

Influence of the sintering conditions on the physical properties of the ceramic PFN multiferroics

Dariusz Bochenek · Zygmunt Surowiak ·
Józef Krok-Kowalski · Jana PoltieroVa-Vejpravova

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Abstract An influence of compacting conditions on applied properties of the multiferroic $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PFN) ceramics synthesized by the columbite method and powder calcination technique is presented in this work. The obtained specimens were subjected to X-ray and chemical composition homogeneity analyses, magnetic tests, electric direct current conductivity and electromechanical tests. Differences in the degree of diffuseness, densities and a grain size were observed depending on the sintering method. The dielectric and magnetic parameters as a function of temperature were measured. The tests confirmed that PFN powder compacting by a hot uniaxial pressing method had an advantageous influence on the crystalline structure ordering and the ceramics microstructure, what improves the applied properties of the material.

Keywords Multiferroics · Ferroelectrics · PFN · Ceramics · Synthesis · Sintering

D. Bochenek (✉) · Z. Surowiak
Department of Materials Science, University of Silesia,
2, Śnieżna St.,
Sosnowiec 41-200, Poland
e-mail: dariusz.bochenek@us.edu.pl

J. Krok-Kowalski
Institute of Physics, University of Silesia,
14, Uniwersytecka St.,
Katowice 40-007, Poland

J. PoltieroVa-Vejpravova
Department of Condensed Matter Physics, Charles University,
Ke Karlovu 5,
121 16 Praha 2, The Czech Republic

1 Introduction

The ferroic is a general term covering ferromagnetics (FM), ferroelectrics (FE), ferroelastics (FES) and ferrotoroides. Those three groups of materials are called “simple (primary) ferroics”. The family of ferroics includes also antiferromagnetics (AFM), ferrimagnetics (FIM), antiferroelectrics (AFE), ferrielectrics (FIE), antyferroelastics (AFES) and ferroelastics (FIES). Materials showing at least two out of four possible ordered states are called multiferroics.

The ferroics and multiferroics, belong to smart family materials [1]. They are defined as materials which have some properties that can be altered and controlled by external stimuli (magnetic, electric, mechanical, thermal). Smart materials can be used in many technology fields such as automation, control process, robotics, material processing, aerospace engineering, automotive and electronic industry, defense technology, medical technology and biotechnology.

The $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PFN) ceramics belongs to a group of the multiferroics, in which at the specified ranges of temperatures there is simultaneous ordering of the electric subsystem (ferroelectric ordering at $T < T_{CE} \approx 114^\circ\text{C}$) and magnetic subsystem (antiferromagnetic ordering at $T < T_N \approx -130^\circ\text{C}$). Multiferroics of that type form a family called ferroelectromagnetics (FEM). PFN has a structure of the perovskite type with a general formula of $\text{A}(\text{B}'\text{B}'')\text{O}_3$, where in octahedral positions B' and B'' ions of iron and niobium place themselves at random, whereas lead places itself in position A [2, 3]. The materials of this group show a wide isomorphism what allows to place appropriate

cations in positions B, obtaining materials for different types of applications.

The PFN ceramics is an interesting material to produce a lot of electronic and electromechanical equipment. High spontaneous polarization and presence of the Fe^{3+} cations in the B octahedral positions create conditions for coexistence of ferroelectricity and magnetism what can be used in new types of memory [4, 5]. The PFN application possibilities are limited by lead ($V_{\text{Pb}}^{//}$) and oxygen ($V_{\text{O}}^{\bullet\bullet}$) vacancies formed in the technological process and cations Fe^{2+} , which cause an increase in electric conduction and dielectric losses. There is also a problem of repeatability of the technology process to produce a pure perovskite phase (without a pyrochlore phase) with the optimum and stable properties of the ceramics.

One of the most important factors which decides that equipment and electronic elements built on the PFN ceramics base would be reliable, with stable parameters, is an appropriately conducted technology and an optimum selection of technological conditions (purity of initial components, degree of refinement, methods and conditions used for synthesis, sintering and compacting etc.). At present new effective and economical techniques to optimize the manufacturing process of those materials are being looked for.

In case of the PFN ceramics a lot of special techniques of powder synthesizing are used such as molten salt synthesis, reaction sintering, columbite, sol-gel, co-precipitation method [6–8]. Each of those methods has both disadvantages and advantages and it requires using special technological conditions and accuracy of the process performance.

A process to produce the PFN ceramics includes two main stages such as: a synthesis and sintering (compacting). The results of investigations are further continuation of experimental investigations begun in work [9] by the authors, in which the PFN synthesis process was presented. This article defines sintering of the synthesized PFN powders and their compacting to a form of the ceramic. Physical properties of the PFN ceramics obtained by the free sintering method (FS) and the hot uniaxial pressing method (HUP) were compared in the article.

2 Experiment

The columbite method to obtain the PFN ceramics is based on a two-stage synthesis of the component powders. In the first stage the FeNbO_4 (ferroniobate) is obtained from a mixture of Fe_2O_3 (99% purity) and Nb_2O_5 (>99,9% purity), in the second stage by adding the PbO (>99% purity) lead oxide to powdered FeNbO_4 , a final product is obtained in a form of the PFN powder. In order to limit the effects of the

PbO loss during the technological process and possibility to form lead vacancies in the PFN ceramics, the lead oxide was added in excess. The initial components in the first and second stage were mixed for 8 h.

Synthesizing was conducted by a technique of calcining of the mixed oxides according to the following reactions: $\text{Fe}_2\text{O}_3 + \text{Nb}_2\text{O}_5 \rightarrow 2\text{FeNbO}_4$ (I stage) and $\text{FeNbO}_4 + 2\text{PbO} \rightarrow 2\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (II stage).

In the first stage the ferroniobate was synthesized at the temperature of: 1000°C for 4 h, in the second stage the optimum synthesis conditions of the mixture of FeNbO_4 and PbO powders turned out to be $T=800^\circ\text{C}$ and $t=3$ h. Compacting (sintering) of the ceramics was conducted by the FS (free sintering) method in the conditions: $T_s=1050^\circ\text{C}/t_s=2$ h or the HUP (hot uniaxial pressing) method in the conditions: $T_s=1000^\circ\text{C}/t_s=1$ h/ $p_s=20$ MPa.

In the FS method the compacts obtained from the PFN powder (formed in a shape of discs, in the steel matrix by the cold uniaxial pressing) were placed in the corundum crucibles, in the Al_2O_3 bed. Free compacting (sintering) was conducted in the electric chamber furnace of a Termod KS-1350 type, where atmospheric pressure was the sintering medium. An adjustable temperature control ensured its linear increase and good stability (a furnace temperature measurement error was $\pm 0.3\%$).

Compacting (sintering) by the hot uniaxial pressing method was conducted on the laboratory stand of USSK-1 type, which was equipped with an electronic system which enabled to program temperature changes and recording of the specimen thermal expansion during the technological process. The atmospheric air was the medium in the HUP method. The main parameters deciding about grain sizes and porosity of the material sintered, and at the same time influencing physical properties of the ferroelectric ceramics are: a sintering temperature, a pressing pressure and sintering time (the time of holding the specimen sintered at the sintering time). There is crystallite growth of the ceramics sintered with a temperature increase. A compacting rate was controlled by the pressure applied and the sintering temperature in the hot pressing process.

The X-ray examinations were made on a polycrystalline diffractometer of the Phillips firm with a Cu lamp and a graphite monochromator. X-ray images were taken at room temperature in an angle range of 2θ $20^\circ \div 95^\circ$, with a step $\Delta 2\theta=0.02^\circ$ and measurement time $t_p=4$ s/step. The data processing was made by use of X'Pert HighScore and FullProf 2000 program. The microstructure examinations were made by a SEM scanning microscope with the field emission, HITACHI S-4700, and with EDS Noran Vantage system, dielectric measurements were performed on a capacity bridge of a QuadTech 1920 Precision LCR Meter type, with a heating rate of $0.5^\circ/\text{min}$, at different frequency of the measurement field (from 100 Hz to 20 kHz) and

electromechanical tests were made with use of a Philtec Inc. D63 sensor, whereas an examination of the hysteresis loop with use of a high voltage feeder of a Matsusada Precision Inc. HEOPS-5B6 type. The dc measurements were carried out with the use of the Cahn magnetic balance in the temperature range of -268°C to 37°C .

The real density was determined by measuring the mass and volume of the specimens and $\rho_{\text{theor}}=8.457 \text{ g/cm}^3$ was taken as the X-ray density [7], and the percentage content of the P_f perovskite phase was calculated from the following relationship:

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

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

3 Results and discussion

An X-ray spectrum of the PFN ceramics synthesized by the two stage method of calcination of powders is presented in Fig. 1. X-ray examinations at room temperature ($T_r < T_C$) confirm a single phase character of a material with the tetragonal structure of the PFN ceramics (no pyrochlore phase was found). The PFN compacting method does not have a significant influence on the parameters and a size of a unit cell (Table 1).

The PFN ceramics obtained by the HUP method, comparing to the PFN specimen obtained by FS, has a greater density (near the theoretical value—Table 1), thereby lower porosity. The different density of the FS and HUP samples is connected with weight loss induced by evaporation, elimination of porosity, grain size growth and distribution, and densification of ceramics with the increase of sintering temperature, which is confirmed by the SEM (Fig. 2). By analyzing the SEM images obtained it can be stated that the PFN ceramic specimens are characterized by a

Table 1 Influence of the sintering method on the basic parameters of the PFN ceramics.

Parameters	Sintering method	
	FS	HUP
$\rho_{\text{exp}} [\text{g/cm}^3]$	8.19	8.28
$\rho_{\text{exp}}/\rho_{\text{theor}} \times 100 [\%]$	96.9	97.9
$a [\text{\AA}]$	4.0140 (6)	4.0169 (7)
$c [\text{\AA}]$	4.029 (2)	4.034 (1)
$V \times 10^6 [\text{pm}^3]$	64.91	65.09
$\rho_{\text{DC}} \text{ at } T_r [\Omega\text{m}]$	6.66×10^8	4.32×10^8
$\rho_{\text{DC}} \text{ at } T_m [\Omega\text{m}]$	5.22×10^6	1.18×10^6
$E_a \text{ at } T < T_m [\text{eV}]$	0.423	0.816
$E_a \text{ at } T > T_m [\text{eV}]$	0.991	1.019
$P_f [\%]$	100	100
$T_m [^{\circ}\text{C}]$	102	105
ϵ_r	3600	4100
$(\tan\delta)_{T_r}$	0.017	0.016
ϵ_m	9600	12700
$(\tan\delta)_{T_m}$	0.022	0.020
ϵ_m/ϵ_r	2.80	3.09
α	1.78	1.71
$P_R [\mu\text{C/cm}^2]$	11.10	13.70
$E_C [\text{kV/mm}]$	0.43	0.46
$S_{\text{rest}} [\%]$	0.0087	0.0059
$H_v [\%]$	27.29	11.68

compact non-porous structure with densely packed and well-formed grains. The PFN specimens obtained by the hot uniaxial pressing method show greater homogeneity and lower average grain size ($\bar{r} \approx 1.33 \mu\text{m}$) in comparison with the specimens obtained by free sintering ($\bar{r} \approx 1.48 \mu\text{m}$). Smaller and more prismatic grains of the ceramics sintered by the HUP method decide about its greater density and lower porosity comparing to the density of the ceramics compacted by the FS method. Detailed and systematic examinations of an influence of conditions and a method of the ceramics sintering on broadening the X-ray reflexes showed that more prismatic grains were less mechanically stressed, and a degree of their defects was also lower [10].

Tests of the composition homogeneity by a point and surface method of spectroscopy with the EDS energy

Fig. 1 The X-ray diffraction pattern of the PFN ceramics: (a) free sintering (FS) (b) hot uniaxial pressing (HUP)

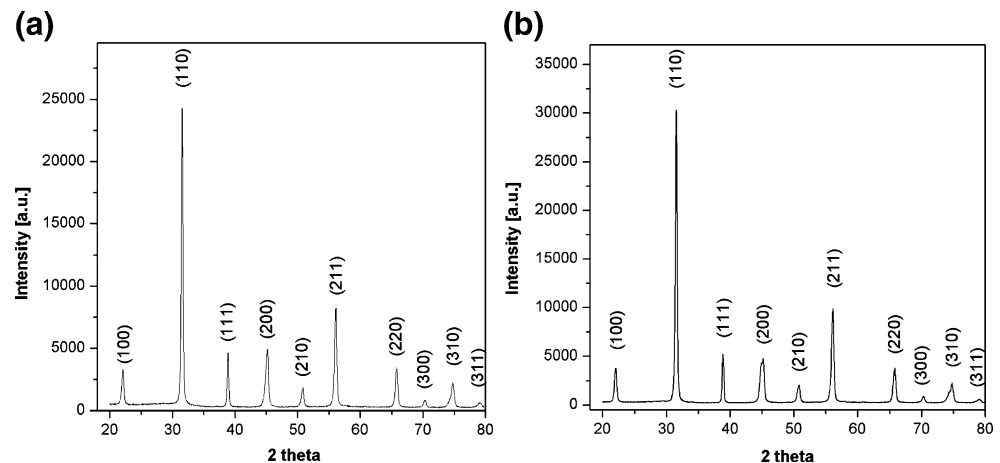
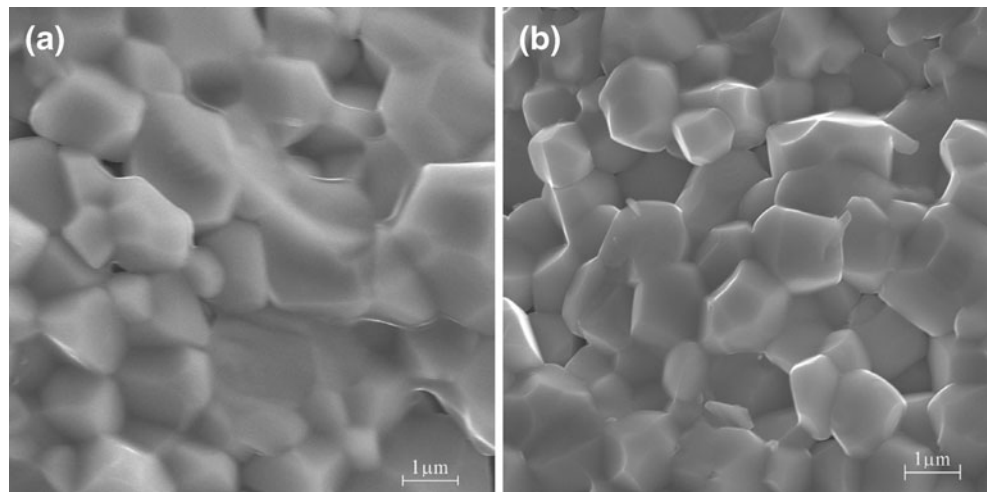


Fig. 2 Influence of the sintering method on the SEM image microstructure of the fracture of the ceramics: (a) free sintering (FS) (b) hot uniaxial pressing (HUP)



dispersion (Fig. 3) confirmed the qualitative composition of the specimens in question. The EDS examinations obtained are comparable to the assumed proportions of the initial components, calculated by stoichiometry, while obtaining the PFN material. In the case of the ceramics compacted by the free sintering method: PbO=67.74%, Fe₂O₃=12.08%, Nb₂O₅=20.18%, whereas in the case of compacting by the hot uniaxial pressing method: PbO=67.73%, Fe₂O₃=12.09%, Nb₂O₅=20.18%. It shows that the sintering method does not have an influence on stoichiometry of the chemical composition of the PFN ceramics.

The microstructure and crystalline structure of the ceramics depends on many factors, among others, on the technological process, types of basic materials, kinetics of the phase transitions, conditions of grain growth, a method of synthesizing, time and a method of powder compacting etc. An appropriately performed technology has a decisive influence on a character of the crystalline structure and

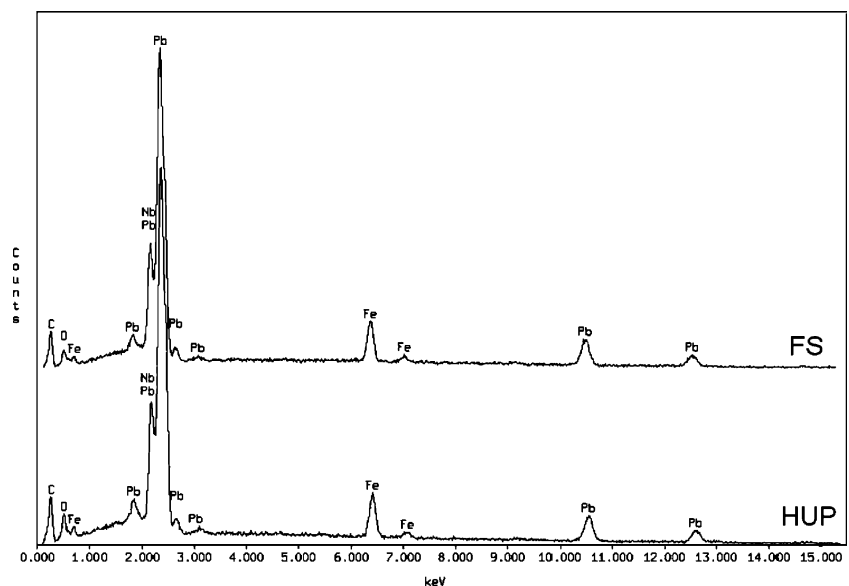
microstructure of the ceramics, what in turn influences its later properties and the applied parameters of the ceramics.

The $\ln\rho_{DC}(1/T)$ dependences for the PFN ceramics specimens are presented in Fig. 4. The freely sintered ceramics has slightly higher values of specific resistance ρ_{DC} . The specific resistance values and the calculated activation energies (E_a) in the ferroelectric ($T < T_m$) and paraelectric ($T > T_m$) phases are presented in Table 1. The activation energy for the specimens in question was calculated according to Arrhenius' law:

$$\rho = \rho_0 \exp\left(\frac{E_a}{k_B T}\right) \tag{2}$$

where: ρ_0 —pre-exponential factor, k_B —Boltzmann's constant, T —absolute temperature, E_a —the activation energy associated with the preponderant conduction mechanism in the analyzed temperature region which can be calculated from the slope of $\ln\rho_{DC}$ vs. $1/T$ plot. The PFN specimen

Fig. 3 The EDS analysis image of the element distribution for the PFN ceramics



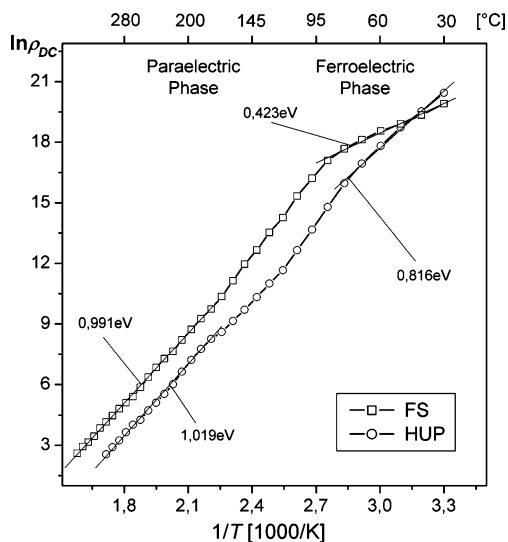


Fig. 4 Influence of the sintering method on the dependence of the direct current specific resistance (ρ_{DC}) vs. inverse temperature ($1/T$) for the PFN ceramics

obtained by the HUP method shows higher values of the activation energy, both in the ferroelectric and paramagnetic phase.

For the DC conductivity, the value of $E_a=0.423$ eV in the ferroelectric phase region ($T < T_m$) for ceramic specimens obtained by FS method is in correspondence with the extrinsic conductivity associated with small polarons and oxygen vacancies [2]. This value is smaller than the value of $E_a=0.816$ eV calculated from the specimens obtained by HUP method. This difference can be associated with the greater presence of Fe^{2+} ions and oxygen vacancies generated in specimen by the succession of processes precursor obtainment and sintering condition of the PFN

ceramics. Lower electric conduction of the PFN ceramics obtained by the HUP hot uniaxial pressing method is also connected with the appropriately formed microstructure, the densely packed grain and lower porosity.

Temperature dependences of permittivity (ϵ) and dielectric loss tangent ($\tan\delta$) for the ceramic PFN specimens are presented in Fig. 5. The PFN ceramics obtained by the hot uniaxial pressing method has higher values of the maximum permittivity (ϵ_m) in comparison with the specimen obtained by the free sintering method.

The investigation (Figs. 5 and 6) results show that independently on the sintering method (FS or HUP), the PFN ceramics is characterized by a diffusion phase transition from the ferroelectric into paraelectric phase (there is no point phase transition, but it takes place in a certain temperature area).

A character of the phase transition diffusion shows a degree of the crystalline structure ordering. When ordering is greater a phase transition taking place in a narrow temperature range is observed. It has a positive influence on the applied parameters of that kind of the ceramics.

The temperature dependence of the permittivity (ϵ) far from temperature T_m is well described by the linear Curie–Weiss law. Near T_m temperature dependence $\epsilon(T)$ is approximated by the quadratic Curie–Weiss law:

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

where T_m —the temperature at which electric permittivity reaches its maximum (ϵ_m), C —a temperature independent function, α —an exponent showing a diffusion degree of the transition from the ferroelectric to paraelectric phase. Where the value of exponent is $\alpha=1$, thus it points to

Fig. 5 Dependences of the permittivity (ϵ) and dielectric loss tangent ($\tan\delta$) on the temperature (T) function for PFN ceramics obtained by the (a) free sintering method and (b) hot uniaxial pressing method

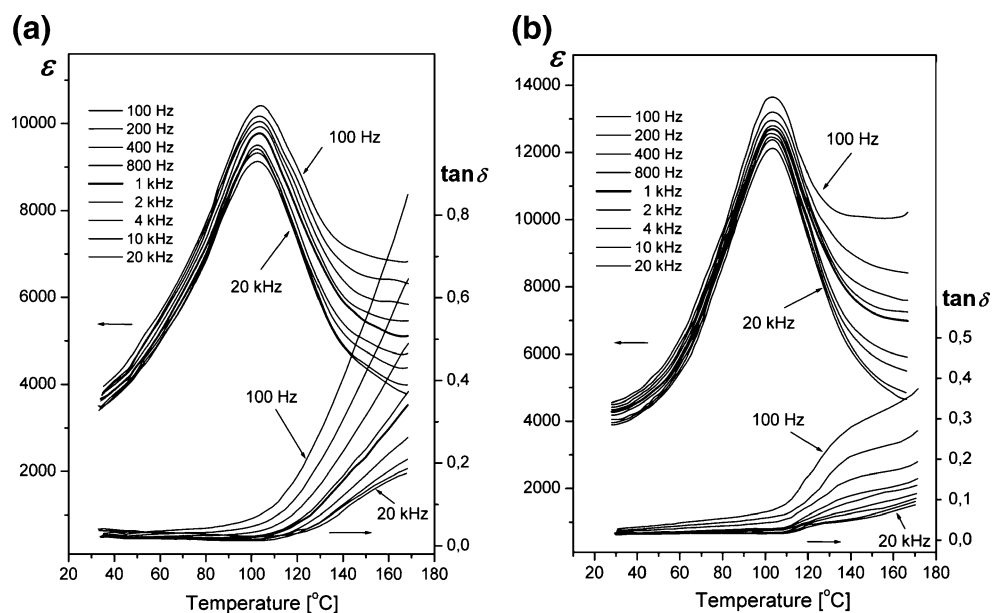
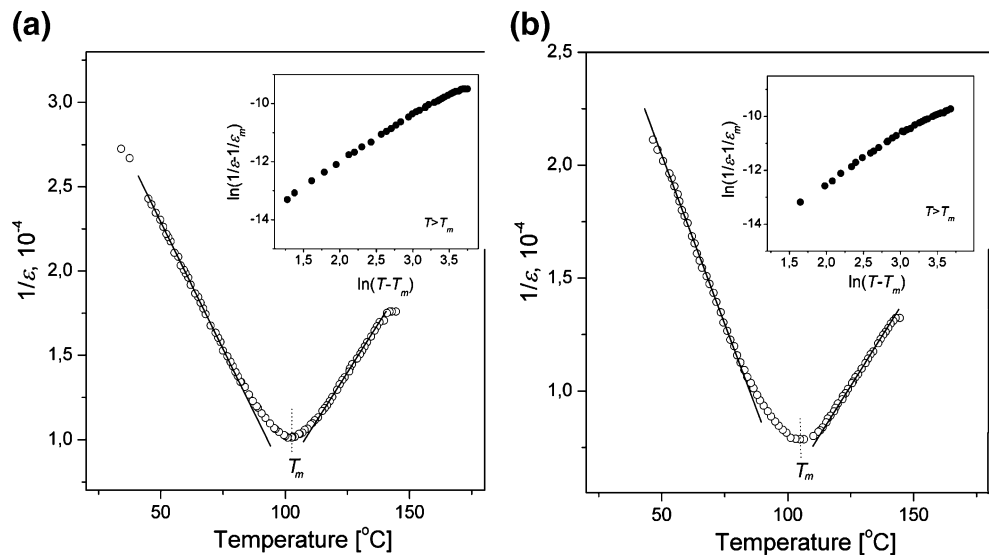


Fig. 6 Temperature dependences of reciprocal dielectric permittivity for PFN ceramics obtained by the free sintering (a) and hot uniaxial pressing (b), measured at the frequency of 1 kHz. Insert plots of $\ln(1/\varepsilon - 1/\varepsilon_m)$ vs. $\ln(T - T_m)$ at temperatures higher than T_m



behaviour according to the Curie–Weiss law when $1 < \alpha \leq 2$ then the phase transition has a diffusive character [5]. A character and a degree of the phase transition diffusion can be determined also as a ratio of the maximum electric permittivity to the electric permittivity at room temperature ($\varepsilon_m/\varepsilon_r$). The dielectric parameters, for $\nu=1$ kHz, and the calculated values of the α diffusion exponent and values $\varepsilon_m/\varepsilon_r$ for the PFN ceramics are presented in Table 1.

The phase transition diffusion is connected with a random distribution of Fe^{3+} and Nb^{5+} ions in the B positions of the perovskite lattice, what results in forming microscopic areas with different Curie temperatures. In comparison with the PFN ceramics sintered freely, a specimen sintered by the hot uniaxial pressing method has higher values of the maximum electric permittivity, and the

phase transition from the ferroelectric to paraelectric phase takes place at higher temperatures. Applying an external pressure at high sintering temperature facilitates a contact among the compact grains (accelerating diffusion processes) and allows partial ordering of the crystallographic orientation of particular grains of the ceramic microstructure. Those factors favour a uniform distribution of the Nb and Fe ions in the B sublattice of the compound, that is why the PFN ceramics obtained by the HUP method shows a lower degree of the diffusion phase transition than a specimen compacted by the free sintering.

The dielectric losses of the PFN ceramics obtained by the two stage synthesis method by the powder calcination are low. In the case of the freely sintered ceramics from room temperature to T_m the dielectric losses maintain at constant low level, and above the phase transition temper-

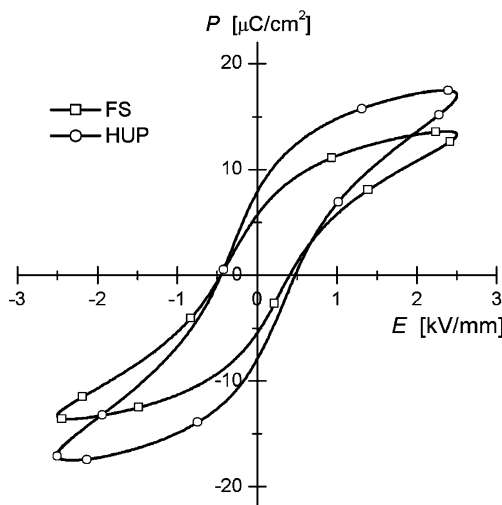


Fig. 7 The electric hysteresis loops ($\nu=1$ Hz) for the PFN ceramics compacted by the free sintering method (FS) and the hot uniaxial pressing method (HUP)

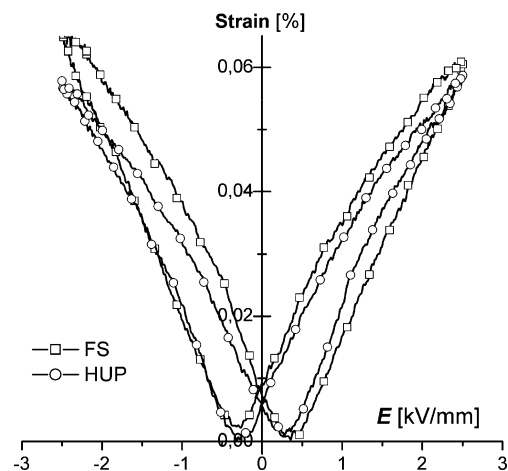


Fig. 8 Loops of a relative deformation in a function of the electric field ($\nu=1$ Hz) for the PFN ceramics compacted by the free sintering method (FS) and the hot uniaxial pressing method (HUP)

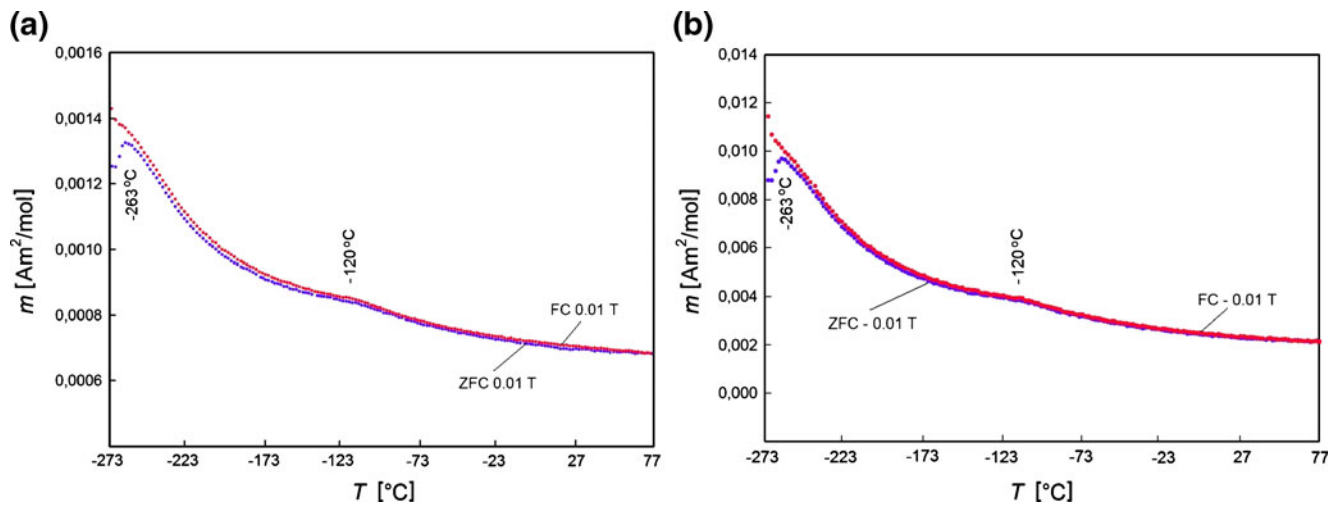


Fig. 9 Temperature dependence of zero field cooled (ZFC) and field cooled (FC) magnetization recorded in field of 0.01 T for ceramic PFN samples: (a) FS, (b) HUP

ature they increase rapidly. The ceramics sintered by the hot uniaxial pressing method shows lower dielectric losses in the whole measurement area and it has a similar character of the $\tan\delta(T)$ curve course. For this specimen a rapid increase in the dielectric losses occurs at about 20°C above the phase transition. In the case of the FS ceramics the dielectric losses are higher what is connected with an increase in electric conduction, above temperature T_m . Too high temperature and too long sintering time has a disadvantageous influence on the ceramic microstructure (too great increase in the grain growth, an increase in mechanical stresses etc.). The HUP method enables to lower the temperature and to shorten time of sintering and it limits porosity and excessive grain growth, leading to obtain the ceramics with lower dielectric losses.

Electric hysteresis loops of the PFN ceramic specimens, tested at room temperature T_r , at $\nu=1$ Hz frequency, are

presented in Fig. 7. The ceramic specimens have a narrow hysteresis loop, what proves that the material is polarized weakly. The PFN ceramics compacted by the free sintering method shows lower remanent polarization values ($P_R \approx 11.10 \mu\text{C}/\text{cm}^2$) and a lower values of coercive field ($E_C \approx 0.43 \text{ kV}/\text{mm}$) in comparison with a specimen compacted by the hot uniaxial pressing method, in a case of which $P_R = 13.70 \mu\text{C}/\text{cm}^2$ and $E_C = 0.46 \text{ kV}/\text{mm}$. The free sintered specimen is characterized by a greater degree of hysteresis saturation at 2.5 kV/mm field. A finer and less defected grain is one of the factors influencing higher polarization values for the HUP specimen.

The PFN ceramics shows a high concentration of free charge carriers. In spite of it, the PFN ceramics deformation loop (Fig. 8) is characterized by symmetry under an influence of a changeable electric field, what is characteristic for ferrosoft materials with a small internal field and

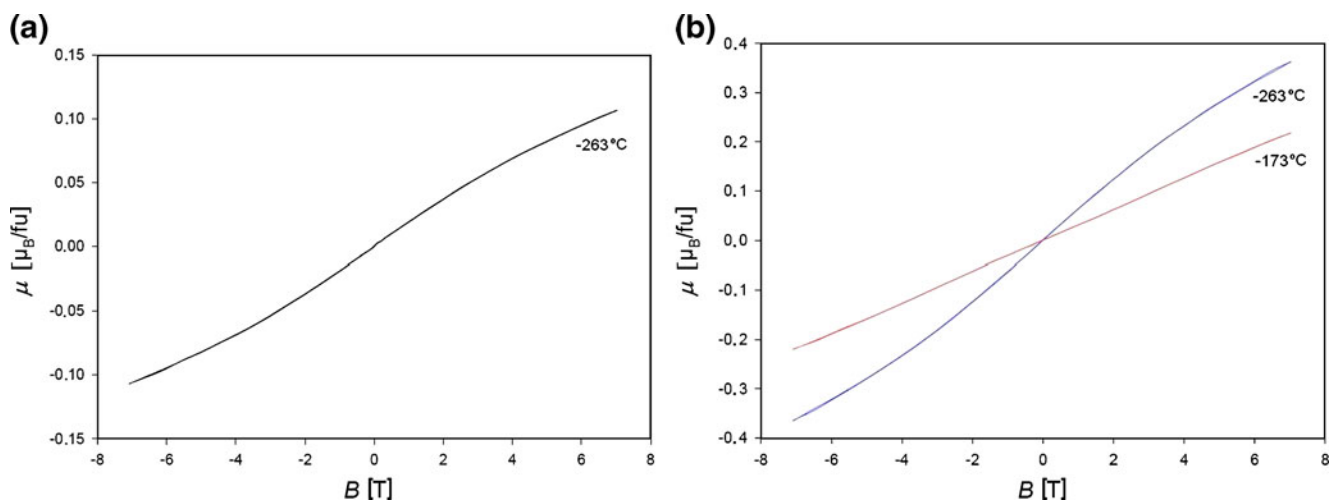


Fig. 10 Hysteresis magnetic loops for the PFN ceramic samples: (a) FS and (b) HUP

low values of the coercive force field. The characteristic loops in a shape of “wings of a butterfly” show relatively low values of remanent stresses and hysteresis. A distortion factor (H_S) presented in Table 1, was calculated on the basis of deformation loop, according the following relation:

$$H_S = \left(\frac{H_{half}}{S_{max}} \right) \cdot 100\%, \quad (4)$$

where: H_{half} —deformation hysteresis for a half of the maximum electric field value [%], S_{max} —deformation for the maximum electric field [%].

Magnetic examinations of the synthesized PFN powder, from which ceramic specimens were obtained, are presented in Fig. 9. On the temperature courses of the magnetization (in zero field cooled (ZFC) and field cooled (FC) recorded in field of 0.01 T) two weak and broad maxima are observed at the temperature of $T_{N1} \approx -120^\circ\text{C}$ and $T_{N2} \approx -263^\circ\text{C}$, which may be connected with presence of magnetic phase transitions. The authors of works [11] and [12] obtained the similar results with two ranges in which the Curie–Weiss law is met. A change of the sintering conditions does not have an influence of the m (T) of the PFN ceramics. However, differences between FS and HUP are observed on the $\mu(B)$ magnetic hysteresis loops (Fig. 10). The magnetic hysteresis for PFN ceramics is seen at -263°C revealing the presence of weak FM behaviour. Higher values of μ possesses the PFN ceramics received by the hot uniaxial method (Fig. 10(b)).

4 Conclusions

The $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) ceramics obtained by a two stage method of powder mixture synthesizing and a calcination technique is free from the undesirable pyrochlore phase, it has a fine-grained microstructure with a well-formed grain and it shows low values of electric conduction and dielectric losses. It improves properties and parameters of such a ceramics (high values of density, polarization and electric permittivity).

Hot uniaxial pressing enables to lower the sintering temperature and to shorten the specimen holding time at the maximum temperature. It has a positive influence on a degree of crystalline structure and microstructure perfectness (including an average grain size). The ceramics of

such a microstructure shows better physical properties and it has the optimum applied parameters.

The physical properties of the electroceramic depend indirectly on the production conditions. The production conditions have a direct influence on the chemical composition, the crystalline structure, the microstructure and the domain structure of the electroceramic, whereas its physical properties are a complex function of the factors mentioned, describing a structure and a physical state of the electroceramic in a microscopic (atom) and macroscopic (“higher than atom”) scale. All those factors are shaped during the ceramics production process and they depend both on the method and conditions of the compacting and sintering process.

Thus, in order to obtain the PFN ceramics with the best properties and optimum applied parameters it is recommendable to perform compacting of the synthesized powder by the HUP hot uniaxial pressing method.

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