Multicomponent complex oxide media – the basics of the functional materials for electronic engineering: the selection of the promising compositions for assessing the ferrohardness

K P Andryushin, S I Dudkina, L A Shilkina, I N Andryushina, D I Rudskiy, I A Verbenko, L A Reznichenko

Southern Federal University, Research Institute of Physics, Stachki Ave., 194, Rostov-on-Don, Russia

Corresponding author’s e-mail: kpandryushin@gmail.com

Abstract.

According to the optimal technological regulations, the solid solutions of two four-component systems based on lead titanate-zirconate and alkali metal niobates were prepared: (1-x) Na_{0.875}Li_{0.125}NbO_{3} – xPbTi_{0.5}Zr_{0.5}O_{3} (0.05 ≤ x ≤ 0.95, Δx = 0.025 - 0.10) and (1-x) Na_{0.875}K_{0.125}NbO_{3} – xPbTi_{0.5}Zr_{0.5}O_{3} (0.0 ≤ x ≤ 1.0, Δx = 0.05 - 0.10). The electrophysical parameters of the solid solutions of these systems were determined and the degree of their ferrohardness and efficiency was assessed according to the main characteristics: the relative permittivity of the polarized samples, $\varepsilon_{33}/\varepsilon_{0}$, the mechanical quality factor, $Q_{m}$, the coefficient of electromechanical coupling of the radial vibration mode, $K_{p}$, the piezomodule, $|d_{31}|$. It was shown that, depending on the chemical composition and the position of the solid solutions on the phase diagram of the systems, they can be characterized by different degrees of the ferrohardness and efficiency, which made it possible to select promising compositions: ferrohard ones – for the converters with high specific power (in step-down piezotransformers, piezoelectric motors, etc.); of the medium ferrohardness – for highly sensitive receivers of the ultrasonic vibrations (telemetry sensors, automatic control systems, etc.); ferrosoft materials with high efficiency – in the low-frequency devices (microphones, hydrophones, deflectors of the optical systems, robotics devices, etc.).

1. Introduction

The current stage in the development of the science of the materials and their use in piezoelectric engineering and other technical areas are characterized by the achievement of a certain saturation region for the parameters of the elements and devices based on them. At the same time, the needs of the technique pose for materials science the tasks that require not only a significant outstep of a number of the characteristics beyond the "usual" limits, but also the ability to vary the properties of the materials, achieving the necessary combination of their parameters.

A natural step towards the creation of new highly efficient piezoceramic materials was the transition from the two- and three-component systems to the multicomponent ones, MS, based on complex oxide media, first of all, lead titanate-zirconate (PZT) [1-4], which was first performed in our team [5, 6]. Exactly in these systems it was possible to obtain the combinations of the parameters necessary for various fields of application. Such MS can be written as: Pb(Zr_{1-\alpha}Ti_{\alpha})O_{3} – $\sum_{n}(Pb\beta_{1-\gamma}B_{\gamma}\alpha'O_{n}$), where $n = 2-4$, $\alpha = 1/2, 1/3, 1/4$ depending on the valences of $B'\gamma$ and $B''\alpha'$: a) at $B''\alpha'$ – Mg (II), Ni (II), Zn (II), Co (II), Mn (II), Cd (II), Fe (II), Ca (II); $\alpha = 1/2$ for $B'\gamma$ – W (VI) and $\alpha = 1/3$...
for $B' – Nb$ (V), $Sb$ (V), $Ta$ (V); b) at $B' – Bi$ (III), $Sn$ (III) $\alpha = 1/2$ for $B' – Nb$ (V), $Sb$ (V), $Ta$ (V); c) at $B' – Li$ (I) $\alpha = 1/4$ for $B' – Nb$ (V), $Sb$ (V), $Ta$ (V).

The components of the four-, five- and six-component systems were selected based on the results of the studies of the three-component systems described in the patent literature, as well as on the results obtained in a number of cases in our works [5, 6]. Based on the data on the phase diagrams and physical properties of the ternary systems, a program of the studies of the most promising MS was compiled, including not only the choice of the components, but also the choice of the regions of the compositions with the optimal properties, which made it possible to reduce the volume of the experimental studies [5, 6].

An important role in the development of the work on the search and creation of new highly efficient piezoceramic materials was played by the developed method for determining the boundaries of the morphotropic regions (MR) (the regions of a structural phase transition in the vicinity of which the electrophysical parameters are extreme) in the MS of the complex oxides, which is as follows. According to the position of the MR in the k-component systems that make up the investigated k-component system, the MR of the latter is approximated in the region of the compositions with the maximum piezoelectric parameters by a part of the dimension space ($k$-2). The X-ray structural studies and measurements of the electrophysical parameters [5, 7] are performed for the compositions of the selected area.

As the studies have shown, the MS have a number of significant advantages over their constituent binary and ternary systems: a) with an increase in the number of the system components, the dimensionality of the MR grows (the isometric section of the phase diagram of the k-component system has a $k$-1 dimensional MR in the case of a two-phase transition), which significantly expands the choice of the solid solutions, SS, with a given combination of the parameters; b) the introduction of the new components that form a solid solution with the components of the original system allows one to change the composition and, consequently, the parameters of the solid solution in a wide range and obtain a wide variety of the material properties. Due to this, on the basis of one MS, the materials for various fields of application can be obtained, which is convenient for their production; c) with an increase in the number of the system components, the efficiency of the SS increases; d) with an increase in the number of the components to 4-6, as a rule, the manufacturability of the systems improves. This is probably due to the fact that the heterovalent substitutions with an increase in the set of the ions included in the solid solution lead to the formation of an additional concentration of the point defects, which provide an intensive course of the diffusion processes, and, consequently, the sintering process, the formation of an optimal microstructure and physical properties of the ceramics [5, 6].

In the studied MS, the regularities that relate the electrophysical and structural parameters both in the vicinity of the MR and in wider concentration ranges and make it possible to establish the relationship between the concentration dependences of the parameters with the areas of application of the piezoelectric ceramics are considered. Depending on the type of the cations B included in the complex oxides, MS differ in the degree of the ferrohardness. The ferrohardness (FH) of the ferroelectric ceramics is determined to a large extent by the magnitude of the local elastic stresses arising during the reorientation of the domains. With an increase in these voltages, the FH increases, ferroelectric ceramics is determined to a large extent by the magnitude of the local elastic stresses.
Thus, with an increase in the FH, the parameters $\delta$, $E_c$, $Q_M$, $V_i^p$, $T_c$ increase, while $e_{31}/e_0$ and $\tan \delta$ decrease. The electromechanical coupling coefficients, in particular $K_p$, most fully characterize the effect of the energy conversion in the piezo materials and are the most important parameters characterizing their efficiency. As a rule, they decrease with the growth of the FH. The piezomodule $|d_{31}|$, which depends both on $K_p$ and $e_{33}/e_0$ ($d \sim \sqrt{e^T \cdot K}$), should also decrease with increasing ferrohardness.

The recently increased interest in the environmentally friendly compositions based on alkali metal niobates, AMN [8-11], as well as in combined media connecting in their basis the representatives of this group and PZT-groups of the functional materials made it necessary to assess the FH and the efficiency of the SS of the corresponding systems, which became the goal of the research.

2. Objects, methods for obtaining and researching the samples

The objects of the study were the solid solutions of two four-component systems of the type $(1-x)Na_{0.875}Li_{0.125}NbO_3 - xPbTi_0.5Zr_0.5O_3$ (1) and $(1-x)Na_{0.875}K_{0.125}NbO_3 - xPbTi_0.5Zr_0.5O_3$ (2). Pure ceramics with a sufficiently high relative density ($\sim 95\%$) were prepared by the two-stage solid-phase synthesis followed by sintering by the hot pressing method (1) or by the conventional ceramic technology (2) [12-15]. Their electrophysical characteristics were determined in accordance with [16]: $e_{33}/e_0$, $Q_M$, $K_p$, $|d_{31}|$.

The assessment of the ferro-hardness (efficiency) of the SS was performed using the coefficients $P$, which make it possible to judge their degree of the FH and efficiency [17]. These coefficients represent the ratio of the parameters of the systems under consideration to the values of these parameters of the known industrial analogs PZT-8, PZT-4, PZT-5 N [18], which are the samples of the hard material of medium hardness and soft, respectively. In this regard, the coefficients can acquire the indices "h", "m", "s". $Q_M$ and $(e_{33}/e_0)^{-1}$ are taken as the parameters characterizing the FH, which increase with the growth of the FH. The efficiency is estimated by the parameters $K_p$ and $|d_{31}|$.

Taking into account the values of $Q_M$, $(e_{33}/e_0)^{-1}$, $K_p$, $|d_{31}|$ of the compositions PZT-8 ($Q_M=1000$; $(e_{33}/e_0)^{-1}=1/1000$; $K_p=0.5$; $|d_{31}|=93$ pC/N); PZT-4 ($Q_M=500$; $(e_{33}/e_0)^{-1}=1/1300$; $K_p=0.58$; $|d_{31}|=123$ pC/N); PZT-5 ($Q_M=65$; $(e_{33}/e_0)^{-1}=1/3400$; $K_p=0.65$; $|d_{31}|=274$ pC/N), the coefficients $P_{Q_0}$ (h), $P_{Q_0}$ (m), $P_{Q_0}$ (s); $P_{(e_{33}/e_0)^{-1}}$ (h), $P_{(e_{33}/e_0)^{-1}}$ (m), $P_{(e_{33}/e_0)^{-1}}$ (s); $P_{K_p}$ (h), $P_{K_p}$ (m), $P_{K_p}$ (s); $P_{|d_{31}|}$ (h), $P_{|d_{31}|}$ (m), $P_{|d_{31}|}$ (s) were calculated in the SS of the systems under study.

3. Experimental results. Discussion

Tables 1, 2 show the electrophysical characteristics of the SS of the studied systems, and tables 3, 4 show their coefficients of the hardness $P_{Q_0}$, $P_{(e_{33}/e_0)^{-1}}$, and efficiency, $P_{K_p}$, $P_{|d_{31}|}$. The coefficients closest to one (for each of the four parameters) are marked in bold, which allow judging the degree of the FH and the efficiency of the analyzed systems.

| $x$ | $e_{33}/e_0$ | $|d_{31}|$, pC/N | $K_p$ | $Q_M$ |
|-----|-------------|-----------------|------|-------|
| 0.05 | 289         | 9.3             | 0.108| 358   |
| 0.10 | 476         | 12.2            | 0.114| 240   |
| 0.15 | 845         | 13.2            | 0.092| 216   |
| 0.20 | 970         | 15.7            | 0.065| 174   |
| 0.30 | 950         | 14.0            | 0.058| 200   |
| 0.40 | 970         | 15.2            | 0.054| 210   |
| 0.50 | 1000        | 15.9            | 0.072| 250   |
| 0.60 | 1100        | 20.1            | 0.150| 248   |
| 0.70 | 1425        | 64.9            | 0.317| 134   |
| 0.725 | 2000     | 85.6            | 0.550| 125   |
Table 2. Main electrophysical parameters of the solid solutions of the four-component system of the type \((1-x)\text{Na}_{0.875}\text{K}_{0.125}\text{NbO}_3 - x\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3\). [13-15]

| \(x\) | \(\varepsilon_{33}/\varepsilon_0\) | \(|d_{31}|\), pC/N | \(K_p\) | \(Q_M\) |
|------|-----------------|-----------------|------|------|
| 0.00 | 449             | 14.9            | 0.099| 113  |
| 0.10 | 1032            | 11.2            | 0.060| 53   |
| 0.20 | 1468            | 12.4            | 0.041| 79   |
| 0.30 | 1424            | 4.9             | 0.018| 215  |
| 0.40 | 1400            | 34.2            | 0.034| 138  |
| 0.60 | 1685            | 55              | 0.220| 210  |
| 0.65 | 1032            | 11.2            | 0.060| 53   |
| 0.70 | 1270            | 50.6            | 0.167| 181  |
| 0.75 | 847             | 30.2            | 0.180| 100  |
| 0.80 | 849             | 61.3            | 0.320| 114  |
| 0.85 | 875             | 48.7            | 0.188| 168  |
| 1.0  | 805             | 11.0            | 0.007| 417  |

Since the absolute values of the electrophysical parameters of the SS of these systems differ significantly from the corresponding characteristics in the known materials PZT-8, PZT-4, PZT-5H, in the studied systems, as can be seen from Tables 3 and 4, there are significant deviations of the \(P\) coefficients from one. Nevertheless, the attention is drawn to the several facts common to both systems: according to different parameters, the systems can be attributed to different degrees of the FH, which is influenced by both the compositional (chemical) composition of the solid solutions and their position on the phase diagrams of the systems.

Table 3. Coefficients of the ferro-hardness and efficiency of the solid solutions of the four-component system of the type \((1-x)\text{Na}_{0.875}\text{Li}_{0.125}\text{NbO}_3 - x\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3\).

| \(x\) | \(P_{0\nu}\) | \(P_{(\varepsilon_{33}/\varepsilon_0)^{-1}}\) | \(P_{K_p}\) | \(P_{[d_{31}]}\) |
|------|-------------|--------------------------------|------------|-------------|
| 0.05 | 0.358       | 0.716                         | 3.5        | 4.5         | 11.7       | 0.22       | 0.19       | 0.17       | 0.09       | 0.08       | 0.03       |
| 0.10 | 0.240       | 0.480                         | 3.7        | 2.1         | 2.7        | 7.14       | 0.23       | 0.197      | 0.18       | 0.13       | 0.09       | 0.04       |
| 0.15 | 0.216       | 0.432                         | 3.3        | 1.2         | 1.5        | 4.02       | 0.18       | 0.16       | 0.14       | 0.14       | 0.10       | 0.05       |
| 0.20 | 0.174       | 0.348                         | 2.7        | 1.03        | 1.34       | 3.51       | 0.13       | 0.112      | 0.10       | 0.17       | 0.13       | 0.06       |
| 0.30 | 0.200       | 0.400                         | 3.1        | 1.05        | 1.37       | 3.50       | 0.12       | 0.10       | 0.08       | 0.15       | 0.11       | 0.05       |
| 0.40 | 0.210       | 0.420                         | 3.2        | 1.03        | 1.34       | 3.51       | 0.11       | 0.09       | 0.08       | 0.16       | 0.12       | 0.06       |
| 0.50 | 0.250       | 0.500                         | 3.8        | 1.00        | 1.30       | 3.4        | 0.14       | 0.12       | 0.11       | 0.17       | 0.13       | 0.06       |
| 0.60 | 0.248       | 0.496                         | 3.8        | 0.91        | 1.18       | 3.1        | 0.3        | 0.26       | 0.23       | 0.22       | 0.16       | 0.07       |
| 0.70 | 0.134       | 0.268                         | 2.06       | 0.7         | 0.91       | 2.4        | 0.6        | 0.55       | 0.49       | 0.69       | 0.52       | 0.24       |
| 0.725| 0.125       | 0.250                         | 1.9        | 0.5         | 0.65       | 1.7        | 1.1        | 0.95       | 0.85       | 0.92       | 0.69       | 0.31       |
| 0.75 | 0.134       | 0.268                         | 2.06       | 0.45        | 0.59       | 1.5        | 1.11       | 0.96       | 0.85       | 1.08       | 0.82       | 0.37       |
the main characteristics (various fields of application: ferro hard – for the converters with high specific power (in step-down proximity to it in different parameters, due to the chemical composition of the compositions and their

The solid solutions of the four-component systems (1 -

in low-frequency devices, etc.

converters of the electronic equipment, including the telemetry sensors, automatic control systems, etc.

in low-frequency devices (microphones, hydrophones, deflectors of optical systems, robotics devices, etc.).

receivers of the ultrasonic vibrations (telemetry sensors, automatic control systems, medical
diagnostics and non-destructive flaw detection devices, etc.); ferro soft materials with high efficiency –
in medium ferro hardness and ferrosoft, respectively.

It is shown that, according to the assessment of the ferrohardness and efficiency degree, the studied

4. Conclusions
The solid solutions of the four-component systems (1-x)Na0.875K0.125NbO3 – xPbTi0.5Zr0.5O3 (0.05 ≤x ≤0.95, Δx = 0.025 - 0.10) and (1-x)Na0.875K0.125NbO3 – xPbTi0.5Zr0.5O3 (0.0 ≤x ≤1.0, Δx = 0.05- 0.10) were prepared by the two-stage solid-phase synthesis followed by sintering by the hot pressing method or by the conventional ceramic technology.

The degree of the ferrohardness and efficiency of the indicated solid solutions was established by the

Table 4. Coefficients of the ferrohardness and efficiency of the solid solutions of the four-

Table 4. Coefficients of the ferrohardness and efficiency of the solid solutions of the type (1-x)Na0.875K0.125NbO3 – xPbTi0.5Zr0.5O3.

| x  | \( P_{QM} \) | \( P_{(33T)}^{01} \) | \( P_{KM} \) | \( P_{d(31)} \) |
|----|--------------|----------------|-------------|-------------|
| 0.00 | 0.113 | 0.226 | 1.74 | 2.22 | 2.89 | 7.56 | 0.20 | 0.17 | 0.15 | 0.16 | 0.12 | 0.05 |
| 0.10 | 0.053 | 0.106 | 0.82 | 0.97 | 1.26 | 3.29 | 0.12 | 0.10 | 0.09 | 0.12 | 0.09 | 0.04 |
| 0.20 | 0.079 | 0.158 | 1.22 | 0.68 | 0.89 | 2.32 | 0.08 | 0.07 | 0.06 | 0.13 | 0.10 | 0.05 |
| 0.30 | 0.215 | 0.43 | 3.31 | 0.70 | 0.91 | 2.39 | 0.04 | 0.03 | 0.03 | 0.05 | 0.04 | 0.02 |
| 0.40 | 0.138 | 0.276 | 2.12 | 0.72 | 0.93 | 2.43 | 0.07 | 0.06 | 0.05 | 0.37 | 0.28 | 0.12 |
| 0.60 | 0.210 | 0.420 | 3.23 | 0.59 | 0.78 | 2.02 | 0.44 | 0.38 | 0.34 | 0.59 | 0.45 | 0.20 |
| 0.65 | 0.053 | 0.106 | 0.82 | 0.97 | 1.26 | 3.29 | 0.12 | 0.10 | 0.09 | 0.12 | 0.09 | 0.04 |
| 0.70 | 0.181 | 0.362 | 2.78 | 0.79 | 1.02 | 2.68 | 0.33 | 0.29 | 0.26 | 0.55 | 0.41 | 0.19 |
| 0.75 | 0.100 | 0.200 | 1.54 | 1.18 | 1.53 | 4.00 | 0.36 | 0.31 | 0.28 | 0.32 | 0.25 | 0.11 |
| 0.80 | 0.114 | 0.228 | 1.75 | 1.18 | 1.53 | 4.00 | 0.64 | 0.55 | 0.49 | 0.66 | 0.50 | 0.22 |
| 0.85 | 0.168 | 0.336 | 2.58 | 1.15 | 1.49 | 3.89 | 0.38 | 0.32 | 0.29 | 0.53 | 0.40 | 0.18 |
| 1.0 | 0.417 | 0.834 | 6.42 | 1.24 | 1.62 | 4.22 | 0.17 | 0.15 | 0.13 | 0.11 | 0.09 | 0.04 |

The results obtained in this work should be used when choosing the promising compositions for the

converters of the electronic equipment, including the telemetry sensors, automatic control systems, medical
diagnostics and non-destructive flaw detection devices, etc.); ferrosoft materials with high efficiency –
in low-frequency devices (microphones, hydrophones, defectors of optical systems, robotics devices, etc.).
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