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PFN CERAMICS SYNTHESIZED BY A TWO-STAGE METHOD

CERAMIKA PFN SYNTETYZOWANA DWUETAPOWĄ METODĄ

In the work the $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ceramics was obtained by a two-stage synthesizing method (columbite method). During the technological process the synthesis took place as a result of powder calcination method. An influence of technological conditions of the first stage of the ferroniobate (FeNbO_4) synthesizing on the crystalline structure, the microstructure, the internal friction and relative density ($\rho_{\text{eksp}}/\rho_{\text{teor}}$) was presented, and they influence basic properties of ($\varepsilon(T)$ and $\tan \delta(T)$, T_m , $S(E)$, $P(E)$) and electric conduction of the PFN ceramics. It has been found that a high temperature of the FeNbO_4 synthesizing does not improve properties of the material and the optimum parameters of the PFN ceramics are obtained while synthesizing of FeNbO_4 at the temperature of 1000 °C for 4 h.

Keywords: Multiferroic, ferroelectromagnetics, PFN ceramics

W pracy otrzymano ferroelektryczną ceramikę $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ dwuetapową metodą syntetyzowania (metodą kolumbitu). Podczas procesu technologicznego synteza odbywała się w wyniku kalcynacji proszków. Przedstawiono wpływ warunków technologicznych pierwszego etapu syntetyzowania żelazo-niobianu (FeNbO_4) na strukturę krystaliczną, mikrostrukturę, tarcie wewnętrzne oraz gęstość względną ($\rho_{\text{eksp}}/\rho_{\text{teor}}$), które wpływają na podstawowe właściwości ($\varepsilon(T)$ i $\tan \delta(T)$, T_m , $S(E)$, $P(E)$) i przewodnictwo elektryczne ceramiki PFN. Stwierdzono, że wysoka temperatura syntetyzowania FeNbO_4 nie poprawia właściwości materiału, a optymalne parametry ceramiki PFN uzyskuje się przy syntetyzowaniu FeNbO_4 w temperaturze 1000 °C przez 4 h.

1. Introduction

The $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) ceramics belongs to a family of perovskite materials with general formula $\text{A}(\text{B}'\text{B}'')\text{O}_3$, where ions of iron Fe and niobium place themselves into positions of B' and B'' at random, and ions of lead Pb in positions A [1, 2]. This material was already discovered in fifties and sixties [3, 4] and it shows multiferroic properties. It means that at the specific temperature ranges PFN is characterized by simultaneous ordering of an electric subsystem (ferroelectric ordering at $T < T_{CE} \approx 110^\circ\text{C}$) and a magnetic subsystem (antiferromagnetic ordering at $T < T_N \approx -130^\circ\text{C}$). In those materials spontaneous magnetization M_s , spontaneous polarization P_s or spontaneous deformation η_s can be changed by a magnetic field H , an electric field E or by a stress σ . Owing to such interesting properties materials of that type can be used, among others, as a dielectric or magnetic medium to build multilayer ceramic condensers (MLCC), microwave resonators and

filters, to build adjustable transducers, sensors and detectors, multistate memory elements, electrostriction actuators, microadjusters etc. [5 - 8]. Ferroelectromagnetics in components and equipments of that type are used in a form of volumetric or thin layer ceramic elements.

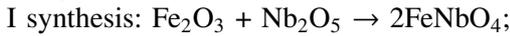
Properties of the PFN ceramics depend, to a great degree, on technological parameters of its production. During a process of the PFN ceramics production there are a lot of barriers which hamper to obtain a material of good and stable parameters. It includes, among others: occurrence of a second nonferroelectric pyrochlore phase besides a ferroelectric perovskite phase, high electric conduction or dielectric losses. These unfavorable factors limit application possibilities of the PFN ceramics.

An aim of this work was to optimize technological conditions of the $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ceramics production, I-st synthesis of the $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ powders (in the columbite method) and to examine an influence of those conditions on properties of the PFN ceramics.

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2. Experiment

The columbite method to obtain the PFN ceramics consists of two stages of synthesizing component powders. In the first stage the so-called ferroniobate FeNbO_4 is obtained from a mixture of Fe_2O_3 and Nb_2O_5 oxides, in the second stage by adding the PbO lead oxide to the powdered FeNbO_4 a final product is obtained in a form of a synthesized PFN powder. In both stages of the PFN technology synthesizing was made by a technique of calcining of mixed oxides (CMO). The process to synthesize PFN took place in two stages according to the reactions:



A mixture of powdered Fe_2O_3 and Nb_2O_5 oxides was synthesized at temperatures $T_{I\text{-synth}}$ from 1000 °C to 1200 °C for $t_{I\text{-synth}} = 4$ h, whereas in the second stage the synthesis was made in the following conditions: $T_{II\text{-synth}} = 800$ °C / $t_{II\text{-synth}} = 3$ h.

The X-ray measurements were made on a polycrystalline diffractometer of the Phillips firm. Examinations of the FeNbO_4 powder and a microstructure of the PFN ceramics were made by a SEM HITACHI S-4700 scanning microscope. To measure temperature relationships of the internal friction Q^{-1} and the Young modulus E an automatic relaxator of acoustic frequencies of the RAK-3 type was used. Dielectric measurements were made on a capacity bridge of a QuadTech 1920 Precision LCR Meter type. Examinations of the hysteresis loop were conducted by use of high voltage feeder cable of a Matsusad Precision Inc. HEOPS-5B6 type, and measurements of

direct current electric conduction were made by use of μA meter (Tesla multimeter BM518). Real density was determined by a measurement of mass and a volume of the specimens, and $\rho_{\text{rentg}} = 8.457$ g/cm³ was taken as X-ray density [9].

The percentage content of the P_f perovskite phase was calculated from the following relationship:

$$P_f = \frac{I_{110} \cdot 100}{I_{110} + I_{222}} \quad [\%] \quad (1)$$

where I_{110} and I_{222} are intensities of the (110) perovskite and (222) pyrochlore diffraction lines.

3. Examination results and their discussion

Fig.1a presents XRD courses of powders synthesized in stage 1 FeNbO_4 , obtained at different temperatures: at 1000 °C – k1000, at 1050 °C – k1050, at 1100 °C – k1100, at 1150 °C – k1150 and 1200 °C – k1200, and Fig.1b presents cumulative XRD diagrams of the PFN specimens obtained by using those powders: PFN1 – temperature of I-st synthesis 1000 °C, PFN2 – 1050 °C, PFN3 – 1100 °C, PFN4 – 1150 °C and PFN5 – 1200 °C. By X'Pert HighScore oraz FullProf 2000 software JCPDS patterns were matched to the powder X-ray photographs (for the powder specimen k1000 and k1150 (070-2275), for k1050 and for k1100 (16-0374), k1200 (084-1981). From the X-ray analysis it results that at room temperature ($T_r < T_C$) the PFN ceramics specimens in question show tetragonal structure. The lattice parameters determined are presented in Table 1.

TABLE 1

An influence of the I-st FeNbO_4 synthesis on the lattice parameters of the PFN elementary cell

Lattice parameter	PFN1	PFN2	PFN3	PFN4
a [Å]	4.0140(6)	4.0151(6)	4.0153(8)	4.0131(5)
c [Å]	4.0290(2)	4.0320(2)	4.0340(2)	4.0310(1)
P_f [%]	100	100	97.3	95.6

In the XRD diagrams it can be noticed that a pure perovskite phase occurs for the PFN compositions with the lowest temperature of the I-st FeNbO_4 synthesis (1000 °C ÷ 1050 °C). For higher temperatures of the I-st FeNbO_4 synthesis there is a small amount of nonferroelectric pyrochlore phase ($\text{Pb}_3\text{Nb}_4\text{O}_{13}$), of which amount increases with an increase in the FeNbO_4 synthesizing temperature.

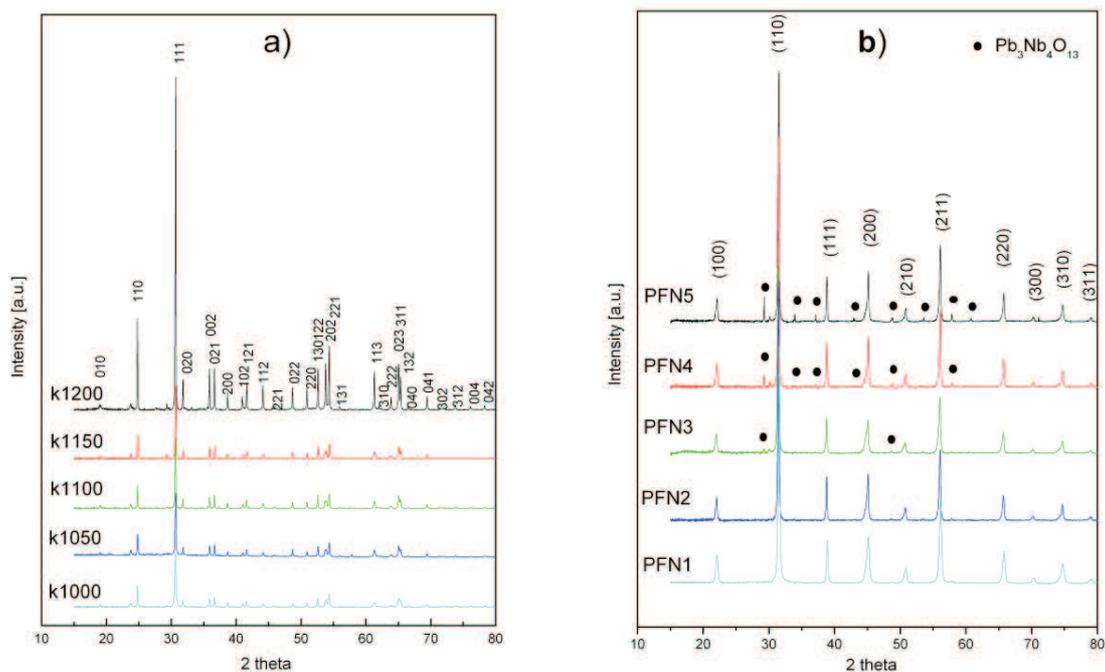


Fig. 1. X-ray spectra of the FeNbO_4 powders (a) and the PFN ceramics sintered freely e (b), of different FeNbO_4 synthesizing temperature

With an increase in the 1-st FeNbO_4 synthesis temperature, an increase in a size of the powder grain agglomerate, from which the PFN specimens were obtained, is observed in the SEM powder images of the PFN material (Fig.2). This increase is also visible in the photographs of the fractures of the PFN ceramics specimens obtained from those powders (Fig.3). The spec-

imen of the 1-st synthesis temperature equal 1000 °C is characterized by greater density of the microstructure with a smaller and well-formed grain. Higher temperatures of the 1-st synthesis cause excessive grain growth what results in an increase in porosity and density of the ceramic PFN.

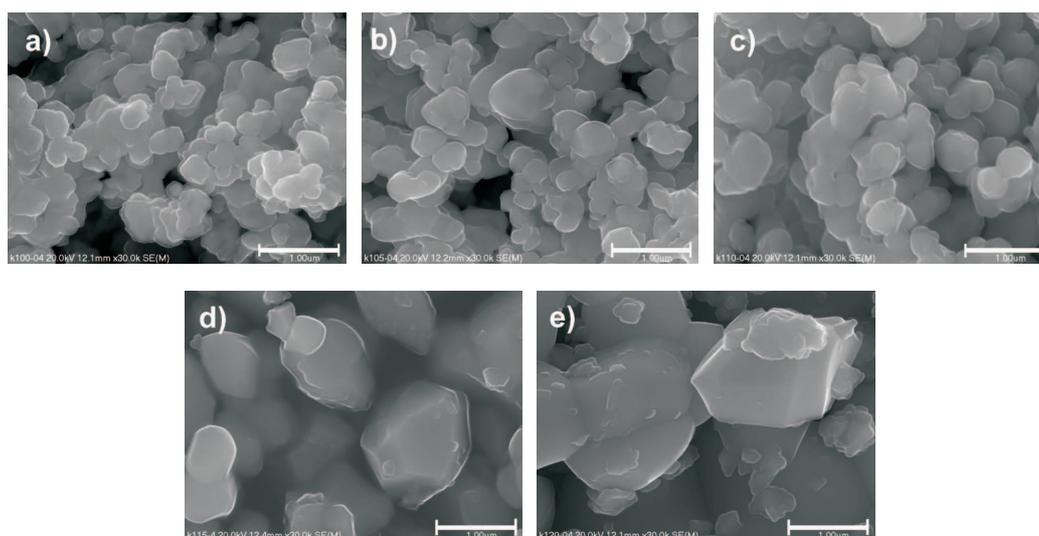


Fig. 2. An influence of the 1-st synthesis temperature on a size of the FeNbO_4 powders: a) 1000 °C, b) 1050 °C, c) 1100 °C, d) 1150 °C, e) 1200 °C (magnification. x 30 thou)

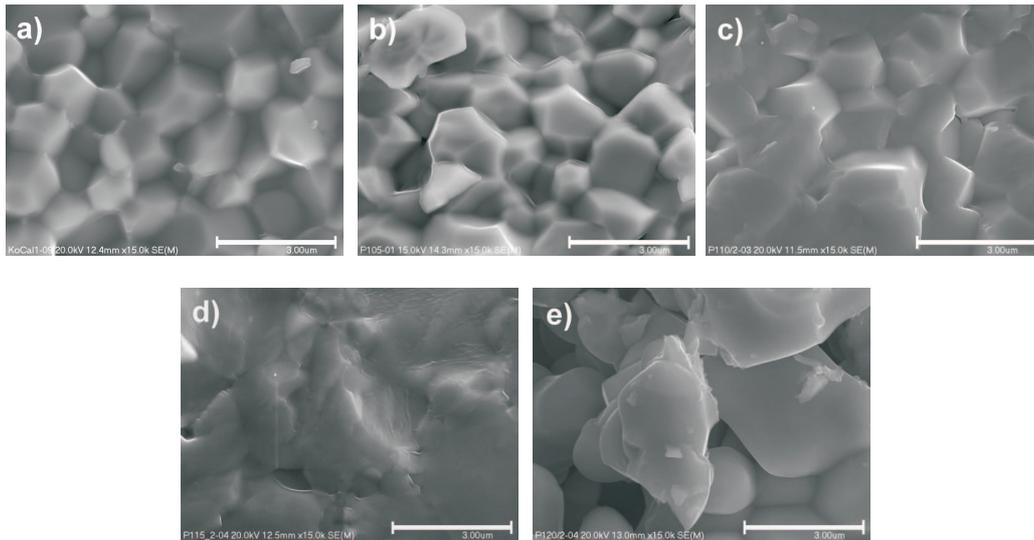


Fig. 3. An influence of the FeNbO₄ synthesis on the PFN ceramics microstructure: a) PFN1, b) PFN2 , c) PFN3, d) PFN4, e) PFN5 (magnification. x15thou)

The technology conducted by a two-stage method of synthesizing (a columbite method) by powder calciantion enables to obtain a final product in a form of the PFN ceramics of high density (near theoretical one). In the case of the PFN specimen at the I-st synthesis

temperature of 1200 °C no further results are given due to high porosity of the specimens and clearly worse properties significantly different from the other series of the ceramic PFN specimens.

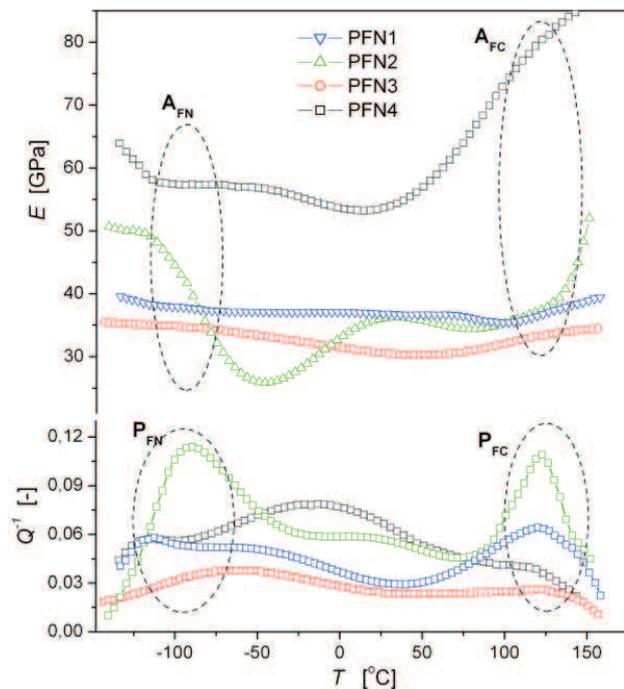


Fig. 4. Temperature relationships of $Q^{-1}(T)$ and $E(T)$ for the PFN ceramics

Fig.4 presents temperature relationships of the $E(T)$ Young modulus and the $Q^{-1}(T)$ internal friction obtained for series of the specimens of the PFN ceramics made at

different temperatures of the FeNbO₄ synthesis. In the temperature range from ~ 90 °C to ~ 150 °C changes of the E value are clearly visible in a form of the A_{FC}

minimum presence. The A_{FC} minima observed correlate with the P_{FC} maxima visible on the $Q^{-1}(T)$ relationships. Presence of the P_{FC} peak connected with an increase in the Young modulus E above the A_{FC} minimum, shows that it is responsible for the ferroelectric \leftrightarrow paraelectric phase transition. The lowest values of the mechanical losses Q^{-1} are observed for the ceramic PFN3 specimens (about $0.01 \div 0.03$), whereas the highest Q^{-1} values has the PFN2 ceramics (about $0.01 \div 0.11$). In a case of the Young modulus, values for ceramic PFN1, PFN2, PFN3 specimens are in a range from ~ 30 GPa to ~ 50 GPa in the whole temperature range. For ceramic PFN4 the Young modulus E values are much higher and they are from about 65 GPa to 90 GPa. It may show that there are additional stresses, which were formed during the specimen production process. For all compositions of the PFN specimen series characteristic broadening diffusion of the phase transition is observed. In the temperature range from about -140 °C do ok. -90 °C, for all PFN specimens in question, the maximum on the $Q^{-1}(T)$ relationship and the A_{FN} minimum on the $E(T)$ relationship correlating with it can be also observed. This maximum is connected with a magnetic transition taking place in the PFN ceramics and it is most visible for specimen PFN2, what may show the strongest magnetic properties from the PFN specimen series.

With an increase of the $FeNbO_4$ synthesizing temperature, at room temperature, the direct current specific

resistance decreases (Table 2). There is similar tendency at the phase transition temperature. The PFN ceramics in the ferroelectric phase is a linear relationship in a function of the temperature converse for the direct current conduction according to the Arrhenius law:

$$\sigma = \sigma_0 \exp\left(\frac{E_{Act}}{k_B T}\right), \quad (2)$$

where k_B is a Boltzman's constant, E_{Act} is activation energy, T – the absolute temperature. From the analysis of straight lines to experimental results values of the activation energy E_{Act} (in the paraelectric and ferroelectric phase) were calculated and they are presented in Table 2. In the $\ln \sigma(1/T)$ diagram in the area of the phase transition a characteristic inflexion of curves, where there is a great difference of the activation energy E_{Act} in the paraelectric and ferroelectric phase, is observed (Fig.5). In the PFN ceramics majority of free charge carriers are electrons generated by the Fe^{2+} iron ions, which behave as donor centers [2]. The E_{Act} values obtained are much higher than values of energy (0.1 eV) connected with a change of valence of iron $Fe^{3+} \leftrightarrow Fe^{2+}$ and they designate conduction connected with a jump of free charge carriers and formation of oxygen vacancies during sintering at high temperatures. The values obtained are in accordance with examinations of the authors of the work [6].

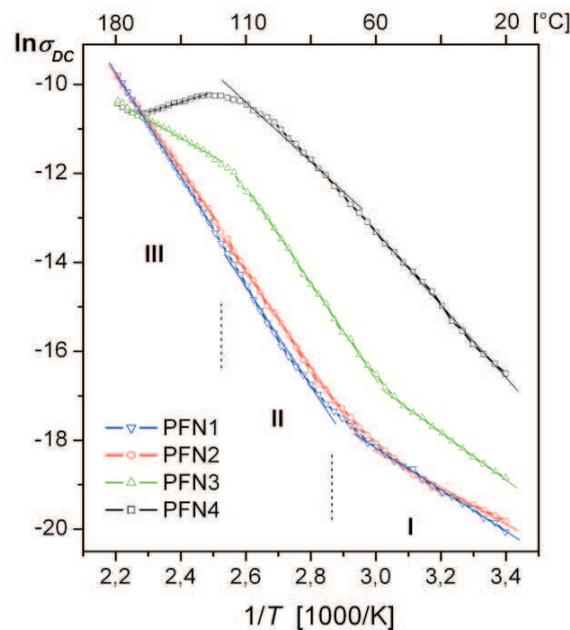


Fig. 5. An influence of the $FeNbO_4$ synthesis temperature on $\ln \sigma_{DC}(1/T)$ for the PFN ceramics

The temperature of the phase transition in the PFN ceramics does not depend on the frequency of the measurement field. Temperature relationships of electric permittivity of the PFN ceramics for 1kHz frequency of the measurement field in the cooling cycle are presented in Fig.6. In the diagrams it is visible that an increase in the temperature of the 1-st FeNbO₄ synthesis causes an increase in the Curie temperature and slight differences in the maximum values of electric permittivity. The highest values of the maximum electric permittivity have specimens PFN, for which the 1-st FeNbO₄ synthesis temperature was in the range of 1050 ÷ 1100 °C. The lowest values of electric permittivity show the specimen of the lowest temperature of the I-st FeNbO₄ synthesis.

The $\varepsilon(T)$ maxima are not sharp. It means that the phase transition from the ferroelectric to paraelectric

phase does not take place at a specific temperature, but in a certain area of temperatures (a diffused phase transition). The diffused character of the phase transition in the PFN ceramics is connected with a random distribution of Fe³⁺ and Nb⁵⁺ ions in positions B of the perovskite lattice. It leads to formation of microscopic areas with different Curie temperature. Parameter α being a degree of diffusion of the phase transition was calculated according to the formula:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = C(T - T_m)^\alpha, \quad (3)$$

where $(\varepsilon_m/\varepsilon_r)$ – the temperature at which electric permittivity reaches its maximum (ε_m), C – constant. The calculated values of the α parameter are presented in Table 2.

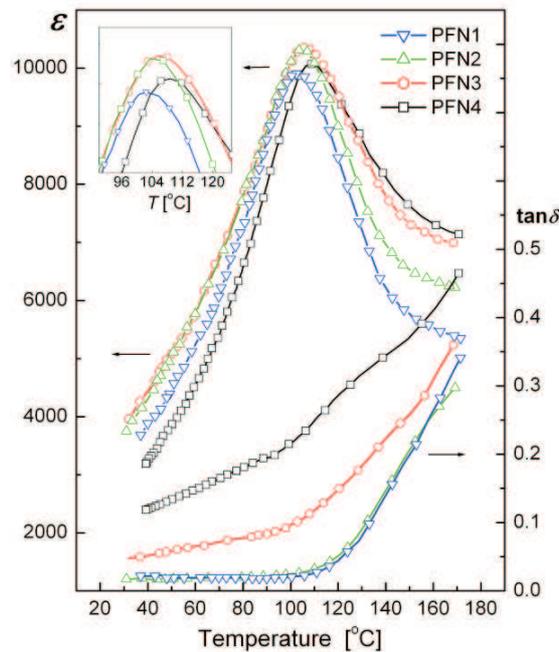


Fig. 6. An influence of the FeNbO₄ synthesis temperature on the temperature relationships of the ε electric permittivity and the $\tan \delta$ tangent of the dielectric loss angle for the PFN ceramics

The I-st FeNbO₄ synthesis temperature influences value of the dielectric losses of the PFN ceramics (Fig.6). With an increase of a temperature in the ferroelectric phase the dielectric losses increase slowly, whereas above the phase transition temperature (in the paraelectric phase), there is a rapid growth of the dielectric losses. It is connected both with a decrease in electric resistance of the grains themselves and grain boundaries (a temperature effect of the synthesis connected with

irreversible chemical changes in the grain boundaries during sintering at high temperatures).

In the $\tan \delta(T)$ diagrams it can be observed that in the whole measurement area dielectric losses increase with an increase in the I-st FeNbO₄ synthesis temperature. The highest dielectric losses show specimens of the I-st synthesis temperature $T_{I-synth} = 1150$ °C (PFN4), the lowest specimens with the lowest I-st synthesis temperature $T_{I-synth} = 1000$ °C (PFN1) and 1050 °C (PFN2).

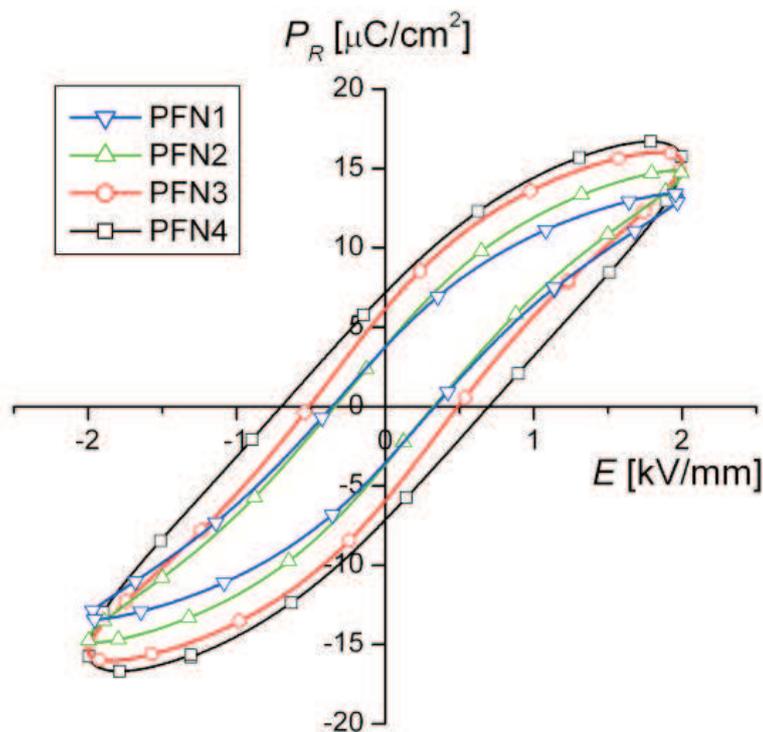
TABLE 2

An influence of the I-st FeNbO₄ synthesis temperature on the basic parameters of the PFN ceramics

Specimen designation	PFN1	PFN2	PFN3	PFN4
FeNbO ₄ synthesis conditions	$T = 1000\text{ }^{\circ}\text{C};$ $t = 4\text{ h}$	$T = 1050\text{ }^{\circ}\text{C};$ $t = 4\text{ h}$	$T = 1100\text{ }^{\circ}\text{C};$ $t = 4\text{ h}$	$T = 1150\text{ }^{\circ}\text{C};$ $t = 4\text{ h}$
$\rho_{\text{exp.}} [\text{g}/\text{cm}^3]$	8.2	7.5	8.1	6.7
$\rho_{\text{exp.}} / \rho_{\text{teor.}} [\%]$	96.9	88.2	96.0	80.0
$T_m [^{\circ}\text{C}]$	103	105	104	108
$(\rho_{DC})_{Tr} [\Omega\text{m}]$	5.16×10^8	4.12×10^8	1.53×10^8	1.47×10^7
$(\rho_{DC})_{Tm} [\Omega\text{m}]$	1.57×10^6	1.18×10^6	2.10×10^5	3.20×10^4
E_{Act} at I [eV]	0.404	0.461	0.354	0.707
E_{Act} at II [eV]	0.961	0.930	0.920	0.578
E_{Act} at III [eV]	1.004	0.356	0.914	0.193
ϵ_r	2220	3100	3200	2930
$(\tan\delta)_{Tr}$	0.017	0.049	0.046	0.093
ϵ_m	9900	10350	10250	10050
$(\tan\delta)_{Tm}$	0.020	0.023	0.107	0.234
ϵ_m / ϵ_r	4.46	3.34	3.20	3.43
α	1.60	1.73	1.79	1.83

At the room temperature measurements of the electric hysteresis loop ($P_R(E)$) of the series of the ceramic PFN specimens in question were conducted, for $\nu = 1\text{ Hz}$, and they are presented in Fig.7. The specimens of the material in question have a narrow hysteresis loop what shows that this material is weakly polarized. The $P_R(E)$

diagrams show that higher temperatures of the FeNbO₄ synthesizing increase maximum polarization, although it is by expense of a loss of the loop saturation at relatively low field (2.0 kV/mm). The electric hysteresis loop for ceramic PFN1 begins to saturate at a field of 2.0 kV/mm.

Fig. 7. An influence of the FeNbO₄ synthesis temperature on the electric hysteresis loop of the PFN ceramics

Looking for a compromise between obtaining the PFN material without an undesirable pyrochlore phase, of high density, an appropriate microstructure and with high values of electric permittivity, and a material with the lowest dielectric losses and low electric conduction, it can be stated that in the process of the PFN production by the columbite method, the optimum temperature of the I-st FeNbO₄ synthesis at time $t_s = 4$ is the temperature $T_s = 1000$ °C.

4. Summing up

An inappropriate selection of the parameters of the Pb(Fe_{1/2}Nb_{1/2})O₃ production causes that the ceramic may have non-perovskite pyrochlore phase, high dielectric losses and electric conduction what results in lack of application possibilities of such ceramic. The two stage synthesis of PFN, using synthesizing by sintering of a loose mixture of a powder (calcination) and use of specific technological conditions reduces disadvantageous factors significantly. The ceramic PFN specimens, for which the FeNbO₄ synthesizing temperature is in the range from 1000 °C to 1050 °C have a pure perovskite ferroelectric phase, and their structure is characterized by fine well-formed grains. Correctly formed crystalline structure and a microstructure of the PFN ceramics have an advantageous influence on the electro-physical parameters of the material.

The conducted comprehensive examinations of the ceramic PFN specimens of a different temperature of the FeNbO₄ synthesizing have shown that the optimum electro-physical parameters and advantageous material prop-

erties are obtained for the PFN ceramics of which the temperature of the I-st FeNbO₄ synthesis is $T_{I-synth} = 1000$ °C, and the synthesizing time is $t_{I-synth} = 4$ h.

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