OPEN ACCESS
JOURNAL OF ADVANCED DIELECTRICS
Vol. 12, No. 4 (2022) 2244001 (4 pages)

DOI: 10.1142/S2010135X22440015

Dielectric spectroscopy of solid solutions based on sodium–potassium–cadmium in the temperature range (10 ÷ 900) K

M. O. Moysa,[*,‡] K. P. Andryushin,[*] A. V. Pavlenko,[†] S. P. Kubrin[*] and L. A. Reznichenko[*]

[*]*Research Institute of Physics, Southern Federal University, 194 Stachki Avenue 344090, Rostov-on-Don, Russia*

[†]*Southern Scientific Centre, Russian Academy of Sciences, Chehov av. 41, 344000 Rostov-on-Don, Russia*

[‡]maksim.moysa@mail.ru

Received 11 May 2022; Revised 25 June 2022; Accepted 14 July 2022; Published 3 August 2022

This paper studies the dielectric spectra of solid solutions (SS) of the system $(1 - x - y)NaNbO_3$–$xKNbO_3$–$yCdNb_2O_6$ $y = 0.075$, $x = 0.05 \div 0.30$ in the temperature range (10 ÷ 900) K. The formation of a local maximum was established in the interval (260 ÷ 300) K at small x values, which, as $KNbO_3$ increases, is gradually blurred and becomes an inflection point. Detected in SS with $x = 0.05 \div 0.10$, the shift of the maxima of dependences $\varepsilon'/\varepsilon_0(T)$ and $\varepsilon''/\varepsilon_0(T)$, depending on the frequency of the electric field at the temperature ranges (300 ÷ 304) K and (258 ÷ 271) K, is not related to relaxation. This anomaly may indicate a crystallographic disorder to A and B positions. The conclusion is made about the expediency of using the obtained results for the development of functional ferroactive materials.

Keywords: Dielectric spectroscopy; lead-free ceramics; KNN.

1. Introduction

Ferroceramic materials are of great technical importance due to their ability to convert mechanical energy into electrical energy and *vice versa*. This determines their use as primary information converters of measuring and control systems. In the last decade, these objects have been widely used in new fields, such as high-power transformers, micromotors, and energy collection devices.[1–3] Solid solutions (SS) based on zirconate–titanate–lead (PZT) were used as the basis of ferroactive materials, due to their excellent piezoelectric and ferroelectric properties.[4–6] In connection with the directives adopted by the European Parliament,[7,8] the researchers are seeking to replace lead-containing compositions with environmentally friendly ones. The most promising are the SS of the binary system $(1 - x)$ $NaNbO_3$–$xKNbO_3$ (KNN) due to the high values of the piezoelectric constants.[9,10] Since the above have exhausted almost all their possibilities, the researchers are making the transition to multicomponent compositions based on them.

Considering that the molecular design of SS based on components from various structural families can lead to a fundamental change in the physical properties of the material, we decided to construct a three-component system $(1 - x - y)NaNbO_3$–$xKNbO_3$–$yCdNb_2O_6$, which was the object of research in several of our works.[13–15] In this paper, we have studied the dielectric spectra of these SS in the range (10 ÷ 900) K. This topic is of particular interest for practical applications, and in particular, polar dielectrics used in electronic products when exposed to alternating electric fields of various frequencies at temperatures close to helium (active exploration of outer space) and extremely high.

2. Objects and Methods of Research

2.1. *Objects of research*

The objects of the study were SS systems $(1 - x - y)NaNbO_3$–$xKNbO_3$–$yCdNb_2O_6$ $y = 0.075$, $x = 0.05 \div 0.30$, $\Delta x = 0.05$.[13] Reagent-grade sodium hydrocarbonate ($NaHCO_3$, 99%), potassium hydrocarbonate ($KHCO_3$, 99%), niobium (Nb_2O_5, 99%) and cadmium (CdO, 99%) oxides were used as raw materials (LLC "Rostechnohim", Rostov-on-Don, Russia). The samples were obtained by solid-phase synthesis in two stages and sintered using conventional ceramic technology with elements of grain landscape texturing ($T_{synth.1} = 1220$ K, $\tau = 5$ h, $T_{synth.2} =$ 1240 K, $\tau = 10$ h; $T_{sint} = 1145 \div 1200$ K, $\tau_{sint} = 2$ 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 Ø10 mm × 1 mm. Before metallization, the samples were calcined at a temperature $T_{calc.} = 770$ 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.

[‡]Corresponding author.

2.2. *Research methods*

The temperature dependences of the real and imaginary parts of the relative complex permittivity $\varepsilon^*/\varepsilon_0 = \varepsilon'/\varepsilon_0 - i\varepsilon''/\varepsilon_0$ (ε_0 = $8.75 \cdot 10^{-12}$ F/m is the dielectric constant) at T = (300–900) K and the frequency range $f = 25 \div 10^6$ Hz were carried out on unpolarized samples using a measuring stand based on the Agilent 4980A LCR meter.

In the temperature range (10 ÷ 330) K, the latter were measured using a precision impedance analyzer (model 6500 B, Wayne Kerr Electronics, Great Britain). The samples were cooled using a closed-type helium refrigerated cryostat CCS-150 (model 22, manufactured by Janis Research Company, USA). Temperature control was carried out by means of the LakeShore 331 temperature controller, which allows keeping the set temperature with an accuracy of ± 0.01 K. During the measurement, the samples were in the vacuum chamber of the cryostat, and the vacuum was created by the turbomolecular pump Boc Edwards.

3. Experimental Results and Discussion

Figure 1 shows the dependencies $\varepsilon'/\varepsilon_0(f, T)$ for T = (10 ÷ 900) K, built on the basis of this work and combined with the results.[13]

All the studied SS at the Curie temperature (T_C) are characterized by the formation of a maximum of $\varepsilon'/\varepsilon_0$, which has

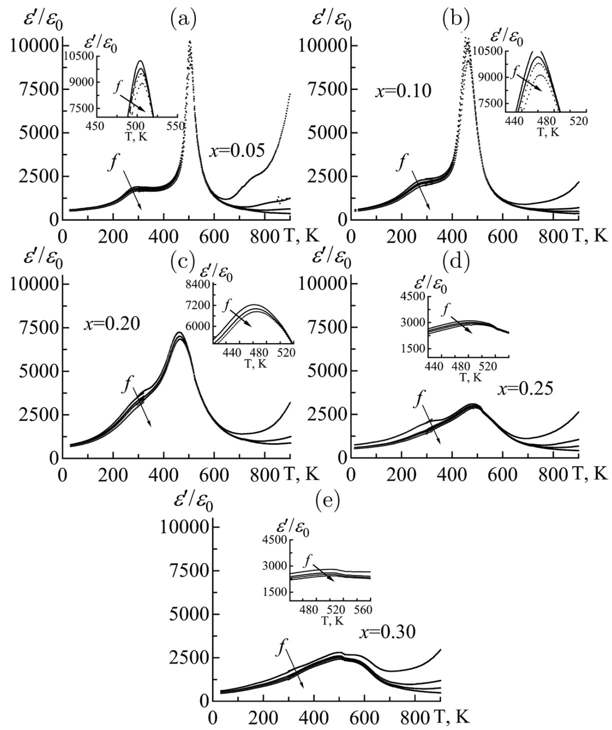

Fig. 1. Dependencies $\varepsilon'/\varepsilon_0(T)$ SS of the system $(1-x-y)NaNbO_3$–$xKNbO_3$–$yCdNb_2O_6$ with y = 0.075, x = 0.05 ÷ 0.30 T = (10 ÷ 900) K and f = (1000 ÷ 500000) Hz.

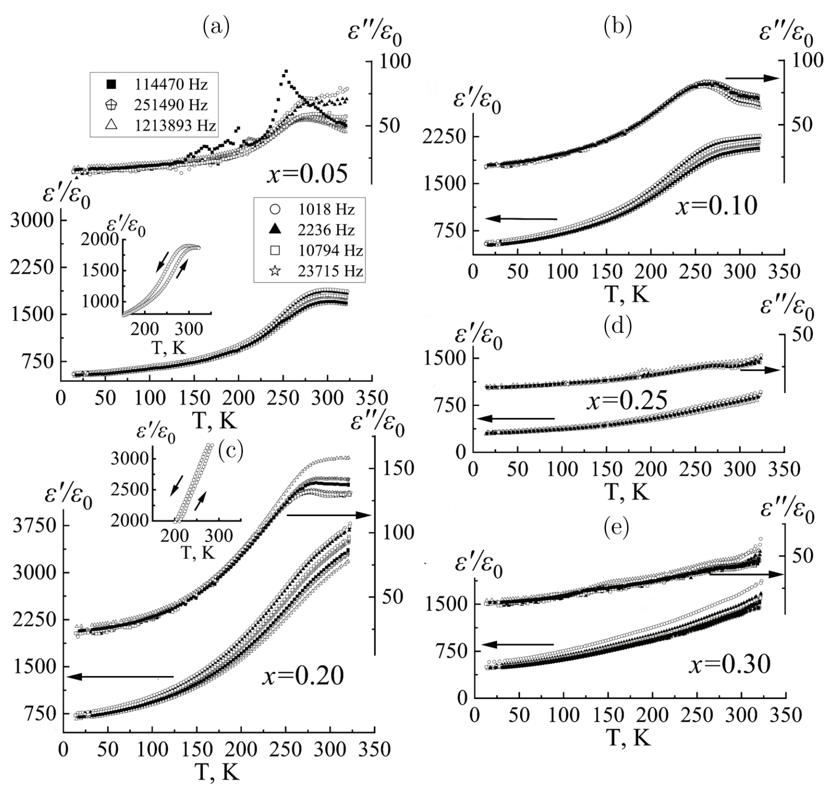

Fig. 2. Dependencies $\varepsilon'/\varepsilon_0\ (T)$, $\varepsilon''/\varepsilon_0\ (T)$ SS of the system $(1-x-y)NaNbO_3$–$xKNbO_3$–$yCdNb_2O_6$ with y = 0.075, x = 0.05 ÷ 0.30 T = (10 ÷ 330) K and f = (1000 ÷ 1213000) Hz.

a relaxation character, characterized by a shift of $\varepsilon'/\varepsilon_0$ towards higher temperatures with an increase in f.

At the same time, the weak dispersion $\varepsilon'/\varepsilon_0$ is noticeable to the left of T_C, increases in T_C and disappears to the right of it up to T~550 K. It should be noted that an increase in the content of $KNbO_3$ ($x > 0.15$) leads to a gradual blur in a wide temperature range of maximum $\varepsilon'/\varepsilon_0$ at T_C, with a noticeable dispersion before T_C, at the time of T_C and after T_C and an increase in $\varepsilon'/\varepsilon_0$. Attention is drawn to the fact of the occurrence of the anomaly $\varepsilon'/\varepsilon_0$ in the temperature range (~630 ÷ 900) K: A rapid increase of $\varepsilon'/\varepsilon_0$ at $f = 1000$ Hz. The observation is associated with a change in the valence state of niobium ions ($Nb^{4+} \rightarrow Nb^{5+}$). In addition to the main extremum $\varepsilon'/\varepsilon_0$ at T_C, at T ~ 270 K, a small local maximum $\varepsilon'/\varepsilon_0$ is formed (Figs. 1(a) and 1(b)), which gradually erodes as x increases and forms an inflection point (Figs. 1(c) and 1(d)). The low-temperature range is discussed in more detail below.

Figure 2 shows the dependences of $\varepsilon'/\varepsilon_0(f, T)$ and $\varepsilon''/\varepsilon_0(f, T)$ of the studied SS in the cooling mode at $T = (10 \div 330)$ K. Inserts (Figs. 2(a) and 2(c)) show the forward and reverse course of the dependence $\varepsilon'/\varepsilon_0(f, T)$.

It is established that the change of $\varepsilon'/\varepsilon_0(T)$ and $\varepsilon''/\varepsilon_0(T)$ occurs according to the exponential law. However, it is necessary to highlight the following features. In SS with $x = 0.05$ (T ~ (275 ÷ 300) K) and $x = 0.10$ (T ~ (260 ÷ 270) K), the formation of dependence maxima $\varepsilon'/\varepsilon_0(T)$, $\varepsilon''/\varepsilon_0(T)$, which are characterized by a shift to the region of higher temperatures with an increase in f, respectively, was revealed.

In SS with $x = 0.20$, the formation of three regions characterized by different rates of change of the dependences $\varepsilon'/\varepsilon_0$ and $\varepsilon''/\varepsilon_0$ was revealed (Fig. 2(c)). Thus, in the interval T ~ (270 ÷ 330) K, a decrease in $\varepsilon'/\varepsilon_0$ occurs, while a platform section is characteristic for $\varepsilon''/\varepsilon_0$; at T ~ (175 ÷ 270) K, an increase in the rate of change of both dependencies is observed; in the range T ~ (10 ÷ 175) K, the angles of inclination $\varepsilon'/\varepsilon_0$ and $\varepsilon''/\varepsilon_0$ are significantly reduced. In SS with $0.25 \le x \le 0.30$ (Figs. 2(d) and 2(e)), there is no formation of anomalies in the entire temperature range studied.

It is found that for SS with $x < 0.25$, a weak dispersion of $\varepsilon'/\varepsilon_0$ and $\varepsilon''/\varepsilon_0$ is present up to T ~ 200 K. In the temperature range T ~ (150 ÷ 200) K, its gradual decrease occurs, after which the dispersion of these dependencies is practically not observed. In SS with $0.25 \le x \le 0.30$, this anomaly is absent in the entire temperature range of the research.

The revealed characteristics in SS with $x = 0.05 \div 0.10$ at ~275 K were checked for the presence of relaxation processes. Figure 3 shows that in SS with $x = 0.05 \div 0.10$, the dependence $\varepsilon'/\varepsilon_0(\omega)$ decreases monotonically up to $\omega \sim 10^6$ as the frequency increases. In SS with $x = 0.05$, a similar behavior is characteristic of $\varepsilon''/\varepsilon_0(\omega)$. At $x = 0.10$, $\varepsilon''/\varepsilon_0(\omega)$ increases, reaching a maximum value at $\omega \sim 10^6$.

The dependences $\varepsilon''/\varepsilon_0(\varepsilon'/\varepsilon_0)$ have a power-law character of behavior at $x = 0.05$ and exponential at $x = 0.10$, which does not correspond to any of the distributions of the relaxation process theory. All of the above indicates that ferroelectrics

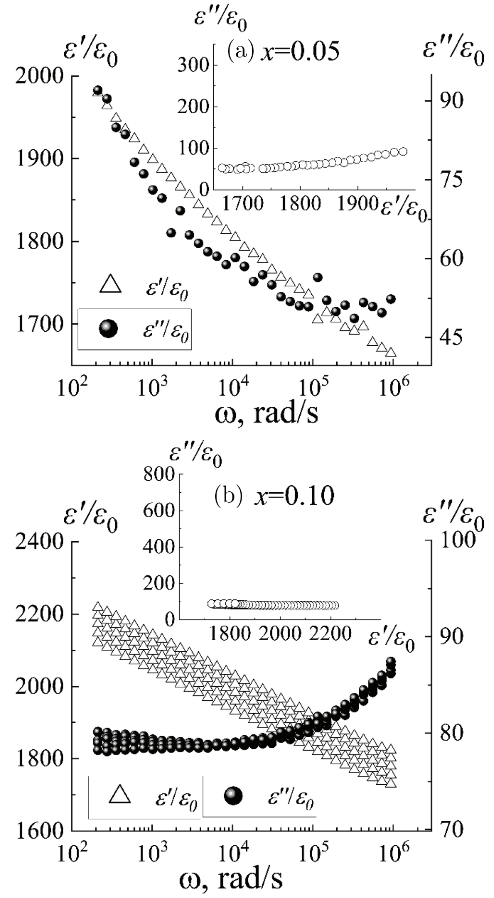

Fig. 3. The dependences $\varepsilon'/\varepsilon_0(\omega)$, $\varepsilon''/\varepsilon_0(\omega)$ and $\varepsilon''/\varepsilon_0(\varepsilon'/\varepsilon_0)$ of the SS system $(1 - x - y)NaNbO_3$–$xKNbO_3$–$yCdNb_2O_6$ with $y = 0.075$, (a) $x = 0.05$ in the temperature range (258 ÷ 271) K (b) $x = 0.10$ in the range (300 ÷ 304) K.

$x = 0.05 \div 0.10$ in the temperature ranges (258 ÷ 271) K and (300 ÷ 304) K are not relaxors. The fact that the maxima of the values ε' and ε'' shift in temperature depending on frequency may indicate a crystallographic disorder at the A and B positions of the SS.

The observed formation of a maximum on the dependences $\varepsilon'/\varepsilon_0(T)$ and $\varepsilon''/\varepsilon_0(T)$ with a low content of $KNbO_3$ and its gradual disappearance with an increase in the content of this component is probably due to the suppression of R→O.[11,12] However, this assumption requires additional radiographic studies.

4. Conclusions

(1) The dielectric spectra SS of the system $(1 - x - y)$-$NaNbO_3$–$xKNbO_3$–$yCdNb_2O_6$ with $y = 0.075$, $x = 0.05 \div 0.30$ have been investigated in the low-temperature range (10 ÷ 900) K.

(2) It is established that in the range (260–300) K, at first, at small values of x, a small local maximum is formed, which gradually (as the system is enriched with

potassium niobate) erodes and turns into an inflection point at significant concentrations of $KNbO_3$.

(3) In SS with $x = 0.05 \div 0.10$, a shift of the maxima of the dependences $\varepsilon'/\varepsilon_0(T)$ and $\varepsilon''/\varepsilon_0(T)$ depending on the frequency of the electric field in the temperature ranges $(300 \div 304)$ K and $(258 \div 271)$ K, respectively, was revealed, which are not associated with relaxation. Presumably, this is due to crystallographic disorder at the A and B positions.

(4) In the SS with $x = 0.20$, the formation of three regions characterized by different rates of dependence changes at temperatures of 270 K and 175 K. These anomalies are probably caused by structural instabilities present in this object.

The obtained results should be taken into account when developing piezotechnical devices for various fields of their application, including in the range of extremely low and high temperatures.

Acknowledgments

The research was supported by the Strategic Academic Leadership Program of the Southern Federal University ("Priority 2030").

This report is presented at the 10th Anniversary International Conference on "Physics and Mechanics of New Materials and Their Applications" (PHENMA 2021), Divnomorsk, Russia, May 23–27, 2022.

References

[1]H. Kim, Y. Tadesse and S. Priya, *Piezoelectric Energy Harvesting, Energy Harvesting Technologies* (Springer, New York, 2009).

[2]S. Priya, Advances in energy harvesting using low profile piezoelectric transducers, *J. Electroceram.* **19**,167 (2007).

[3]E. Hollenstein, D. Damjanovic and N. Setter, Temperature stability of the piezoelectric properties of Li-modified KNN ceramics, *J. Eur. Ceram. Soc.* **27**, 4093 (2007).

[4]E. Cekas, G. Janusas, A. Guobiene, A. Palevicius, A. Vilkauskas and S. Urbaite, Design of controllable novel piezoelectric components for microfluidic applications, *J. Sensors* **18**, 4044 (2018).

[5]H. Wang, S. Xia, M. Ma and Z. Li, Anisotropic growth kinetics and electric properties of PZT-5H single crystal by solid-state crystal growth method, *J. Am. Ceram. Soc.* **105**, 3238 (2022).

[6]J. Huang, M. Yao, J. Lin and X. Yao, Enhanced mechanical properties and excellent electrical properties of PZT piezoelectric ceramics modified by YSZ, *J. Mater. Lett.* **307**, 131006 (2022).

[7]Directive 2002/95/EU of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electronic equipment, *Official J. Eur. Union*. **L. 37**, 19 (2003).

[8]Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment, *Official J. Eur. Union*. **L. 174**, 88 (2011).

[9]T. Zheng, J. Wu, D. Xiao and J. Zhu, Recent development in lead-free perovskite piezoelectric bulk materials, *Prog. Mater. Sci.* **98**, 552 (2018).

[10]X. Lv, J. Zhu, D. Xiao, X. X. Zhang and J. Wu, Emerging new phase boundary in potassium sodium-niobate based ceramics, *Chem. Soc. Rev.* **49**, 671 (2020).

[11]L. Egerton and D. M. Dillon, Piezoelectric and dielectric properties of ceramics in the system potassium—sodium niobate, *J. Am. Ceram. Soc.* **42**, 438 (1959).

[12]N. Zhang, X. Lv, X.-X. Zhang, L. Jing, S.-W. Yang and J. Wu, Low-temperature dielectric relaxation associated with NbO_6 octahedron distortion in antimony modified potassium sodium niobate ceramics, *J. Mater. Sci. Technol.* **115**, 189 (2022).

[13]M. O. Moysa, A. V. Nagaenko, L. A. Shilkina, K. P. Andryushin, I. N. Andryushina, L. A. Reznichenko, D. I. Rudskiy and A. G. Rudskaya, The influence of the internal structure on the polarization properties of the solid solutions of the three-component system of the sodium–potassium–cadmium niobates, *Ferroelectrics* **575**, 64 (2021), doi: 10.1080/00150193.2021.1888228.

[14]K. Andryushin, L. Shilkina, I. Andryushina, A. Nagaenko, M. Moysa, S. Dudkina and L. Reznichenko, Features of the structure and electrophysical properties of solid solutions of the system $(1 - x - y)$ $NaNbO_3$–xKNbO3y$Cd_{0.5}NbO_3$, *Materials* **14**, 4009 (2021), doi:10.3390/ma14144009.

[15]M. O. Moysa, K. P. Andryushin, S. P. Kubrin, I. N. Andryushina and L. A. Reznichenko, Dielectric spectroscopy, piezoelectric and ferroelastic properties of solid solutions of the three-component system $(1 - x - y)$ $NaNbO_3$–$x$$KNbO_3$–$y$$CdNb_2O_6$ in the temperature range (10-330) K, *J. Phys. Conf. Ser.* **1942**, 012027 (2021), doi:10.1088/1742-6596/1942/1/012027.