Ceramic materials with special electrical properties based on niobates of alkali and alkaline earth metals: technology, structure, macro-responses, applications

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Abstract. The article describes the electrophysical properties research results of the solid solution based on sodium and strontium niobates. The obtained data indicate the preservation of piezoelectric activity in the paraelectric range. The research results will be of interest in the development of diagnostic devices for heat-loaded structures and radio engineering.

1. Introduction

The development of modern technology is associated with the use of functional materials capable of operating at high temperatures, changing pressures, limiting speeds, as well as under conditions of exposure to high-frequency electromagnetic fields.

One of the most important requirements for such materials is the requirement for the stable piezoelectric state realizations for a long time at elevated temperatures. When creating high-temperature modules, the greatest attention should be paid to ceramic materials that have a high temporary retention of parameters, chemical resistance in aggressive environments, and, most importantly, low cost in mass production.

Among such high-temperature ferroelectric-piezoceramic materials, there are six groups that have a high Curie temperature \( T_C \), and, accordingly, high limiting operating temperatures. These are perovskites [1], tungsten bronzes [2], Bi-containing [3] and Aurivillius phases [4], pseudo-ilmenites [5], perovskite-like layered [6]. The latter, in contrast to the others listed, deserve the main attention, due to their high Curie temperature, exceeding 1500K [7].

Due to the high Curie temperature, the study of such objects is complicated, and therefore there is no reliable information on phase equilibria in solid solution (SS) systems with the participation of layered compounds \( \text{Ca}_2(\text{Sr}_2)\text{Nb}_2\text{O}_7 \). The state diagrams of \( \text{Sr}(\text{Ca})\text{O}-\text{Nb}_2\text{O}_5 \) with many different chemical compounds have a number of features that limit their widespread use. These features are due to the multistage solid-phase processes and sensitivity to the technology of their manufacture; the presence of areas of morphotropic, polymorphic and reconstructive transformations in the systems \( \text{NaNbO}_3-\text{Sr}(\text{Ca})_2\text{Nb}_2\text{O}_7 \).
Therefore, the study of these condensed media is relevant when conducting practice-oriented scientific research [8].

Previously, when analyzing X-ray data, we plotted phase x diagrams of the selected SS systems, determined the regions of structural instabilities in them of various types, caused by reconstructive phase transitions (perovskite-layered structures), a change in the cell multiplicity (quadruple-doubled monoclinic subcell (M) of rhombic (R) cells), the coexistence of either phases of different symmetry (rhombic (R) + cubic (C)), or phase states (R (M\(_4\)) + R (M\(_2\))) [9].

The aim of this study was to establish the regularities of the formation of macro-responses (dielectric, piezoelectric) in SS based on sodium niobate with the participation of a layered perovskite-like compound - strontium pyroniobate.

2. Experimental

The objects of research were SS composition (1-x)Na\(_3\)O\(_3\)-xSr\(_2\)O\(_3\) with 0.00≤ x ≤ 1.00 (Δx=0,025).

The SSs selected for the study were prepared by a two-stage method of solid-phase reactions at synthesis temperatures (1230÷1500)K and duration of firing (3÷4) h., followed by sintering using conventional ceramic technology at certain temperatures, T\(_{SN}\), from the range (1520÷1660)K within (2÷3) h.

The sintered samples were cut into disks with a diameter of about 10 mm and a thickness of (1.0 ÷ 1.5) mm. Electrodes made of silver-containing paste were applied to flat surfaces by two-time firing of samples at a temperature of 1070K for 0.5 h.

Polarization was carried out in a polyethylene siloxane liquid at 450 K and an electric field (3÷7) kV / mm within 25 min.

X-ray studies were carried out by powder diffraction using a DRON-3 diffractometer (Bragg-Brentano focusing scheme, Co\(_K\alpha\) radiation).

The determination of the experimental (ρ\(_{EXP}\)) density of the samples was carried out by the method of hydrostatic weighing, where octane was used as a liquid medium, while ρ\(_{EXP}\) was calculated by the formula:

\[
ρ_{exp} = \frac{ρ_{\text{C8H18}} m_1}{m_2 - m_3 + m_4}
\]

(1)

where \(ρ_{\text{C8H18}}\) – octane density, \(m_1\) – dry workpiece weight, \(m_2\) – weight of workpiece saturated with octane, \(m_3\) – weight of saturated workpiece, weighed in octane with suspension, \(m_4\) – weight of the workpiece hanger.

The X-ray density (\(ρ_{\text{xray}}\)) was calculated using by the formula:

\[
ρ_{\text{xray}} = 1.66 \times \frac{M}{V}
\]

(2)

where \(M\) is the weight of the formula unit in grams, \(V\) is the volume of the perovskite cell in Å.

Relative density (\(ρ_{rel}\)) was calculated by the formula:

\[
ρ_{rel} = \frac{ρ_{exp}}{ρ_{\text{xray}}} \times 100
\]

(3)

The microstructure of the samples was studied using a laser microscope KEYENCE VK-9700.

Studies of the dependences of the relative permittivity up to \(ε(ε_0)\) and after \(ε(ε_0)/ε_0\) polarization versus temperature at various frequencies \(f\) of the alternating electric measuring field was carried out using an Agilent E4285A precision LRC meter in the temperature (300 ÷ 900)K and frequencies(20÷10\(^6\)Hz range).

The Piezomodule determinations d\(_{33}\) under pressure (2t/cm\(^2\)) was carried out using the installation "Rubin-2".
3. Results and discussion

Figure 1 shows fragments of SS microstructures of the studied system, including basic compounds of NaNbO₃, Sr₂Nb₂O₇. The isometric type of grain structure is characteristic of NaNbO₃ and solid solutions near it. Crystallites have the shape of a cube, which is displayed on the plane of the polished section by its various sections - squares, rectangles, trapezoids, triangles. In conjunction with the study of the relative density (~ 92%) can speak about the acceptance of this technology and the reliability and validity of the results.

![Figure 1](image)

**Figure 1.** Fragments of NaNbO₃ microstructures.

**Figure 2.** Fragments of (1-x)NaNbO₃-xSr₂Nb₂O₇ microstructures.

Figure 1-4 shows the dielectric dependence ($\varepsilon/\varepsilon_0$, $\varepsilon_{33}^\prime/\varepsilon_0$, $T_C$) and piezoelectric ($d_{33}$) SS system studied characteristics belonging perovskite area ($x \leq 0.20$). It can be seen that the dielectric spectra of all solid solutions are characteristic of ferro-antiferroelectric media with the maxima $\varepsilon/\varepsilon_0$ at $T_C$. In this case, the transition to the paraelectric state as the systems are enriched with strontium In this case, the transition to the paraelectric state as the systems are enriched with strontium pyrobiote is blurred with a shift of the $T_C$ to the low-temperature region. A rapid growth regions $\varepsilon/\varepsilon_0$ is formed in the vicinity of (500 ÷ 600) K. This anomaly begins at temperatures greater, the higher the frequency of the alternating electric field (Fig.3) $T_C$ behavior against the background of an increase in the content of the layered compound indicates the instability of the ferroelectric state in the system. This instability is due to the presence of the strontium component (Fig. 4). All the observed effects are associated, to a certain extent, with the development of crystal-chemical disorder in the system upon the introduction of a Sr₂Nb₂O₇ non-structural component into NaNbO₃. Moreover, the presence in the compositions of the variable valence ion (Nb) contributes to the formation in the system when recovering Nb⁵⁺→Nb⁴⁺ oxygen vacancies according to the scheme.

$$A_{1}^{1+}Nb_{1-y}^{5+} Nb_{y}^{4+} O_{3-y/2}^{2-} \square_{y/2}$$ (4)

($\square$-designation of vacancies)

In the case of Nb it takes place at temperatures (500÷600)K [10,11], which leads to the instability of the properties of SS in this area and as a result, frequency-dependent behavior $\varepsilon/\varepsilon_0$. The change in the dependence of the piezomodule, $d_{33}$ for all compositions is equally regular. In the vicinity of (350...
÷ 500) K, the values of $d_{33}$ decrease. Attention is drawn to the facts of the practical constancy of $d_{33}$ up to $T_c$. In the paraelectric phase up to 500K, the values of $d_{33}$ are retained. The described phenomena are a consequence of the smearing of the phase transition to the paraelectric state (Figure 5).

![Figure 3. Thermal frequency dependence of $\varepsilon/\varepsilon_0$](image)

**Figure 3.** Thermal frequency dependence of $\varepsilon/\varepsilon_0$

![Figure 4. Dependencies of $T_c(x)$](image)

**Figure 4.** Dependencies of $T_c(x)$

![Figure 5. Dependences of the piezomodule $d_{33}$ on temperature ($T_c$ are indicated in brackets)](image)

**Figure 5.** Dependences of the piezomodule $d_{33}$ on temperature ($T_c$ are indicated in brackets)

![Figure 6. Dependencies of $\varepsilon_{33}^T/\varepsilon_0$ and $d_{33}$](image)

**Figure 6.** Dependencies of $\varepsilon_{33}^T/\varepsilon_0$ and $d_{33}$

It is clearly seen that changes in the dielectric and piezoelectric characteristics correlate with the phase diagram of the state of the system: the extrema $\varepsilon_{33}^T/\varepsilon_0$ and $d_{33}$ are localized at or near the interphase boundaries.

The data analysis allows to predict the possibility of using materials investigated in diagnostic devices of thermally loaded structures and radio engineering.

4. Conclusion

The research of the electrophysical properties of the objects under study showed the preservation of piezoelectric activity in the paraelectric region, which is of interest in the development of diagnostic devices for heat-loaded structures and radio engineering.
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