

R. ZACHARIASZ*, D. BOCHENEK*

PROPERTIES OF THE PZT TYPE CERAMICS ADMIXED WITH BARIUM AND NIOBIUM

WŁAŚCIWOŚCI CERAMIKI TYPU PZT DOMIESZKOWANEJ BAREM I NIOBEM

In this work a PZT type ceramics of the composition $\text{Pb}_{0.90}\text{Ba}_{0.10}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.951}\text{Nb}_{0.049}\text{O}_3$ was obtained by a method of sintering simple oxides in the solid phase at high temperature. The X-ray examinations and examinations of a microstructure, an internal friction, dielectric and piezoelectric properties and a hysteresis loop of the ceramics obtained were made. The electrophysical parameters of the ceramics obtained show a possibility to use that type of material as a bimorphic and ignition transducers, and high values of piezoelectric parameters and electric permittivity to build band-pass filters.

Keywords: electric properties, internal friction, PZT ceramics, transducers

W niniejszej pracy otrzymano piezoceramikę typu PZT o składzie $\text{Pb}_{0.90}\text{Ba}_{0.10}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.951}\text{Nb}_{0.049}\text{O}_3$ metodą spiekania prostych tlenków, w fazie stałej, w wysokiej temperaturze. Przeprowadzono badania rentgenowskie, mikrostrukturalne, tarcia wewnętrznego, właściwości dielektrycznych, piezoelektrycznych oraz pętli histerezy otrzymanej ceramiki. Elektrofizyczne parametry otrzymanej ceramiki wskazują na możliwości zastosowania tego materiału jako bimorficzne i zapłonowe przetworniki, a wysokie wartości parametrów piezoelektrycznych i przenikalności elektrycznej umożliwiają jego wykorzystanie do budowy filtrów pasmowych.

1. Introduction

The $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) ceramics is one of the basic piezoelectric materials used in the modern electrical engineering. It is connected with its ferroelectric electromechanical and pyroelectric properties. PZT has a structure of the (ABO_3) , perovskite type, in which cations Ti^{4+} and Zr^{4+} take positions B in a random way, whereas cations Pb^{2+} occupy positions A [1]. Owing to wide range isomorphism of the $(1-x)\text{PbZrO}_3 - (x)\text{PbTiO}_3$ two component solid solution, which enables to substitute appropriate cations of admixtures in a place of zirconium Zr and titanium Ti, multi-component solid solutions called the PZT type ceramics are made on its base [2]. An appropriate selection of a composition, technological conditions and appropriate admixtures enables to obtain the PZT type ceramics being used as different types of piezoelectric transducers, electric band-pass filters, transformers, generators, servomotors and amplifiers, electrooptic materials or pyroelectric elements [3 - 6]. Besides appropriate values of electrophysical parameters, materials for that type of applications must show high temperature stability of resonance

frequency ($\Delta f_r/f_r < 0.2 \%$) and other parameters. Sharpness of pass band for a piezoelectric filter is influenced by a mechanical quality factor (Q_m) of the piezoceramic and should be equal to an inverse of a resonance stability coefficient (e.g. for $\Delta f_r/f_r = 0.001$, $Q_m = 1000$), whereas the pass band width without including inductance is proportional to a square of an electromechanical coupling coefficient. Thus, without including an induction coil, a crystal filter with coefficient $k_{ij} \approx 0.1$ can pass a band of the width not greater than 1 % of average frequency, whereas a PZT piezoceramics disk with $k_p = 0.5$ pass a band with the width of 10 % comparing to average frequency [7].

Since stability of resonance frequency f_r of the piezoceramic based on the $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ two component solid solution is small ($\Delta f_r/f_r > 0.5 \%$), the base PZT solid solution is admixed with appropriate admixtures to improve temperature and time stability of its parameters.

In the work a PZT type ceramics admixed with barium and niobium was obtained and comprehensive X-ray and microstructure examinations, examinations of dielectric and piezoelectric properties and hysteresis loop

* UNIVERSITY OF SILESIA, DEPARTMENT OF MATERIALS SCIENCE, 41-200 SOSNOWIEC, 2 ŚNIEŻNA STR., POLAND

of the ceramics obtained were conducted regarding possibilities of its application to build electric filters.

2. Experiment

The material tested was the PZT type ceramics admixed with barium and niobium of the composition $\text{Pb}_{0.90}\text{Ba}_{0.10}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.951}\text{Nb}_{0.049}\text{O}_3$ (PZT1). The initial components were oxides: lead PbO , zirconium ZrO_2 , titanium TiO_2 , niobium Nb_2O_5 and barium carbonate BaCO_3 . The PZT ceramics was synthesized by sintering of a mixture of simple oxides in the solid phase (a pressing method) in the following conditions: $T_{\text{synth}} = 850^\circ\text{C}$, $t_{\text{synth}} = 2$ h. Compacting was made by a free sintering method as a result of sintering twice in the following conditions: $T_{s1} = 1200^\circ\text{C} / t_{s1} = 3$ h and $T_{s2} = 1300^\circ\text{C} / t_{s2} = 3$ h. After baking twice the ceramic specimens were ground, polished and then, silver electrodes were spread by a paste burning method.

The X-ray examinations were made on a polycrystalline diffractometer of the Phillips firm with a Cu lamp and a graphite monochromator. The microstructure examinations were made by a SEM scanning microscope with field emission, HITACHI S-4700, and with EDS Noran Vantage system. Elemental distribution and microstructures were revealed by transmission electron microscope (TEM) Model JEM-3010 JEOL. Measurements of the $Q^{-1}(T)$ internal friction and the Young modulus $E(T)$ were made by an automatic relaxator of acoustic

frequencies of a RAK-3 type, 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 whereas an examination of the hysteresis loop with use of a high voltage feeder of a Matsusada Precision Inc. HEOPS-5B6 type.

In order to examine the piezoelectric parameters, ceramic PZT1 was poling by a low temperature method (high voltage) with use of a high voltage feeder of a Matsusada Precision Inc. HEOPS-5B6 type, in the following conditions: the poling temperature $T_{\text{pol}} = 165^\circ\text{C}$, the poling time $t_{\text{pol}} = 0.5$ h and the poling field in a range of $E_{\text{pol}} = 10 \div 40$ kV/cm. Poling of the specimens by the low temperature method took place at a temperature much lower than the Curie temperature of the PZT1 ceramics, in the silicon oil medium, being protection of the specimen against breakdown and possibilities to use high value of poling fields. The examinations of the piezoelectric parameters were made by a resonance-antiresonance method.

3. Examination results

The X – ray examinations of the ceramics with the composition of $\text{Pb}_{0.90}\text{Ba}_{0.10}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.951}\text{Nb}_{0.049}\text{O}_3$ (Fig.1), have confirmed that it belongs to a group of materials with a perovskite structure.

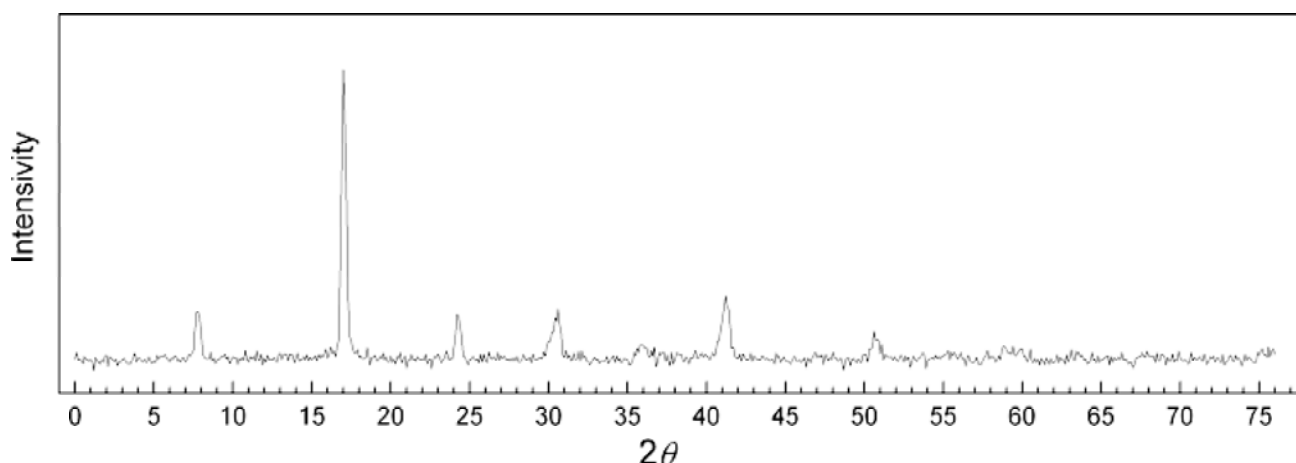


Fig. 1. The X-ray spectrum for ceramic PZT 1 at room temperature

Fig.2a and Fig.2b present TEM images of PZT1 ceramics and (Fig.2c, d) their diffraction patterns. A domain structure of the PZT1 ceramics is characterized by not wide domains and a low degree of domain structure ordering. There is a high concentration of struc-

tural twins (namely 90 degree structural domains) with 90 degree boundaries between them. A structure with cross-hatched tweeds can be observed in Fig.2a, whereas in Fig.2b characteristic longitudinal domains in a shape of needles with single twins and a complex of domains

are visible. It is possible to notice a few wedge-shaped domains sticking in complex another domains. It is characteristic for domain structure of the PZT type ceramics. Electron diffraction pattern of the PZT1 ceramics (Fig.

2c ,d) shown that studied material is correctly crystallized.

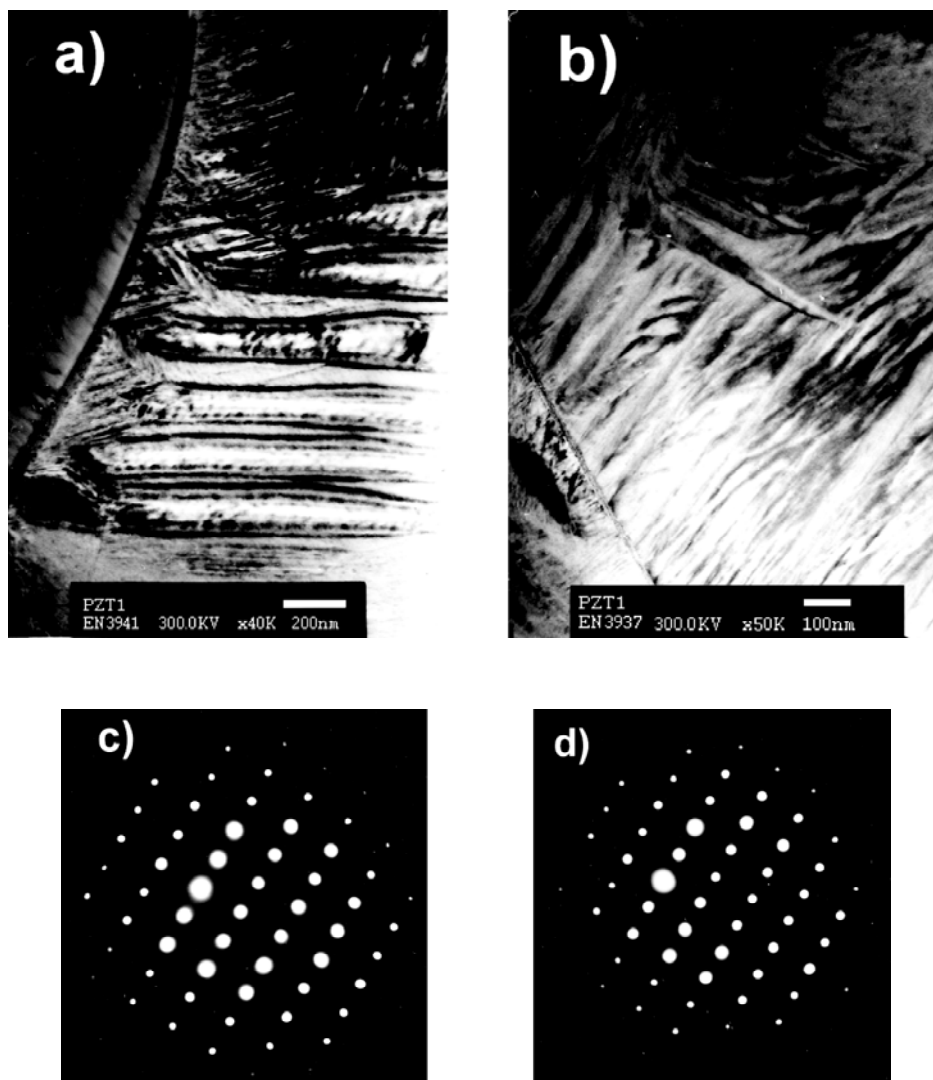


Fig. 2. TEM image domain-twinning structure of the PZT1 ceramics (a) for magnification x 40 k (with zig-zag domains) and (b) for magnification x 50 k (needles, single-variant tweeds and band domains), (c) and (d) corresponding electron diffraction pattern of PZT1

A microstructure photograph of a fracture of the PZT type ceramics is presented in Fig.3. This material is characterized by a non-porous structure with a densely packed and well-formed grain (the average grain size $\bar{r} < 2\mu\text{m}$).

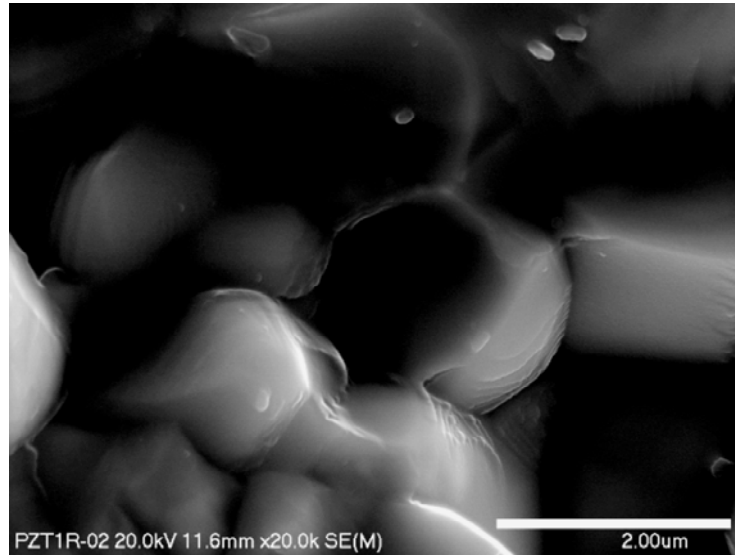


Fig. 3. SEM photographs of a fracture microstructure of PZT1 ceramics

Fig. 4 presents temperature relationships of the internal friction $Q^{-1}(T)$ and the dynamic Young modulus $E(T)$, obtained during a cycle of heating \leftrightarrow cooling for the specimen. On the $Q^{-1}(T)$ curve during the heating process there is a small maximum P1 at the temperature of $T_{P1} = 77^\circ\text{C}$, and then a slight increase in the internal friction takes place, until a P2 wide peak at the temperature of $T_{P2} = 229^\circ\text{C}$ appears. With further temperature increase a rapid increase in the internal friction is observed (peak P3). In the area of presence of maxima P1, P2 and P3 on the $Q^{-1}(T)$ curve, a decrease in a value of the dynamic Young modulus E was observed in a form of characteristic minima A1, A2, and A3 (Fig.4. rela-

tionships of $E(T)$). Those values were respectively: $E_{A1} = 100$ GPa in the area of presence of peak P1, $E_{A2} = 99$ GPa in the area of maximum P2 and $E_{A3} = 90$ GPa in the area of peak P3. In the cooling process after completing the heating cycle analogical changes of the relationships of $Q^{-1}(T)$ and $E(T)$ were observed and there was a difference that maxima P1, P2, and P3 moved toward lower temperatures and they were present at: $T_{P1} = 61^\circ\text{C}$, $T_{P2} = 215^\circ\text{C}$, $T_{P3} = 361^\circ\text{C}$ respectively. On the $E(T)$ curve determined for the specimen cooling process there was a decrease in the E value in the whole temperature range, and in the area of peak P1 the E_{A1} value was 98 GPa, for peak P2 – $E_{A2} = 97$ GPa, whereas $E_{A3} = 87$ GPa.

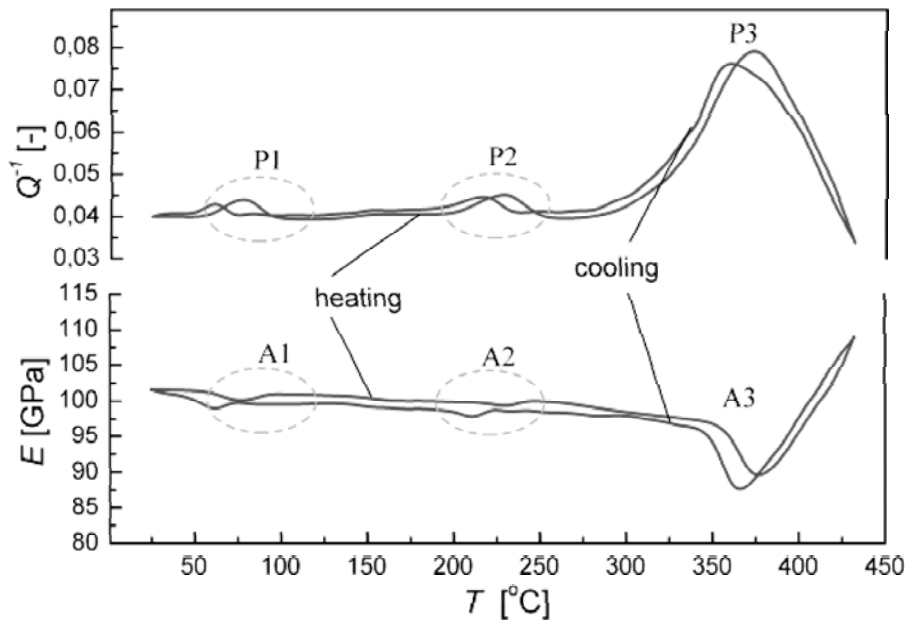


Fig. 4. Temperature relationships of $Q^{-1}(T)$ and $E(T)$ obtained for ceramic PZT1 during the heating \leftrightarrow cooling cycle

Height of maxima P1 and P2 and their temperature position depends on a lot of factors, such as e.g.: measurement frequency, a rate of heating and cooling of a specimen, additional defects of a structure introduced as a result of heating in the vacuum atmosphere or irradiation [9]. According to Arrhenius law and on basis of temperature measurements of presence of particular

peaks and measurement frequency of the specimen in question values of the activation energy E_{Act} (on basis of half width of the $Q^{-1}(T)$ curve) and the pre-exponential factor for peaks P1 and P2 were determined. The calculated values of the parameters are presented in Table 1.

TABLE 1

Values of activation energy E_{Act} and a pre-exponential factor τ_o for PZT1 for a heating \leftrightarrow cooling cycle

	P1 heating	P1 cooling	P2 heating	P2 cooling
T_p [°C]	77	61	229	215
E_{Act} [eV]	1.14	1.03	1.82	1.71
τ_o [s]	$(6.81) \cdot 10^{-15}$	$(4.65) \cdot 10^{-16}$	$(8.19) \cdot 10^{-21}$	$(2.13) \cdot 10^{-22}$
Q_m^{-1} [-]	0.044	0.041	0.045	0.043

Peak P2 reflects an initial increase in a number of domains what also results in an increase in a value of the internal friction. However, a phenomenon of a decrease in mobility of the domain walls is connected with an increase in a number of domains, and it causes a decrease in a value of the internal friction in the area before the Curie temperature. Activation parameters of peak P1 point to relaxation processes connected with mutual interaction of point defects (mainly oxygen and lead vacancies) and domain walls (mainly 90 °). Those defects were introduced in the PZT1 ceramics structure both in the technological process and as a result of admixing with the Nb₂O₃ oxide. The E_{Act} values obtained, being within ranges from 1.14 eV to 1.03 eV for a process of heating and cooling of the specimen, respectively, are connected with a migration process of point defects in the materials of the PZT type [8].

Presence of the P3 characteristic maximum on the $Q^{-1}(T)$ curve, correlating with occurrence of a visible minimum on the $E(T)$ relationship is connected with a phase transition taking place for the ceramics with the composition in question. This phenomenon is connected with a phase transition from a ferroelectric phase to a paraelectric phase (temperature Curie T_C) and with a simultaneous transition of a tetragonal structure in regular one [9]. An analysis made for peak P3 for three different measurement points of ceramic PZT1 confirmed that it was responsible for a phase transition of ferroelectric \leftrightarrow paraelectric (no temperature transition of its position was observed). With an increase in the measurement frequency a decrease in the P3 height was observed (Fig.5).

Changes taking place in the area of the P3 peak presence, connected with a phase transition are described by a relationship of J.F. Delome and P.F. Gobin, which

says that they are proportional to a rate of temperature changes of the specimen in question and to the amount of mass taking part in the phase transition and inversely proportional to resonance frequency of the specimen vibrations [10]. This relationship can be written in a form of the formula:

$$Q^{-1} = \frac{KG}{\omega} \cdot \frac{\partial m}{\partial T} \cdot \frac{\partial T}{\partial t}, \quad (1)$$

where: K – material constant, G – shear modulus, ω – frequency of the specimen vibration ($\omega = 2\pi f$, f – frequency of the specimen vibration), $\frac{\partial m}{\partial T}$ – amount of the substance taking part during the phase transition, $\frac{\partial T}{\partial t}$ – a rate of temperature changes (during a heating or cooling cycle).

As it results from relationship (1), for ceramic PZT1, height of maximum Q_m^{-1} for peak P3 is inversely proportional to resonance frequency of the specimen vibrations, what is reflected by the $Q^{-1}(1/f)$ curves in Fig.5.

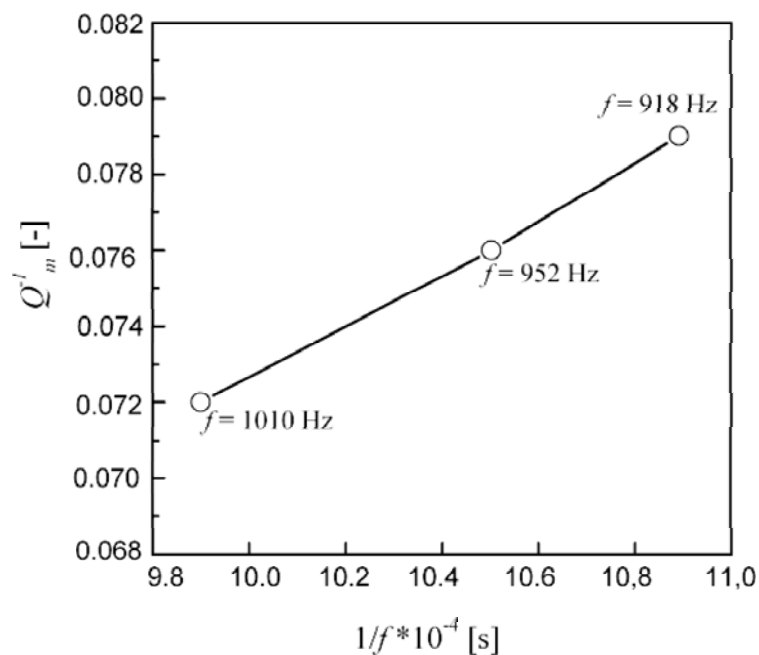


Fig. 5. Dependence of height of the P3 phase transition peak on the converse of the resonance frequency of the specimen vibrations

The PZT type ceramics shows temperature changes of electric permittivity in the temperature function typical for ferroelectrics (Fig.6). The phase transition temperature, for the measurement field $\nu = 1$ kHz is $T_m = 361^\circ\text{C}$. For the measurement field $\nu = 1$ kHz, at room temperature T_r , the PZT1 ceramics has high values of electric permittivity ($\epsilon_{Tr} = 1200$), whereas at the phase transition temperature ($\epsilon_{Tm} = 5500$).

Temperature courses of dielectric losses for the com-

position in question show typical behaviour for materials of the PZT type. In the area of the phase transition a characteristic decrease in the $\tan \delta$ values is observed, and then after exceeding the phase transition temperature there is their rapid increase. The PZT1 ceramics shows low dielectric losses and for the measurement field frequency $\nu = 1$ kHz, tangent values of the dielectric loss angle are: $\tan \delta_{Tr} = 0.016$ for the room temperature and $\tan \delta_{Tc} = 0.074$ for the phase transition temperature.

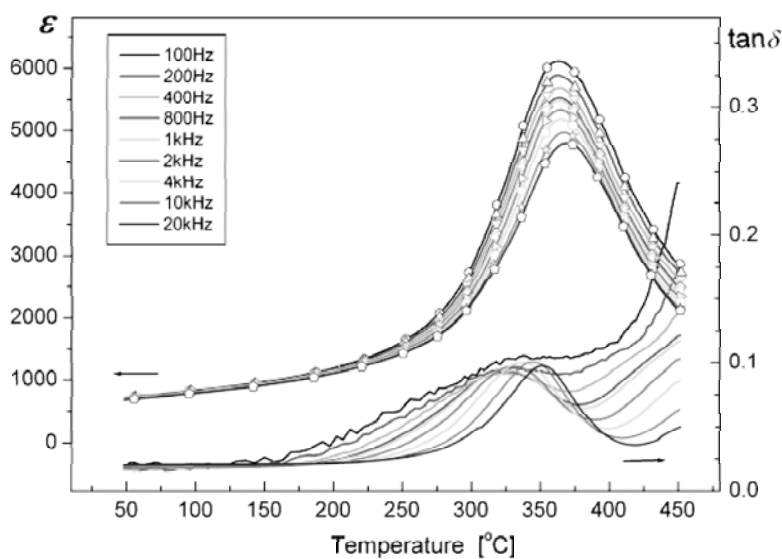


Fig. 6. Dependences of electric permittivity (ϵ) and a tangent of the dielectric loss angle ($\tan \delta$) on a temperature (T), for the PZT type ceramics

Fig.7 presents an electric hysteresis loop obtained at room temperature for the PZT type ceramics composition in question. This material is classified into ferrosoft materials, which in changeable electric fields, is easily prone to repolarization. The electric hysteresis loop shows high values of residual and spontaneous polarization, (saturation of the hysteresis loop) and a big coercion

field. For the applied external variable electric field 3.5 kV/mm, the value of the residual polarization is $P_r = 23.38 \mu\text{C}/\text{cm}^2$ and the value of the coercion field is $E_C = 1.55 \text{ kV}/\text{mm}$. Changes in values of P_r and E_C with an increase in the external electric field E_{\sim} are presented in Table 2.

TABLE 2

Changes in values of P_r and E_C with an increase in the external electric field E_{\sim}

E_{\sim}	2.0 kV/mm	2.5 kV/mm	3.0 kV/mm	3.5 kV/mm
$E_C [\mu\text{C}/\text{cm}^2]$	1.063	1.40	1.48	1.55
$P_r [\mu\text{C}/\text{cm}^2]$	13.49	20.40	22.10	23.38

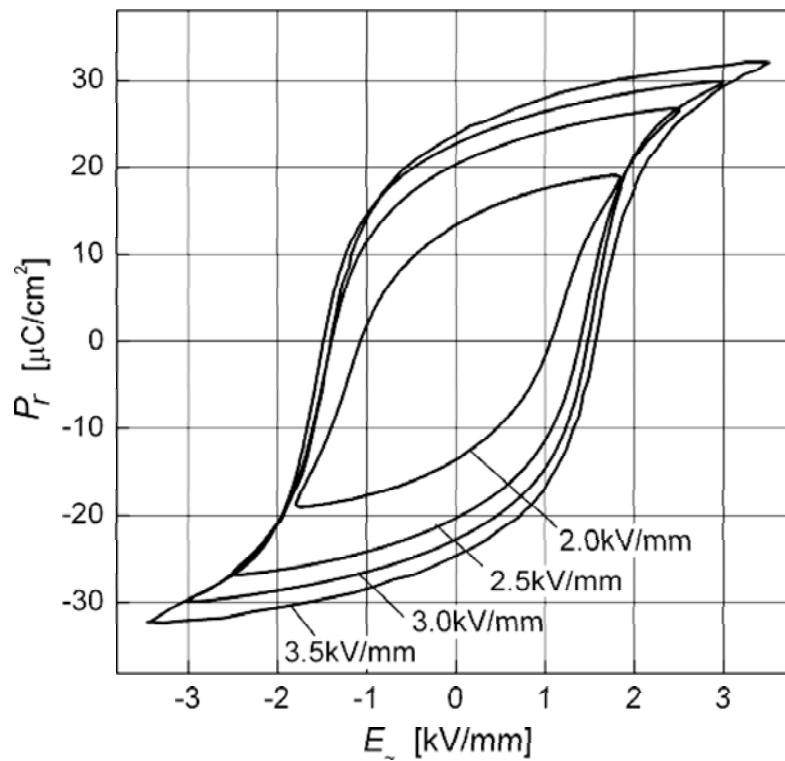


Fig. 7. Hysteresis loops for the PZT1 ceramics for $E_{\sim} = 2.0 \text{ kV}/\text{mm}$, $2.5 \text{ kV}/\text{mm}$, $3.0 \text{ kV}/\text{mm}$ and $3.5 \text{ kV}/\text{mm}$

Values of piezoelectric parameters and their temperature and time stability depend, to a high degree, on a way and poling conditions. An influence of values of the poling field E_{pol} on the selected parameters for ceramic PZT1 poling by a low temperature method in the conditions: $T_{pol} = 165^{\circ}\text{C}$, $t_{pol} = 30 \text{ min}$. With an increase in the poling field E_{pol} intensity there is an increase in values of piezoelectric parameters, electromechanical coupling factor k_p , k_{31} , piezoelectric modulus d_{31} , g_{31} , a speed of the acoustic wave propagation V_R and antiresonance frequency/resonance frequency ratio f_a/f_r of the ceramic PZT-1. With the poling field E_{pol} increase,

however, there is a decrease in values of elastic susceptibility S_{11}^E and electric permittivity ϵ_{33}^T . The optimum parameters for piezoceramic PZT1 are obtained for the poling field $E_{pol} = 3.5 \text{ kV}/\text{mm}$.

TABLE 3

An influence of poling field on the piezoelectric parameters of PZT1 ceramics poling by a low temperature method in the conditions:

$$T_{pol} = 165^{\circ}\text{C}, t_{pol} = 30 \text{ min}$$

E_{pol}	1.0 kV/mm	1.5 kV/mm	2.0 kV/mm	2.5 kV/mm	3.0 kV/mm	3.5 kV/mm	4.0 kV/mm
k_p	0.54	0.57	0.58	0.59	0.60	0.61	0.61
k_{31}	0.28	0.30	0.31	0.32	0.33	0.33	0.33
$d_{31} \times 10^{-12}$ [C/N]	152.7	163.4	168.4	170.1	172.1	174.3	172.7
$g_{31} \times 10^{-3}$ [Vm/N]	9.14	9.79	10.03	10.33	10.41	10.63	10.66
f_a/f_r	1.137	1.146	1.168	1.175	1.180	1.186	1.187
$S_{11}^E \times 10^{-12}$ [m ² /N]	17.22	17.08	17.05	16.79	16.83	16.69	16.39
$\varepsilon_{33}^T \times 10^{-11}$ [F/m]	1670.3	1668.8	1667.7	1645.8	1641.5	1632.8	1628.7
V_r [m/s]	1923	1931	1931	1932	1934	1936	1941

4. Summing up

A choice of an appropriate technological process to obtain the PZT type ceramics has an essential influence on electric parameters of the ceramics, including temperature and time stability of the resonance frequency. The method to obtain ceramic $\text{Pb}_{0.90}\text{Ba}_{0.10}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.951}\text{Nb}_{0.049}\text{O}_3$ used in this work enables to get the ceramics having its high applied parameters. Adding barium Ba^{2+} and a soft admixture of Nb^{5+} to the base composition of the PZT type ceramics causes an increase in the electric permittivity value ε and piezoelectric parameters and it also leads to a decrease in dielectric losses at high temperatures. Owing to it, this material can be used to build piezoelectric filters used in multi-channel telephony, telemetry, to analyze signals in multi-stage amplifiers of medium frequency etc. High values of piezoelectric modules and values of electromechanical coupling coefficient ($k_p > 0.5$) much higher than quartz, allowed an application of this type of the ceramics for band filters, in which adjustment accuracy of 10^{-3} is sufficient.

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