Dielectric spectroscopy, piezoelectric and ferroelastic properties of solid solutions of the three-component system (1-x-y) NaNbO3 – xKNbO3 – yCdNb2O6 in the temperature range (10-330) K

M O Moysa, K P Andryushin, S P Kubrin, I N Andryushina and L A Reznichenko

Southern Federal University, Scientific Research Institute of Physics, Stachki av. 194, 344090, Rostov-on-Don, Russia.
maksim.moysa@mail.ru

Abstract. A solid solution of the three - component system 0.8NaNbO3 – 0.15KNbO3-0.05CdNb2O6 was prepared by two-stage solid-phase synthesis followed by sintering using conventional ceramic technology. An experimental study of the dielectric, piezoelectric, and ferroelastic characteristics of the latter in the low-temperature range (10÷330) K. The conclusion is made about the expediency of using the obtained results in the development of functional ferroactive materials based on sodium – potassium – cadmium niobates and devices with their participation.

1. Introduction
Solid solutions (SS) based on sodium niobate (SN) are lead-free materials that can replace toxic, lead-containing ceramics, including those with the participation of compositions of the composition PbTiO3-PbZrO3 (PZT). SS based on SN have a unique combination of properties, the achievement of which in PZT materials is fundamentally impossible [1-3]: high speed of sound (~ 6 km / s) against the background of relatively low dielectric constant; - which makes them promising for microwave applications. Electrophysical characteristics similar to the popular PZT media are the solid solutions of the binary systems (Na, K) NbO3 [4] and NaNbO3-CdNb2O6 [5]. However, in view of the fact that the capabilities of these basic systems are practically exhausted, we decided to make the transition to a three-component system based on them. The latter led to an expansion of the dimensionality of the morphotropic region and, as a consequence, an increase in the efficiency of the materials obtained. In [6, 7], we found the optimal conditions for the preparation of the solid solution of the (Na, K) NbO3 - CdNb2O6 system, plotted the phase diagram of its states, and determined the composition - structure - properties correlations.

This work is a continuation and development of our earlier studies of solid solutions of the composition (1-x-y) NaNbO3 - xKNbO3 - yCdNb2O6. In view of the fact that the modern materials science trend is associated with research at low temperatures (active development of the Arctic region
and outer space), it seemed relevant to study the dielectric spectroscopy, piezoelectric and ferroelastic properties of the SS of the above system in the temperature range (10 ÷ 330) K.

2. Experiments

The objects of study were SS of the (1-x-y) NaNbO3 – xKNbO3 – yCdNb2O6 system with y= 0.05, x= 0.15. The samples were obtained by solid-phase synthesis in two stages and sintered using conventional ceramic technology (CCT) (T_synth.1=1220 K, τ=5 h., T_synth.2= 1240 K, τ=10 h.; T_sint.= .=1190 K, τ=2 h).

Sintered ceramic blanks were subjected to mechanical processing (cutting along the plane, grinding along flat surfaces and ends) in order to obtain measuring samples of Ø10mm x 1mm. Before metallization, the samples were calcined at a temperature Тcalc.=770 K for 0.5 h. to remove organic matter residues and degrease surfaces in order to increase the adhesion of the metal coating to ceramics. The electrodes were applied by double firing a silver-containing paste at a temperature of 1070 K for 0.5 h.

Dielectric spectra were studied on unpolarized samples in the temperature range (10÷330) K using a Wayne Kerr 6500 B precision impedance analyzer, which allows measurements of capacitance and dielectric losses, tgδ, with high accuracy in the frequency range from 20 Hz to 2 MHz. In this case, the real, \( \varepsilon'/\varepsilon_0 \), and imaginary, \( \varepsilon''/\varepsilon_0 \), parts of the relative, complex dielectric constant were calculated.

The electrophysical parameters of the polarized samples in the temperature range (10÷330) K were measured using precision LCR meters Agilent 4980A by the resonant antiresonance method. At the same time, the relative permittivities, \( \varepsilon_{33}^T/\varepsilon_0 \), dielectric losses in a weak field (tangent of dielectric loss angle, tgδ), piezoelectric module, \( |d_{31}| \), piezoelectric coefficient (piezoelectric sensitivity), \( |g_{31}| \), coefficient of electromechanical coupling were determined simultaneously planar vibration mode, \( K_p \), mechanical quality factor, \( Q_m \), Young’s modulus, \( Y_{11} \), speed of sound, \( V_{11} \).

The samples were cooled using a CCS-150 closed-type helium refrigerated cryostat manufactured by Cryogenics. Temperature control was carried out using a LakeShore 331 temperature controller, which allows maintaining the set temperature with an accuracy of ± 0.01K. During measurements, the samples were placed in the vacuum chamber of a cryostat, and the vacuum was created with a Boc Edwadrs turbomolecular pump.

3. Results and discussion

Fig. 1 shows the dependences \( \varepsilon'/\varepsilon_0(T) \) and \( \varepsilon''/\varepsilon_0(T) \) for samples of SS 0.8NaNbO3 - 0.15KNbO3 - 0.05CdNb2O6 during cooling and heating (forward and reverse) (T = (10 ÷ 330) K).

The formation of three regions of dependences \( \varepsilon'/\varepsilon_0(T) \) and \( \varepsilon''/\varepsilon_0(T) \) with different rates of change in \( \varepsilon'/\varepsilon_0 \) and \( \varepsilon''/\varepsilon_0 \) (i.e., the angle of inclination of these dependences) was found. Upon cooling in the temperature range (325 ÷ 230) K, a smooth decrease in the above dependences is observed; upon reaching 230 K, the rate of change in the dependences \( \varepsilon'/\varepsilon_0(T) \) and \( \varepsilon''/\varepsilon_0(T) \) sharply increases, forming a quasi-minimum, up to 160 K After passing the above point in the temperature range (160 ÷ 10) K, the slope angle \( \varepsilon'/\varepsilon_0(T) \) and \( \varepsilon''/\varepsilon_0(T) \) decreases significantly. Upon heating, the investigated dependences have an exponential form, and the anomalies \( \varepsilon'/\varepsilon_0 \) and \( \varepsilon''/\varepsilon_0 \), at T = 160 K and 230 K, are much less pronounced. It was also revealed that, both during cooling and heating, a weak dispersion of \( \varepsilon'/\varepsilon_0 \) and \( \varepsilon''/\varepsilon_0 \) is present up to T ~ 250K. Up to T ~ 175 K, it gradually decreases, after which a change in dispersion is practically not observed.
Dependences $\varepsilon'/\varepsilon_0(T)$, $\varepsilon''/\varepsilon_0(T)$ for solid solution samples of composition $0.8\text{NaNbO}_3 - 0.15\text{KNbO}_3 - 0.05\text{CdNb}_2\text{O}_6$ for frequencies $f = 1018-1213893$ Hz.

Figure 1.

In fig. 2 shows the temperature dependences of the relative permittivity and the tangent of the dielectric loss angle of polarized samples of the same composition. It was found that these dependences have a form similar to that observed in unpolarized samples: upon cooling in the previously indicated temperature ranges, there are inflection points $\varepsilon_{33}'/\varepsilon_0$, $\tan\delta$ at the same temperatures. When heated, these anomalies are weakened. It should be noted that, upon cooling, dielectric losses undergo a jump at a temperature of 160 K, in contrast to unpolarized samples. When heated, as the temperature rises, $\tan\delta$ tends to grow linearly.

Figure 2.

In fig. 3 shows the dependences of the piezoelectric (Fig. 3 a) and ferroelastic (Fig. 3 b) characteristics of SS of the composition $0.8\text{NaNbO}_3 - 0.05\text{KNbO}_3 - 0.15\text{CdNb}_2\text{O}_6$ in the temperature range (10-300) K. In fig. 3 shows the dependences of the piezoelectric (Fig. 3 a) and ferroelastic (Fig. 3 b) characteristics of SS of the composition $0.8\text{NaNbO}_3 - 0.05\text{KNbO}_3 - 0.15\text{CdNb}_2\text{O}_6$ in the temperature range (10-300) K.
Figure 3. Dependences of piezoelectric (a) and ferroelastic (b) characteristics of SS of composition
composition 0.8NaNbO₃ - 0.05KNbO₃ - 0.15CdNb₂O₆ in the temperature range (10-300) K.

It was found that the piezoelectric properties (Fig. 3a) exhibit extreme behavior at the previously
designated temperatures of 160 and 230 K, which coincides with the anomalies in unpolarized samples.
Thus, $K_P$ experiences a strong “disturbance” in the form of a maximum at 230 K. After the indicated
temperature, this value begins to abruptly drop to 160 K, forming a minimum of the $K_P(T)$ dependence.
Further, as the temperature decreases, the system stabilizes and reaches practically the same values of
the value that were at room temperature. Parameters $|d_{31}|$ and $|g_{31}|$ tend to be reciprocal: $|g_{31}|$ increases,
experiencing extrema at temperatures of 160 K and 230 K, and $|d_{31}|$ decreases, reaching a plateau-like
area at 160 K.

It should be noted that the effect of temperature on the ferroelastic properties of the samples under
study is not so significant. Fluctuations of the dependences $Y_{11}^E$ and $V_1^E$ at $T = 160$ K are present both
during cooling and during heating; however, they are not as pronounced as piezoelectric properties.
Another distinctive feature of these characteristics is the presence of significant hysteresis above $T \sim
230$K. Thus, it has been established that the elastic subsystem of the samples under study reacts weakly
to changes in the external temperature. An exception is the mechanical quality factor, $Q_M$, which
demonstrates the extreme nature of the dependence $Q_M(T)$ in both cases.

The low-temperature anomalies revealed during the experiment are likely due to structural
instabilities present in this object, which requires additional X-ray studies. The fact that they manifest
themselves differently during cooling and heating of the samples may be due to a defect situation. Thus,
upon cooling from room temperature, the defects present in the experimental sample contribute to the
electrophysical properties. As they approach the minimum temperature, their gradual freezing occurs
and their effect on macro-properties is leveled. During heating, due to the fact that a state of relative
equilibrium has been established in the sample, the external activation energy is not enough to excite
the defective matrix of the object.
The implementation of sufficient $K_p$ values at high $V_f^1$ and average $\varepsilon_{33}^R/\varepsilon_0$ (Fig. 3) in the range (10-160) K allows us to recommend this SS as the basis for functional materials used in high-frequency technology, operated at critically low temperatures.

4. Conclusions
• Received a solid solution of the system $0.8\text{NaNbO}_3 – 0.15\text{KNbO}_3 – 0.05\text{CdNb}_2\text{O}_6$
• The dielectric spectra, piezoelectric and ferroelastic properties of the above-mentioned solid solution have been investigated in the low-temperature range (10÷330) K
• The formation of three regions of dependences $\varepsilon'/\varepsilon_0(T)$ and $\varepsilon''/\varepsilon_0(T)$ with different rates of change in their angle of inclination at temperatures of 160 K and 230 K.
• It was revealed that, both during cooling and heating, a weak dispersion of $\varepsilon'/\varepsilon_0$ and $\varepsilon''/\varepsilon_0$ is present up to $T \sim 250$ K. Up to $T \sim 175$ K, it gradually decreases, after which a change in the dispersion is practically not observed
• It was found that anomalies at temperatures of 160 K and 230 K also manifest themselves in the dependences of the piezoelectric and ferroelastic characteristics in the form of extrema.

The results obtained should be taken into account when developing piezoelectric devices for various fields of their application, including in the low temperature range.

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

References
[1] Safari A, Hejazi M, et al 2012 Lead-Free KNN-Based Piezoelectric Materials Springer New-York. 5 pp 139-175.
[2] Egerton L, Dillon D M, et al 1959 Piezoelectric and Dielectric Properties of Ceramics in the System Potassium—Sodium Niobate Journal of the American Ceramic Society 42 pp. 438-442
[3] Smiga W, Konieczny K, et al 1998 Dielectric properties of Li$_{0.003}$Na$_{0.997}$NbO$_3$ ceramics Ferroelectrics 216 pp 53-61
[4] Koruza J, Bell A J et al 2018 Requirements for the transfer of lead-free piezoceramics into application J. Materiomics 4 pp. 13-26. https://doi.org/10.1016/j.jmat.2018.02.001.
[5] Lewis B, et al 1956 Structure and Phase Transitions of Ferroelectric Sodium Cadmium Niobates Journal of Electronics and Control 1 pp. 646-664
[6] Reznichenko L A, Verbenko I A, Andryushin K P, et al 2010 Lead-free long ago Piezoceramic Materials and Devices pp 1-69
[7] Andryushin K P, et al 2012 Sodium solutions of sodium- potassium-cadmium. Preparation, structure, electrophysical and thermofrequency properties LAP LAMBERT Academic Publishing 61