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FUNCTIONAL MATERIALS

Polarization and acoustic properties of barium-modified lead-free potassium–sodium niobate ceramics

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Abstract. Results of polarization and polarization switching in samples prepared by solid phase synthesis of the $(1\text{-}x)(K_{0.5}Na_{0.5})(Nb_{0.93}Sb_{0.07})O_3$–$x$$BaTiO_3$ + 0.5mol%MnO_2 system at x = 0.01, 0.02, and 0.04 (KNNS7–xBT) studied over a wide range of temperatures are reported. The observed features of the dielectric nonlinearity at the ferroelectric and structural phase transitions in the materials are described. The dielectric response data of the samples of different contents of the admixture in the KNNS7–xBT ceramics are compared with the behaviour of their elastic properties.

Key words: ferroelectrics, relaxors, ceramics, solid solutions, dielectric permittivity, polarization, elastic properties.

1. INTRODUCTION

Lately, because of the toxicity of lead and lead compounds, the interest in ferroelectric materials without lead has grown considerably. Potassium–sodium niobate (KNN) – a solid solution of ferroelectric $KNbO_3$ and anti-ferroelectric $NaNbO_3$ – is one of such materials. The most interesting for application is the $(K_{0.5}Na_{0.5})NbO_3$ compound on the morphotropic phase boundary [1–3] the ferroelectric phase transition (PT) in which proceeds at $T_C \approx 670$ K. Below that temperature KNN has a tetragonal crystal lattice and a structural tetragonal-to-orthorhombic PT proceeding at $T_{o\text{-}t} \approx 470$ K.

The KNN modified by a small amount of admixture is known for a substantial change of its properties [2–7]. A detailed study of structural transformations at the low-temperature PT and around T_C [8] unravelled the behaviour of lattice parameters in the $(K_xNa_{1-x})NbO_3$ compounds with the temperature. A conclusion of different phases coexisting in the modified ceramics over a wide range of temperatures improving the piezoelectric properties of the material is drawn on the basis of the obtained results. A lower T_C and broadening of the PT in KNN is also achieved by admixtures isovalent to Nb. In the $(K_{0.5}Na_{0.5})(Nb_{0.93}Sb_{0.07})O_3$ (KNNS7) compound $T_C \approx 550$ K and $T_{o\text{-}t} \approx 410$ K. A very small admixture of barium efficiently modifies electrical properties. Studies [5,6] point to improved electromechanical parameters of KNN modified by addition of $BaTiO_3$ or $BaZrO_3$. Regardless of the numerous studies of lead-free ferroelectric ceramics a series of questions related to relaxation processes of polarization at structural PTs remain unanswered.

This study aims at presenting a completer overview of the effects of admixtures such as $BaTiO_3$ on the properties of the KNN system by examining over a wide range of temperatures the behaviour of the dielectric, elastic, and polarization characteristics in the $(1\text{-}x)(K_{0.5}Na_{0.5})(Nb_{0.93}Sb_{0.07})O_3$–$x$$BaTiO_3$ + 0.5mol%MnO_2 (KNNS7–xBT) ferroelectric ceramics system of x = 0.01, 0.02, and 0.04.

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2. SAMPLES AND METHODS

Ceramic samples of $(1\text{-}x)(K_{0.5}Na_{0.5})(Nb_{0.93}Sb_{0.07})O_3$–$x BaTiO_3$ + 0.5mol%MnO_2 were prepared by conventional ceramics technology [5,6]: from finely ground oxides and carbonates by solid phase thermo-chemical reaction: calcination at 1100–1200 K, sintering at 1300–1500 K. For dielectric measurements the sample plates of the size 10 mm × 5 mm × 0.5 mm were supplied with conductive silver paste electrodes.

The dielectric response in weak fields (linear response) was studied with an E7-15 RLC measuring device, in medium and strong fields by analysis of polarization loops obtained at frequencies 1–10 Hz on a modified Sawyer–Tower circuit.

The velocity of longitudinal acoustic waves was measured by resonance techniques in bar samples 12–18 mm long and 1.5–2 mm thick. The electrodes were applied to the large faces after which the samples were polarized under the applied field $E = 10$ kV/cm at $T \approx 370$ K and cooled to room temperature T_{room} under the field.

3. EXPERIMENTAL RESULTS

The behaviour of a number of parameters of the KNNS7–xBT ceramics at different concentrations of the modifying admixture of $BaTiO_3$ is illustrated in Figs 1, 2, and 3. As seen from Fig. 1a, two anomalies are apparent on the temperature curve of the dielectric permittivity $\varepsilon'(T)$: a step and a maximum. The step-like anomaly on the $\varepsilon'(T)$ curve in the compound without BT is known to indicate the range of the structural PT from the orthorhombic to the tetragonal phase ($T_{o\text{-}t}$) at heating the sample [6]. The temperature range of the step-like anomaly in ostensibly pure KNNS7 extends over 380 to 410 K and in the case of KNNS7–0.01BT over 350 to 370 K (Fig. 1a, insert). The maximum on the $\varepsilon'(T)$ curve exhibits the temperature of the ferroelectric PT at $T_C \approx 540$ K. The temperature T_C is about 10 degrees lower compared with the data of [6]; the average temperature of the step-like range on the $\varepsilon'(T)$ curve (regarded as the temperature of the structural PT) dropped by almost 30 degrees. Thus, at the BT concentration of $x = 0.01$ in particular the temperature $T_{o\text{-}t}$ considerably decreases.

The remnant polarization $P_r(T)$ as a function of temperature in the range of $T_{o\text{-}t}$ is presented in Fig. 1b. The data are obtained from polarization loops at frequency 10 Hz and $E \approx 18$ kV/cm (the insert of Fig. 1b illustrates polarization loops under different fields E_{max} at one of the studied temperature points). The step-like anomaly here is also seen as a noticeable reduction of the $P_r(T)$ curve within the range from $T \approx 340$ to $T \approx 370$ K. The

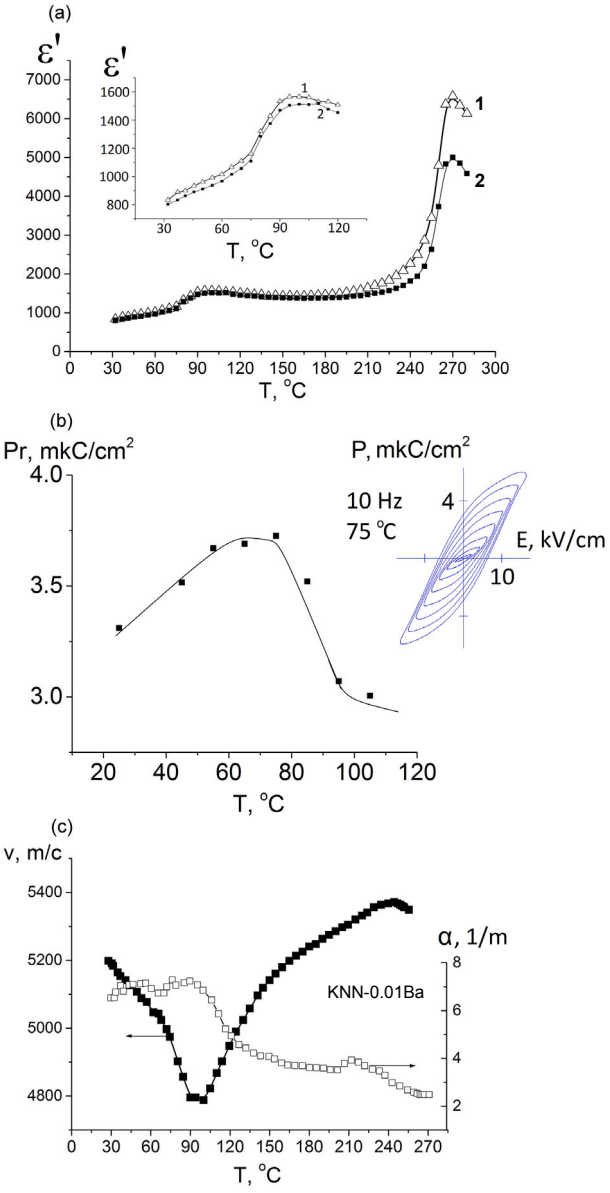

Fig. 1. KNNS7–0.01BT ceramics: (a) dielectric permittivity $\varepsilon'(T)$ under weak fields (**1** – 100 Hz, **2** – 1000 Hz, insert – in the range of $T_{o\text{–}t}$); (b) remnant polarization $P_r(T)$ determined from polarization loops at 10 Hz (insert – polarization loops at different fields E_{max}); (c) velocity $v(T)$ and absorption $\alpha(T)$ of sound.

shape of the loops has a pronounced slope from where it follows that the ratio is small (around 0.5). On the one hand, such behaviour may indicate a considerable coercive field, which is consistent with the polarization data of the compound without BT [6] and a substantial reduction of $P_r(T)$ at $T < 330$ K with the decrease of the temperature. For that reason the maximum values of polarization are not reached at E_{max} used in the present study. On the other hand, in this case the decrease of

polarization may be related to structural inhomogeneity of the material because of the presence of BT.

The behaviour of the velocity $v(T)$ and the coefficient of absorption $\alpha(T)$ of the longitudinal acoustic wave in the range of temperatures including $T_{o\text{-}t}$ and T_C is illustrated in Fig. 1c. The pattern and the magnitude of the $v(T)$ and $\alpha(T)$ curves are rather typical of ceramics [9–11]. The temperature $T \approx 370$ K at the minimum velocity of the acoustic wave determines the temperature of the structural PT. The $v(T)$ curve has a fracture in the range of $T \approx 340$ K where $\alpha(T)$ has a minor additional maximum. Since the domain structure in ferroelectric materials has a substantial effect on the elastic properties, the observed fracture might be related to the change of the domain state of the sample when at heating the PT temperature is being approached. It is in good agreement with the behaviour of $P_r(T)$ at $T \approx 340$ K: the drop of the magnitude of P_r (Fig. 1b).

The behaviour of the parameters in compounds of higher contents of $BaTiO_3$ (Fig. 2 and Fig. 3) allows of the following conclusion: in KNNS7–0.02BT T_C continues shifting to lower temperatures ($T_C \approx 500$ K), approximately by 40–45 degrees with regard to KNNS7–0.01BT. The range of the structural PT is also reduced from $T \approx 340$ K to $T \approx 370$ K while broadening of the ferroelectric and structural PTs is increased. A 'tail' of $\varepsilon'(T)$ at lower temperatures in KNNS7–0.02BT appears at a frequency of 100 Hz (Fig. 2a), which is most likely related to the growth of the contribution to conductivity with the increasing content of BT. The value of $\varepsilon'(T)$ is elevated in the whole range of temperatures studied. However, the dispersion of ε' (the difference of its values at 1000 and 100 Hz) in KNNS7–0.02BT is distributed over the whole range of temperatures whereas in the KNNS7–0.01BT compound the dispersion of $\varepsilon'(T)$ is pronounced only around T_C.

The behaviour of the dielectric response in KNNS7–0.02BT at weak fields is in good agreement with the data on polarization (Fig. 2b). The magnitude of the remnant polarization at the same E_{max} substantially increases (almost three times at room temperature) compared to KNNS7–0.01BT. The same follows from the shape of polarization loops (Fig. 2b, insert), showing that the ratio P_r/P_{max} also increases (~0.6). The features of polarization switching in the compound point to the formation of a more homogeneous polarization under the applied field and to a stable domain state emerging in the material. As seen from Fig. 2b, the range of temperatures of dropping $P_r(T)$ or the step on the $P_r(T)$ curve around $T_{o\text{-}t}$ extends from $T \approx 320$ K to $T \approx 350$ K.

The presence of homogeneous polarization in the KNNS7–0.02BT compound is also displayed by the

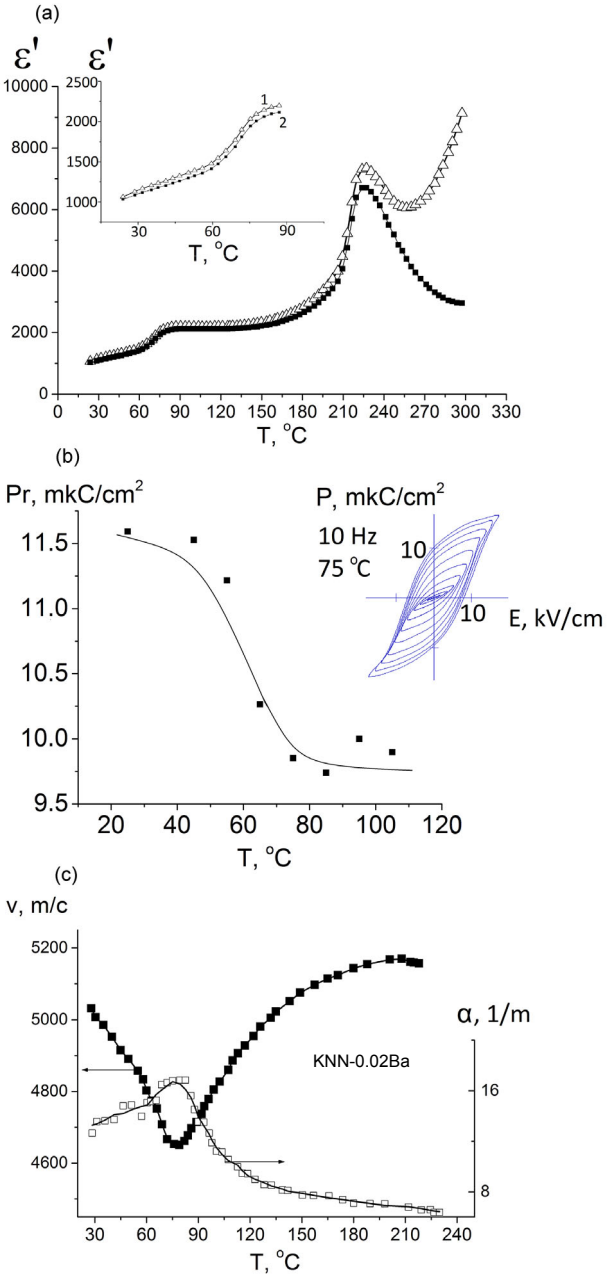

Fig. 2. KNNS7–0.02BT ceramics: (a) dielectric permittivity $\varepsilon'(T)$ under weak fields (**1** – 100 Hz, **2** – 1000 Hz, insert – in the range of $T_{o\text{–}t}$); (b) remnant polarization $P_r(T)$ determined from polarization loops at 10 Hz (insert – polarization loops at different fields E_{max}); (c) velocity $v(T)$ and absorption $\alpha(T)$ of sound.

behaviour of the elastic properties. The minimum of $v(T)$ is distinctly observed at $T \approx 350$ K (Fig. 2c), which is the temperature of the maximum of $\alpha(T)$. The fracture on the $v(T)$ curve below $T_{o\text{-}t}$ is located at 330 K. Comparison to the behaviour of the remnant polarization $P_r(T)$ curve (Fig. 2b) on which the step starts around $T \approx 320$ K suggests that it is related to the change of the

domain structure approaching the PT temperature as in the case of KNNS7–0.01BT.

Substantial differences in the behaviour of the presented parameters are observed in KNNS7–0.04BT (Fig. 3). The high-temperature 'tail' of $\varepsilon'(T)$ at a frequency of 100 Hz practically levels the maximum at

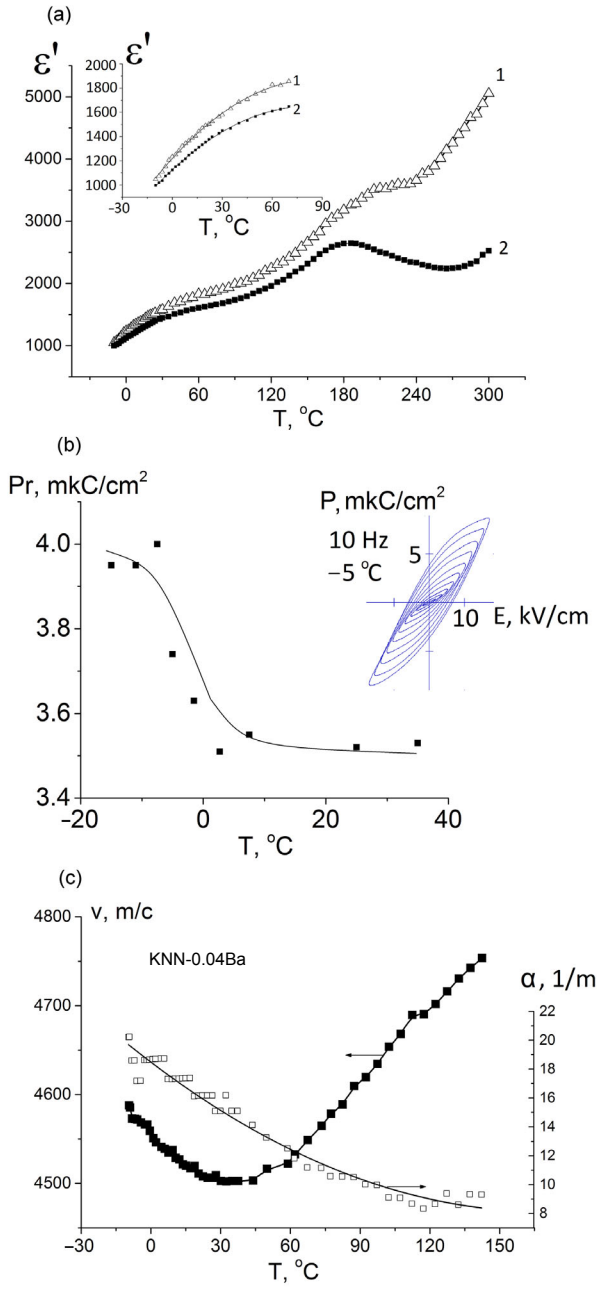

Fig. 3. KNNS7–0.04BT ceramics: (a) dielectric permittivity $\varepsilon'(T)$ under weak fields (**1** – 100 Hz, **2** – 1000 Hz, insert – in the range of T_{o-t}); (b) remnant polarization $P_r(T)$ determined from polarization loops at 10 Hz (insert – polarization loops at different fields E_{max}); (c) velocity $v(T)$ and absorption $\alpha(T)$ of sound.

the ferroelectric PT (Fig. 3a), indicating a considerable contribution of conductivity. The dielectric permittivity at 1000 Hz reveals a strongly broadened maximum of $\varepsilon'(T)$ at 450 K – a further decrease of the mean temperature of the PT by about 45–50 degrees compared with the KNNS7–0.02BT compound. The low-frequency dispersion of ε' here is increased over the whole range of temperatures including the low-temperature bounds (Fig. 3a, insert). Instead of a step on the $\varepsilon'(T)$ curve at the structural PT observed in compounds of smaller BT concentrations here the anomaly appears as a smooth bent around 295 K, which might suggest the end of PT beginning at $T \approx 260$ K or even a lower temperature. Most likely the reason of the strongly broadened PTs in KNNS7–0.04BT is a considerable heterogeneity of the material as evidenced by the behaviour of polarization (Fig. 3b). In the given case a noticeable decline of $P_r(T)$ begins at $T \approx 260$ K and continues within a relatively wide range of temperatures (approximately up to 50 degrees). The polarization loops at $T \approx 270$ K presented in the insert of Fig. 3b have a glass-like shape as in disordered ferroelectric relaxors [12,13], which means it does not saturate at increasing the applied field E_{max}.

The conclusion about a substantial heterogeneity of the KNNS7–0.04BT compound is consistent with $v(T)$ and $\alpha(T)$ presented in Fig. 3c, from where it follows that the velocity of the acoustic wave is lower compared with other compounds while its minimum is practically like a plateau extending from 300 to 320 K. The absorption curve $\alpha(T)$ of relatively higher α values is monotonously declining over the whole range of temperatures. Such substantial broadening of the anomalies is observed in ferroelectric relaxors [9–11].

4. CONCLUSIONS

The study of the effects of $BaTiO_3$ admixtures on the properties of the KNNS7 ferroelectric ceramics revealed the following:

- The growth of the BT content broadens and shifts to lower temperatures the low-frequency maximum of $\varepsilon'(T)$ corresponding to the ferroelectric PT by ~10 degrees at $x = 0.01$, by ~55 degrees at $x = 0.02$, and by ~100 degrees at $x = 0.04$.
- The mean temperature T_{o-t} of the step-like anomaly on the $\varepsilon'(T)$ curve determining the structural PT decreases with the growth of BT content by ~30 degrees at $x = 0.01$, by ~40 degrees at $x = 0.02$, and by ~120 degrees at $x = 0.04$.
- The growth of the BT content increases the conductivity of the material.

- The range of temperatures of a noticeable decrease of the remnant polarization $P_r(T)$ around $T_{o\text{-}t}$ substantially extends with the growth of the BT content the pattern of polarization loops transforming them to the shape characteristic of ferroelectric relaxors.
- In polarized KNNS7 samples containing BT an anomaly displayed at heating by a minimum of the acoustic wave velocity $v(T)$ distinctly indicates the temperature $T_{o\text{-}t}$ of the structural PT in the KNNS7–0.01BT compound $T_{o\text{-}t} \approx 370$ K, in KNNS7–0.02BT $T_{o\text{-}t} \approx 350$ K, and in the KNNS7–0.04BT compound the $v(T)$ minimum is substantially broadened to a plateau ranging from 300 to 320 K indicating a substantial heterogeneity of the material's structure at BT content of $x = 0.04$.
- It can be deduced that the most favourable polarization and elastic properties are exhibited by the compound of $x = 0.02$.

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Baariumiga modifitseeritud pliivaba KNN-keraamika polarisatsioon ja akustilised omadused

Karlis Bormanis, Anver I. Burkhanov, Andris Sternberg, Aleksandr V. Zhirkov, Maija Antonova, Anna Kalvane ja Reinis Ignatans

Tahkefaasi sünteesi abil saadud $(1\text{-}x)(K_{0,5}Na_{0,5})(Nb_{0,93}Sb_{0,07})O_3$–$x$BaTiO$_3$ + 0,5mol%MnO_2 (x = 0,01, 0,02 ja 0,04 (KNNS7–xBT)) proovides uuriti suures temperatuuri vahemikus polarisatsiooni vaheldumist. Kirjeldati nende materjalide dielektrilise mittelineaarsuse ja ferroelektriliste ning struktuursete faasiüleminekute omadusi. Erineva lisandite sisaldusega KNNS7–xBT keraamikates võrreldi dielektrilise koste ja elastsete omaduste käitumist.

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