Modification as a method of directed change in the properties of ferro-piezoceramics

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Abstract. Solid-phase synthesis followed by sintering using conventional ceramic technology produced ceramics based on the binary system of solid solutions (Na, Li) NbO3. The influence of superstoichiometric modification with nickel oxide on the internal structure (crystalline, grain) and macroresponses of the analyzed media is established. Based on the analysis of piezoelectric and ferroelastic properties, the prospects of using materials in various electronic devices are shown.

1. Introduction

One of the most effective methods for changing the physical properties of ferroelectrics is the method of introducing small (no more than 10 at. %) additives of monoxides of various elements (modification). The great potential of this method is due to the existence of a significant amount of metal monoxides and their combinations capable of dissolving in complex oxides, in particular, in ferroelectric (FE) oxides with a perovskite-type structure (OSP) over a wide concentration range, as well as oxides of elements forming when introduced into the initial objects "melt" (B2O3, SiO2, V2O5, .......), and, finally, additives of combined action that affect the properties of the initial systems due to the formation of a liquid phase (LP) and cation-exchange interaction I'm with the base (modifying glass). The undoubted advantage of the method is the ability, while preserving the complex of specific properties of the modified objects, to slightly change the values of some parameters in the right direction by slightly varying their composition.

In the case of a significant change (improvement) in the ceramic and technological characteristics of the materials being modified, as well as such changes in the dielectric and piezoelectric parameters, which can be considered as “tuning” them to the target values, the modification is represented by the parameter optimization method. Changes in these characteristics to such an extent that leads to the formation of a new set of properties, allows modification to be considered as a method of creating qualitatively new materials with adjustable parameters [1].

From a theoretical point of view, the establishment of general patterns of changes in physical properties during OSP modification provides information on the composition – structure – property relationships, which allows us to consider it as a method for studying the FE state. Thus, the modification results have a
A wide range of applications – from basic research to technology processes at the atomic-molecular level, in connection with this, the urgency of the FE OSP modification problem becomes clear.

According to bibliographic data, the modification of solid solutions (SS) based on the PZT system (Pb(Ti,Zr)O₃) is most fully studied. At the same time, the possibilities of modifying the system itself are now practically exhausted. Multicomponent lead-containing SSs were examined quite deeply in this regard. The analysis and generalization of the vast experimental material (more than 300 combinations of modifying oxides are known for the PZT system alone) allowed us to classify all known modifiers of these systems and, on this basis, establish general patterns of change in their physical properties. This was successfully used in predicting the properties of ferro-piezoelectric ceramic materials (FPCM) and in finding the optimal ways to create them [1]. The possibilities of modifying SS based on sodium niobate (SN) have been little studied. The only exception is the NaNbO₃ – KNbO₃ system [2]. Recently, attention has been paid to another “niobate” system — NaNbO₃ – LiNbO₃, as well as multicomponent systems with its participation [3].

The advantages of the latter: increased dimensionality of the morphotropic region and, as a result, expanded choice of SS with given combinations of parameters; expanding the possibilities of SS formation with a wide variety of properties; increasing the efficiency of SS and improving their manufacturability; as well as the absence of toxic elements in their composition; – make these compositions very promising for industrial applications.

The table shows the formulas and quasi-chemical equations of cationic modification of the SS system (Na, Li) NbO₃.

By cationic is meant modification by elements other than those constituting the base, by vacancy, change in the defective state of the base without a qualitative change in its chemical composition (only the concentration of the AO component or the degree of oxidation of the B component varies). Despite the conventionality of such a division (in the first case, the formation of vacancies also takes place, and in the second, the chemical composition changes), it seems legitimate, since in each of the options the leading mechanism of the formation of a new set of properties is highlighted (or, primarily, due to the influence of the crystal chemical characteristics of the modifiers, either due to the quantity and "quality" of vacancies).

The scheme presents variants of stoichiometric (isovalent vacancy-free and heterovalent with the formation of vacancies, the position of which in the crystal structure may be different) and superstoichiometric isomorphic substitution of ions in AB, AB sublattices. Moreover, with A-substitutions (I), only the case with nMA > nA * (that is, nM = 2, 3) is considered, since the valency is ΩM = 1; for B-substitutions, the possibilities with nM < B are described (that is, nMB = 6, 4, 3). Isovalent modification is implemented with nMA = 1, nMB = 5. In combined modification, when ions in both cationic sublattices are replaced, a compensation variant is possible that excludes the appearance of vacancies (nMA = 2 and nMB = 4, nMA = 3 and nMB = 3), or the path associated with their appearance in A, B, AB positions.

With the introduction of modifiers in excess of stoichiometry, the variants of changes in the crystal lattice of the base can be greater than with their introduction stoichiometrically. The cation modifier can become regular nodes of the matrix crystal, which leads to the formation of vacancies in the cationic and oxygen sublattices (cation A forms vacancies in the B and O sublattices, cation B in the A and O sublattices); can be embedded in the lattice, displacing the main component, can itself be embedded in the lattice, or will be present as an impurity, distributed in the intergranular space.

In connection with the foregoing goal, the work was to establish the laws governing the formation of the internal structure (crystalline, grained) and macroresponses (dielectric, ferroelastic, piezoelectric) SS with the participation of (Na, Li) NbO₃ superstoichiometrically modified with nickel oxide. The choice of this dopant is due to its crystal-chemical specificity, which provides an improvement in the entire set of electrophysical properties of the base SS [4].
2. Objects. Methods for producing and research samples
SSs based on the (Na1-xLix) NbO3 system (composition – Na0.86625Li0.12375Sr0.01Nb0.988Al0.01O3 (Basis) were chosen as objects of study. The modification was performed stoichiometrically with a concentration step of 0.5 mass %. In this case, simple NiO oxide was used as additives. Solid-phase synthesis was carried out in two stages: \( T_{\text{syn}} = (850 - 870) \, ^\circ\text{C} \) (depending on the composition), for \( t_1 = t_2 = 6 \) hours, sintering using conventional ceramic technology at a variable temperature, \( T_{\text{sp.}} \), equal to \((1180, 1200) \, ^\circ\text{C}\) for 1 hour. Samples were made in different geometries to determine the effect of habit on electrophysical characteristics.

The phase composition and completeness of the synthesis were checked by X-ray diffraction on a DRON-3 diffractometer using filtered Ckα radiation from Ckα (Bragg-Brentano focusing). The experimental, \( \rho_{\text{exp.}} \), Density of the samples was determined by hydrostatic weighing in octane. The grain structure was studied using a JSM – 6390L scanning electron microscope (JTOL) (Japan) with a system of microanalyzers from Oxford instruments (Great Britain).

Measurements of the electrophysical parameters of SS were carried out in accordance with OST 11 0444-87. In this case, we determined the relative permittivities of polarized, \( \varepsilon_{33t} / \varepsilon_0 \), and non-polarized, \( \varepsilon / \varepsilon_0 \), samples, the dielectric loss tangent of polarized samples, \( \tan \sigma_{pp} \), piezoelectric modules, \( |d_{33}| \), \( d_{33} \), the electromechanical coupling coefficient of the planar oscillation mode, \( K_P \), mechanical quality factor, \( Q_m \), speed of sound, \( v \), piezosensitivity, \( g_{33} \), and acoustic impedance, \( z \), \( (g_{33} = d_{33} / \varepsilon_{33t} \) and \( z = \rho_{\text{exp.}}, \) Where \( \rho_{\text{exp.}} \) is the experimental density of the samples). The Curie temperature, \( T_C \), was established on the basis of thermofrequency measurements carried out in the temperature range \((20–700) \, ^\circ\text{C}\) and frequencies of 25 Hz – 1 MHz using an Agilent E4980A precision LCR meter.

3. Experimental results, discussion
Fig. 1. shows the dependence of the parameters of the perovskite cell and the homogeneous parameter Strain SS \( \delta \) versus NiO concentration. In the range \( 0 \leq x \leq 1.0 \), two phases coexist in SS – the rhombohedral (Rh) and rhombic (R (M2) doubled monoclinic subcells) (M2), but their ratio changes with increasing x, the amount of the latter decreases and in the range \( 1.0 < x < 2.0 \) TR becomes almost single-phase – Rh.

![Figure 1.](image-url)
In fig. 1, it is seen that at the point $x = 1.5$, the cell volume and the angle $\alpha$ sharply decrease: $\Delta V = -0.07 \text{Å}^3$, $\Delta \alpha = -0.06^\circ$. At $x > 1.5$, the cell parameters practically do not change with $x$, with the exception of the volume, which increases slightly, while the phase composition changes smoothly. In fig. 2, it is seen how, with increasing NiO concentration, the intensity of the lines of the P (M) phase gradually increases, that is, SS again becomes biphasic, but the amount of P (M) phase is much smaller than Pe.

Thus, upon superstoichiometric modification of SS based on (Na, Li) NbO$_3$ with nickel oxide, the latter is embedded in the crystal lattice of the initial SS, substantially changing its phase composition.

In fig. 3, Fragments of the microstructure of the studied ceramics are presented, indicating fine-grained and densest packing of crystallites. The porosity of ceramics is point, intergranular, and insignificant. An increase in the NiO content leads to a refinement of the grain landscape and densification of the ceramic frame, probably due to the formation of small amounts of liquid phases.

Figures 4–6 illustrate the dependences of the dielectric, ferroelastic, and piezoelectric characteristics of SS on the concentration of the introduced dopant, and Fig. 7 – thermofrequency "behavior" $\varepsilon / \varepsilon_0$ and $\tan \delta$.

It is clearly seen that enrichment of the base SS with nickel leads to a decrease in $\varepsilon_{33}T / \varepsilon_0$, $\tan \delta$, and an increase in $Q_m$ (TSP = 1190 °C), which indicates an increase in the degree of ferro rigidity of SS. The mechanism of the latter can be related to the following.

In the case of substitution of alkali metal ions for higher-charged cations (Ni$^2+$), anionic excess SSs are likely to form, in which excess oxygen can be located either in internodes or in positions shifted from internodes.
Figure 3. Fragments microstructures of the investigated SS

Figure 4. Dependences of the dielectric characteristics of solid solutions based on (Na, Li) NbO3 modified with NiO. (On the left $T_{sp} = 1190 \, ^{\circ}C$, on the right $T_{sp} = 1205 \, ^{\circ}C$, solid lines samples $\varnothing 10 \, mm$, dashed $\varnothing 20 \, mm$)

Figure 5. Dependences of the ferroelastic characteristics of solid solutions based on (Na, Li) NbO3 modified with NiO. (Left – $T_{sp} = 1190 \, ^{\circ}C$, right – $T_{sp} = 1205 \, ^{\circ}C$, solid lines – samples $\varnothing 10 \, mm$, dashed – $\varnothing 20 \, mm$)

X=0.0

X=0.5

X=1.0

X=1.5

X=2.0

X=2.5

X=3.0

$\tan \delta_{a.p.}$

$\tan \delta_{b.p.}$

$\varepsilon_{33} / \varepsilon_{0}$

$\varepsilon_{33} / \varepsilon_{0}$

$T_{C}, ^{\circ}C$

$T_{C}, ^{\circ}C$

$\varepsilon_{33} / \varepsilon_{0}$

$\varepsilon_{33} / \varepsilon_{0}$

$\tan \delta_{a.p.}$

$\tan \delta_{b.p.}$

$\varepsilon_{33} / \varepsilon_{0}$

$\varepsilon_{33} / \varepsilon_{0}$

$T_{C}, ^{\circ}C$

$T_{C}, ^{\circ}C$

$\varepsilon_{33} / \varepsilon_{0}$

$\varepsilon_{33} / \varepsilon_{0}$

$\tan \delta_{a.p.}$

$\tan \delta_{b.p.}$

$\varepsilon_{33} / \varepsilon_{0}$

$\varepsilon_{33} / \varepsilon_{0}$

$T_{C}, ^{\circ}C$

$T_{C}, ^{\circ}C$
In the latter case, such a situation forms a defective subsystem, including, among other things, Willis clusters of different types, differing in combinations of vacancies and various types of internodes.

This causes the effects of strong local ordering (short range order). Note that the excess of anions accumulates mainly on certain crystallographic planes.

O2– ions located in internodes can initiate additional distortion of atomic groups, creating their own dipole moment. Considering the well-known tendency of niobate ceramics to self-organize defective structures [5] by ordering them and forming microdomains, we can assume the influence of the latter on the total dipole moment of the system, the degree of ferroelectric rigidity, and, consequently, the coercive force, dielectric constant, piezoelectric sensitivity, and mechanical quality factor. As shown experimentally, in the studied SS modified with NiO, the degree of ferro rigidity does increase.

The dielectric spectra of SS are characteristic of alkali metal niobates with a pronounced maximum $\varepsilon / \varepsilon_0$ at the Curie point, the rapid increase of $\varepsilon / \varepsilon_0$ in the paraelectrical region at temperatures higher, the higher the frequency of the electric measuring field associated with the restoration of Nb5+ → Nb4+ and the emergence of vacancies [6]. Moreover, in modified TPs, this process develops at higher temperatures [7–8].
4. Conclusion
The results obtained are appropriate to consider when developing electronic devices that use the materials in question.

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