

# STABILITY OF MECHANICAL AND DIELECTRIC PARAMETERS IN PZT BASED CERAMICS

JAN ILCZUK, JUSTYNA BLUSZCZ, RADOSŁAW ZACHARIASZ

University of Silesia, Faculty of Computer and Material Sciences,  
Department of Material Science  
3, Źeromskiego St., 41-200 Sosnowiec, POLAND  
rzachari@us.edu.pl

*The  $(Pb_{0.9}Ba_{0.1})(Zr_{0.53}Ti_{0.47})O_3 + 2\% \text{ mol. } Nb_2O_5$  ceramics were prepared from high purity synthesized ceramic powders by a classical sintering method. Internal friction  $Q^{-1}$  and Young's modulus  $E$  were measured as a function of temperature for the sample in the initial state and after  $\gamma$  irradiation 5 R dose. Two internal friction peaks P1 and P2, related to oxygen vacancies and domain walls, respectively, were observed in all measurements. In addition, a minimum in modulus  $E$  associated with a phase transition internal friction peak P3 appearing at curie temperature was observed. The internal friction results indicate the changes of concentration of oxygen vacancies and the domain structure, which will be helpful in the utilities of the PZT ceramics in transducers, ultrasonic generators, wave filters, etc.*

## INTRODUCTION

Lead titanate zirconate  $Pb(Zr_xTi_{1-x})O_3$  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. [1-7]. Generally, all those applications need low electrical and mechanical losses. The ferroelectric ceramics belong to combination  $ABO_3$  type, with 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, 8]. 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.

It can be the result of mechanical treatment of the ceramic obtained or its irradiation with molecules or photons with high energy. In investigation of stability of the real structure PZT materials in the recent years, is a method of the internal friction (IF). This non-destructive method, basing on measurements of the mechanical losses, the extraction the essential conclusions about changes in the microstructure makes possible [9-14].

Mechanical losses, like magnetic or dielectric, occur in the tested material as a result of existence of the internal dissipation mechanism of energy externally supplied. Dissipation of energy of mechanical vibrations is connected with irreversible material transition into new state of equilibrium. The transition of a solid into a new state of equilibrium does not take place immediately but within certain period of time, leading to formation of the following inelastic effects: mechanical deceleration, differences in phases between stress and deformation, dissipation of energy of mechanical vibrations.

The ceramic ferroelectric materials in the temperature range below Curie temperature, are formed of domains, namely areas with the same direction of spontaneous polarization. Presence of domains in a ferroelectric crystal will be one of the reasons for dissipation of energy of mechanical vibrations. Phase transformations taking place in the material in question and presence and interaction of point defects (inherit and inserted) with the domain walls will be a reason for dissipation of mechanical energy.

In the present study, the temperature dependencies the Young's modulus  $E$ , the internal friction  $Q^{-1}$ , dielectric permittivity  $\epsilon$  and the tangent of dielectric loss angle  $\text{tg}\delta$  were measured for the initial state and  $\gamma$  irradiated samples on doped ceramics of the PZT type.

## 1. SAMPLES AND EXPERIMENTAL PROCEDURES

Doped PZT ceramics, with the chemical composition  $(\text{Pb}_{0.9}\text{Ba}_{0.1})(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 + 2\%$  mol.  $\text{Nb}_2\text{O}_5$  was the material tested.

This ceramics is a material with the chemical composition, which includes a dual-morphotropic and tetragonal areas. It is characterized by high dielectric values ( $\epsilon_{33}^T/\epsilon_0 > 1300$ ,  $\text{tg}\delta = 0,024$ ) and electromechanical coupling coefficient ( $k_p > 0,5$ ). Due to good mechanical parameters ( $E = 102$  GPa at  $T = 293$  K) and high stability of parameters at elevated temperatures, the ceramics is used in electromechanical transducers of low frequency[15].

Ceramic bodies were fabricated from high purity synthesized ceramic powders by a classical sintering method. They were sintered at 1523 K for 2h. Samples in discs ( $10 \times 1$ )  $\text{mm}^2$  and rectangular bars ( $30 \times 10 \times 0,9$ )  $\text{mm}^3$  form were obtained from sintered block. Next all samples were ground and polished and after that electrodes were deposited on their surface by the silver paste burning method.

Some ceramic samples were subjected to irradiation of  $\gamma$  radiation. The spring the radiation was Ir-192 about 1.354 TBq activity. The samples were radiated by 5 R radiation dose, at  $k_\gamma = 0.5$  ionization constant.

Ceramic samples in the shape of discs, to measurements dielectric properties (capacity bridge of the BM 595 Tesla type) were used.

The temperature dependencies of the  $Q^{-1}(T)$  and  $E(T)$  were determined while heating at a constant rate of 3 K/min. for samples in the shape of rectangular bars (in the initial state and after irradiation 5 R dose). Additionally, for the samples in the initial state, the temperature dependencies  $Q^{-1}(T)$  in three different frequencies: 918, 952 and 1010 Hz were obtained (at a constant heating rate of 3 K/min.). The internal friction  $Q^{-1}(T)$  was measured with a resonance mechanical spectrometer of the RAK- 3 type controlled by a computer [11].

To quantitative qualification of the internal friction the logarithmic decrement of suppression was used:

$$\delta = \frac{1}{N} \ln \frac{A_0}{A_N}, \quad (1)$$

where:

$A_0$  – initial amplitude of deformation.

$A_N$  – amplitude after realization N vibrations.

The values of the Young's modulus E were calculated on the ground of the measurements of resonance frequency f vibration of the sample, conducted simultaneously with the internal friction measurements, using with dependence:

$$E = 94,68 \left( \frac{l_r}{h} \right)^3 \cdot \frac{m_d}{b} \cdot f^2, \quad (2)$$

where:

$l_r$ ,  $h$ ,  $b$  and  $m_d$  – respectively: length, thickness, width and mass of vibratile part of sample.

## 2. INVESTIGATION RESULTS AND DISCUSSION

Figure 1 shows the curves of internal friction  $Q^{-1}(T)$  and Young's modulus  $E(T)$  obtained with  $(\text{Pb}_{0.9}\text{Ba}_{0.1})(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 + 2\% \text{ mol. Nb}_2\text{O}_5$  ceramics. The  $Q^{-1}(T)$  curve shows three peaks called P1, P2, P3, located respectively at  $T_1 = 350 \text{ K}$ ,  $T_2 = 502 \text{ K}$  and  $T_3 = 646 \text{ K}$  for the sample in the initial state (before irradiation) and at  $T_1 = 362 \text{ K}$ ,  $T_2 = 513 \text{ K}$  and  $T_3 = 634 \text{ K}$  for the sample after irradiation 5 R dose.

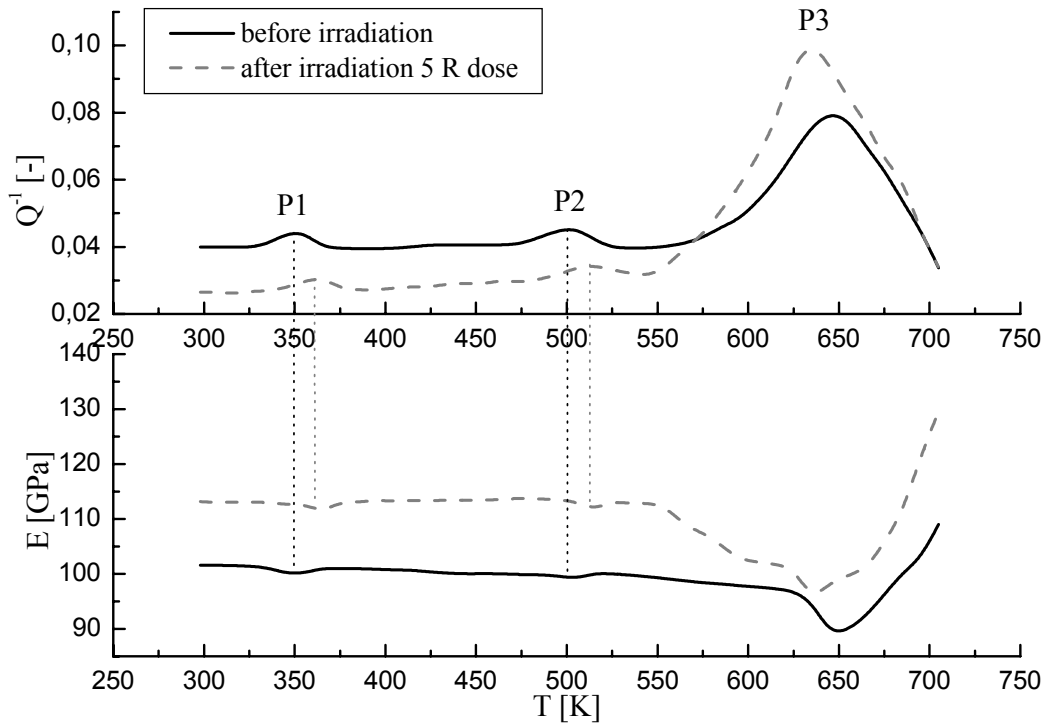


Fig. 1. Temperature dependencies  $Q^{-1} = f(T)$  and  $E = f(T)$  obtained for the PZT ceramics in the initial state (before irradiation) and after irradiation 5 R dose

The P1 and P2 peaks of internal friction are correlated to the anomalies on the E(T) curve. It was observed that values of the Young's modulus E decreased in the area of presence of the P1 and P2 peaks. For the sample after irradiation 5 R dose, decrease in the background value of internal friction and displacement of the temperature of the P1 and P2 peaks towards higher temperatures were observed. The P1 peak is associated with the short-distance diffusion of oxygen vacancies and the P2 peak is related to the movement of domain walls.

According to the Arrhenius equation, the relaxation rate can be written as [16]:

$$\tau = \tau_o \exp\left(\frac{H}{kT}\right), \quad (3)$$

where:

- $\tau_o$  – the inverse of frequency factor,
- H – the activation energy,
- k – Boltzman's constant,
- T – the absolute temperature.

The value of the activation energy was obtained on the base half width of the curve  $Q^{-1}(T)$ :

$$H = \frac{2.63 \cdot k \cdot T_1 \cdot T_2}{T_2 - T_1}, \quad (4)$$

where  $T_1$  and  $T_2$  are temperatures for  $\frac{1}{2} Q^{-1}_{\max}$  respectively.

From the above results on the peak temperature, the activation energy H and  $\tau_o$  of peaks are determined for P1 and P2 peaks as Table1.

Tab. 1. Parameters of the P1 and P2 peaks

	P1	P2	P1	P2
	before irradiation		after irradiation 5 R dose	
$\tau_o$ [s]	$(6.81 \pm 0.04) \cdot 10^{-15}$	$(8.19 \pm 0.04) \cdot 10^{-21}$	$(7.72 \pm 0.04) \cdot 10^{-17}$	$(9.14 \pm 0.04) \cdot 10^{-22}$
H [eV]	(1.14 ± 0.02)	(1.82 ± 0.02)	(0.98 ± 0.02)	(1.74 ± 0.02)
T [K]	350	502	362	513

The values of activation energy H and relaxation time  $\tau_o$ , obtained for the P1 peak are typical values for interaction between oxygen vacancies and domain walls. It confirmed that the P1 peak came from the thermally activated relaxation process [12]. The large activation energy and short relaxation time  $\tau_o$  may be understood by the fact that P2 peak is close to the Curie temperature. Therefore, we thought that the motion of domain walls should have a dominant role in the mechanism of the peak in PZT ceramics. According to Wang's model [17], in ferroelectric phase, the change of the spontaneous polarization vector with temperatures below  $T_C$  resulted in the fast variation of the density of domain walls, the viscous coefficient of domain walls, and the interaction among domain walls. When the temperature was near the Curie temperature  $T_C$ , the increase of the density of domain walls led to an increase in internal friction. On the other hand, the distance between domain walls

decreased and resulted in a decrease in mobility of the domain walls due to their mutual interactions, thus leading to a decrease in internal friction. The compromise of the above two factors brought about on internal friction P2 peak. on the figure 3, the domain structure of the obtained ceramics is shown.

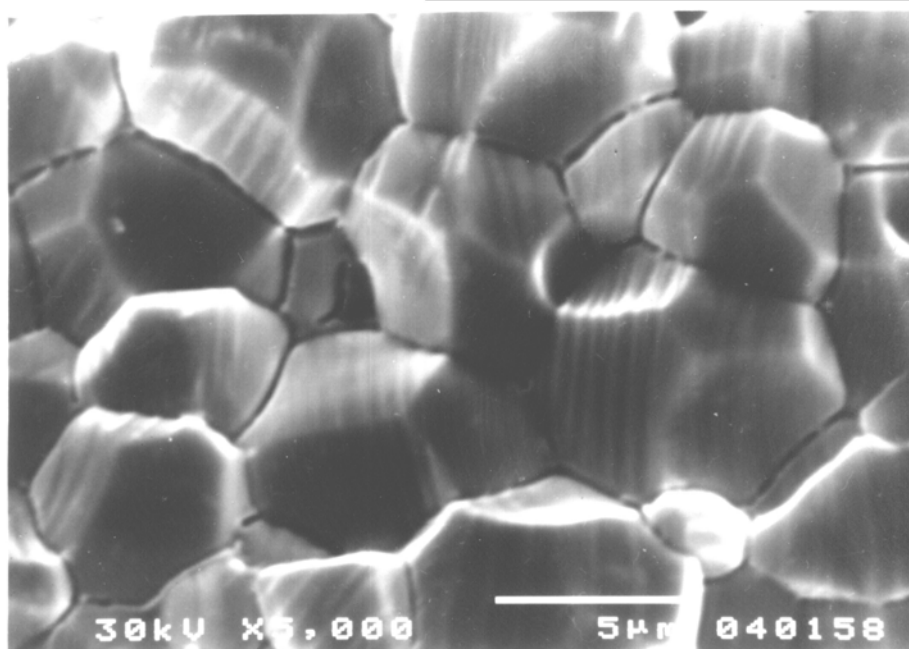


Fig. 2. Microstructure of the investigated ceramics obtained in the temperature of 293 K

The P3 peak originates from the ferroelectric – paraelectric phase transformation (Curie temperature  $T_C$ ). In the phase transition point, for the sample after irradiation 5 R dose, distinct increase of height of the maximum P3 was observed, and additionally, movement of this P3 maximum towards lower temperatures (from 646 k to 634 K). Changes connected with phase transition and temperature shift of internal friction P3 peak were also observed in  $E(T)$  dependencies. An increase in the internal friction in the curie temperature area is connected with an increase in the amount of new phase formed within the phase already existing [18].

Figure 3 presents temperature dependencies of the internal friction  $Q^{-1}(T)$  observed for the P1, P2 and P3 peak position, obtained for the sample before irradiation in the different frequencies: 918, 952, 1010 Hz during the heating process.

During performing measurements at different frequencies, changes in the temperature position of the P1 and P2 peaks were observed – displacement these peaks towards higher temperatures with an increase of the measurement frequency. These two peaks have a relaxation behavior because they are frequency dependent. For the P1 peak, the magnitude of the relaxation time ( $\tau_0 = (6.81 \pm 0.04) \cdot 10^{-15}$  s) is coherent with a point defect relaxation and the P1 relaxation peak could be due to interaction between domain walls and oxygen vacancies because the activation energy ( $H = 1.14 \pm 0.02$  eV) for diffusion of oxygen vacancy is about 0.9 eV. Concerning the P2 peak, its activation energy is high (about 1,82 eV). Therefore it is deduced that P2 peak can not only result from the diffusion of oxygen vacancies or other point defects. To understand the mechanisms of the P2 peak in detail further investigations are required.

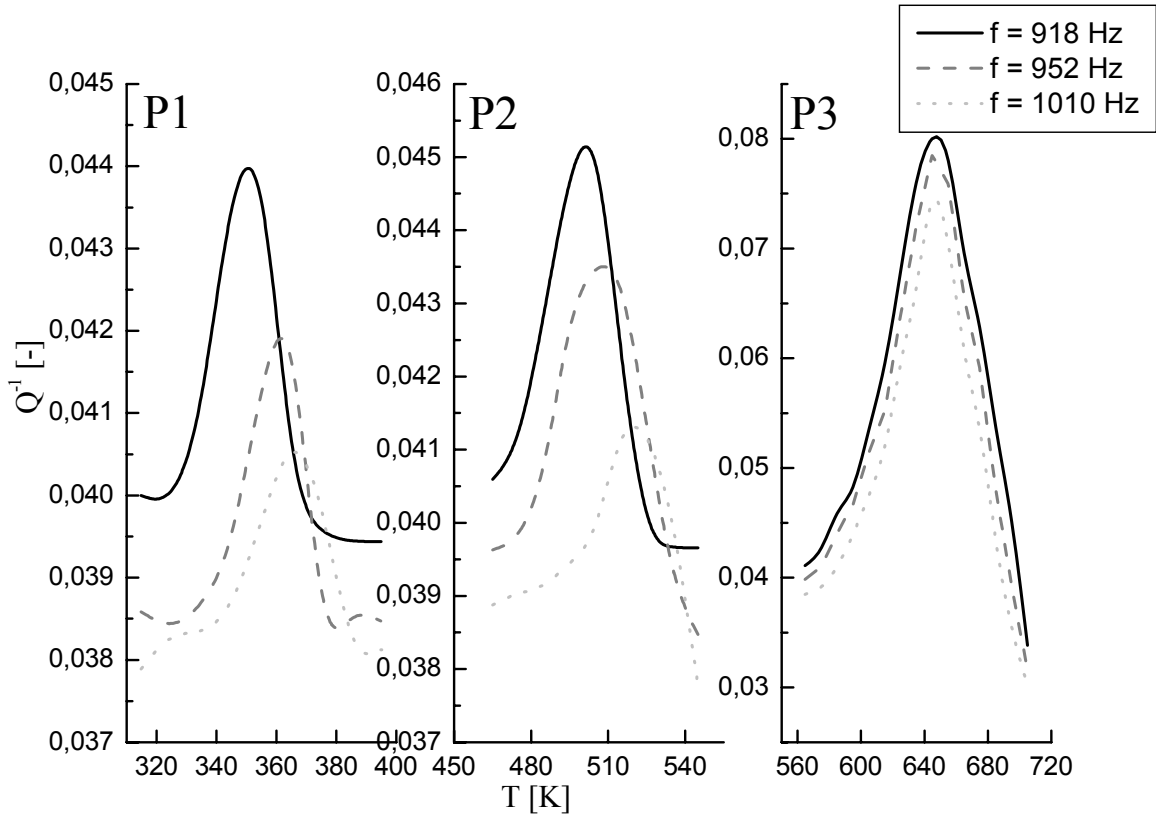


Fig. 3. Temperature dependencies  $Q^{-1} = f(T)$  for the P1, P2 and P3 peak position obtained for the sample in the initial state for three different frequencies while heating with a temperature ramp rate of about 3 K/min.

On the base of the J. F. Delorme'a and P. F. Gobin model, description on the curve  $Q^{-1} = f(T)$ , connected with the phase transition (peak P3 on the figure 3) was made [19]. The relative change of the volume undergoing to phase transition are shown in this model. These changes are the function of the heating and cooling processes. Thus the following formula was derived:

$$Q^{-1} = \frac{KG}{\omega} \cdot \frac{\partial m}{\partial T} \cdot \frac{\partial T}{\partial t}, \quad (5)$$

where:

$K$  – material constant,

$G$  – shear modulus,

$\omega$  - periodicity of the sample;  $\omega = 2\pi f$  ( $f$  – frequency),

$\frac{\partial m}{\partial T}$  - the volume of substance undergoing the phase transition in unit temperature change,

$\frac{\partial T}{\partial t}$  - the rate of the temperature changes (during heating or cooling processes).

Height of the internal friction peak, connected with the phase transition is directly proportional to rate of the temperature changes and inversely proportional to resonance frequency changes, what was introduced in the formula 5. The obtained dependence between height of the P3 peak and frequency finds agreement with the Delorme'a – Gobina model (fig. 3).

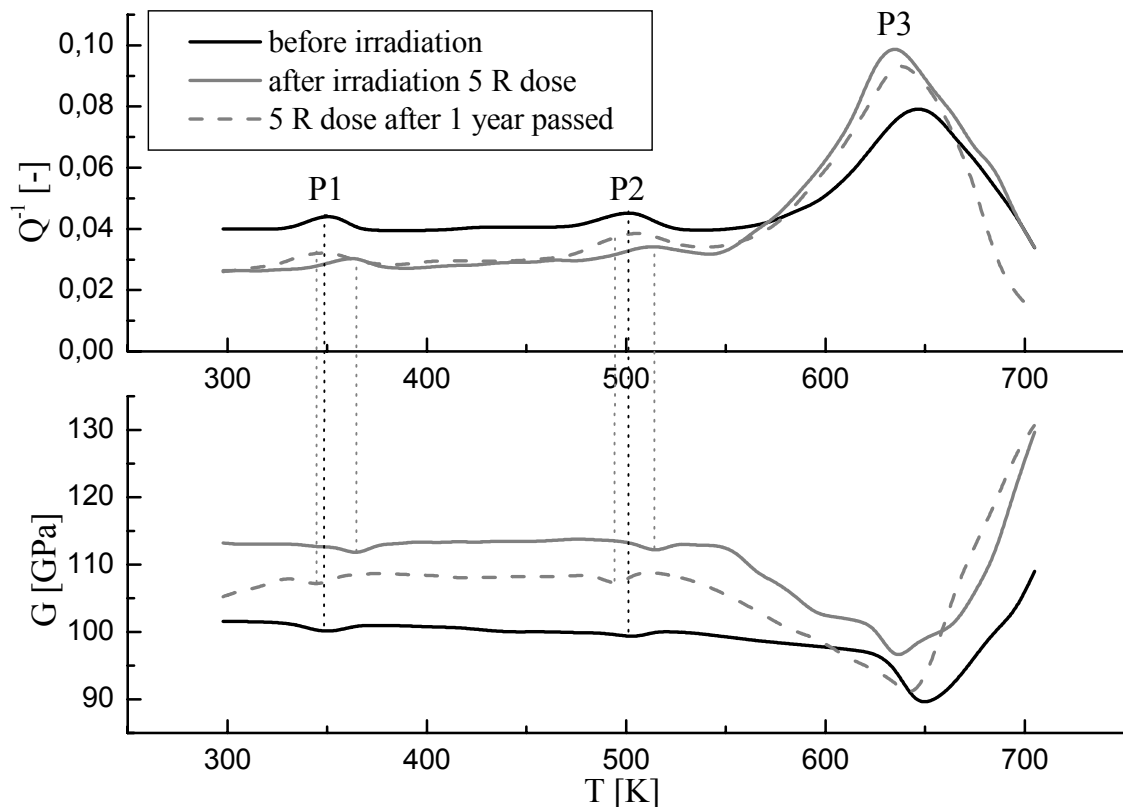


Fig. 4. Temperature dependencies  $Q^{-1} = f(T)$  and  $E = f(T)$  obtained for the PZT ceramics in the initial state (before irradiation), after irradiation 5 R dose (directly and after 1 year passed)

In order to verify our hypothesis, we intend to stabilize the concentration of oxygen vacancies for the samples after irradiation 5 R dose. One of the sample was examined just after one year passed. Temperature dependencies  $Q^{-1}(T)$  and  $E(T)$  for the sample are shown on the figure 4 by the dash line. On the base of the measurements, movement of P1 and P2 peaks towards lower temperatures and mild phase transition to paraelectric state was observed: respectively: for the P1 peak from 358 K to 348 K, for the P2 peak from 513 K to 498 K, for the P3 peak from 634 K to 643 K. Additionally, increase in value of background of internal friction took place, but only to the phase transition point. Changes connected with phase transition and temperature shift of each of internal friction peaks were also observed in  $E(T)$  dependencies. In the room temperature, the values of the Young modulus  $E$  were carried out respectively: 102 GPa for the sample before irradiation, 114 GPa for the sample after irradiation 5 R dose, 105 GPa for the sample after irradiation 5 R dose after one year passed.

Figure 5 shows the curves of permittivity  $\varepsilon(T)$  and dielectric loss  $\text{tg}\delta(T)$  as a function of temperature for the sample before and after irradiation 5 R dose during heating. The  $\varepsilon(T)$  curves show peak in the temperature range about 605 K to 635 K corresponding with the Curie temperature and with the P3 peak on the dependencies  $Q^{-1} = f(T)$ . Additionally, for the sample after irradiation 5 R dose, decrease in value of dielectric permittivity  $\varepsilon$  and movement of the phase transition peak towards lower temperatures were observed, in comparison to sample before irradiation. On the curve  $\text{tg}\delta(T)$  we can observe decreasing of the values of the  $\text{tg}\delta$  for the sample after irradiation 5 R dose. From the practical point of view this phenomena gives beneficial influence on the stability of the dielectric parameters. The stability of the parameters is still preserved despite the passage of time (one year).

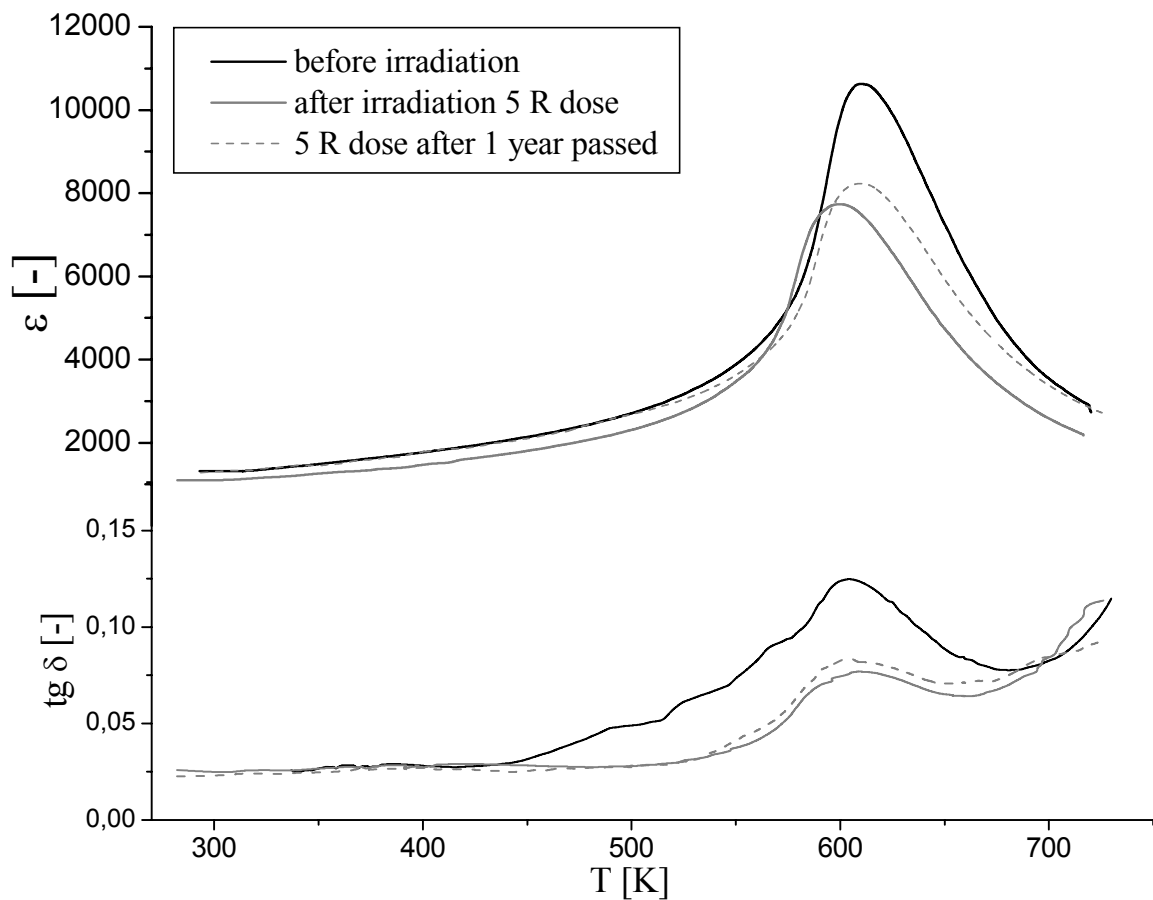


Fig. 5. Temperature dependencies  $\varepsilon = f(T)$  and  $\text{tg}\delta = f(T)$  obtained for the PZT ceramics in the initial state (before irradiation), after irradiation 5 R dose (directly and after 1 year passed)



### 3. CONCLUSIONS

1. On the temperature dependencies of the internal friction  $Q^{-1}$ , obtained for the multi-component ceramics of the PZT type before and after  $\gamma$  irradiation, three maxima of the internal friction were observed. Maximum P3 connected with the transformation phase (ferroelectric-paraelectric) and the relaxation peaks P1 and P2 in the ferroelectric phase.
2. The P1 peak is associated with the short-distance diffusion of oxygen vacancies and the P2 peak is related to the movement of domain walls.
3. Irradiation of piezoceramics of the  $\gamma$  radiation causes formations and accumulations of considerable numbers of point defects. These defects can fasten weakly or strongly the domain boundaries. First of all, these oxygen vacancies, because the solutions of the  $ABO_3$  type can reduce atoms of oxygen comparatively easy [20-21]. The investigated PZT ceramics belong also to these solutions.
4. Permanent fasten of domain structure, characteristic for PZT ceramics is caused both by point defects. Results of these are decreasing values of the internal friction and increasing mechanical strength of ceramics. It can be observed in changes of Young's modulus  $E$  presented in this work.
5. Increase in the internal friction background value, dielectric permittivity  $\epsilon$  and  $\text{tg}\delta$  and also a mild phase transition for the samples irradiated and examined just after one year passed, is caused by disappearance of oxygen vacancies anchoring particular domain walls, increase in their mobility and ease of re-orientation.

### REFERENCES

- [1] B. Jaffe, W. R. Jr. Cook, H. Jaffe, Piezoelectric Ceramics, Academic Press, p.271, London and New York 1971.
- [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] Y. Tomikawa, T. Ogasawa, Ultrasonic motors: construction, characteristics, applications, Ferroelectrics, 91, 13-178, 1989.
- [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] B. Noheda, D. E. Cox, G. Shirane, J. A. Gonzalo, L. E. Cross, S. E. Park, Applied Physics Letters, 74(14), 2059-2061, 1999.
- [9] S. A. Gridnev, Ferroelectrics, 112, 107-127, 1990.
- [10] A. Puskar, Internal Friction of Materials, Cambridge International Science Publishing, Cambridge 2001.
- [11] R. Zachariasz, J. Ilczuk, A. Chrobak, Ceramics, 66, 710-715, 2001.
- [12] B. L. Cheng, M. Gabbay, M. Maglione, Y. Jorand, G. Fantozzi, Journal de Physique IV, Vol. 6, 647-650, 1996.
- [13] B. Bruś, R. Zachariasz, J. Ilczuk, Physica Stat. Solidi (a), 201, 798-802, 2004.
- [14] J. Ilczuk, Molecular & Quantum Acoustics, 23, 167-174, 2002.
- [15] J. Ilczuk, J. Dudek, Z. Surowiak, Molecular & Quantum Acoustics, 18, p.101, 1997.

- [16] A. S. Nowick, B. S. Berry, *Anelastic Relaxation in Crystalline Solids*, Academic Press, Chap. 3, New York 1972.
- [17] Y. N. Wang, W. Y. Sun, X. H. Chen, H. M. Shen, B. S. Lu, *Physica Stat. Solidi (a)*, 102, p. 279, 1987.
- [18] J. Ilczuk, J. Dudek, Z. Surowiak, *Molecular & Quantum Acoustics*, 19, p.108, 1998.
- [19] J. F. Delorme, P. F. Gobin, *Metaux, Corr. Ind.*, 573, 185-192, 1973.
- [20] E. M. Bourim, H. Idrissi, B. L. Cheng, M. Gabbay, G. Fantozzi, *J. De Physique, IV*, 6, C8-633-636, 1996.
- [21] J. Jimenez, J. Vicente, *J. Phys. D: Appl. Phys.*, 31, 130-136, 1998.