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Synthesis of potassium-sodium niobate powder in water vapor for piezoelectric ceramics manufacturing

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In this work, for the first time, single-phase potassium-sodium niobate powder with a primary particle size of $0.3-3.1\,\mu$m was synthesized in a water vapor medium at a temperature of 260°C and a pressure of 4.69 MPa. Two different techniques, the traditional one and laser stereolithography, were applied to produce powder-based ceramics with a density reaching 80−85% of the theoretical value. A set of the most important piezoelectric characteristics was studied for the prepared ceramics. The obtained preliminary results indicated the prospect of improving the phase, structural, and piezoelectric properties of potassium-sodium niobate ceramics by controlling the parameters of powder synthesis in water vapor and enhancement of the sintering conditions.

Keywords: piezoelectric ceramics, complex oxide synthesis, potassium-sodium niobite, laser stereolithography.

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Ceramic materials based on potassium-sodium niobate ($K_{0.5}Na_{0.5}NbO_3$, KNN) are regarded as the most viable lead-free alternative to widely used, but toxic lead zirconate titanate ($Pb(Zr,Ti)O_3$, PZT) [1]. A high Curie point and temperature stability of piezoelectric parameters are the advantages of KNN over the other possible PZT substitutes [2]. The problems arising in sintering (narrow sintering range, difference between the diffusion coefficients of K^+ and Na^+, and volatility of these ions at high temperature [3]) act as an important limiting factor for the substitution of PZT ceramics with KNN on a large scale. These issues lead to the formation of secondary phases and nonuniform grain growth and exert a profound negative effect on the piezoelectric properties of the obtained material [2]. It is a crucial point for the KNN ceramics technology to shift the sintering range toward lower temperatures. The development of novel approaches to synthesis of sintering-active KNN powder is one of the ways to solve this problem [4]. It has been demonstrated earlier that subcritical water vapor and supercritical water fluid are efficient media for synthesis of simple and complex oxides (base materials for the production of ceramics) [5]. Specifically, $BaTiO_3$ synthesized under such conditions was superior in its phase and morphological characteristics to a similar powder prepared by solid-phase synthesis [6]. $BaTiO_3$ and $MgAl_2O_4$ powders had a distinctly low water content compared to the products of hydrothermal solution synthesis [7,8]. The mentioned features of synthesized powders contribute to an increase in the density of ceramic materials (piezoelectric ceramics included [9]). The aim of the present study is to estimate the feasibility of application of synthesis in water vapor to KNN powder for subsequent production of piezoelectric ceramics. In addition to the traditional molding method, we used laser stereolithography apparatus (SLA) that is regarded as a promising technique for fabrication of products of an intricate shape, but still remains poorly explored in relation to KNN ceramics [10,11].

KNN powder was synthesized in laboratory stainless-steel autoclaves with a volume of 200 ml. A reagent mixture with a mass of 134.724 g (the mole ratios of KOH, NaOH, and Nb_2O_5 used to prepare it were as follows: KOH/NaOH = 5, $NaOH/Nb_2O_5 = 1.1$) was treated in water vapor at a temperature of 260°C and under an equilibrium pressure of 4.69 MPa for 24 h. An excess amount of alkalies in the mixture is needed to sustain the process at the end stage and ensure that Nb_2O_5 is processed fully. The excess of potassium ions over sodium ions is due to the difference in their mobilities under hydrothermal conditions. The obtained product was rinsed with distilled

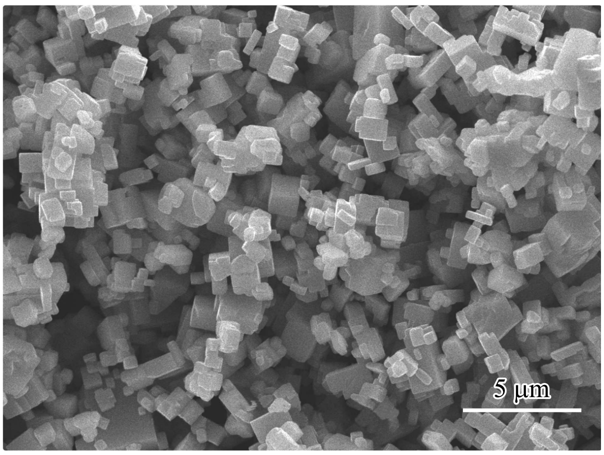

Figure 1. Morphology of the synthesized KNN powder.

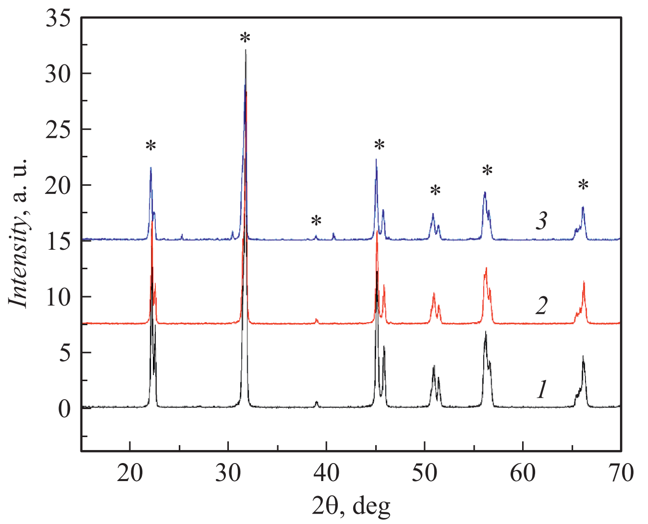

Figure 2. Diffraction patterns of samples of synthesized powder (*1*) and KNN ceramics produced following the traditional process (*2*) and with the use of SLA (*3*). Asterisks denote reflections corresponding to orthorhombic phase $K_{0.5}Na_{0.5}NbO_3$.

water to remove excess alkalies and dried in air at 70°C for 12 h. The traditional ceramic processing technology involved preparing mold powder with 5 wt.% of paraffin and uniaxial pressing under 100 MPa. Polymer-ceramic pastes based on di- and triacrylate monomers and KNN powder with a filling of 52.45−52.47 vol.% were prepared for SLA ceramic processing. Organic binders were removed in air under temperature conditions specified in [12]. The samples were sintered in air at a temperature of 1100°C for 1 h.

Particles of the synthesized powder have a prismatic shape, which is typical of KNN, and range in size from 300 nm to 3.1 μm (Fig. 1). The positions of major reflections in the diffraction patterns of the powder and the ceramic material (Fig. 2) correspond to orthorhombic modification $K_{0.5}Na_{0.5}NbO_3$ (#2300499, Crystallography Open Database [13]). In addition to these reflections, the pattern for the SLA ceramic material features weak reflections of secondary phases, which may be associated with the formation of polyniobates in the process of sintering due to the fact that K^+ and Na^+ have high and significantly different volatility values [2].

The mechanical compaction of powder in the course of uniaxial pressing facilitates contact between powder particles and is conducive to microstress on their surface. In SLA processing, interparticle contacts form primarily at the debinding stage. The local packing of particles is almost loose. Under equal sintering conditions, the average grain size in samples subjected to pressing (2.6 μm) is higher than the corresponding size in samples after SLA (1.9 μm; see Fig. 3). Compared to pressed KNN ceramics (Figs. 3, *a*, *b*), SLA samples are less uniform, which is manifested in the presence of alternating regions with different degrees of packing and the formation of large pores up to several tens of micrometers in size (Figs. 3, *c*, *d*). Pressed samples have somewhat higher values of the relative density (80% on average), which was measured by the kerosene saturation method, than SLA samples (77% on average; see the table).

The results of measurements of piezoelectric parameters of KNN ceramic samples are listed in the table. The molding method has no significant influence on the studied characteristics. Under similar material density values, the piezoelectric parameters of samples obtained here are comparable to the data from other studies. Low dielectric losses of ceramics produced in the traditional way (samples

Properties of KNN ceramics produced following the traditional process and with the use of laser stereolithography

Method technique	description designation/source	T_{sint}, °C	ρ_{rel}, %	ε	tg δ	R, MΩ	d_{33}, pC/N	d_{31}, pC/N
This study								
Traditional	KNN-T1	1100	78	411	0.358	0.13	48	−29
	KNN-T2		83	206	0.015	0.17	74	−57
	KNN-T3		85	209	0.012	0.19	83	−65
With the use SLA	KNN-A1		80	571	0.404	0.23	60	−48
	KNN-A2		78	246	0.033	0.24	71	−55
	KNN-A3		66	314	0.042	0.23	64	−45
Data from other studies								
Traditional	[4]	970	79	197	0.04	–	86	–
		1000	81	205	0.04	–	113	–
		1030	86	206	0.05	–	114	–
		1060	88	362	0.05	–	119	–
		1090	89	130	0.09	–	46	–
	[14]	1070	91	310	0.03	–	75	–
	[15]	1100	91	199	0.03	–	85	–
	[16]	1130	81	434	0.062	–	–	–

Note. T_{sint} is the sintering temperature, ρ_{rel} is the relative density, ε is the permittivity, tg δ is the dielectric loss tangent, R is the resistance, and d_{33} and d_{31} are piezoelectric moduli.

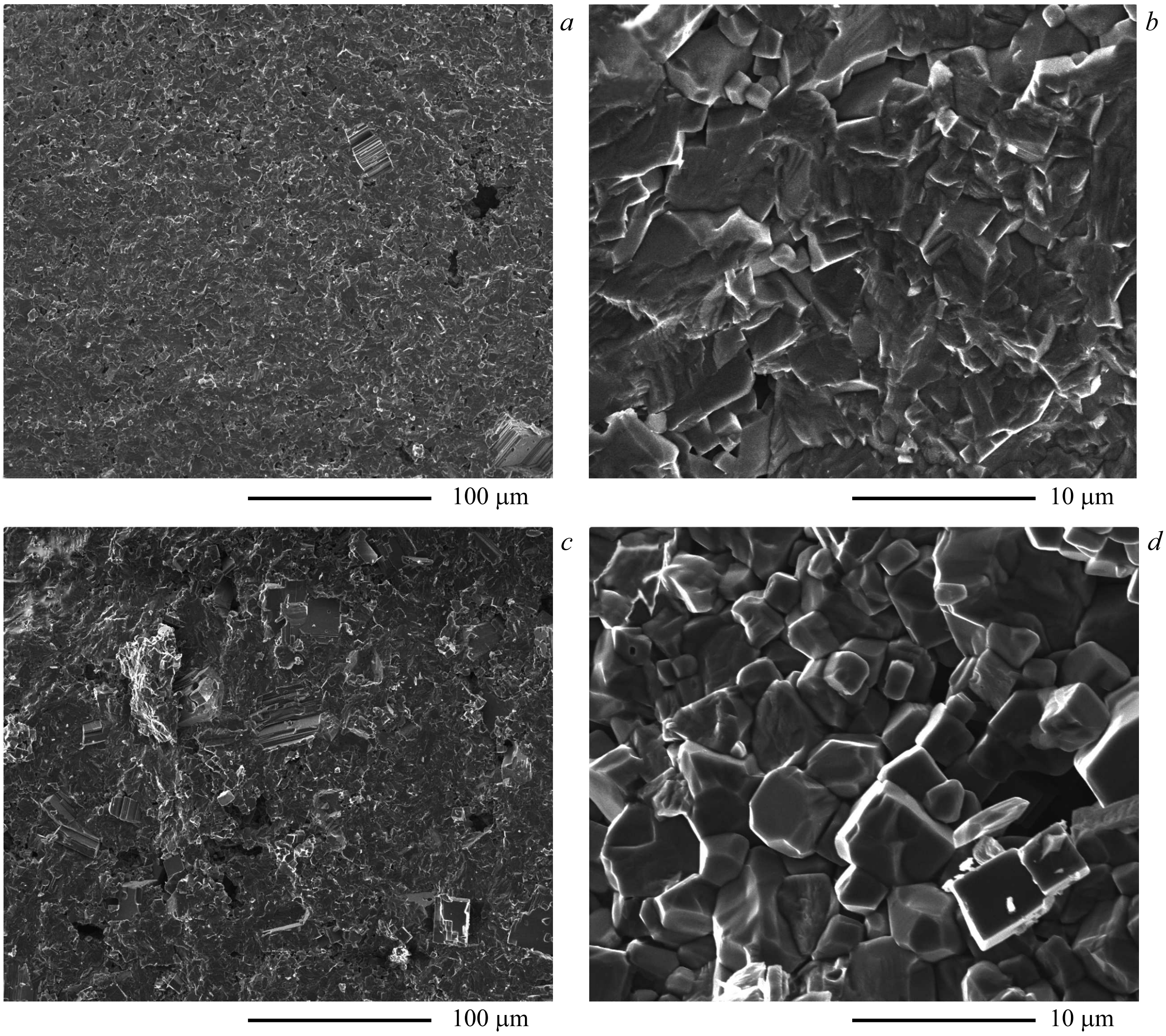

Figure 3. Microstructure of KNN ceramics produced following the traditional process (a, b) and with the use of laser stereolithography (c, d).

KNN-T2 and KNN-T3) and the high permittivity of samples after SLA are worthy of note. The increase in density of KNN ceramics observed at higher sintering temperatures is often accompanied by a d_{33} reduction due to partial evaporation of K^+ and Na^+ ions [4]. The smallness of d_{33} values determined in the present study is likely attributable to the fact that the sintering conditions were more severe than those set in the considered examples from scientific literature. The stoichiometry violation in sintering may be the reason why certain samples (KNN-T1 and KNN-A1) feature elevated dielectric losses.

Ceramic materials with their phase, structural, and piezoelectric parameters being close to the ones known from literature were produced by traditional and additive methods without optimization of processing conditions from KNN powder that has been synthesized in water vapor for the first time. A further refinement of powder morphology via adjustment of the synthesis conditions should help improve the sintering characteristics of powder and reduce the temperature needed for sintering of dense ceramics without any alteration of the initial ratio of ions of alkali metals and with fine piezoelectric parameters.

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Conflict of interest

The authors declare that they have no conflict of interest.

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