

FERROELECTRIC AND FERROELECTROMAGNETIC CERAMICS IN A VIEW OF POSSIBILITIES TO BE USED IN ELECTROACOUSTIC

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Ferroelectric ceramics were born in the early 1940's with the discovery of the phenomenon of ferroelectricity as the source of the unusually high dielectric constant in ceramic barium titanate capacitors. Since that time, they have been the heart and soul several multibillion dollar industries, ranging from high-dielectric-constant capacitors to later developments in piezoelectric transducers, positive temperature coefficient devices, and electrooptic light valves. Various ceramic formulations, their form, fabrications, functions, and future are described in relation to their ferroelectric nature and specific areas of applications. This paper is intended to illustrate practical uses of ferroelectric and ferroelectromagnetic ceramics obtained and investigated by the authors.

INTRODUCTION

The ferroelectric (PZT, PLZT) and ferroelectromagnetic (PFN) ceramics belongs to the solid solutions with the combination of ABO_3 type structure.

Lead titanate zirconate $Pb(Zr_xTi_{1-x})O_3$ (PZT) ceramics are one of the most common piezoelectric materials in industry. They are used as transducers between electrical and mechanical energy, such as phonograph pickups, air transducers, underwater sound and ultrasonic generators, delay-line transducers, wave filters, piezoelectric micromotors, microrobots, actuators, etc. [1-8]. Generally, all those applications need low electrical and mechanical losses. The ferroelectric ceramics has a pronounced maximum in dielectric constant

and piezoelectric effects in the proximity of the morphotropic transformation at Zr/Ti ratio between 0.52 and 0.55 [1,9]. The study of PZT modified with some additives is studied widely in order to improve their properties. However the modifications generally lead to the creation of undesirable defects due to a lack of compensation in some of the components. The nature and concentration of the components, the shaping procedure of green bulk, the sintering temperature and atmosphere are the controlling factors which provide the suitable properties for applications. The changes properties of these materials are possible by inserting point structural defects. $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ crystallizes with the ABO_3 type structure in which the A-site is occupied by Pb^{2+} ions; Zr^{4+} and Ti^{4+} are accommodated on the B-site (Fig. 1). The influence of various substitutions in the A and B-site of PZT unit cell has been studied by numerous investigators.

The PLZT formula $(\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3)$ assumes that La^{3+} substitutes for Pb^{2+} in the A-site and the B-site vacancies are created for electrical balance. The composition of PLZT is routinely represented by the notation $x/(1-y)/y$, which denotes the amount of La/Zr/Ti, given in mole fractions or mole per cent. The PLZT type ceramic may be used for electro-optic and has a potential use in non-volatile memories, transducers, modulators, etc. [10-12].

The $\text{Pb}(\text{Fe}_x\text{Nb}_{1-x})\text{O}_3$ ferroelectromagnetic ceramics, called shortly PFN, belongs to a family of materials with a perovskite structure with the $\text{A}(\text{B}'\text{B}'')\text{O}_3$ general formula, where in positions A Pb ions substitute themselves, and in octahedral positions B' and B'' ions of Fe and Nb in a random way [13]. The PFN material is characterized by two ordered antiferromagnetic and ferroelectric sub-systems. A change from the paramagnetic to ferroelectric phase takes place at about 143 K temperature, whereas a change from the paraelectric to ferroelectric phase occurs at about 383 K temperature [14]. The PFN is an optimal ceramic material to produce multilayered ceramic capacitors. Owing to their large capacitance, highly compact design and reliability, these capacitors have become promising candidates for electronic devices [15].

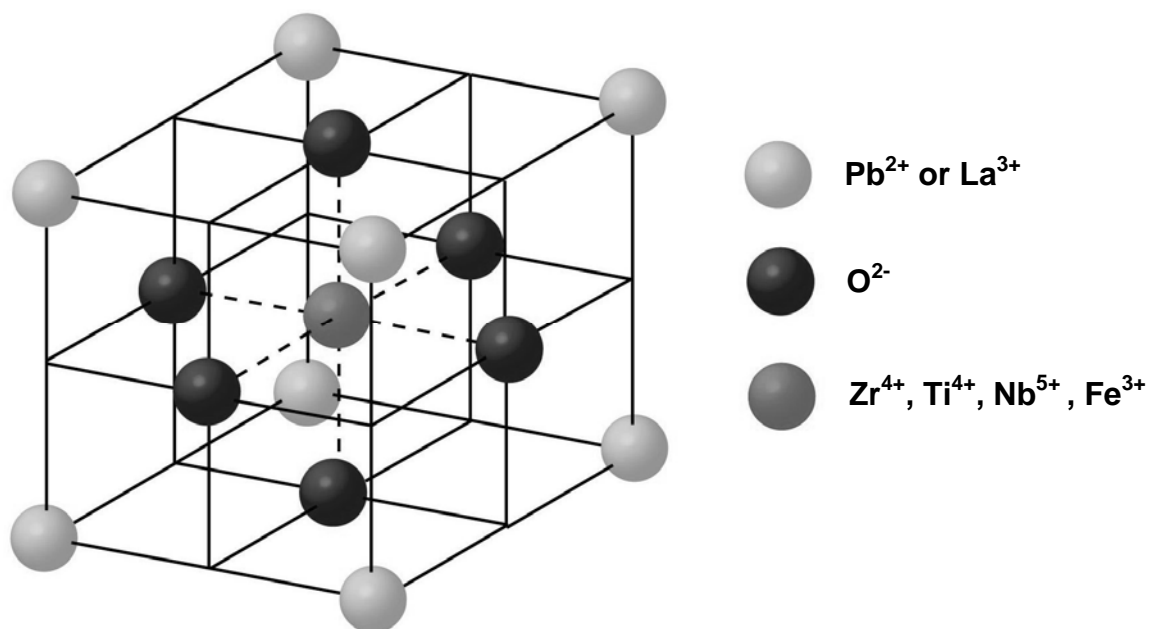


Fig.1 The elementary cell of ABO_3 type structure

1. THE PZT CERAMICS

In the work, comprehensive researches of the converters produced on the base of PZT were made. They were performed for five compositions with „hard” and „soft” dopants (table 1).

Tab.1 Chemical compositions of the PZT ceramics used in the researches

	Chemical composition	Zr/Ti	Dopants		
				hard	soft
Cc* 1	$(\text{Pb}_{0.94}\text{Sr}_{0.06})(\text{Zr}_{0.46}\text{Ti}_{0.54})\text{O}_3$ + 0.25% wt. Cr_2O_3	46/54	Sr	Cr	-
Cc* 2	$(\text{Pb}_{0.94}\text{Ba}_{0.06})(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ + 0.15% wt. Cr_2O_3 + 0.1% wt. MnO_2	52/48	Ba	Cr, Mn	-
Cc* 3	$(\text{Pb}_{0.94}\text{Sr}_{0.06})(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ + 0.25% wt. Cr_2O_3	50/50	Sr	Cr	-
Cc* 4	$(\text{Pb}_{0.9}\text{Ba}_{0.1})(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ + 1.67% wt. Nb_2O_5	53/47	Ba	-	Nb
Cc* 5	$\text{Pb}(\text{Zr}_{0.70}\text{Ti}_{0.30})\text{O}_3$ + 0.15% wt. Cr_2O_3 + 0.1% wt. MnO_2	70/30	-	Cr, Mn	-

*Cc – Chemical composition

In the tested materials the positions B, took up by the Zr and Ti ions, were partly substituted by „hard” dopants of the Cr^{2+} (Cc 1, 2, 3 and 5). Whereas, additionally in these positions for the Cc 2 and 5, a dopant of the Mn^{2+} was substituted. As it is known, the ions of the Pb^{2+} occupy the positions A in the PZT ceramics. For Cc 1 and 3 the ions of Pb^{2+} were partly occupied by the Sr^{2+} and Ba^{2+} ions. In the case of Cc 4, „soft” dopant of the Nb^{5+} substituted in the positions B and ions of the Ba^{2+} substituted in the positions A have been used. The conducted modification of the basic chemical composition was purposeful with the point of view of a future experiment. In the comparison to non-modified compositions of the PZT, improvement of the piezoelectric properties (electromechanical coupling coefficient k_p) as well as decreasing the temperature of phase transition (Curie temperature T_C) are caused by addition of the Ba^{2+} and Sr^{2+} . Analyzing the content of Zr/Ti, it should be emphasized that the samples of ceramics with Cc 1 to 4 belong to morphotropic area, whereas the sample with Cc 5 to the area with rhombohedral structure [17]. The material to build converters with different dielectric and piezoelectric parameters, applicabled in different disciplines of acoustoelectronics, has been received.

Tab.2 The electric parameters for the investigated PZT converters

Cc	T_C [K]	ε in T_p	ε in T_C	$\text{tg}\delta$ in T_p	$\text{tg}\delta$ in T_C	k_p	$d_{31} \times 10^{12}$ [C/N]	$S_{11}^E \times 10^{13}$ [m ² /N]	$E_C \times 10^6$ [V/m]	P_r [C/m ²]
Cc 1	644	620	9800	0.009	0.342	0.37	45	95	0.62	0.012
Cc 2	638	1170	12800	0.007	0.208	0.59	120	130	0.72	0.043
Cc 3	633	900	10000	0.012	0.325	0.35	65	115	0.52	0.013
Cc 4	585	1400	11000	0.023	0.036	0.50	120	145	1.06	0.177
Cc 5	592	400	11700	0.037	0.211	0.25	20	86	0.49	0.074

*Cc – Chemical composition

As shown in the table 2, the best set of electrical parameters possesses the ceramics with the Cc 2: high temperature of phase transition $T_C = 638$ K, high values of the electric permittivity ε , piezoelectric modulus d_{31} , and electromechanical coupling coefficient k_p as well as the lowest values of the $tg\delta$. The ceramics with Cc 1, 2 and 3, with „hard” dopants Cr^{2+} and Mn^{2+} , is characterized by low values of the $tg\delta$ (in the range $0.007 \div 0.012$), high Curie temperature T_C . But on other hand, they have low values electric permittivity ε (with the exception of Cc 2, in which thanks to additional doping of Ba^{2+} , the values of $\varepsilon = 1170$ were obtained). The values of k_p are contained in the range $0.35 \div 0.59$. In the case of the ceramics with Cc 4, with “soft” dopant Nb^{5+} , distinct growth of the ε is observed (to the values 1400). This Cc 4 has high values of piezoelectric modulus d_{31} as well as elastic susceptibility S_{11}^E , too. However, the dopants of niobium causes distinct growth of the $tg\delta$ to the values about 0.023 in the room temperature. It is unprofitable from the point of view of it’s practical use in the ceramics Cc 4. The temperature of phase transition T_C for the converters with Cc 4 shifts to 585 K and it is lowest in the comparison to other chemical compositions. The high values of the $tg\delta$ and low values of the ε in the converters with the Cc 5 is caused by the change of the content $Zr/Ti = 70/30$ and the transition from morphotropic to rhombohedral phase. As it is shown, the values of piezoelectric parameters: k_p , d_{31} i S_{11}^E for Cc 5 are lowest, too (Fig. 2).

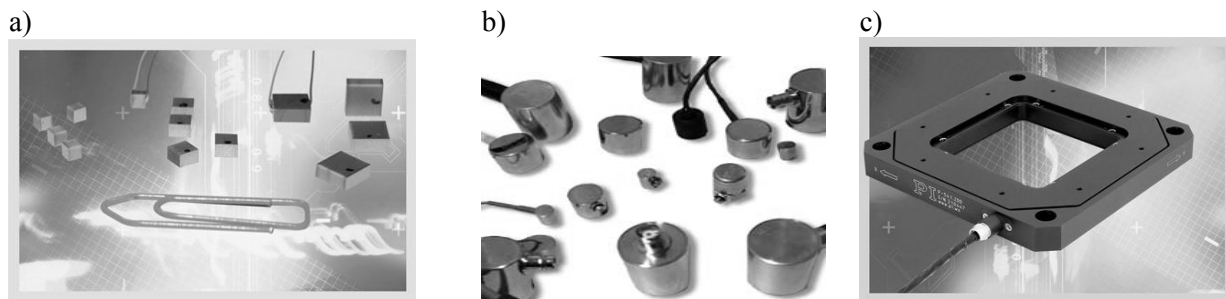


Fig.2 Applications of PZT: a) PZT capacitors, b) acoustic emission transducers, c) piezo nanopositioning stages for microscopy

In the ceramic converters with Cc 4, doping Nb^{5+} and Ba^{2+} , the following parameters are observed: high values of the polarization $P_r = 0.177$ C/m² and of the coercive force $E_C = 1.06 \times 10^6$ V/m. In the case of ceramics with Cc 2, doping Ba^{2+} and “hard” dopants Cr^{2+} i Mn^{2+} , clear fall values of the P_r to 0.043 C/m² and of the E_C to 0.72×10^6 V/m is visible. Whereas Cc 1 and 3 with „hard” dopants Cr^{2+} i Mn^{2+} and doping Sr^{2+} instead Ba^{2+} , show definitely lower values of the polarization P_r as well as low values of the coercive force E_C (table 2). The ceramics with Cc 5 is characterized by low values of the coercive force $E_C = 0.49 \times 10^6$ V/m.

2. THE PLZT CERAMICS

The aim of this part of work was to obtain solid solution of the PLZT from ferroelectric phase with constant ratio $Zr/Ti=50/50$ and variable concentration of La^{3+} ions:

- **$Pb_{0.95}La_{0.05}(Zr_{50}Ti_{50})_{0.9875}O_3$ - PLZT 5/50/50**
- **$Pb_{0.95}La_{0.10}(Zr_{50}Ti_{50})_{0.975}O_3$ - PLZT 10/50/50**

and investigate electromechanical properties of obtained ceramics.

The measurements of the temperature dependences of $\epsilon(T)$ and $\text{tg}\delta(T)$ were obtained as a aim of detailed analysis of the changes in the area of phase transition. The nature of the temperature dependences of $\text{tg}\delta(T)$ in the range of temperatures below phase transition is connected with dissipation of energy to polarization of the domains. But above the phase transition temperature (T_C) losses of energy are related with electric conductivity. For both chemical composition of PLZT type ceramics the temperature dependences of $\epsilon(T)$ has a relaxor character with diffuse phase transition between ferroelectric and paraelectric phase.

Tab.3 Basic parameters of the PLZT measured at 293K [10]

Parameter	Value	
% mol La	5	10
electric permittivity ϵ [-]	1450	1650
dielectric losses $\text{tg}\delta$ [-]	0.020	0.004
electromechanical coupling coefficient k_p [-]	0.33	0.32
piezoelectric modulus $d_{31} \cdot 10^{11}$ [C/N]	2.24	6.36
acoustic velocity V_R [m/s]	2446	2030
elastic susceptibility $S_{11}^E \cdot 10^{11}$ [m ² /N]	1.61	1.32
elastic susceptibility $S_{12}^E \cdot 10^{12}$ [m ² /N]	-7.53	-5.06
elastic modulus $C_{11}^E \cdot 10^{-10}$ [N/m ²]	6.17	7.56
density ρ [kg/m ³]	7542	7315
Poisson's ratio ν [-]	0.46	0.38
resonance frequency f_r [kHz]	229	266.2

The k_p coefficient characterizes a part of electric energy transformed into mechanical energy while applying an external electric field. It can also characterizes a part of mechanical energy transformed into the electric energy, in a case when the mechanical stress is applied to the samples. The k_p value is always lower than unit, because during transformation of one type of energy into other a part of energy is dispersed. The values of k_p coefficient as well as for PLZT 5/50/50 and PLZT 10/50/50 are almost the same and respectively are 0.33 and 0.32.

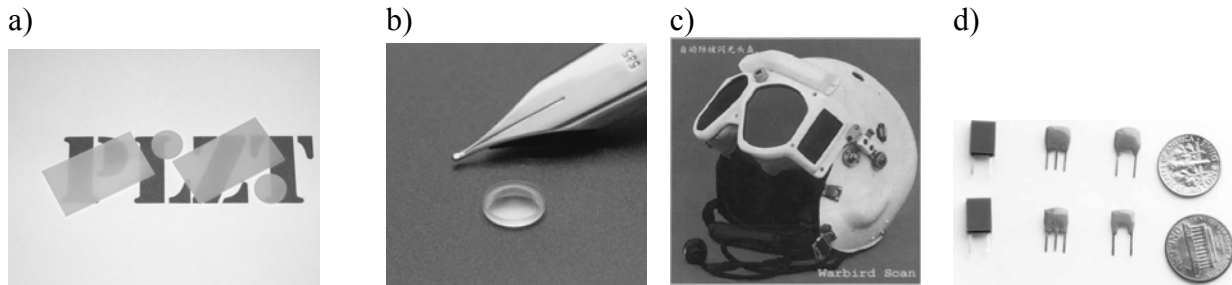


Fig.3 Applications of PLZT: a) samples of transparent PLZT ceramics obtained by the authors, b) transparent ceramics lens used in digital cameras, c) anti-flash goggles for nuclear operations, d) PLZT capacitors

Obtained PLZT type ceramic samples are characterized by low values of dielectric losses of angle $\text{tg}\delta=1\div1.5\%$ and high values of electric permittivity $\epsilon=11000\div12000$ (at room temperature). The measurement of the temperature dependences of ϵ let to obtained the temperature of phase transition (T_C). The value of T_C is decreasing with increasing of La content. Lanthanum has also significant influence for level of diffuse phase transition (Fig. 3).

3. THE PFN CERAMICS

The $\text{Pb}(\text{Fe}_{1-x}\text{Nb}_x)\text{O}_3$ was obtained by two methods. In the first synthesizing took place as a result of sintering of compacts from a mixture of PbO , Fe_2O_3 and Nb_2O_5 oxides in the conditions $T_{\text{synth}}=850^\circ\text{C}/t_s=4\text{h}$ (PFN1), whereas in the second calcining of mixed oxides (CMO) was used in the conditions $T_s=850^\circ\text{C}/t_s=4\text{h}$ (PFN2). Compacting of the synthesized PFN powders was made by the FS free sintering method. For PFN1 as a result of sintering of compacts twice in the conditions: $T_s=950^\circ\text{C}/t_s=4\text{h}$ and $T_s=1050^\circ\text{C}/t_s=4\text{h}$, whereas for PFN2 in the conditions: $T_s=1050^\circ\text{C}/4\text{h}$.

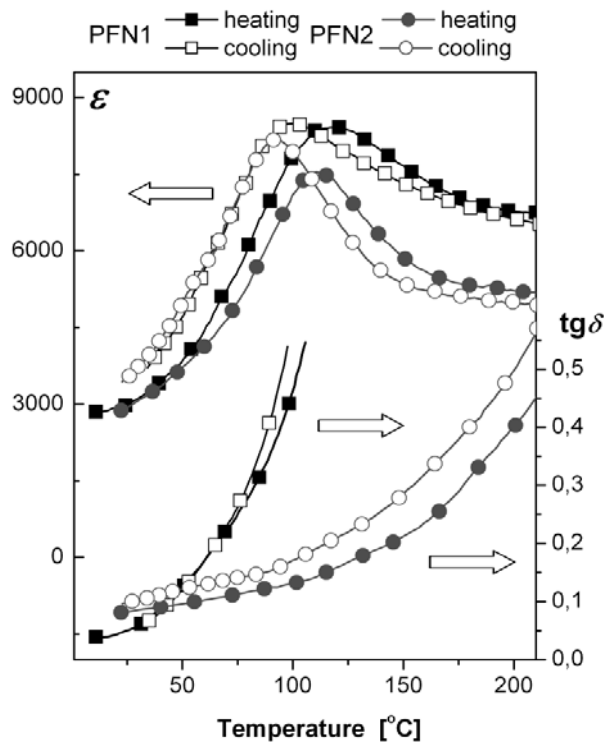


Fig.4 Diagrams of the $\epsilon(T)$ and $\text{tg}\delta(T)$ relationships for the PFN ceramic specimens in question [15]

In the PFN ceramics the pyrochlore non-ferroelectric phase is formed first (at 500°C), whereas the perovskite ferroelectric phase begins to appear above that temperature. Co-existence of those phases is obtained at the temperature of 700°C , whereas the pure perovskite phase at 750°C [6]. The CMO method used in the one-stage synthesis enables to minimize the pyrochlore phase during the PFN ceramics production. Percentage content of the P_{perow} perovskite phase for PFN1 and PFN2 is 94.58% and 96.77%, respectively.

Tab.4 Presentation of parameters of the PFN ceramic specimens in question (heating cycle)

	$\rho_{exp} \times 10^3$ [kg/m ³]	ρ_{exp}/ρ_{ther} x100 [%]	T_m [K]	ϵ_r	$(tg\delta)_{Tr}$	ϵ_m	$(tg\delta)_{Tm}$
PFN1	7.636	90.29	114	2900	0.052	8420	0.71
PFN2	8.180	96.72	110	2890	0.062	7530	0.14

Diagrams of relationships of electric permittivity and dielectric losses in the temperature function for the tested compositions of the PFN ceramics are presented in fig.4. The PFN ceramics obtained by the compact synthesizing method has slightly higher values of electric permittivity in comparison with specimen PFN2 obtained as a result of powder calcinng. However, the conducted temperature tests of dielectric losses (fig.4) show that the dielectric losses for specimen PFN1 are much higher than for specimen PFN2, with simultaneous high tendency to their increase with the temperature.

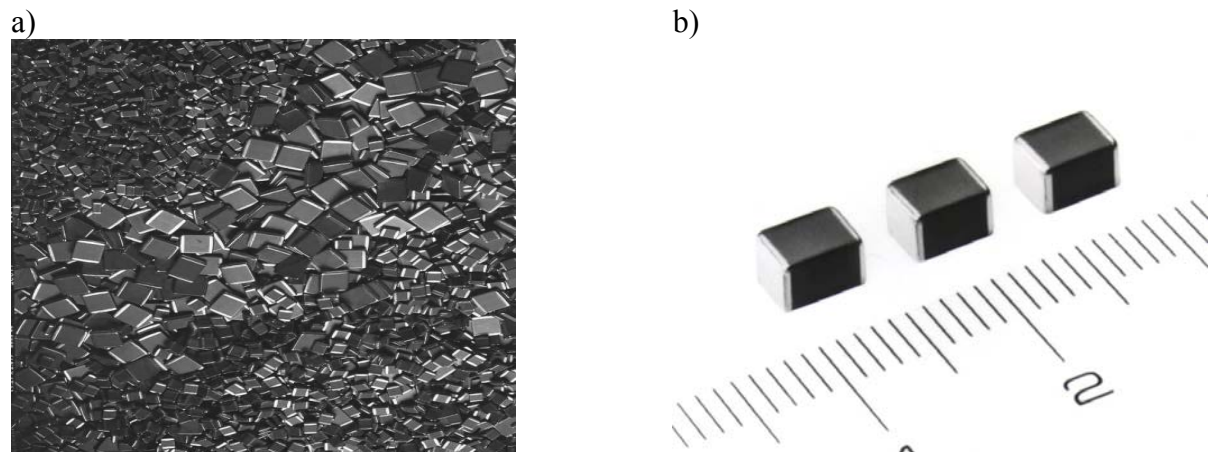


Fig.5 Applications of PFN: a) Multi-layered ceramic capacitors (MLCC) contain palladium, b) MLCC and Chip Resistors

5. CONCLUSIONS

Present market trends continue to show that the future for ferroelectric and ferroelectromagnetic ceramics is bright and continuous to get even brighter as the transition is made from passive to electrically active “smart” and “very smart” materials. In this regard a smart material senses a change in the environment and using an external feedback control system makes a useful response, as in a combined sensor/actuator ceramic.

In the future, more and more applications for nonlinear, electrostrictive relaxor materials, such as PLZT will emerge as the relentless drive toward miniaturization and integration continues. Indeed, this very trend will also encourage more materials research efforts to develop better ferroelectric and electrostrictive ceramics.

REFERENCES

1. J. Ilczuk, *Ceramics*, 103(1), 83-96, 2008.
2. J. Wallaschek, Piezoelectric ultrasonic motors, *J. Intell. Mat. Syst. Structures*, 6, 71-73, 1995.
3. Y. Yamayoshi, H. Hirose, Ultrasonic motors not using mechanical friction force, *Int. J. Appl. Electr. Mat.*, 3, 179-182, 1992.
4. A. Zarycka, R. Zachariasz, M. Czerwiec, J. Ilczuk, J. Rymarczyk, *Journal de Physique IV* 137, 193-196, 2006.
5. A. Kumada, A piezoelectric ultrasonic motor., *Jap. J. Appl. Phys.*, 24, 739-741, 1985.
6. E. Flint, C. Liang, C. A. Rogers, Electromechanical analysis of piezoelectric stack active member power consumption, *J. Intell. Mat. Syst. Structures*, 6, 117-124, 1995.
7. F. P. Sun, Z. Chandhry, C. Liang, C. A. Rogers, Truss structure integrity identification using PZT sensor actuator, *J. Intell. Mat. Syst. Structures*, 6, 134-139, 1995.
8. Y. Xu, *Ferroelectric materials and their application*, North-Holland, New York, 1991.
9. B. Noheda, D. E. Cox, G. Shirane, J. A. Gonzalo, L. E. Cross, S. E. Park, *Applied Physics Letters*, 74(14), 2059-2061, 1999.
10. M. Czerwiec, R. Zachariasz, J. Ilczuk, *Archives of Acoustics* 32(4), 59-64, 2007.
11. C. L. Hulang, B. H. Chen, Wu L., *Solid State Comm.*, 130, 19, 2004.
12. E. M Bourim, H. Tanaka, M. Gabbay, G. Fantozzi, B. L. Cheng, *J. Appl. Phys.*, 91, 6662, 2002.
13. K. Wójcik, K. Zieleniec, M. Mulata, *Ferroelectrics*, 289, 107, 2003.
14. O.N. Iwanov, E.A. Skriptchenko, M.E.Pryakhina, *Ferroelectrics*, 294, 145, 2004.
15. R. Zachariasz, J. Ilczuk, *Archives of Acoustics* 32(4), 111-116, 2007.
16. M. Jenhi, E.H.El. Ghagraoui, H. Balli, M.El. Aatmani, M. Rafiq, *Ann. Chim. Sci. Mat*, 23, 151, 1998.
17. R. Zachariasz, D. Bochenek, *Journal de Physique IV* 137, 189-192, 2006.