Phase formation, structure, and properties of the solid solutions in a system based on $K_{0.5}Na_{0.5}NbO_3$ and $Ca_2Nb_2O_7$

E V Glazunova, I A Verbenko, I A Shilkina, A V Nagaenko and I A Reznichenko

Institute of Physics, Southern Federal University, 194, Stachki Ave., Rostov-on-Don, 244090, Russia

E-mail: kate93g@mail.ru

Abstract. This study reports the creation of the solid solutions $(1-x-y)K\bar{N}bO_3-yNa\bar{N}bO_3-xCa_2Nb_2O_7$ system, with $y=0.50$, $0.0\leq x\leq 0.1$, $\Delta x=0.025$ using solid-state reaction and sintering by conventional ceramic technology. The mechanisms and patterns of formation of the microstructure and dielectric properties of received solid solutions are established. The most probable mechanism of the formation of defects in the structure of $(1-x-y)K\bar{N}bO_3-yNa\bar{N}bO_3-xCa_2Nb_2O_7$ solid solutions was determined.

1. Introduction

Knowing the importance of preserving the environment resulted in the adoption of a directive banning the use of toxic elements (RoHS 2002/95/EC) [1] in some fields of science and technique. In this regard, lead-free piezoceramic has become increasingly popular among researchers in recent years. One of the most promising bases for lead-free piezo materials is the system of potassium-sodium niobate (K, Na)NbO$_3$ (KNN). In recent decades, this system has been intensively investigating due to the proximity of its piezoelectric characteristics to the PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) materials used in industry [2] as well as through the possibility to produce materials with a large amount of stored energy [3]. However, producing KNN-ceramic is difficult due to the properties of materials are dependent on thermodynamic prehistory (conditions of the production) [4-6]. It is known from the literature that obtaining ceramic based on KNN-system is associated with several chemical and technological difficulties. Such as hydrolysis of parent substances, a narrow spacing optimal synthesis and sintering temperatures, high volatility of alkaline components at relatively low temperatures that lead to producing ceramic with low density and high conductivity. These problems are being addressed through the introduction of various modifiers.

Pyrotriobate calcium (Ca$_2$Nb$_2$O$_7$) has a high temperature of phase transition~1700 K [7]. Solid solutions of the KNN-based systems have high values piezoelectric characteristics. Consequently, in conjunction, they can provide the right combination of properties to develop modern generation high-temperature devices.

Thus, the establishing of the correlations between phase formation, structure, and properties in the $(1-x-y)K\bar{N}bO_3-yNa\bar{N}bO_3-xCa_2Nb_2O_7$ solid solutions are relevant.

2. Experimental section

The $(1-x-y)K\bar{N}bO_3-yNa\bar{N}bO_3-xCa_2Nb_2O_7$ solid solutions with $y=0.50$, $0.0\leq x\leq 0.1$, $\Delta x=0.025$ were the subjects of this study. The solid solutions were prepared using a two-stage solid-state reaction at $T_1=1250-1270$ K, $T_2=1400-1420$ K for 6 h followed by sintering using conventional ceramic technology.
at $T_{\text{int}} = 1400\text{–}1550 \text{ K}$ for 2 h. The raw powders were NaHCO$_3$ (99 %), KHCO$_3$ (99 %), Nb$_2$O$_5$ (98 %), and pre-synthesized Ca$_2$Nb$_2$O$_7$.

X-ray diffraction was conducted using a DRON 3.0 diffractometer (using CoK$_\alpha$ radiation with Bragg-Brentano focusing). The content of impurity phases was estimated from the relative intensity of their strong line: $\frac{I}{I_1} \cdot 100\%$, where $I$ is the intensity of the strong line of the impurity phase, $I_1$ is the intensity of the strong line of the perovskite phase.

The microstructural measurements were performed by using a JSM – 6390L scanning electron microscope.

The dielectric permittivity was measured in a temperature range $T = 300\text{–}900 \text{ K}$ at frequencies of 1 kHz–1 MHz using Agilent 4980A and Wayne Kerr 6500B precision LCR meter.

3. Results and discussion

An X-ray phase analysis of the $(1-x-y)$KNbO$_3$ – $y$NaNbO$_3$ – $x$Ca$_2$Nb$_2$O$_7$ system with $y=0.50$, $0.0 \leq x \leq 0.1$, $\Delta x=0.025$ system showed that all of the solid solutions had perovskite-type structures.

![Figure 1. Triangle of Gibbs phases of the $(1-x-y)$KNbO$_3$ – $y$NaNbO$_3$ – $x$Ca$_2$Nb$_2$O$_7$ system with marked experimental points.](image)

**Figure 1.** Triangle of Gibbs phases of the $(1-x-y)$KNbO$_3$ – $y$NaNbO$_3$ – $x$Ca$_2$Nb$_2$O$_7$ system with marked experimental points.

![Figure 2. X-ray diffraction peaks of the solid solutions in the $(1-x-y)$KNbO$_3$ – $y$NaNbO$_3$ – $x$Ca$_2$Nb$_2$O$_7$ system (the pseudocubic (PsC) phase peaks are marked by stars, the cubic (C) phase peaks are marked by triangles, and the layered perovskite-like phase peaks are marked by arrows).](image)

**Figure 2.** X-ray diffraction peaks of the solid solutions in the $(1-x-y)$KNbO$_3$ – $y$NaNbO$_3$ – $x$Ca$_2$Nb$_2$O$_7$ system (the pseudocubic (PsC) phase peaks are marked by stars, the cubic (C) phase peaks are marked by triangles, and the layered perovskite-like phase peaks are marked by arrows).
In figure 2 is shown that on X-ray patterns of the solid solutions with $x=0.00-0.05$ the indices of the diffraction peaks are corresponding to the perovskite axes. The X-ray phase analysis also demonstrated that the solid solutions with $x=0.10$ had peaks of the layered perovskite phase. Traces of this phase are also visible on the X-ray diffraction pattern of the solid solution with $x=0.075$.

The initial solid solution $K_{0.5}Na_{0.5}NbO_3$ has a monoclinic distorted subcell. When the $Ca_2Nb_2O_7$ is introduced into the parent solid solution, it decays into two solid solutions with larger and smaller cell parameters. The symmetry of a solid solution with a smaller cell parameter is cubic. The solid solution with a large parameter is very heterogeneous, therefore, it is not possible to reliably determine its symmetry. We designated its symmetry as pseudocubic. When increased the concentration of $Ca_2Nb_2O_7$ the volume of the cubic cell decreases that associated with K→Ca substitution ($R(K^+)=1.33 \text{ Å}$ $R(Ca^{2+})=1.04 \text{ Å}$) (see Table 1).

As the concentration of $Ca_2Nb_2O_7$ increases in the range of $0.00 \leq x \leq 0.10$, a number of phase transitions occur in this system: monoclinic (M) $\rightarrow$ M+ pseudocubic (PsC) $\rightarrow$ PsC + cubic (C) (see figure 3 and Table 1).

Table 1. Parameters of cell and density of ceramics of the $(1-x-y)KnBO_3 - yNaNbO_3 - xCa_2Nb_2O_7$ solid solutions

| $x$   | symmetry | $a$, Å  | $b$, Å  | $\beta$ (°) | $V$, Å$^3$ | $\rho_{exp}$ g/cm$^3$ | $\rho_{xr}$ g/cm$^3$ | $\rho_{rel}$, % |
|-------|----------|---------|---------|-------------|-----------|----------------|-----------------|-------------|
| 0.000 | M        | 3.997   | 3.938   | 90.29       | 62.91     | 3.89           | 4.54            | 85.73       |
| 0.025 | M+       | 3.990   | 3.935   | 90.31       | 62.63     | 3.95           | 4.64            | 85.19       |
|       | PsC      | 4.005   |         |             |           | 64.26          |                 |             |
| 0.050 | C+       | 3.937   |         |             |           | 61.01          | 4.89            | 75.25       |
|       | PsC      | 3.990   |         |             |           | 63.53          |                 |             |
| 0.075 | C+       | 3.934   |         |             |           | 60.91          | 5.03            | 72.77       |
|       | PsC      | 3.981   |         |             |           | 63.38          |                 |             |
| 0.100 | C        | 3.936   |         |             |           | 60.97          | 5.22            | 72.79       |

As $Ca_2Nb_2O_7$ increases in the range of $0.00 \leq x \leq 0.10$, a number of phase transitions occur in this system: monoclinic (M) $\rightarrow$ M+ pseudocubic (PsC) $\rightarrow$ PsC + cubic (C) (see figure 3 and Table 1).

Figure 3. Phase diagram $(1-x-y)KnBO_3 - yNaNbO_3 - xCa_2Nb_2O_7$ system.

Fragments of microstructures of the $(1-x-y)KnBO_3 - yNaNbO_3 - xCa_2Nb_2O_7$ solid solutions are shown in figure 4. The analysis of figure 4 shows that pure $Na_{0.5}K_{0.5}NbO_3$ has a cubic form grain. The grain boundaries are equilibrium. The packing of the structure is dense and consists of large crystallites with an average grain size of $d \approx 15 \text{ μm}$. If the concentration of the component $x$ increases, the grain size decreases significantly, but the character of the grain landscape remains up to $x=0.05$. An anisometric type of grain structure is observed in which needle and lamellar grains which are characteristic to layered pyrobiobates, which can be nuclei of a new layered phase [9] are formed on the background of cubic crystallites ($x$ above 0.075). The orientation of such grains is chaotic therefore different sections of elongated prisms are observed. The size of such grains is 5-10 μm.
The temperature dependence of dielectric constant demonstrated two extrema in the (480–550) K and (680–750) K regions at \(x=0.0\), corresponding to phase transitions between the rhombohedral→tetragonal and tetragonal→cubic phases, respectively. The dependences of the \(\varepsilon/\varepsilon_0\) at \(x=0.025\) and \(x=0.05\) are characterized by a strong frequency dispersion (starting at 550 K) at the point of the phase transition at a frequency of 1 kHz. The maxima of the dielectric constant on the dependences are weakly. At frequencies above 1 kHz, the strong dispersion begins to appear at 700K, and shifted as the frequency increases to the higher-temperature region (figure 5).

This behavior may be related to the increasing number of free charge carriers at domain boundaries emerging from the adding of bivalent calcium into the system. The charged boundaries of grains interact with an alternating electric field, which leads to the appearance of Maxwell-Wagner type polarization. Further, contribution to the polarization mechanism may be due to the appearance of ceramic-air interphases during the formation of the pores and vacancies. Let’s consider the possible means of their formation. At producing solid solutions with a perovskite-type structure, the adding of compounds like \(\text{Ca}_2\text{Nb}_2\text{O}_7\) leads to an excess of oxygen octahedrons concerning the cations occupying the A-position.

**Figure 4.** Fragments of microstructure of the \((1-x-y)\text{KNbO}_3 – y\text{NaNbO}_3 – x\text{Ca}_2\text{Nb}_2\text{O}_7\) system solid solutions.
Figure 5. Temperature dependence of the dielectric constant $\varepsilon/\varepsilon_0$ and loss tan$\delta$ of the $(1-x-y)\text{KNbO}_3 - y\text{NaNbO}_3 - x\text{Ca}_2\text{Nb}_2\text{O}_7$ solid solutions with a) $x=0.0$; b) $x=0.025$; c) $x=0.05$ at frequencies of 1 kHz-1 MHz.

At low concentrations $\text{Ca}_2\text{Nb}_2\text{O}_7$, such an excess can be offset by the formation of vacancies in the A sublattice, which must be reflected in increasing the unit cell volume of the perovskite structure $\text{A}_{1-x}\text{M}_x^{2+}(\text{Nb}^{5+}\text{O}^{2-3})_{1+x}$, where $\text{M}_x^{2+}$ – divalent cation.

However, this trend is less pronounced when compared to potassium replacement by the smaller calcium $\text{Ca}$ ($\text{R} (\text{Ca}^{2+}) = 1.04$ Å, $\text{R} (\text{K}^+)=1.33$ Å). Furthermore, the clustering and annihilation of vacancies take place when their accumulation in the A-sublattice via the crystallographic shift with the formation of linear, planar, and block superstructures [10].

Furthermore, the partial loss of oxygen with the formation of vacancies occurs at temperature rise, as in any oxide compounds. Besides, the relatively low reduction temperature of niobium-containing complex oxides ($\approx 450$ ° C) deals with a variable valence of Nb and is correlated with increases in electrical conductivity at increasing frequency in the compounds of this group [11]. This process lasts
up to 750 K. Reduction of niobium occurs according to the scheme $A^{1+} \text{Nb}^{5+}_{1-x} \text{Nb}^{4+}_x \text{O}^{2-}_{5-x/2} \text{vac}_{x/2}$, where $\text{vac}_{x/2}$ - vacancies in the oxygen sublattice, with the emergence of point defects. The interaction of two types of coexisting defective systems can lead to additional Maxwell-Wagner type maximums, changes in the nature of dispersion processes and their energy characteristics.

Conclusions
The correlations between composition, crystal structure, microstructure, and dielectric responses in the $(1-x-y)\text{KNbO}_3 - y\text{NaNbO}_3 - x\text{Ca}_2\text{Nb}_2\text{O}_7$ solid solutions were established. The most likely mechanism of the formation of defects in the structure was established.

Acknowledgments
The study was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (State task in the field of scientific activity, scientific project No (0852-2020-0032)/(BA30110/20-3-071F) using the equipment of the Collective Use Center “Electromagnetic, Electromechanical and Thermal Properties of Solids” of the Research Institute of Physics.

References
[1] Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment, Official Journal of the European Union 13 pp 10–24
[2] Lee M K, Yang S A, Park J J and Lee G J 2013 Proposal of a rhombohedral-tetragonal phase composition for maximizing piezoelectricity of (K,Na)NbO$_3$ ceramics, Scientific Reports 9 pp 4195
[3] Xiang Zh, Di H, Zhongbin P et al 2021 Enhancement of recoverable energy density and efficiency of lead-free relaxor-ferroelectric BNT-based ceramics, Chemical Engineering Journal 406 pp 126818
[4] Reznitchenko L A et al 2012 Ferroelectrics, relaxors, multiferroics with different thermodynamic prehistory, Nova Science Publishers (Monograph «Piezoceramic Materials and Devices») pp 1-50
[5] Malic B et al 2005 Alkaline-earth doping in (K,Na)NbO$_3$ based piezoceramics, Journal of the European Ceramic Society 25 pp 2707–2711
[6] Nagaenko A V, et al 2020 Multi-element ferroactive materials based on KNN-PZT compositions with fundamentally different physical properties, Heliyon 6 pp 3497
[7] Tomashpolsky Yu Ya, Matyuk V M, Sadovskaya N V 2016 Formation of a Surface Phase with the Matrix Composition in a Ca$_2$Nb$_2$O$_7$ Single Crystal, Inorganic Materials 52 pp 791–795
[8] Zubarev J Y et al 2019 Intercalation of water molecules from the air into perovskite and layered structures formed in the system of NaNbO$_3$–Ca$_2$Nb$_2$O$_7$, Heliyon 5 pp e02786
[9] Titov S V et al 2000 Clustering of the structure preceded by concentration phase transitions, Letters in J.Tech. Phys 26 pp 9–16
[10] Rao C N R, Gopalakrishnan J, 1990 New Directions in Solid State Chemistry. Structure, synthesis, properties, reactivity and materials design, New York. Cambridge university Press pp 519
[11] Vezzoli G G 1982 Electrical properties of NbO$_2$ and Nb$_2$O$_5$ at elevated temperature in air and flowing argon, Phys. Rev. B 26 pp 3954-3957