Physics of the Solid State, 2022, Vol. 64, No. 13

06,04

# Features of polarization of piezoelectric ceramics based on sodium niobate

© O.V. Malyshkina[1], M. Ali[1], A.I. Ivanova[1], I.A. Chernyshova[2], D.V. Mamaev[1]

[1] Tver State University,
Tver, Russia
[2] St. Petersburg State University,
St. Petersburg, Russia
E-mail: Olga.Malyshkina@mail.ru

*Received July 3, 2021*
*Revised July 3, 2021*
*Accepted July 7, 2021*

Comparative studies of the pyroelectric properties and structural features of sodium niobate and sodium-potassium niobate ceramics obtained under different technological conditions for the synthesis of sodium niobate have been carried out. X-ray phase analysis revealed the existence of an additional phase with the chemical formula $NaNb_{10}O_{18}$ in sodium niobate ceramic samples that do not exhibit ferroelectric properties. It is shown that the temperature conditions for the synthesis of the sodium niobate material determine the nature of the macroscopic polarization of the samples of both pure sodium niobate and sodium-potassium niobate.

**Keywords:** piezoelectric ceramics, lead-free materials, polarization, pyroelectric effect.

DOI: 10.21883/PSS.2022.13.52317.159

## 1. Introduction

Studies of ferroelectric ceramics based on sodium niobate (NN) began at the same time [1], when the studies of lead-containing materials [2,3]. The latter have found industrial application due to high values of piezoelectric moduli and other dielectric characteristics. The introduction of restrictions on the use of lead-containing materials, documented in the legislation of the European Union (Directiv 2002/95/EC) and in the technical regulation of the Eurasian Economic Union „On the restriction of the use of hazardous substances in electrical and radio-electronic products“ (TR EAEU 037/2016) forced to return at the beginning of the XXI century to the search for modified compositions based on lead-free ceramics, including those based on sodium niobate [4–8]. Since modified compositions of lead zirconate titanate have a main industrial application [9], a new stage in the study of lead-free piezoelectric ceramics resulted in extensive studies of the influence of alkali and rare earth metals modifiers and in the construction of multicomponent systems based on sodium-potassium niobate (KNN) [10]. The KNN system was chosen primarily due to a number of optimistic publications [11,12], and the possibility of constructing for it a phase diagram [13]. At the same time, the most effective ceramics based on KNN were obtained in the area of polymorphic transition between tetragonal and orthorhombic phases, that results in the appearance of phase transition fatigue effect even with insignificant heating of the ceramics, and significantly limits the range of possible practical applications [14,15]. Other solid solutions based on sodium niobate ceramics [1,11,13] are being pretty widely studied. Not a modified sodium niobate, though it has been studied for quite a long time [1,16], continues to be an interesting study subject. This is due to the large number of heterogeneous phase transitions of this ceramics [16–19] in the temperature range 360−640°C, that allows to influence its properties by varying fusion temperature of this material within insignificant limits. In fact, as we have shown earlier [20], a change in fusion temperature of sodium niobate composition, even without adding modifying additives, results in a significant change of final samples properties. They can exist at room temperature in a stable ferroelectric phase, when, according to the literature, a sodium niobate crystal is a model antiferroelectric [21].

The purpose of this study was to determine structural mechanisms of the appearance of antiferroelectric phase in sodium niobate ceramics and to study the uniformity of the polarized state of NN and KNN ceramics samples. The latter is relevant not only scientifically, but also practically, since the uniformity of macroscopic polarization is basic for the use of piezoelectric ceramics.

## 2. Methods of obtaining and studies

Samples of sodium niobate and sodium-potassium niobate ceramics were obtained by solid-phase synthesis method and studied on the equipment of the Research Equipment Sharing Center of Tver State University.

Solid-phase synthesis of $NaNbO_3$ material to obtain NN ceramics was carried out in three different ways: single synthesis at a temperature ($T_{\text{synth}}$) 650°C (NN650) or 700°C (NN700); double synthesis both at $T_{\text{synth}} = 700$°C (NN700-700) and the first at $T_{\text{synth}} = 650$°C, the second at $T_{\text{synth}} = 700^\circ$C (NN650-700). For KNN ceramics, the $KNbO_3$ material was synthesized by double synthesis (the first at $T_{\text{synth}} = 650^\circ$C, the second at $T_{\text{synth}} = 700^\circ$C). $NaNbO_3$ is also using double synthesis, but at different synthesis temperatures: I batch: both temperatures 700°C (KNN1), II batch: the first synthesis at $T_{\text{synth}} = 650^\circ$C, the second at $T_{\text{synth}} = 700^\circ$C (KNN2).

The samples were pressed in the form of tablets with a diameter of 10.4 mm and a thickness of 1–2 mm under 5 atmosphere pressure. The samples were sintered at a temperature of 1100°C for 4 h.

The structure and elemental composition were investigated by scanning electron microscopy (SEM) using JEOL JSM-6610LV microscope (Japan). To determine the grain structure, the secondary electron mode (SEI) was used, with an accelerating voltage 10–14 kV, shown at the bottom of the image, the scale mark is also working distance 11 mm, probe current 5 pA. The investigation with the help of reflected (BEC) electrons allowed to specify the compositional (in terms of elemental composition) contrast. The analysis of the elemental composition was carried out in an analytical complex of a scanning electron microscope using an INCA Energy + spectrometer with an energy dispersion of X-ray quanta (Oxford Instruments, Great Britain). Oxford INCA Energy 350 energy dispersive X-ray microanalysis system allows the determine mass and atomic fractions (concentration) of chemical elements in samples.

The phase composition was determined by X-ray powder diffraction method on DRON-7 diffractometer, radiation Cu–K$\alpha$. The obtained X-ray images were interpreted on the basis of the Science Park of St. Petersburg State University (RC XRDRS) in the software packages PDXL and TOPAS version 5.0.

The presence and direction of spontaneous polarization in the samples were determined by the dynamic pyroelectric effect method [22].

## 3. Experimental findings and their discussion

X-ray phase analysis of NN samples showed the existence of two phases in these samples (Fig. 1).

The main phase — $NaNbO_3$ corresponds to the lueshite mineral, which has a structure similar to perofskite [23,24]. The lueshite structure can be presented as a framework of octahedrons [$NbO_6$], which cavities include Na atoms [25].

Additional phase — $NaNb_{10}O_{18}$. The existence of $NaNb_{10}O_{18}$ phase and its crystallographic characteristics were considered by the authors for the first time [26]. The niobium valence in this chemical formula is 3.5+. This valence, most likely, means that the structural unit contains two or more (an even number) formula units, in which the valence of Nb atoms alternates (3+ and 4+). Possible oxidation states of Nb (5, 4, 3, 2 and 1) allow such a valence.

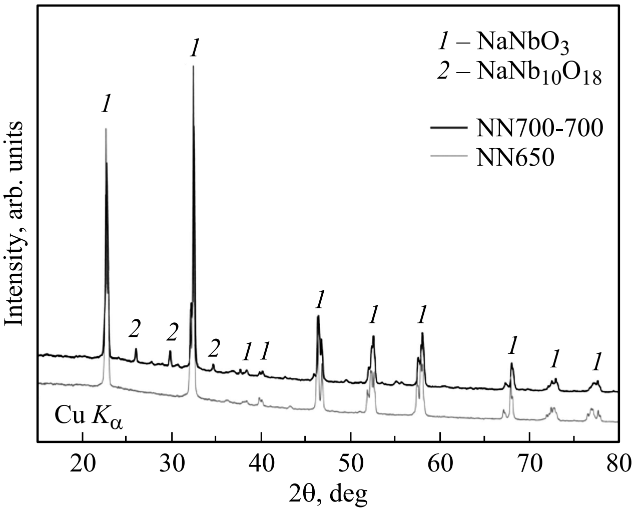

**Figure 1.** X-ray image of NN650 and NN700-700 samples.

The presence of an additional phase depends on the NN material synthesis conditions. So, the samples with a single synthesis (NN650 and NN700) has no additional phase. And NN700-700 sample includes about 10%. The increase of sintering temperature up to 1400°C did not change the percentage of the additional phase.

Studies of the grain structure and ferroelectric properties have shown their significant dependence on the presence of the additional phase in the NN material. For example, the grain of samples without an additional phase (Fig. 2, *a, b*) is by an order larger than of the samples with 10% content (Fig. 2, *c*).

In the course of analyzing the elemental composition, we obtained and processed the spectra recorded on the samples surface in different grains. If the samples NN650 and NN700 show insignificant scatter of the content of Na, Nb and O elements over the grains, then in the material NN700-700 a number of grains contain a significantly lower Na amount. The content (in molar percent) of elements for

**Table 1.** Content of elements in NN materials, molar %

| Parameter | O | Na | Nb |
|---|---|---|---|
| *Chem. formula* $NaNbO_3$ | 60 | 20 | 20 |
| NN650, NN700 | | | |
| Average in experiment | 61 | 18 | 21 |
| NN650-700 | | | |
| Average in experiment | 63 | 17 | 20 |
| NN700-700 | | | |
| Average in experiment 1 | 62 | 18 | 20 |
| Average in experiment 2 | 72 | 9 | 19 |
| *Chem. formula* $NaNb_{10}O_{18}$ | 62 | 3.5 | 34.5 |

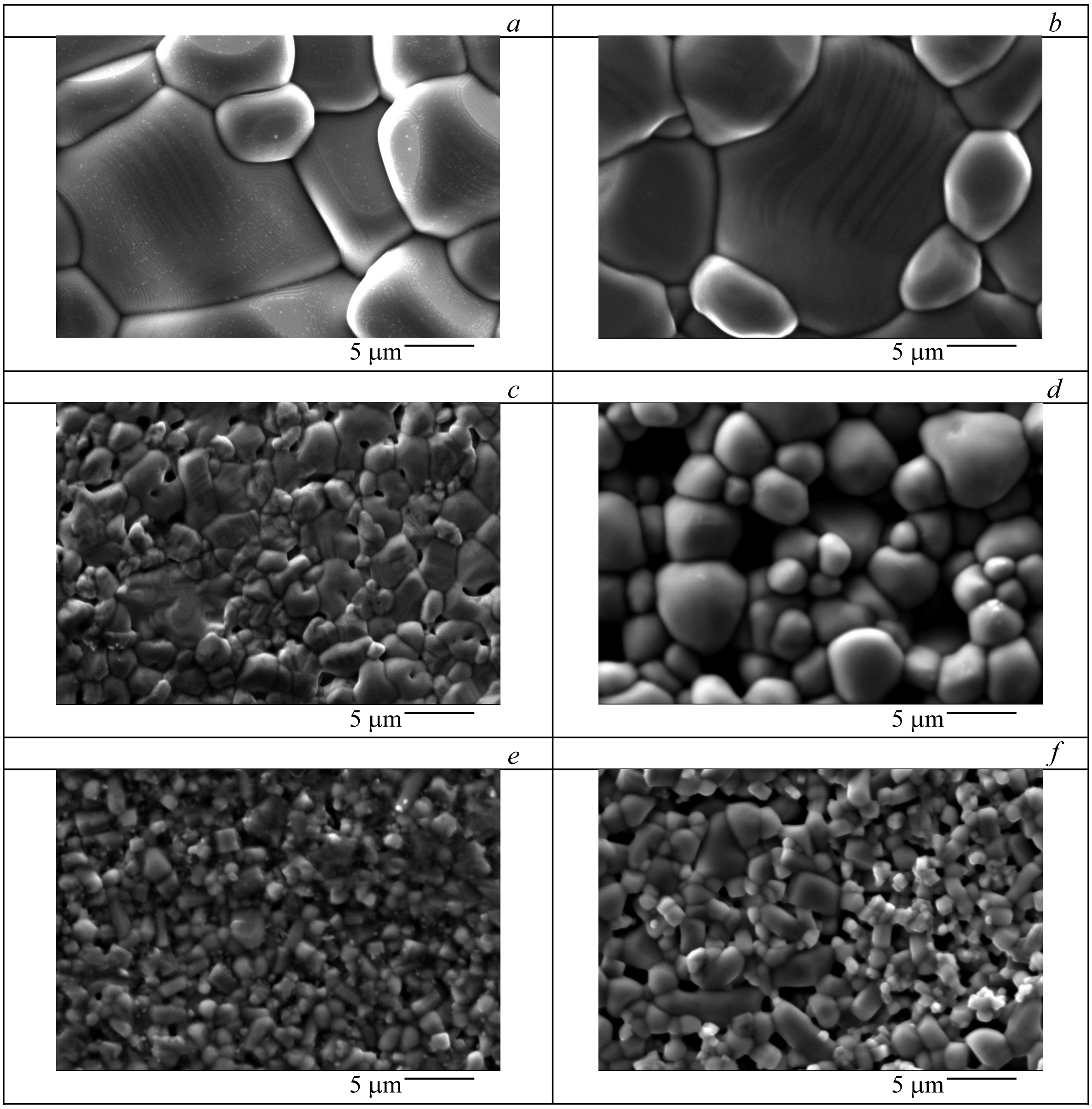

**Figure 2.** SEM-images of the surfaces of samples NN650 (*a*), NN700 (*b*), NN700-700 (*c*), NN650-700 (*d*), KNN1 (*e*) and KNN2 (*f*). Scale bar 5 $\mu$m.

materials NN, calculated by the chemical formula and the average value obtained in the course of the experiment are given in Table 1. In ceramics NN650, NN700, NN650-700 and in most grains of ceramics NN700-700 the content of Na, Nb and O elements differs insignificantly from the chemical formula $NaNbO_3$, there is only a slight decrease in the number of sodium atoms in comparison with niobium atoms and increased oxygen content. At the same time, in grains with a reduced Na content (material NN700-700) the ratio O : Na : Nb does not correspond to the chemical formulas $NaNb_{10}O_{18}$ and $NaNbO_3$, therefore both phases are present in these grains.

Thus, the performed structural studies showed that the presence of switchable electric polarization in the samples of ceramics NN650 and NN700, and its absence in ceramics NN700-700, which was shown by us earlier [20], is due to the absence (presence) of $NaNb_{10}O_{18}$ phase in the structure of the samples.

Since the majority of practical applications of ferroelectric ceramics as piezoacoustic transducers are based on longitudinal or transverse oscillations in alternating electric fields, their implementation requires working bodies with uniform polarization over the sample thickness. To analyze the state of polarization in the samples, we have used dynamic pyroelectric effect method [22], that allows to determine not only the presence of spontaneous polarization, but also its direction in the sample. Prior measuring the pyrocurrent, the samples were poled in a DC electric field of 1.5 kV/mm.

**Table 2.** Dependence of the pyrocurrent of the ceramics based on NN on the synthesis conditions

| Synthesis conditions $NaNbO_3$ | Pyrocurrent, $10^{-10}$ A | |
|---|---|---|
| | Side $-P_s$ | Side $+P_s$ |
| NN | | |
| 1 synthesis 650°C | 0.7 | 0.56 |
| 1 synthesis 700°C | 0.4 | 0.16 |
| 2 synthesis 700°C 700°C | 5.2 | 0.48 |
| 2 synthesis 650°C 700°C | 0.52 | 0.52 |
| KNN | | |
| 2 synthesis 650°C 700°C | 0.64 | 0.64 |
| 2 synthesis 700°C 700°C | 2.12 | 0.14 |

As a source of heat current a 60 mW IR laser was used. The measurements were made on the sides of the samples corresponding to the positive ($+P_s$) and negative ($-P_s$) ends of the spontaneous polarization vector (Table 2).

Although ceramic samples NN650 and NN700, according to [20], have macroscopic polarization, fixed by the dielectric hysteresis loop, the distribution of polarization over the thickness of the samples poled in a DC electric field is nonuniform. These samples, like NN700-700 ones, have a polarization gradient directed from the side $-P_s$ to the side $+P_s$. And for the sample NN700-700 both the gradient value and pyrocurrent value on the side $-P_s$ significantly exceed the similar values observed for samples NN650 and NN700. Since the type of dielectric hysteresis loops of NN700-700 ceramics allows the presence of an antiferroelectric state [20] in the sample, it can be assumed that it is this state that contributes to such an uneven redistribution of the space charge inducing additional polarization inside the sample.

Since KNN ceramics is considered as an alternative substitute for PZT material, the polarization uniformity was also checked on polarized samples of this material. The KNN700-700 material has a polarization gradient similar to the composition of NN700-700 (Table 2). This means that exactly the technological process of synthesizing sodium niobate material is the reason for the presence of a polarization gradient in the final samples.

It is interesting to note that a uniform polarization distribution over the thickness of the samples (Table 2) was obtained in the samples of ceramics NN650-700 and KNN2; i.e. in those compositions, for which sodium niobate material was synthesized using the same double synthesis technology with temperatures 650°C first synthesis and 700°C second synthesis.

In comparison with the structure of industrial PZT ceramics [27,28], the grain size of samples NN650-700 and KNN2 (Fig. 2, *d* and *f*) is maximum close to the structure observed in PZT samples.

## 4. Conclusion

The studies carried out have shown that by varying the temperature mode of sodium niobate material synthesis, one can significantly influence the ferroelectric properties of ceramics based on this material. So, although the natural polycrystalline material NN (leushite) has antiferroelectric properties [24], we managed to synthesize NN ceramics, which have ferroelectric properties at room temperature.

In the course of studies, we have found that a single synthesis, on the one hand, allows to obtain NN ceramics with clearly observable ferroelectric properties, both at the micro and macroscopic levels. On the other hand, we could not obtain uniform polarization in a DC electric field for these samples. Perhaps, in this case, the large grain size (up to 20 $\mu$m) has a negative effect. It should be noted here that the grain size of industrial PZT ceramics samples does not exceed 5–6 $\mu$m. Exactly the same grain size was observed in this study for samples NN650-700 and KNN2, in which we could obtain a uniform polarization distribution over the thickness, that is evidenced by the same value of pyroresponse observed on opposite sample sides.

At the same time, the materials with a sufficiently large polarization gradient (NN700-700 and KNN1), after clarifying the physical reasons for the manifestation of such a gradient, can find practical application in piezoelectric sensors with bending oscillations, in which specially designed bimorphs are currently used.

### Conflict of interest

The authors declare that they have no conflict of interest.

## References

[1] L. Egerton, D.M. Dillon. J. Am. Ceram. Soc. **42**, *9*, 438 (1959).
[2] G.A. Smolensky. ZhTF (in Russian) **20**, *2*, 137 (1950).
[3] G.A. Smolensky. Usp. fiz. Nauk (in Russian) **62**, *1*, 41 (1957).
[4] B. Malic, A. Bencan, T. Rojac, M. Kosec. Acta Chim. Slov. **55**, *4*, 719 (2008).
[5] V.I. Ivanenko, E.P. Lokshin, O.G. Gromov, V.T. Kalinnikov. Sintez segnetoelektricheskih i lyuminescentnyh slozhnyh oksidov redkih elementov. Izd-vo Kol'skogo nauchnogo centra RAN, Apatity (in Russian) (2009). 153 p.
[6] L.A. Reznichenko, I.A. Verbenko, K.P. Andryushin. Fazovye perekhody, uporyadochennye sostoyaniya i novye materialy (in Russian) **11**, 30 (2013).
[7] J. Wu, D. Xiao, J. Zhu. Chem. Rev. **115**, *7*, 2559 (2015).
[8] J. Rodel, K.G. Webber, R. Dittmer, W. Jo, M. Kimura, D. Damjanovic. J. Eur. Ceram. Soc. **35**, 1659 (2015).
[9] Materialy p'ezokeramicheskie OST II 0444-87. (in Russian) Date of introduction since 01.01.1988.
[10] Sh. Zhang, R. Xia, Th.R. Shrout. J. Electroceram. **19**, 251 (2007).
[11] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura. Nature **432**, *7013*, 84 (2004). doi: 10.1038/nature03028.
[12] L.E. Cross. Nature **432**, *7013*, 24 (2004).

[13] B. Malic, J. Koruza, J. Hrescak, J. Bernard, K. Wang, J. Fisher, A. Bencan. Materials **8**, 811 (2015).

[14] E. Hollenstein, D. Damjanovic, N. Setter. J. Eur. Ceram. Soc. **27**, *13–15*, 4093 (2007).

[15] K. Higashide, K.-I. Kakimoto, H. Ohsato. J. Eur. Ceram. Soc. **27**, *13–15*, 4107 (2007).

[16] H.D. Megaw. Ferroelectrics **7**, *1–4*, 87 (1974).

[17] Yu.I. Yuzyuk, P. Simon, E. Gagarina, L. Hennet, D. Thiaudiere, V.I. Torgashev, S.I. Raevskaya, I.P. Raevskii, L.A. Reznitchenko, J.L. Sauvajol. J. Phys: Condens. Matter. **17**, *33*, 4977 (2005).

[18] V.S. Bondarev, A.V. Kartashev, M.V. Gorev, I.N. Flyorov, M.S. Molokeev, S.I. Raevskaya, D.V. Suzdalev, I.P. Raevsky. FTT (in Russian) **55**, *4*, 752 (2013).

[19] N.N. Kraynik. Izv.AN SSSR. Ser. fiz. (in Russian) **28**, *4*, 643 (1964).

[20] O.V. Malyshkina, M. Ali, E.V. Barabanova, A.I. Ivanova. Ferroelectrics **567**, *1*, 197 (2020).

[21] P. Vousden. Acta Cryst. **4**, **6**, 545 (1951).

[22] V.A. Golovnin, I.A. Kaplunov, O.V. Malyshkina, B.B. Ped'ko, A.A. Movchikova. Fizicheskie osnovy, metody issledovaniya i prakticheskoe primenenie p'ezomaterialov. Tekhnosfera, M. (2013). 272 p. (in Russian)

[23] A.C. Sakowski-Cowley, K. Łukaszewicz, H.D. Megaw. Acta Cryst. B **25**, 851 (1969).

[24] R.H. Mitchell, B.J. Kennedy K.S. Knight. Phys. Chem. Minerals **45**, 77 (2018).

[25] D.O. Mischuk, O.I. V'yunov, O.V. Ovchar, A.G. Belous. Neorgan. Materialy (in Russian) **40**, *12*, 1508 (2004).

[26] J. Kohler, A. Simon. Z. Anorg. Chem. **572**, 7 (1989).

[27] S.I. Pugachev, I.A. Embil', O.V. Malyshkina, A.A. Topchiyov. Morskie intellektual'nye tekhnologii (in Russian) **2**, *2(24)*, 60 (2014).

[28] O.V. Malyshkina, A.Yu. Eliseev, V.A. Golovin, A.V. Dayneko, A.I. Ivanova, E.V. Barabanova. Poverkhnost'. Rentgenovskie, sinhrotronnye i nejtronnye issledovaniya (in Russian) **9**, 40 (2015).