Influence of polyaniline on the electrophysical properties of lead-free ceramics

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Abstract. The effect of polyaniline additives on the dielectric and piezoelectric properties of a composite based on a multi-component system of sodium-potassium niobate was studied in the paper. The behavior of dielectric characteristics, electromechanical and piezoelectric properties of the system was studied. The critical concentration of polyaniline influencing the formation of an electromechanical connection between ferroactive inclusions and piezoelectric properties was determined.

1. Introduction

In recent decades, much attention has been paid to the creation of composite materials, as well as environmental protection. As a result, there is an increasing number of investigations that focus on environmentally-friendly (lead-free) materials. One of the most attractive and studied groups of lead-free materials, promising as an active ferroelectric phase of composites, are systems based on alkali metal niobates. Herewith, a significant number of works are devoted to the study of ceramics based on the $\text{K}_{1-x}\text{Na}_x\text{NbO}_3$ (KNN) system. These solid solutions have several advantages due to the crystal-chemical properties of their constituent cations: high dielectric constant, manufacturability, Curie temperature ($T_c$) $> 400$ K, providing a wide range of practical applications [1-3]. The piezoelectric properties of polycrystalline materials based on KNN are close to the most common industrial ceramics of the $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$ (PZT) system [4-5], which will allow the use of lead-free materials of this system in the already known technological schemes.

Composite materials with an active ferroelectric phase have several advantages in comparison with single-phase polycrystalline materials, which significantly expand the prospects for their use, both in terms of parametric design and in terms of technical production capabilities. An increase in the spectrum of possible resonant frequencies, the range of piezo sensitivities and acoustic impedance, and, most importantly, the emergence of possibilities for controlling these characteristics provides the prospect of using these materials in piezo acoustic [6]. A significant decrease in the temperatures of formation of the final topology’s active elements provides the use of appropriate precursors in additive technological solutions.
One of the most popular polymers often used to create composite systems is polyaniline (PANI). It attracts the attention of researchers due to its potential application in various fields of technics. It can be used to absorb electromagnetic radiation and to create antistatic and anticorrosive coatings [7-9]. Compared to other conductive polymers, PANI has the highest chemical stability. The main problem associated with the practical application of PANI is that the materials from these polymers in a free state exhibit low strength and lack of elasticity.

Because of the above, obtaining and establishing the regularities of the formation of properties in composite materials based on a ceramic matrix, which provides the material with the necessary mechanical integrity, strength, and elasticity, and a conducting polymer is a current task.

Thus, the purpose of this work is to establish the effect of the PANI additive on the electrophysical properties of multicomponent solid solutions based on KNN.

2. Experimental section
The K$_{0.4324}$Na$_{0.5076}$Li$_{0.06}$Nb$_{0.864}$Ta$_{0.094}$Sb$_{0.06}$O$_3$ solid solutions with 1.5% wt. (Fe$_2$O$_3$ + Bi$_2$O$_3$) and CuNb$_2$O$_6$ is the subjects of this study. The raw powders were NaHCO$_3$ (99.9%), KHCO$_3$ (99%), Li$_2$CO$_3$ (98%), Nb$_2$O$_5$ (98%), Ta$_2$O$_5$ (99.9%), Sb$_2$O$_5$ (99.9%), Fe$_2$O$_3$ (99%), Bi$_2$O$_3$ (99.9%), CuO (99.99%). The solid solutions were prepared using a two-stage solid-state reaction at $T_1 = 1273$ K for 6 h, $T_2 = 1373$ K for 6 h. PANI was added before sintering. In the work, there were used five schemes for modifying solid solutions: No 1) 0 wt.% PANI, No. 2) 5 wt.% PANI, No. 3) 10 wt.% PANI, No. 4) 15 wt.% PANI, No. 5) 20 wt.% PANI.

The billets were sintered by hot pressing (with external pressure applied) using a modernized unit UGPE-2 [10, 11]. Optimal sintering temperature modes are $T_{\text{sint.}} = 1363$ K, $P = 200$ kg/cm$^2$, $\tau_{\text{sint.}} = 60$ min. The pressure was applied at room temperature and maintained at the stages of temperature rise and isothermal holding. During the cooling process, the applied pressure was removed. The sintered samples were being sanded to a thickness of 0.2 mm on an LPSh surface grinder.

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: $I/I_1 \cdot 100\%$, 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 samples were polarised in oil in a chamber with PES 5 K at $T=150$ °C and 3.4 kV. The electrophysical parameters were measured using Agilent 4980A and Wayne Kerr 6500B precision LCR meters via the resonance – antiresonance method [24, 25] at room temperature. The piezo modules were measured using APC International, Ltd.Piezo d33Test System. The temperature dependence $\varepsilon'/\varepsilon_0$ was measured in a temperature range $T = 300$ - 900 K at frequencies of 20 Hz-1 MHz.

3. Experimental section
An X-ray phase analysis showed that the K$_{0.4324}$Na$_{0.5076}$Li$_{0.06}$Nb$_{0.864}$Ta$_{0.094}$Sb$_{0.06}$O$_3$ solid solution with 1.5% wt. (Fe$_2$O$_3$ + Bi$_2$O$_3$) and CuNb$_2$O$_6$ was pure after the second stage of the synthesis. An X-ray phase analysis also showed that after sintering in the solid solution there are lines of an impurity phase - Li$_2$K$_3$Ta$_5$O$_{15}$ (up to 14%).

The dependence of the relative density on the concentration of the PANI additive is shown in fig. 2. The density of composites changes non-monotonically but generally decreases. This is logical because at high temperatures (at sintering) PANI almost completely is burned out (up to 90-95%), and a porous structure with a small PANI inclusion is formed. The non-monotonic change in density is most likely associated with the nature of the PANI distribution in the bulk of the composite.

In fig. 3 are shown the graphs of the dependences $\varepsilon'/\varepsilon_0$ and $\varepsilon''/\varepsilon_0$ on temperature are shown. An analysis of the dependencies is shown that an anomaly in the region of 500 - 600 K is observed, which corresponds to the ferroelectric phase transition between the cubic and tetragonal phases. Also, the
dependences showed that with an increase in the PANI concentration to 15wt.% the value of the $\varepsilon'/\varepsilon_0$ in maximum decreases and then begins to increase. The maximum $\varepsilon'/\varepsilon_0$ shifts to the region of higher temperatures (Fig. 3). Herewith, a significant increase in the frequency dispersion of the material is observed.

![Figure 1](image1.png)

**Figure 1.** X-ray diffraction peaks (a) microstructure (b) of the solid solutions in the $K_{0.4324}Na_{0.5076}Li_{0.06}Nb_{0.864}Ta_{0.094}Sb_{0.06}O_3$ solid solutions with 1.5% wt. $(Fe_2O_3 + Bi_2O_3)$ and $CuNb_2O_6$ under optimal conditions (the $Li_2K_3Ta_5O_{15}$ peaks are marked by circles).

The values of the main dielectric and piezoelectric parameters of the investigated solid solutions are shown in table 1. As shown in an analysis of table 1, the dielectric constant in the system under study experiences a maximum at a PANI additive concentration of 5wt.%. This can be explained by the specific distribution of PANI in the bulk of the matrix (PANI particles are isolated from each other by a dielectric layer and only slightly contact each other in the bulk of the composite).

![Figure 2](image2.png)

**Figure 2.** Dependence of the relativity density of $K_{0.4324}Na_{0.5076}Li_{0.06}Nb_{0.864}Ta_{0.094}Sb_{0.06}O_3$ solid solutions with 1.5% wt. $(Fe_2O_3 + Bi_2O_3)$ and $CuNb_2O_6$ on the concentration of the PANI additive.

Dependence of the relative density on the concentration of the PANI additive is shown in fig. 2. The density of composites changes non-monotonically but generally decreases. This is logical because at high temperatures (at sintering) PANI almost completely is burned out (up to 90-95%), and a porous structure with a small PANI inclusion is formed. The non-monotonic change in density is most likely associated with the nature of the PANI distribution in the bulk of the composite. The piezoelectric modulus $d_{33}$ at a concentration PANI of 5wt.% as whole decreases, which can be associated with a decrease in the relative area of the piezo active phase. The discontinuity of the piezo active phase in
the transverse direction, which prevents mechanical deformation of the composite in the indicated direction results in a sharp decrease in $d_{31}$.

**Figure 3.** Dependences $\varepsilon'/\varepsilon_0$ and $\varepsilon''/\varepsilon_0$ of $K_{0.4324Na_{0.5076}Li_{0.06}Nb_{0.864}Ta_{0.094}Sb_{0.06}O_3}$ solid solutions with 1.5% wt. ($Fe_2O_3 + Bi_2O_3$) and $CuNb_2O_6$ with the addition of 0% PANI (a), 5wt.% PANI (b), 10wt.% PANI (c), 15wt.% PANI (d), 20wt.% PANI (e) on temperature.
The electromechanical coupling coefficient $K_p$ changes non-monotonically. This can be due to the combined effects decrease of the piezoelectric modulus $d_{31}$ and a change of the dielectric constant. The main reason for the decrease in $K_p$ is the discontinuity of the piezo active phase in the transverse direction.

### Table 1. Dielectric and piezoelectric parameters of K$_{0.4324}$Na$_{0.5076}$Li$_{0.06}$Nb$_{0.864}$Ta$_{0.094}$Sb$_{0.06}$O$_3$ solid solutions with 1.5% wt. (Fe$_2$O$_3$ + Bi$_2$O$_3$) and CuNb$_2$O$_6$ at the addition PANI.

|       | $\rho$, g/cm$^3$ | $C_p$, pF | $\tan\delta$ | $\varepsilon/\varepsilon_0$ | $K_p$ | $K_{31}$ | $V_{1E}\cdot10^3$, km/s | $|d_{31}|$, pK/N | $d_{33}$, pK/N |
|-------|------------------|-----------|---------------|-----------------|--------|----------|------------------|----------------|----------------|
| 0 wt% PANI | 4.74 | 690 | 0.013 | 502 | 0.24 | 0.13 | 5.7254 | 25.7 | 163 |
| 5 wt% PANI* | 4.74 | 100 | 0.040 | 943 | 0.25 | 0.14 | 4.9458 | 8.7 | 100 |
| 10 wt% PANI | 4.63 | 369 | 0.050 | 268 | 0.13 | 0.07 | 6.6655 | 8.5 | 26 |
| 15 wt% PANI | 4.65 | 319 | 0.031 | 232 | 0.16 | 0.09 | 6.2422 | 8.4 | 15 |
| 20 wt% PANI* | 4.55 | 19 | 0.200 | 179 | 0.07 | 0.04 | 4.5043 | 2.3 | 10 |

* Square plate

The behavior of the speed of sound $V_{1E}$ is determined by the competing influences of changes in the modulus of elasticity and density. Thus, the decrease in $V_{1E}$ with the addition of 5wt.% PANI is most likely due to the slight increase in density.

The observed, most likely, is associated with the weakening of the electromechanical relationship between the particles of the ferroactive phase. This leads to a sharp increase in the influence of local inhomogeneities, contributing to the blurring of the transition. It happens both due to the uneven distribution of temperature gradients in the bulk of the ceramic (broadening of the maximum of the dielectric constant) and the appearance of a local potential difference on phase boundaries as a result of their different electrical conductivities (increase in frequency dispersion). All this leads to a significant decrease in piezoelectric activity in the range of PANI concentrations over 5 wt. %.

### 4. Conclusions

Critical importance in the formation of macro-responses in the studied ceramics has an inhomogeneity associated with the formation of composite structures of different connectivity.

Composites with a concentration of PANI range of 1-5 wt% PANI can have optimal properties for practical applications. A further increase in the concentration of the organic component (the filler) leads to the disruption of the electromechanical connection between ferroactive inclusions and the degradation of the piezoelectric properties.

### 5. References

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Acknowledgements
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)/(BAZ0110/20-3-071F).