THE STABILITY OF THE PROPERTIES
IN PZT BASED CERAMICS

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1. 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. [1-8]. 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 [1,9]. 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.

It can be the result of mechanical treatment of the ceramic obtained or its irradiation with molecules or fotons 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 [10-15].

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 ε and the tangent of dielectric loss angle tgδ were measured for the initial state and γ irradiated samples on doped ceramics of the PZT type.

2. MATERIAL AND INVESTIGATION METHOD

The ceramics with the following chemical composition $Pb_{0,94}Sr_{0,06}(Zr_{0,5}Ti_{0,5})O_3 + 0,25\%$ wag. Cr_2O_3 was the material tested. This ceramics is a material characterized by dielectric values ($\varepsilon^T_{33}/\varepsilon_0 > 900$, tg$\delta = 0,012$) and electromechanical coupling coefficient ($k_p > 0,35$). Due to good mechanical parameters (E = 86 GPa at T = 293 K) and high stability of parameters at elevated temperatures, the ceramics is used in resonators, filters and supersonic transducers [16].

Ceramic bodies were fabricated from high purity synthesized ceramic powders by a conventional sintering method. They were sintered at 1523 K for 2h. Samples in discs (10×1) mm^2 and rectangular bars $(30 \times 10 \times 0,9)$ 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 γ radiation. The spring the radiation was Ir^{192}. The samples were irradiated by 5 R radiation dose.

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). The internal friction $Q^{-1}(T)$ was measured with a resonance mechanical spectrometer of the RAK- 3 type controlled by a computer [12].

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

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

where:

A_o – 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:

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

where:

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

3. RESULTS AND DISCUSSION

Figure 1 shows the curves of internal friction $Q^{-1}(T)$ and Young's modulus E(T) obtained with $Pb_{0,94}Sr_{0,06}(Zr_{0,5}Ti_{0,5})O_3$ + 0,25% wag. Cr_2O_3 ceramics. The $Q^{-1}(T)$ curve shows three peaks called P1, P2, P3, located respectively at $T_1 = 408$ K, $T_2 = 574$ K and $T_3 = 613$ K for the sample in the initial state (before irradiation) and at $T_1 = 415$ K, $T_2 = 599$ K and $T_3 = 632$ K for the sample 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.
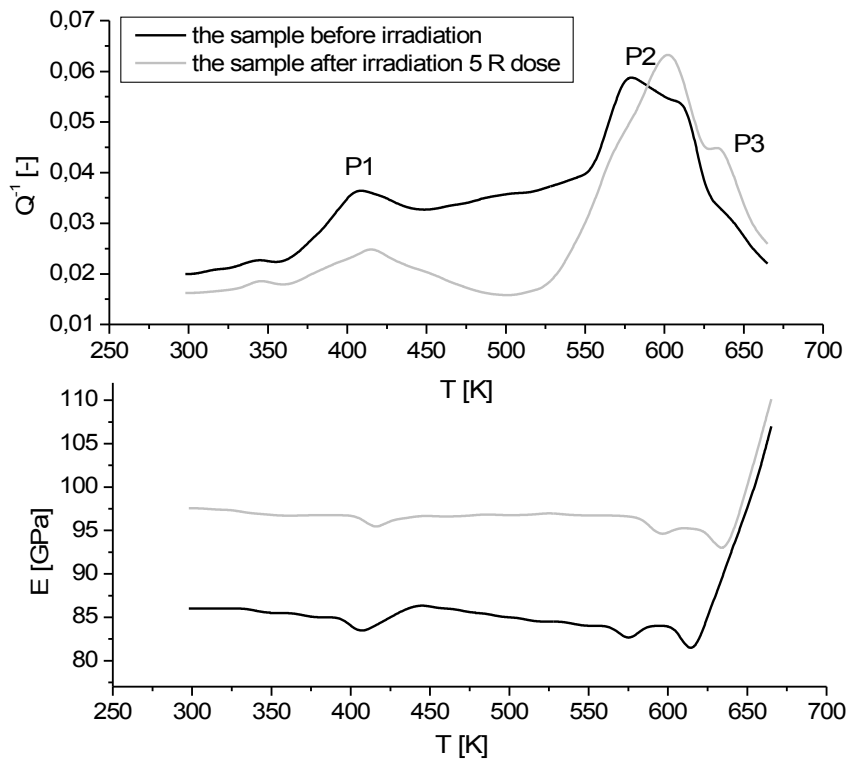
Fig. 1. Temperature dependencies Q^{-1} = f(T) and E = f(T) obtained for the PZT ceramics in the initial state (before irradiation) and after irradiation 5 R dose

According to the Arrhenius equation, the relaxation rate can be written as [17]:

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

where:

τ_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):

$$H = \frac{2.63 \cdot k \cdot T_1 \cdot T_2}{T_2 - T_1}, \tag{4}$$

where T$_1$ and T$_2$ are temperatures for ½ Q$^{-1}_{max}$ respectively.

From the above results on the peak temperature, the activation energy H and τ_o of peaks are determined for P1 and P2 peaks as Table I.

Table I. Parameters of the P1 and P2 peaks

	P1	P2	P1	P2
	before irradiation		after irradiation 5 R dose	
τ_o [s]	$(2.18\pm0.04)\cdot10^{-15}$	$(4.67\pm0.04)\cdot10^{-20}$	$(2.03\pm0.04)\cdot10^{-16}$	$(7.34\pm0.04)\cdot10^{-22}$
H [eV]	(1.11 ± 0.02)	(1.94 ± 0.02)	(1.08 ± 0.02)	(1.78 ± 0.02)
T [K]	408	574	415	599

The values of activation energy H and relaxation time τ_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 [13]. The large activation energy and short relaxation time τ_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 [18], 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.

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 632 K to 613 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 [19].
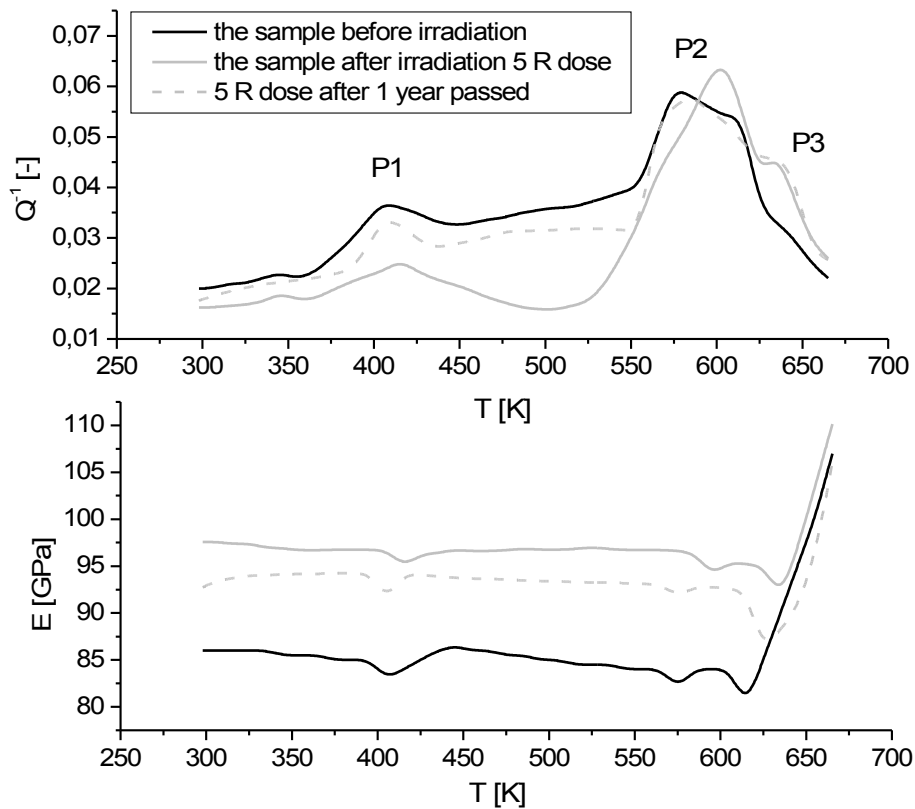
Fig. 2. Temperature dependencies $Q^{-1} = f(T)$ and $E = f(T)$ obtained for the PZT ceramics in the initial state (before irradiation) and after irradiation 5 R dose (directly and after 1 year passed)

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 2 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 415 K to 408 K, for the P2 peak from 599 K to 576 K, for the P3 peak from 632 K to 628 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: 86 GPa for the sample before irradiation, 97 GPa for the sample after irradiation 5 R dose, 92 GPa for the sample after irradiation 5 R dose after one year passed.
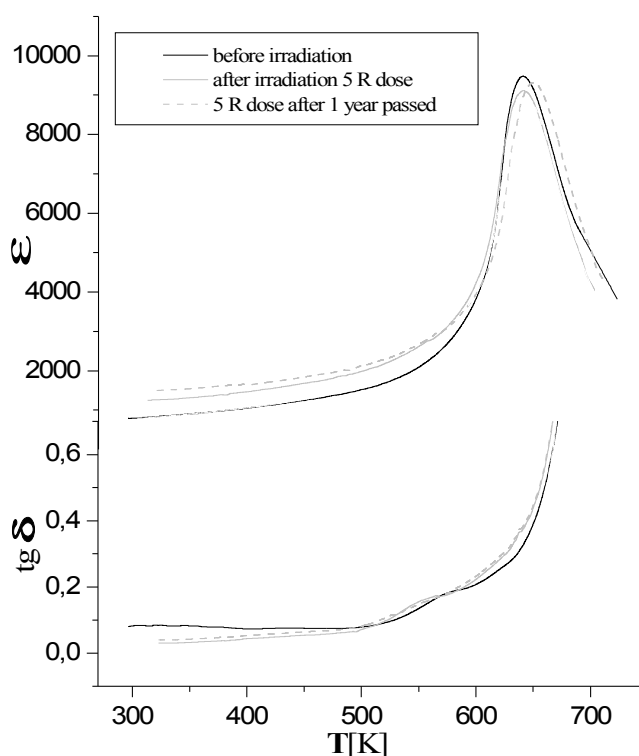
Fig. 3. Temperature dependencies $\varepsilon = f(T)$ and $tg\delta = f(T)$ obtained for the PZT ceramics in the initial state (before irradiation), after irradiation 5 R dose (directly and after 1 year passed)

Figure 3 shows the curves of permittivity $\varepsilon(T)$ and dielectric loss $tg\delta(T)$ 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 615 K to 645 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 ε and movement of the phase transition peak towards lower temperatures were observed, in comparison to sample before irradiation. On the curve $tg\delta(T)$ we can observe decreasing of the values of the $tg\delta$ 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).

4. CONCLUSIONS

1. Irradiation of piezoceramics of the γ radiation causes formations and acumulations of considerable numbers of points 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]. The investigated PZT ceramics belong also to these solutions.

2. Increase in the internal friction background value, dielectric permittivity ε and tgδ 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.

ACKNOWLEDGEMENT

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