x$ on the concentration of PZT: a) $\varepsilon_{33}/\varepsilon_0$, b) $K_p$, c) $d_{33}$, d) $g_{33}$.](image-url)
given stoichiometry of the chemical composition leads to a very serious change in the phase state and structure and, as a result, to a significant spread in the electrophysical properties of SS. This is due to the increased sensitivity of complex oxide media to changes in chemical composition and, importantly, its homogeneity. Aggravating circumstances are solid-phase synthesis, which does not, obviously, ensure the completeness of the reaction; sintering using conventional (traditional) ceramic technology, in which the maximum attainable density of products usually does not exceed (90 ± 95)% of theoretical one; heterovalent ion substitutions in both cationic sublattices, introducing a certain crystallochemical disorder and disordering of the structure.

All this can lead to increased chemical heterogeneity of SS from the regions of morphotropic phase transitions. Indirect confirmation of the validity of this assumption can be achieved by analyzing the piezoresonant signal. So, Figure 11 shows the dependences of the real part of the complex conductivity on the frequency of the measuring signal. The figures show the concentration of PZT(x), as well as the values of the coefficients from Eq. (8), calculated by approximating the piezoelectric response. The contribution of dielectric loss was previously subtracted from the experimental data. a) x = 0.4, b) x = 0.6, c) x = 0.8.

Figure 11. Dependences of the real part of the complex conductivity on the frequency of the measuring signal. The figures show the concentration of PZT(x), as well as the values of the coefficients from Eq. (8), calculated by approximating the piezoelectric response. The contribution of dielectric loss was previously subtracted from the experimental data. a) x = 0.4, b) x = 0.6, c) x = 0.8.

Thus, we can assume that the appearance of additional components in the resonance signal is directly related to the chemical heterogeneity of the objects, leading to the formation of a naturally composite state in them. In this case, attention is drawn to the dependence of the difference between the resonance frequencies of the two components (f) on the concentration of PZT in the system. So, in samples with x = 0.4 and 0.8, belonging to single-phase regions, f is 1671 and 1152 Hz, respectively, and this may be due to compositional fluctuations, and the resulting extended inhomogeneities do not differ much in physical properties, and as a result the resonant response can be, with some error, described by a single-circuit equivalent circuit. On the other hand, the resonance components in the sample of MR2 (x = 0.6) are separated by a significant frequency gap of 8165 Hz, which, as expected, indicates a significant difference in the physical properties of volume units forming the composite structure of heterophase SS.

We performed the micro-XRF study using statistical analysis of the experimental data for the SS with x = 0.2, 0.4. Table 2 shows the initial values of the concentrations for the chemical elements which include in the studied samples.

Using mathematical support of the spectrometer the chemical elements concentrations were determined in the frame of the method of fundamental parameters [13]. For each sample it should been spent about 1.5–2 h for one cycle of measurement. The average values of atomic concentrations are presented in Table 3.

Figure 12 shows the distributions for concentration on two ceramic samples (R and 1, R and 2) collected on the base of fluorescence received from the surface of the sample with x = 0.4. The presented distributions were approximated by Gaussian functions and characterize dependences of the number of surface points containing the same values of atomic concentrations. For all analyzed chemical elements obtained on the tested sample the distributions are given for two samples of ten measurements in each group.

The statistical method for comparison of in pairs samples we applied to all studied ferroceramics. According to the t-criterion for six chemical elements a statistical estimate was performed to compare the average concentrations. This analysis showed that variations of the average concentrations for the chemical elements are not significant. Moreover, the differences in the average concentrations of the samples do not

| Composition | Atomic concentrations |
|-------------|-----------------------|
| Na0.1K0.1Pb0.8Nb0.2Ti0.4Zr0.4O3 | Na 25% K 25% Pb 0% Nb 50% Ti 0% Zr 0% |
| Na0.6K0.4Pb0.3Nb0.2Ti0.3Zr0.3O3 | 0.8(Na0.6K0.4)0.3Nb0.2Pb0.3Ti0.3Zr0.3O3 20% Na 20% K 10% Pb 40% Nb 30% Ti 10% |
| Na0.6K0.4Pb0.3Nb0.2Ti0.3Zr0.3O3 | 0.6(Na0.6K0.4)0.3Nb0.2Pb0.3Ti0.3Zr0.3O3 15% Na 15% K 20% Pb 30% Nb 10% Ti 10% |
| Na0.6K0.4Pb0.3Nb0.2Ti0.3Zr0.3O3 | 0.4(Na0.6K0.4)0.3Nb0.2Pb0.3Ti0.3Zr0.3O3 10% Na 10% K 20% Pb 20% Nb 10% Ti 15% |
| Na0.6K0.4Pb0.3Nb0.2Ti0.3Zr0.3O3 | 0.2(Na0.6K0.4)0.3Nb0.2Pb0.3Ti0.3Zr0.3O3 5% Na 5% K 10% Pb 40% Nb 10% Ti 20% |
| PbTiO3 | 0 0 50% 0 25% 25% |
exceed 1% and the values correspond to the confidence interval $X \pm \Delta X$ (7). Thus, it was found that for all samples the scatter of the concentration values is statistically insignificant, i.e., there is a sufficient degree of homogeneity of the chemical composition of these piezoceramic materials.

The micro-XRF method and the statistical approach to analysis of the experimental data were used to estimate a sensitivity of the method to the changing the chemical composition under variation of technological conditions for the manufacture of piezoceramics. The statistical comparison of concentrations described above was carried out for two

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**Table 3.** The average concentration of chemical elements that make up the samples of ferro-piezoceramics.

|          | $x = 0.0$ | $x = 0.2$ | $x = 0.4$ | $x = 0.6$ | $x = 0.8$ | $x = 1.0$ |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Na       | 25.22     | 20.16     | 15.17     | 9.38      | 5.88      | 0.00      |
| K        | 24.83     | 20.08     | 15.46     | 9.20      | 4.28      | 0.00      |
| Ti       | 0.00      | 4.81      | 9.85      | 15.32     | 20.39     | 24.73     |
| Zr       | 0.00      | 4.54      | 9.54      | 14.54     | 19.68     | 25.31     |
| Nb       | 49.95     | 40.56     | 29.78     | 20.77     | 10.24     | 0.00      |
| Pb       | 0.00      | 9.85      | 20.21     | 30.79     | 39.54     | 49.96     |

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**Figure 12.** Sample $x = 0.4$: Normalized distribution of the number of points containing the same atomic concentrations of the main chemical elements: a) Na, b) K, c) Ti, d) Zr, e) Nb, f) Pb. 1 - fluorescence measured in the first sample of 10 surface areas; 2 - fluorescence measured in a second sample of 10 surface areas.
piezoceramic samples $x = 0.2$, which were fabricated at different sintering temperatures $T_{\text{sint.1}} = 1448K$ and $T_{\text{sint.2}} = 1493K$. It should be noted that sintering temperatures differed by less than 3%. In Figure 13 shows the corresponding component distributions for these two samples, and Table 4 shows the average values of atomic concentrations.

Statistical analysis (t-criterion) of the average intensities and the corresponding concentrations confirms the sample mean concentrations of two chemical elements - 19K and 41Nb - significantly differ at the confidence level of $P = 95%$. In sample 1 ($T_{\text{sint.1}} = 1448K$), the relative content of potassium atoms is greater than in sample 2 ($T_{\text{sint.2}} = 1493K$), while changes in the niobium content occur in the opposite direction. In this case, the atomic concentrations of the remaining components differ slightly.

Figure 14 shows the $\varepsilon/\varepsilon_0$ dependences of all the studied SS taken at a frequency of 1018 Hz in the sample cooling mode. The concentration dependence of $T_c$, constructed from these data, correlating with the course of $\delta(x)$ (Figure 8) and having a minimum at $x \sim 0.5$, located near SS$_2$ (Figure 9), corresponds to the logic of $T_c$ change in systems, extreme components of which do not have common cations. An estimate

![Graphs showing normalized distribution of atomic concentrations](image)

Table 4. Average values of atomic concentrations of the chemical elements that make up the sample $x = 0.2$ ferro-piezoceramics.

| Element | $T_{\text{sint.1}} = 1448K$ | $T_{\text{sint.2}} = 1493K$ |
|---------|-----------------|-----------------|
| Na      | 20.16           | 19.40           |
| K       | 20.08           | 17.55           |
| Ti      | 4.81            | 5.29            |
| Zr      | 4.54            | 4.59            |
| Nb      | 40.56           | 43.12           |
| Pb      | 9.85            | 10.04           |
of the temperature, $T_{\text{Cmin}}$, at the minimum and concentration, $x_{\text{min}}$, at which it occurs, using the formulas:

$$T_{\text{Cmin}} = \left(4T_{11}T_{22} - (T_{12} + T_{21})^2\right) / \left(4(T_{11} + T_{22} - T_{12} - T_{21})\right)$$

(9)

$$x_{\text{min}} = \frac{2(T_{11} - T_{12} - T_{21})}{(2(T_{11} + T_{22} - T_{12} - T_{21}))}$$

(10)

gives the values of $T_{\text{min}}$ and $x_{\text{min}}$, equal to 340K and 0.50, respectively, which is close to experiment (in the formulas $T_{iik}$ - the Curie temperatures of the intermediate compounds of $A_iB_kO_3$).

Figure 15 shows the $P$-$E$ loops ($\sim T = 300K, f = 50$ Hz) of some SS. It can be seen that an increase in the content of PZT leads to their transformation: from narrow with small values of coercive field ($E_c$) and polarization of saturation ($P_s$) - to wide, characterized by more than doubled $P_s$ and increased $E_c$. The aforementioned is associated with an increase in grain size and in the electrical conductivity of SS as the PZT content increases.

4. Conclusion

SS of $(1-x)(Na_{0.5}K_{0.5})NbO_3-xPb(Ti_{0.5}Zr_{0.5})O_3$ ($0.0 \leq x \leq 1.0; \Delta x = 0.025-0.05-0.1$) composition have been obtained by two-stage solid-phase synthesis followed by sintering, using conventional ceramic technology in optimized modes.

X-ray diffraction has shown that after a double synthesis the final formation of the phase composition and structure of SS does not occur. The formation of the stoichiometric SS structure continues during sintering, while the increase in $T_{\text{Cmin}}$, changes their phase composition, cell parameters and does not always lead to an increase in density. The constructed phase diagram of the system is characterized by the existence of two morphotrophic regions with $O + Psc$ ($0.0 < x < 0.25$) and $Psc+T$ ($0.55 < x < 0.75$) phases and three single-phase fields: $O$, $Psc$, $T$.

It has been shown that the average grain size and the uniform strain parameter extremely depend on the sintering temperature, with a maximum and a minimum of $\delta$ at $x \sim 0.4-0.6$, i.e. in the vicinity of the transition from SS1 to SS2. The electrophysical characteristics are extreme near (and at the boundaries) the phase stability, mainly in the vicinity of the $Psc \rightarrow T$ transition, which corresponds to the logic of their change in systems with MR. Statistical analysis of macroresponses of single- and two-phase SS showed their greater scatter in heterophase SS.

The results of microfluorescence studies indicate that for all samples the variation in concentration values is statistically insignificant, i.e. a fairly high degree of homogeneity of the chemical composition takes place.

Analysis of the obtained data revealed three groups of SS-based intelligent materials: with high $K_p, \varepsilon_{33}/\varepsilon_0$, low $V_{1E}$ (near PZT) – for low-frequency applications; with low $\varepsilon_{33}/\varepsilon_0$, high $V_{1E}$ (near KNN) – for high-frequency use; with intermediate values of the piezoelectric parameters (near SS1→SS2 transition), intended for operation in combined equipment complexes.

Declarations

Author contribution statement

Alexandr V. Nagaenko, Konstantin P. Andryushin, Lidiya A. Shilkina, Mikhail I. Mazuritskiy, Inna N. Andryushina, Ekaterina V. Glazunova, Aleksey A. Pavelko, Yuri A. Trusov, Iliya A. Verbenko: Performed the experiments; Wrote the paper.

Figure 14. Temperature dependences of $\varepsilon/\varepsilon_0$ (upon cooling) of all the studied SS ($f = 1018$ Hz).

Figure 15. Dielectric hysteresis loops (on the left) and polarization characteristics (on the right) at $T = 300$ K, ($P_s$ saturation polarization, $P_r$ residual polarization, $E_c$ coercive field).
Shun-Hsyung Chang, Ivan A. Parinov: Analyzed and interpreted the data.
Larisa A. Reznichenko: Conceived and designed the experiments.

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