Microstructure, electromechanical hysteresis and polarization characteristics of solid solutions of the system (Na, K, Cd0.5) NbO3

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Abstract. The phase diagram of the system (1-x-y) NaNbO3 – xKNbO3 – yCdNb2O6 (y=0.25, x=0.05÷0.20) is constructed. The agreement between the microstructure and the phase diagram of the system is demonstrated. A decrease in the polarization characteristics up to the phase transition temperature is detected. The formation of extrema $d_{33}(E)$ in the region of the inflection point on the ascending branch of the half-period $S_{33}$ is revealed. A correlation has been established between the internal structure (crystalline, domain, grain, defect), fundamental electromechanical and polarization properties for solid solutions of the studied system.

1. Introduction

The most widely used piezoelectric materials are solid solutions based on system PbTiO3-PbZrO3 (PZT). This is due to their excellent piezoelectric properties [1-3]. The development of the legislative framework in the field of environmental protection is forcing the search for lead-free materials that can replace PZT ceramics. This will allow to reduce anthropogenic pollution. Among the latter, a special place is occupied by materials based on solid solutions (SS) of sodium niobate (SN) [1, 4-6], which have a unique combination of properties: low specific gravity ($\rho \leq 4.5$ g/cm$^3$), high velocity of sound ($v_R \approx 6$ km/s), a wide range of values of relative dielectric constants ($50 \leq \varepsilon_r/\varepsilon_0 \leq 2000$) and mechanical quality factor ($50 \leq Q_M \leq 2000$) at sufficiently high piezoelectric parameters, the achievement of which in PZT materials is fundamentally impossible.

At the same time, niobate materials have not yet found wide application in equipment, while the number of known SS systems containing PZT has reached several hundred. Among the latter, multicompontent systems have become the basis of materials for various purposes. The range of studied systems based on SN is limited no more than 50 compositions, which not sufficiently investigated and only a few binary systems have found real practical application. This is due to the impossibility of obtaining solid solutions based on SN by traditional methods, which, is associated with the complexity of their crystal structure, the presence of a large number of phase transitions, and the strong dependence of properties on the conditions of structure formation.
This work continues our earlier studies of the system \((1-x-y)\) NaNbO\(_3\) – \(xKNbO_3\) – \(yCd_{0.5}NbO_3\) \([7]\) and is devoted to the establishment of regularities in the formation of the phase picture, grain landscape (microstructure), electromechanical and polarization properties of the SS system in a wide range of external influences (temperatures, constant and alternating electric fields).

2. Experiments

The objects of the study were SS of the composition \((1-x-y)\) NaNbO\(_3\) – \(xKNbO_3\) – \(yCdNbO_3\) system with \(y=0.25\), \(x=0.05\div0.20\), \(\Delta x=0.05\). The samples were prepared by two-stage solid-phase synthesis and sintering using conventional ceramic technology. \((T_{\text{synth.1}}=1220\,\text{K}, \tau=5\,\text{h.}, T_{\text{synth.2}}=1240\,\text{K}, \tau=10\,\text{h.}; T_{\text{sint.}}=(1190\div1200)\,\text{K}\) depending on the composition). NaHCO\(_3\) (“chemically pure”), KHCO\(_3\) (“pure for analysis”), and Nb\(_2\)O\(_5\), CdO (“pure”) were used as the feedstock.

Sintered ceramic blanks were subjected to mechanical processing (cutting along the plane, grinding along flat surfaces and ends) in order to obtain measuring samples of Ø10mm x 1mm. Before metallization, the samples were calcined at a temperature \(T_{\text{calc.}}=770\,\text{K}\) for 0.5 h. to remove organic matter residues and degrease surfaces in order to increase the adhesion of the metal coating to ceramics. The electrodes were applied by double firing a silver-containing paste at a temperature of 1070 K for 0.5 h.

X-ray diffraction studies were performed at room temperature using a DRON-3 diffractometer (filtered Co\(_{K\alpha}\) radiation, Bragg - Brentano focusing scheme). Bulk and ground ceramic objects were studied, which made it possible to exclude the influence of surface effects, voltage and textures arising in the process of obtaining ceramics. The calculation of structural parameters was performed according to standard methods \([8]\).

The obtained samples were polarized using the “hot” polarization method. In this case, the samples were loaded into the chamber with PES-5 polyethylene siloxane liquid at \(\approx 300\,\text{K}\) for 0.5 h., then the temperature was smoothly risen to 423 K, while the field was simultaneously increased from 0 to \((3.0\div4.0)\,\text{kV/mm}\). Under these conditions, the samples were kept for \((20\div25)\) minutes and then cooled under the field to \(\approx 300\,\text{K}\) (room temperature).

A scanning electron microscope JSM – 6390L (JEOL) (Japan) with a system of microanalyzers of the Oxford Instruments company (Great Britain) was used to study the microstructure of sample chips; microscope resolution was up to 1.2 nm at an accelerating voltage of 30 kV (an image in secondary electrons), accelerating voltage limits were from 0.5 to 30 kV, magnification range: from x5 to x300000, beam current was up to 200 nA.

The P–E loops were studied using the Sawyer - Tower scheme, at \(f=50\,\text{Hz}\) and the temperature range of \((290\div431)\,\text{K}\). The values \(P_s\) – the saturation polarization, \(P_r\) – the residual polarization, \(E_c\) – the coercive field were estimated. The narrow temperature range was conditioned by the use of polyethylene siloxane oil with a boiling point of \(\approx 480\,\text{K}\) as an insulator in the measuring cell. To eliminate the effect of hydrozilation, the samples were preliminarily annealed at \(T=670\,\text{K}\).

The curves of unipolar deformation \((S_{33})\) induced by a constant electric field with intensity \(E\) and \((S_{33})\) were recorded on polarized specimens using a specially fabricated test stand at the Research Institute of Physics, Southern Federal University, based on a MIKRON-2 instrument for verifying end gauges, an Agilent 34420 A nanovoltmeter / microohmmeter. The curves of \(S_{33}(E)\) were approximated using the least squares approach. Minimum standard deviation \(r\) was our criterion of the quality of approximation. Inverse piezomodulus \(d_{33}\) was calculated using the equation \(d_{33}=S_{33}/E\).

3. Results and discussion

Figure 1 shows the phase diagram (PD) of the system with \(y=0.25\), which indicates the formation of regions with coexisting phases with different symmetry.
Figure 1. Phase diagram of the \((1-x-y)\) NaNbO\(_3\) – \(x\)KNbO\(_3\)– \(y\)Cd\(_{0.5}\)NbO\(_3\) \(y=0.25, x=0.05\div0.20\).

It is seen that near NaNbO\(_3\) \((x \leq 0.15)\) tetragonal (T) structures with traces of monoclinic (M) structures crystallize. An increase in the content of the KNbO\(_3\) \((0.15 \leq x \leq 0.25)\) leads to the formation of a heterogeneous region with coexisting T- and M- phases. Recrystallization processes occurring against the background of such phase transformations lead to the formation of a kind of grain landscape (Figure 2), which clearly responds to all changes in the crystal structure of the SS. From figure 2 it is clearly seen that the microstructure of ceramics with a very low content of KNbO\(_3\) \((x = 0.05 \div 0.10)\) is close to homogeneous (region I, RI). At \(0.15 \leq x \leq 0.20\), the microstructure is refined, becomes inhomogeneous, and regions with coarse and fine grains appear, the number of which (small) increases with approaching KNbO\(_3\) (region II, RI).

Figure 2. Fragments of the ceramic microstructure of SS of the \((1-x-y)\) NaNbO\(_3\) – \(x\)KNbO\(_3\)– \(y\)Cd\(_{0.5}\)NbO\(_3\) \(y=0.25, x=0.10\div0.20\).

Figure 3. \(P-E\) loops of SS of the composition \((1-x-y)\) NaNbO\(_3\) – \(x\)KNbO\(_3\)– \(y\)Cd\(_{0.5}\)NbO\(_3\) \((y=0.25, 0.05 \leq x \leq 0.20)\) at \(T=300\div420\)K, \(\Delta T=30\)K.
Figure 3 shows the $P$-$E$ loops of the studied SS at $T=300÷420$K, $\Delta T=30$K. It was revealed that, in a SS with $x = 0.05$, the formation of saturated $P$-$E$ loops occurs at a voltage of $U = 700$ V over the entire investigated temperature range (Figure 3a). Exceeding $U = 700$V causes the loop to expand and, consequently, increase energy losses during the polarization reversal cycle. In SS with $0.10 \leq x \leq 0.20$, the permissible voltage at which typical ferroelectric $P$–$E$ loops are formed is $U = (1600 ÷ 1800)$ V (Figure 3 b–d). An increase in temperature leads to a gradual contraction of the loop along the ordinate axis.

Based on the study of the $P$-$E$ loops, the dependences of $(P_s, P_r, E_c)$ ($T$) (Figure 4) have been constructed and approximated by a polynomial of the second degree. It was found that at $x = 0.05$, the inflection point $P_s, P_r$ of characteristics is formed in the temperature range $\sim (360 ÷ 370)$ K. Up to the indicated temperatures $(P_s, P_r)(T)$, the dependences either increase slightly (Figure 4) or do not change. Parameter $E_c$ decreases over the entire research temperature range. The observed anomaly may indicate structural instabilities present in these objects. At $0.15 \leq x \leq 0.20$, the dependences $(P_s, P_r, E_c)$ ($T$) tend to linearly decrease with increasing temperature.

![Figure 4. Dependences of $(P_s, P_r, E_c)(T)$ of SS of the composition $(1-x-y) \text{NaNbO}_3 - x\text{KNbO}_3 - y\text{Cd}_{0.5}\text{NbO}_3$ ($y=0.25, 0.05 \leq x \leq 0.20$).](image1)

Figure 5 illustrates the evolution of $S_{33}$-$E$ loops depending on the concentration of KNbO$_3$. It was revealed that in the investigated SS the dependence $S_{33}(E)$ is characterized by a shape close to the dielectric hysteresis loop. It is also shown that at $x > 0.10$, a gradual narrowing of the loops occurs over the entire range of constant electric field strengths. The resulting loop shape of the investigated SS at low concentrations $x$ may be due to the softness of the structure, and their narrowing with enrichment in potassium niobate is probably a consequence of an increase in the rigidity of the latter and an increase in the heterogeneity of these objects.

From the ascending loop of electromechanical hysteresis, curves $d_{33}(E)$ were obtained at $0.05 \leq x \leq 0.20$ (Figure 6). It was revealed that in SS at $0.05 \leq x \leq 0.10$, the $d_{33}(E)$ curves are characterized by a sharp increase in $d_{33}$ at low values of the constant electric field strength, followed by the formation of extrema in the inflection point area on the ascending branch of the half-period $S_{33}$ [9]. For $x > 0.10$, the $d_{33}(E)$ curves in the region of low fields do not form extrema and increase smoothly. It should be noted that
the curves $d_{33}(E)$ characterizing SS with $0.05 \leq x \leq 0.10$ and $x = 0.20$ reach saturation, i.e. have a plateau-like region. The $d_{33}(E)$ ($x = 0.15$) does not reach saturation in the entire research range of field strengths.

![Graph](image1)

**Figure 5.** $S_{33}-E$ loops of SS of the composition $(1-x-y)\text{NaNbO}_3 - x\text{KNbO}_3 - y\text{Cd}_{0.5}\text{NbO}_3$ ($y=0.25, 0.05 \leq x \leq 0.20$) at $T=300\text{K}$.

![Graph](image2)

**Figure 6.** Curves $d_{33}(E)$ of the SS composition $(1-x-y)\text{NaNbO}_3 - x\text{KNbO}_3 - y\text{Cd}_{0.5}\text{NbO}_3$ ($y=0.25, 0.05 \leq x \leq 0.20$).

4. **Conclusions**
Solid solutions of the three-component system $(1-x-y)\text{NaNbO}_3 - x\text{KNbO}_3 - y\text{Cd}_{0.5}\text{Nb}_2\text{O}_6$ ($y=0.25, x=0.05-0.20$) were obtained. A diagram of the states of the system is constructed. The formation of regions with coexisting phases with different symmetry is detected. The matching of the microstructure and phase diagram of the system is demonstrated. The regularities of the formation of electromechanical and polarization properties of the SS system in a wide range of external influences (temperature, constant and alternating electric fields) have been established. It was found that at $0.05 \leq x \leq 0.10$, the inflection
point $P_s$, $P_r$-characteristics are formed in the temperature range $\sim (360 \div 370) \text{ K}$. It was revealed that in SS at $0.05 \leq x \leq 0.10$, the $d_{33}(E)$ curves are characterized by a sharp increase in $d_{33}$ at low values of the constant electric field strength, followed by the formation of extrema in the inflection point area on the ascending branch of the half-period $S_{33}$. A scientific explanation of the observed phenomena is given.

The obtained results should be considered in the development piezoelectric devices for various applications.

**Acknowledgments**
Research was financially supported by the Ministry of Science and Higher Education of the Russian Federation (State assignment in the field of scientific activity, Southern Federal University, 2020).

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