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RESEARCH ARTICLE

Chemical and technological aspects of increasing the functional characteristics of hard piezoceramics

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Abstract

Objectives. *Ferroelectrically hard piezoelectric ceramics are in demand for high-power applications in piezotransformers, ultrasonic emitters, and piezo motors, which requires a combination of high piezoelectric characteristics and mechanical quality factors in it. The aim of this research was to reveal the main regularities in the microstructure and functional characteristic formation of ferroelectrically hard piezoceramics based on two widespread chemical systems, $Pb(Zr_xTi_{1-x})O_3$ and $(Na_{1-x}K_x)NbO_3$, through various technological modes of production. In this study, two fundamentally different technological ways of forming a dense microstructure on the example of above systems have been employed to obtain the best set of dielectric, piezoelectric, and mechanical parameters for practical applications. In the case of lead-containing ceramics, various sintering technologies have been used, including conventional ceramic, hot pressing, and spark plasma sintering.*
Methods. *The microstructure of the piezoelectric ceramics was investigated using electron microscopy, and the functional characteristics were assessed in terms of mechanical and piezoelectric properties. The density values were determined by hydrostatic weighing in octane, the relative dielectric permittivity was measured using an LCR meter, and the values of the piezoelectric coefficient and mechanical quality factor were gathered using the resonance–antiresonance method.*
Results. *This research has identified that spark plasma sintering technology makes it possible to obtain high-density samples, which contain a homogeneous microstructure and double the figure-of-merit values, for use in high-power piezoelectric devices that operate at piezoresonance frequencies. It also found that the addition of a small amount of $CuNb_2O_6$ ($x = 0.025$) to lead-free solid solutions leads to the formation of a liquid phase during sintering, thereby creating a compacted microstructure with relative density values (96%) that have practical limitations in conventional ceramic technology. An increase in both the piezoelectric and mechanical properties, which leads to a twofold increase in the values of the quality indicator, was also observed.*
Conclusions. *It is possible to increase, and even to double, the functional characteristics of both lead-containing and lead-free ferroelectrically hard piezoceramics by varying the technology used in the manufacturing process. By using spark plasma sintering technology with lead-containing ceramics, it is possible to reduce the optimum sintering temperature by 200°C and the sintering time by more than 20 times, thus reducing production costs.*

Keywords: *piezoceramics, sintering technology, spark plasma sintering, microstructure, piezoelectric properties, mechanical quality factor, liquid phases, figure-of-merit*

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НАУЧНАЯ СТАТЬЯ

Химико-технологические аспекты повышения функциональных характеристик сегнетожесткой пьезокерамики

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Аннотация

Цели. *Сегнетожесткая пьезоэлектрическая керамика востребована при создании устройств, работающих в силовых режимах: пьезотрансформаторах, ультразвуковых излучателях и пьезодвигателях, что требует сочетания в ней высоких пьезоэлектрических характеристик и механической добротности. В этой работе на примере двух широко распространенных химических систем $Pb(Zr_xTi_{1-x})O_3$ и $(Na_{1-x}K_x)NbO_3$ продемонстрированы принципиально различные химико-технологические пути формирования плотной микроструктуры и достижения наилучших, с точки зрения практических применений, наборов диэлектрических, пьезоэлектрических и механических параметров. В случае свинецсодержащей керамики были использованы различные технологии спекания: обычная керамическая, горячее прессование и искровое плазменное спекание. Для повышения функциональных характеристик бессвинцовой керамики был выбран путь, связанный с добавлением медьсодержащего компонента $CuNb_2O_6$ (x) к исходной системе ниобата натрия-калия. Целью настоящей работы стало выявление основных закономерностей формирования микроструктуры и функциональных характеристик сегнетожесткой керамики на основе систем $Pb(Zr_xTi_{1-x})O_3$ и $(Na_{1-x}K_x)NbO_3$, при вариации технологических режимов их изготовления.*

Материалы. *Микроструктура пьезоэлектрической керамики исследовалась методом электронной микроскопии, а функциональные характеристики оценивались по показателям механических и пьезоэлектрических свойств. Значения плотности определялись методом гидростатического взвешивания в октане, относительная диэлектрическая проницаемость была измерена с помощью LCR-метра, а значения пьезоэлектрического коэффициента и механической добротности установлены на основании резонансно-антирезонансного метода.*

Результаты. *Установлено, что применение технологии искрового плазменного спекания позволяет получить высокоплотные образцы свинецсодержащей керамики с однородной микроструктурой и более чем в два раза возросшими значениями показателя качества (figure-of-merit) для ее использования в устройствах силовой пьезотехники, работающих на частотах пьезорезонанса. Обнаружено, что добавка небольшого количества $CuNb_2O_6$ (x = 0.025) к бессвинцовым твердым растворам приводит к образованию в процессе спекания жидкой фазы, в результате чего формируется уплотненная микроструктура с практически предельными для обычной керамической технологии значениями относительной плотности (96%). Наблюдается возрастание как пьезоэлектрических, так и механических свойств, что приводит к двукратному повышению значений показателя качества.*

Выводы. *Вариация технологических режимов изготовления как свинецсодержащей, так и бессвинцовой сегнетожесткой пьезокерамики позволяет существенно (в два раза) повысить ее функциональные характеристики. Использование метода искрового плазменного спекания при изготовлениии свинецсодержащей керамики способствует сокращению как оптимальной температуры процесса на 200 °С, так и продолжительности изотермической выдержки более чем в 20 раз. Такой прием существенно снижает производственные затраты.*

Ключевые слова: *пьезокерамика, технология спекания, искровое плазменное спекание, микроструктура, пьезоэлектрические свойства, механическая добротность, жидкие фазы, показатель качества*

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INTRODUCTION

In recent decades, ceramics based on the $Pb(Zr_xTi_{1-x})O_3$ (PZT) system have become the most popular piezoelectric materials in industry and technology [1]. Through chemical modification of the PZT system, it has been possible to obtain a large number of solid solutions that demonstrate a variety of physical properties. Depending on the chosen modifier, ceramic solid solutions can have both ferroelectrically soft and hard properties. The former are observed in solid solutions in which the Zr^{4+} and Ti^{4+} ions have been partially replaced by ions with a higher formal valence (e.g., Nb^{5+}, Sb^{5+}, or W^{6+}), while in the latter, they are replaced by ions with a lower valence (e.g., Fe^{2+} or Mn^{2+}) [1–4]. Cardinal differences in the physical properties of piezomaterials determine the range of their practical applications. Thus, the creation of high-voltage equipment (such as ultrasonic emitters, piezotransformers, and piezomotors), requires ferroelectrically hard piezoceramics that combine high piezoelectric parameters (piezoelectric coefficients d_{33} and d_{31}, planar and thickness coefficients of electromechanical coupling K_p and K_t) with a mechanical quality factor (Q_m) and low values for the tangent of the dielectric loss angle (tgδ) [5, 6]. However, the role of technological factors in the formation of the microstructure and the functional characteristics of ferroelectrically hard ceramics has been researched to a much lesser extent than in the case of ferroelectrically soft materials. This is largely on account of differences in the influence of the defect subsystem on the growth of crystallites during sintering. In ferroelectrically hard ceramics based on PZT, a slow grain growth is observed [1]; however, the choice of sintering technology and modes can affect the functional characteristics of ferroelectrically hard ceramics based on PZT [7].

The study of lead-free solid solutions with properties similar to PZT ceramics is an important area of research regarding the creation of ferroelectrically hard piezomaterials, given that PZT ceramics contain a substantial amount of lead, an extremely toxic element. One of the most promising lead-free systems is the solid solution of $(Na_{1-x},K_x)NbO_3$ (KNN) [1], which is characterized by its relatively high values of piezoelectric response (d_{33} ~ 80 pC/N, K_p ~ 0.36) [8]. To increase the hardness of KNN-based ceramics, Cu^{2+} ions are introduced into the perovskite structure in the form of various compounds (CuO, $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$, $K_4CuNb_8O_{23}$, and $CuNb_2O_6$) [9–11], which form liquid phases during sintering. This results in a significant decrease in the optimal sintering temperatures, the preservation of the stoichiometry of a given composition, and an increase in the relative densities of ceramics. It also produces a significant increase in the mechanical quality factor Q_m, which favors the use of KNN systems in ultrasonic emitters for medical devices and high-power piezotechnics.

Analysis of the literature demonstrates that there are fundamental differences in the most common technological approaches to improving the functional characteristics of lead-containing (based on PZT) and lead-free (based on KNN) ferroelectrically hard ceramics. Thus, the purpose of this study is to identify the main regularities involved in the formation of the microstructure of ferroelectrically hard ceramics, based on both the PZT and KNN systems, through variations in the technological modes of their manufacture.

EXPERIMENTAL

The study investigates the ferroelectrically hard ceramics of two systems:

$PbZrO_3–PbTiO_3–Pb(Mn_{1/3}Nb_{2/3})O_3–Pb(Zn_{1/3}Nb_{2/3})O_3$ and $0.5NaNbO_3–(0.5–2x)KNbO_3–xCuNb_2O_6$.

In the lead-free ceramics, the concentration of $CuNb_2O_6$ (x) varied: x = 0.025, 0.050, and 0.075. The details of the solid-phase synthesis of PZT and KNN-based compounds are described in [12] and [13], respectively.

The sintering of lead-containing samples was carried out in accordance with the following technologies:

– sintering in the chamber furnace Nabertherm L5/13/P330 (*Nabertherm GmbH*, Germany) at atmospheric pressure (ATM) and sintering temperatures T_{sint} = 1150–1200°C;

– sintering by hot pressing (HP) with uniaxial pressure on the USSK-1 installation (*Piezopribor SBDT*, Southern Federal University, Russia) at sintering temperatures T_{sint} = 1125–1175°C;

– spark plasma sintering (SPS) in a vacuum at uniaxial pressure and current pulses on the SPS515S unit (*Fuji Electronic Industrial Co., Ltd.*, Japan) at sintering temperatures T_{sint} = 930–970°C.

Sintering of lead-free samples with different concentrations of $CuNb_2O_6$ (x) was carried out using conventional ceramic technology at T_{sint} = 1100–1170°C.

The control of the completeness of the sintering process of the studied ceramics was carried out according to the results of X-ray phase analysis (ARL X'TRA diffractometers (*Thermo Fisher Scientific*, Switzerland) and DRON-3.0 (*RPE Burevestnik*, Russia)), microstructure images (JEOL JSM-6390LA scanning electron microscopes (*JEOL*, Japan) and Hitachi TM1000 (*HITACHI*, Japan)), and by the values of the density of sintered piezoelectric ceramics, determined by hydrostatic weighing in octane. In the lead-containing samples, X-ray patterns identified a tetragonal crystal structure and showed no trace of impurity phases [12]. Lead-free solid solutions have orthorhombic symmetry with a monoclinic perovskite subcell, and the content of the low-melting impurity phase depends on the concentration of $CuNb_2O_6$ [13].

Disks with a diameter of 10 mm and a thickness of 1 mm, with silver-containing electrodes applied to the end parts, were used as measuring samples. The main electrophysical characteristics (d_{31}, K_p, Q_m) of the pre-polarized samples were determined at room temperature using a precision impedance meter, Wayne Kerr 6500V (*Wayne Kerr Electronics*, UK), in accordance with OST 11 0444 87. The values of the relative permittivity of the polarized samples ($\varepsilon^T_{33}/\varepsilon_0$) and tgδ were measured using a bench that included the LCR-meter Agilent E4980A (*Agilent Technologies*, USA). The piezoelectric coefficient d_{33} was measured using the APC d_{33}-meter system (*APC International, Ltd.*, USA).

RESULTS AND DISCUSSION

Ferroelectrically hard ceramics based on PZT system

Figure 1 contains images of the microstructure of ferroelectrically hard ceramics based on the PZT system that have been sintered in various ways. A polydisperse grain structure with pore-like inclusions was observed in the ceramic samples sintered at 1150°C (Fig. 1a). When sintering is undertaken using conventional ceramic technology, a strongly pronounced secondary recrystallization, which increases with higher T_{sint} values, is observed (Fig. 1b). In samples sintered at 1200°C (Fig. 1c), a significant amount of the glass phase is observed. The formation of this glass phase leads to a decrease in the experimental density and piezoelectric characteristics (Table 1); at the same time, the values of the mechanical quality factor increase by more than 15% relative to the values observed in the samples with the maximum density (at T_{sint} = 1170°C). Note that residual porosity is observed throughout the entire temperature range of ceramic sintering.

Ceramic samples obtained by the HP method (Fig. 1d–f) do not contain visible residual pores and have a dense structure on account of the mechanical pressure applied during sintering. However, secondary recrystallization is produced as a result of the high temperature (above 1100°C) and the long duration of the sintering process (12 h). Note that this process causes the growth of large crystallites (Fig. 1f), which can reach the size of about 20 μm, on the surface of which small shells are visible-places of local melting of the liquid phase. The formation of an inhomogeneous large-crystal microstructure leads to a decrease in the experimental density and in all the main functional characteristics (Table 1).

All of the ceramic samples sintered by the SPS method had a homogeneous microstructure, with grain sizes not exceeding 5 μm and no visible glass phase inclusions (Fig. 1g–i). It would appear that such a fine-grained microstructure of ceramics is the result of the mechanical pressure applied during the sintering process and its short duration. Note that an increase in the sintering temperature to 970°C did not lead to a significant increase in the average grain size, but rather an increase in the degree of perfection of the crystallites' shape; at the same time, there was an increase in the experimental density value and in all the main functional characteristics (Table 1). An increase in the sintering temperature was seen to have the greatest effect on the increase in the dielectric properties; there was an increase of more than 30% when the T_{sint} changed from 930 to 970°C. This may be due to a change in the electrical conductivity of the grain boundaries, but this requires further investigation using dielectric spectroscopy.

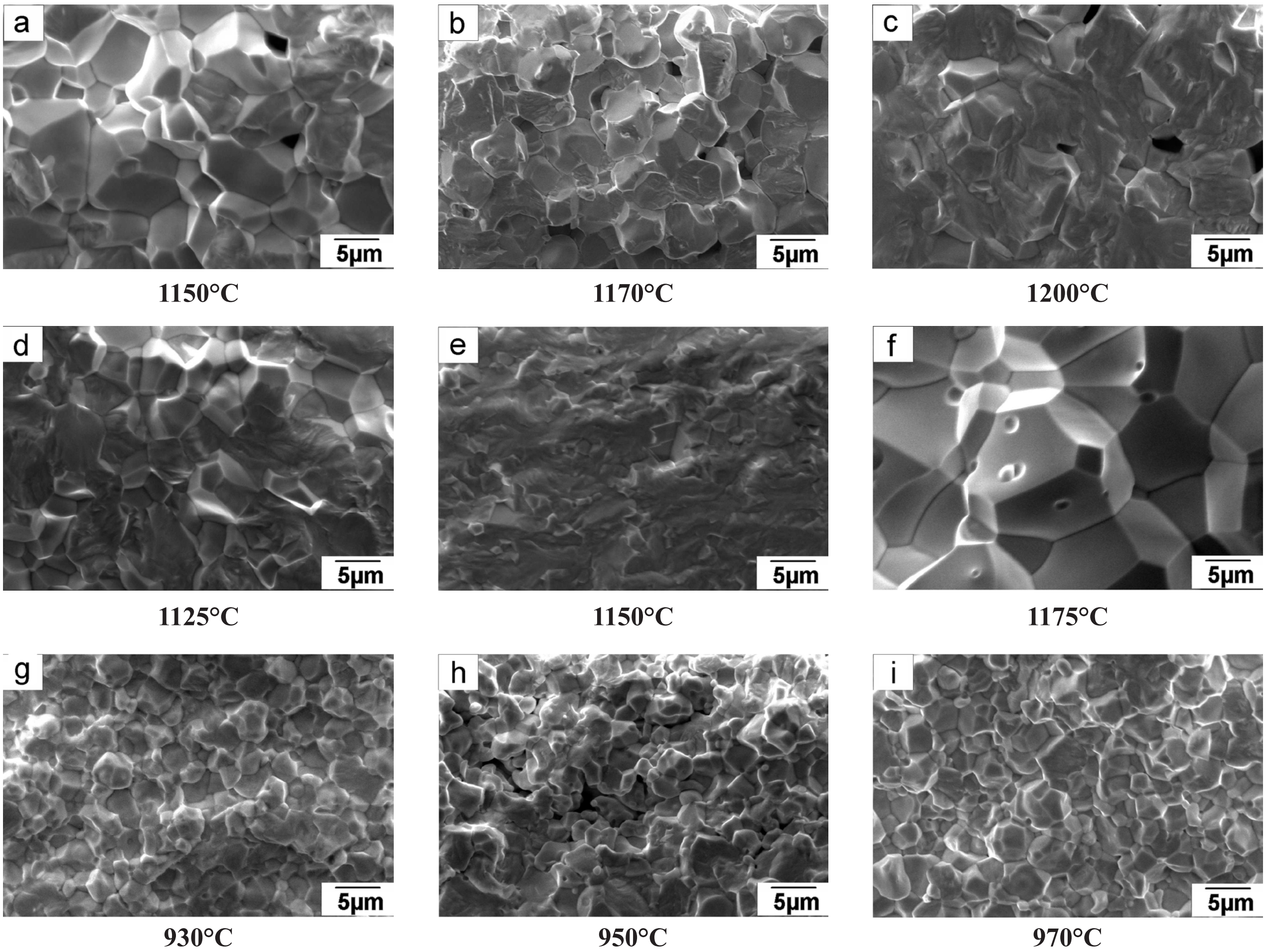

Fig. 1. Fragments of the microstructure of PZT-based ceramics sintered using various technologies: ATM (a–c), HP (d–f), and SPS (g–i).

Table 1. Experimental density and main dielectric, piezoelectric, and mechanical characteristics of ferroelectrically hard ceramics based on PZT sintered using various technologies

Sintering technology	Sintering temperature, °C	Density, g/cm³	$\varepsilon^T_{33}/\varepsilon_0$	d_{31}, pC/N	Q_m
ATM	1150	7.73	1292	115	449
	1170	7.80	1307	125	538
	1200	7.78	1297	119	624
HP	1125	7.67	1399	122	545
	1150	7.72	1415	130	644
	1175	7.70	1387	127	576
SPS	930	7.91	1153	119	912
	950	7.94	1349	127	1012
	970	7.98	1514	129	1090

The choice of sintering technology and mode had the greatest impact on the mechanical quality factor values: in the case of ceramics sintered by the SPS method, Q_m exceeds 1000, which is 70–140% more than the values typically found in the other samples (Table 1). At the same time, the differences in the d_{31} values of samples sintered using different technologies (but with optimal T_{sint}) do not exceed the experimental error. When compared with ceramics sintered using conventional ceramic technology, those sintered by the SPS method are characterized by more than twice the figure-of-merit values, FOM = $K^2 \cdot Q_m$ (where, K is one of the coefficients of electromechanical coupling, depending on the type of device) [14].

The most significant factors that affect the manifestation of physical properties were identified through analysis of data published in literature that is devoted to the establishment of correlations between the technology of ceramic manufacturing, the average size of crystallites, and the macroscopic responses (dielectric, piezoelectric, mechanical) of piezoceramics [15–17]. These include changes in the configuration and size of domains and in the pinning effect of domain walls, which can be enhanced both by increasing the concentration of oxygen vacancies and by reducing the size of crystallites, thus increasing the area of intercrystalline boundaries that can also act as pinning centers [17]. However, in this case, a sharp increase in Q_m did not result in a decrease in the d_{31} values. The ceramics sintered by the SPS and ATM methods were characterized by the very close parameters of the dielectric hysteresis loops [18], which indicates the absence of any significant rearrangement of the domain structure. It is possible that a change in sintering modes can lead to the development of several processes that affect macroscopic responses in different ways, for example, to an increase in the density of the boundaries of 90° domains [15] and to an increase in pinning by intercrystalline boundaries with a decrease in the average grain size. Note that, to date, there is no unambiguous understanding of the relationship between the size of the crystallites and the behavior of their dielectric and piezoelectric properties, while the established correlations even within a single PZT chemical system are contradictory [19].

Ferroelectrically hard ceramics based on the KNN system

Figure 2 shows images of the microstructure of ferroelectrically hard ceramics based on the KNN system that contain different concentrations of $CuNb_2O_6$ (x). It can be seen that the addition of even a small amount of $CuNb_2O_6$ (Fig. 2a and 2b) leads to the formation of a compacted microstructure that includes a significant glass phase content and large individual crystallites. As shown in [13], the addition of $CuNb_2O_6$ to the KNN system leads to the appearance of the impurity phase $K_4CuNb_8O_{23}$. This compound has a low melting point (1050°C), which contributes to the formation of liquid phases during sintering, and as a result, it increases the density of ceramics [20]. The relative density of samples with $x = 0.025$ reaches 96%, which is almost the limit result for unmodified KNN ceramics, even when using SPS [21]. As a result, it is possible to obtain an increase of ~10% in the dielectric and piezoelectric characteristics and an increase of 60% in the mechanical quality factor (see Table 2) when compared to unmodified KNN ceramics sintered using conventional ceramic technology [8]).

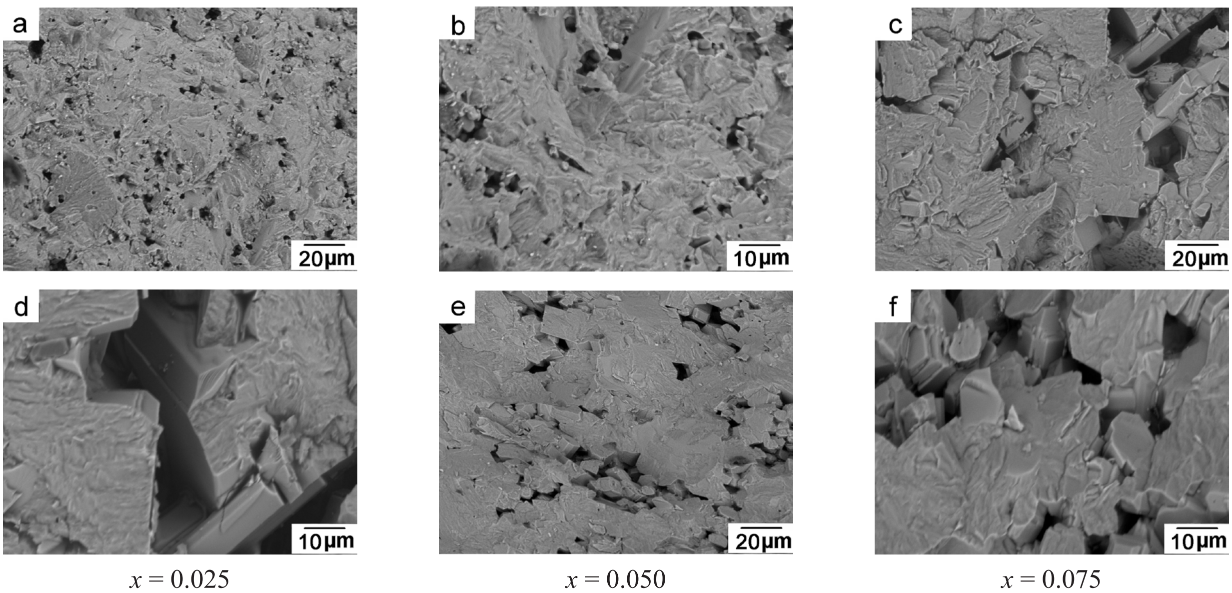

Fig. 2. Fragments of the microstructure of KNN-based ceramics with different concentrations of $CuNb_2O_6$ (x).

Table 2. Experimental density and main dielectric, piezoelectric, and mechanical characteristics of ferroelectrically hard ceramics based on KNN with different concentrations of $CuNb_2O_6$ (*x*)

x	Density, g/cm³	$\varepsilon^T_{33}/\varepsilon_0$	d_{33}, pC/N	Q_m
0.025	4.36	343	88	211
0.050	3.65	253	43	314
0.075	3.55	332	26	290

Further increases in the concentration of $CuNb_2O_6$, to $x = 0.050$ (Fig. 2c and 2d) and 0.075 (Fig. 2e and 2f), led to a spur increase in the content of the impurity phase [13] and a significant decrease in the relative density of ceramics to values below 80%. At the same time, individual cubic-shaped crystallites, with sizes exceeding 20 μm, were observed (Fig. 2c and 2d); this is typically seen in KNN ceramics with Cu-containing additives that form liquid phases [10, 11, 22]. The ceramics of both compositions are characterized by the accumulation of pores around large crystallites, which is likely to be the result of excessive growth that occurred due to the liquid phase, in place of which numerous voids were subsequently formed. As shown in [23], which uses the example of Al_2O_3 with CaO and TiO_2 additives that provoke the formation of liquid phases during sintering, an increase in the content of the TiO_2 additives leads to a sharp increase in the number of crystallites, which prevents their excessive growth and contributes to the formation of a more homogeneous microstructure (Fig. 2e and 2f). When *x* increases, there is a sharp drop in the values of the piezoelectric parameters, while the value of Q_m increases by 50% (Table 2).

Note that in this paper, KNN-based ceramics are made by solid-phase synthesis and are sintered using conventional ceramic technology. However, the use of HP and SPS technologies makes it possible to significantly increase the values of the main piezoelectric characteristics of unmodified KNN ceramics, with the value of d_{33} doubling. For this reason, further study is required with regard to the effect of sintering modes on the properties of ferroelectrically hard ceramics that are based on KNN with $CuNb_2O_6$ additives.

CONCLUSIONS

This paper studies the microstructure features of ferroelectrically hard piezoceramics based on PZT and KNN systems with variations in the chemical and technological modes of their manufacture. In the case of lead-containing ceramics, three different sintering technologies were used: ATM, HP, and SPS. Within each of these, the production modes were optimized in order to obtain samples that had the maximum density and best combinations of functional characteristics. It has been established that SPS is the optimal technology for the application of the studied ferroelectrically hard ceramics in high-power piezotechnics devices operating at piezoresonance frequencies. Ceramics sintered by this method are characterized by a high density, a homogeneous microstructure, and an increase of more than twice the amount of FOM values in comparison with those sintered by conventional ceramic technology. In addition, the use of SPS allowed a reduction of 200°C in the optimal sintering temperature and reduced the sintering time by more than 20 times, which reduces production costs. This technology can also be used in the manufacture of multilayer converters with a low-voltage control, in which the sintering of ceramic layers and the burning of conductive electrodes are combined in one technological operation.

This paper takes a new approach to studying improvements in the functional characteristics of lead-free ceramics, by adding a copper-containing additive $CuNb_2O_6$ (*x*) to the base KNN system, which contributes to the appearance of liquid phases during sintering. It was found that, at $x = 0.025$, a compacted microstructure is formed with relative density values (96%) that have practical limitations in conventional ceramic technology. As a result, there is an increase in both the piezoelectric and mechanical properties, which leads to a twofold increase in the values of the FOM when compared to KNN ceramics. This offers an opportunity for further research on the choice of technology and modes of sintering lead-free ceramics based on the system considered in this paper.

Thus, on the basis of the performed research, it has been established that the choice of chemical and technological modes of manufacturing both lead-containing and lead-free ferroelectrically hard piezoceramics can significantly (twice) increase its functional characteristics.

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Authors' contribution

M.V. Talanov – production and experimental study of dielectric and piezoelectric properties of ceramic samples, interpretation of experimental results, writing the text of the article;

M.A. Marakhovsky – production and experimental study of the dielectric and piezoelectric properties of ceramic samples, study, and description of the microstructure of ceramics based on the lead zirconate–titanate system, discussion of measurement results.

The authors declare no conflicts of interest.

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