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The relaxation phenomena in irradiated PZT type piezoceramics

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The samples of PZT type multi-component piezoceramics $Pb_{0.975}Ba_{0.01}Ca_{0.01}Sr_{0.005}(Zr_{0.52}Ti_{0.48})O_3$ + 1.4 wt.% Bi_2O_3 + 0.3 wt% GeO obtained by hot pressing were shaped as (30×10×0.9) mm^3 plane-parallel plates. Some samples were subjected to polarization by low temperature method (T = 423 K, E_p = 30 kV/cm, t = 30 min), and others were γ-irradiated (200 kGy, ^{60}Co). For all specimens, temperature dependences of the internal friction Q^{-1} and Young's modulus E were determined while heating at a rate of 3 K/min. The $Q^{-1}(T)$ curve shows two peaks P_R and P_F, located for non-irradiated sample at T_R = 380 K, T_F = 640 K, respectively. For samples irradiated at 200 kGy dose, the P_R peak shifts towards higher temperatures, while P_F, towards lower ones. The values of Young's modulus E are decreased in the area of the P_R and P_F peaks. At room temperature, the E value is 133 GPa for the non-irradiated sample and 150 GPa for the irradiated one. The relaxation peak P_R has been shown to be due to the domain boundary interaction with oxygen vacancies while the P_F one is related to the phase transition at the Curie point.

Исследованы образцы многокомпонентной керамики типа ЦТС состава $Pb_{0,975}Ba_{0,01}Ca_{0,01}Sr_{0,005}(Zr_{0,52}Ti_{0,48})O_3$ + 1,4 мас.% Bi_2O_3 + 0,3 мас% GeO, полученной методом горячего прессования. Некоторые образцы поляризованы низкотемпературным методом (T = 423 К, напряженность электрического поля E_p = 30 кВ/см, время τ = 30 мин.), другие облучены γ-лучами (Co-60, 200 кГй). Для всех образцов получены температурные зависимости внутреннего трения Q^{-1} и динамического модуля Юнга E при нагреве со скоростью 3 К/мин. На кривых $Q^{-1}(T)$ для необлученного образца наблюдаются два максимума P_R и P_F при T_R = 380 К и T_F = 640 К. После облучения дозой 200 кГй пик P_R смещается в сторону повышенных температур, а пик P_F — в сторону пониженных температур. В области температур максимумов P_R и P_F динамический модуль Юнга понижается. При комнатной температуре значение E составляет 133 ГПа для необлученного образца и 150 ГПа для облученного. Показано, что релаксационный пик P_R обусловлен взаимодействием доменных границ с кислородными вакансиями, а пик P_F связан с фазовым переходом при температуре Кюри.

Lead titanate zirconates $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) are among the most popular industrial piezoelectric materials, used as transducers, wave filters, micromotors, microrobots, etc. [1–4]. All those applications require generally high piezoelectric constants and low dielectric and mechanical losses in ceramics. The variation of mechanical losses and elastic modulus as function of temperature and excitation frequency can provide direct information on the energy dissipation and phase transitions in the material. Several authors [5, 6] have shown that the mechanical losses in the PZT are associated not only with domain walls motion but also with interaction of point defects with domain walls. The formation and accumulation of considerable numbers of point defects may be caused, among other things, by irradiation of the PZT ceramics with γ radiation. These defects can fasten, weakly or strongly, the domain boundaries. Among the defects, the most important role play oxygen vacancies, because the solutions of the ABO_3 type can reduce oxygen atoms quite easily [7].

This work presents the study results of the multi-component piezo-ceramics of the

PZT type. The temperature dependences of the Young's modulus E and the internal friction Q^{-1}, were measured for the as-prepared doped ceramics samples (prior to irradiation) and γ irradiated ones at 200 kGy dose.

The material used is doped PZT ceramics of the following chemical composition: $Pb_{0.975}Ba_{0.01}Ca_{0.01}Sr_{0.005}(Zr_{0.52}Ti_{0.48})O_3$ + 1.4 wt.% Bi_2O_3 + 0.3 wt% GeO. The ceramics is characterized with high dielectric and piezoelectric properties: $\varepsilon_{33}^T/\varepsilon_0 = 1210$, $tg\Delta = 0.02$, $d_{31} = 60 \cdot 10^{-12}$ C/N, $k_p = 0.3$ and belongs to the soft ferroelectric ceramics from the morphotropic area. Thanks to its good mechanical properties (E = 133 GPa at T = 293 K) and high stability of parameters at elevated temperatures and pressures, it is widely used in industry in vibration and pressure sensors. The ceramics in question were obtained by hot pressing method. The samples were ground, polished to the $30 \times 10 \times 0.9$ mm^3 size and then electrodes on their surface were deposited by the silver paste burning method. Some samples were subjected to polarization by low temperature method (T = 423 K, E_p = 30 kV/cm, t = 30 min), and others were γ-irradiated at 200 kGy dose. The radiation source was ^{60}Co. The mechanical loss, Q^{-1}, and Young's modulus, E, as functions of temperature were measured by a RAK-3 resonance mechanical spectrometer controlled by a computer [7]. At each temperature, the resonance curve of the vibration amplitude was recorded, and Young's modulus (E) was calculated as [7]:

$$E = 94.68\left(\frac{l_r}{h}\right)^3 \cdot \frac{m_d}{b} \cdot f^2, \qquad (1)$$

where l_r, h, b and m_d are the vibrating sample part length, thickness, width and mass, respectively. The $Q^{-1}(T)$ and $E(T)$ were measured in vacuum at the heating rate of 3 K/min. The temperature dependences of the internal friction $Q^{-1} = f(T)$ and the Young's modulus $E = f(T)$ obtained during a heating cycle of a ceramic sample before and after the irradiation with 200 kGy dose, are presented in Fig. 1.

In the $Q^{-1}(T)$ curve obtained for the non-irradiated sample, the following phenomena are observed: (1) the distinct P_R maximum at T_{PR} = 380 K, then (2) a decrease in the internal friction value at temperatures up to about 550 K, next (3) the sharp increase in the internal friction in the form of the P_F peak at the temperature T_{PF} = 640 K. In the areas of the P_R and P_F maxima in the $Q^{-1}(T)$ curve, a decrease in the Young's modulus value E in the form of characteristic minima A_R and A_F (Fig. 1, $E(T)$ dependence) is observed. Those values are E_{AR} = 122 GPa in the area of the P_R peak, E_{AF} = 124 GPa in the area of the P_F maximum. The Young's modulus value determined at room temperature and is 133 GPa.

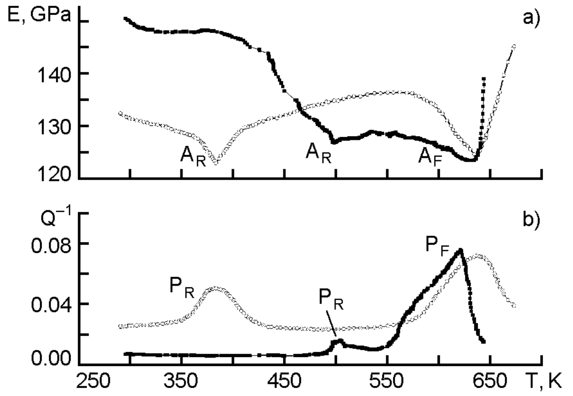

Fig. 1. Temperature dependences $E = f(T)$ (a) and $Q^{-1} = f(T)$ (b) for the tested PZT ceramics before and after the γ irradiation.

For the ceramic samples γ-irradiated at 200 kGy, changes in the $Q^{-1}(T)$ curve are observed: the P_R maximum becomes shifted toward higher temperatures (T_{PR} = 500 K), whereas the P_F maximum, toward lower temperatures (T_{PF} = 620 K). A great decrease in the internal friction value was also observed in the whole temperature range until the P_F peak temperature. The irradiation also causes a considerable decrease in the P_F peak height. Both maxima are close to each other. Similar changes (as for the non-irradiated sample) are observed in the $E(T)$ dependences: in the area of the P_R and P_F peaks, decrease in the Young's modulus E value is observed in the form of the A_R and A_F minima (Fig. 1, the $E(T)$ dependence). Those values are: E_{AR} = 127 GPa and E_{AF} = 122 GPa for the A_R and A_F minima, respectively. It should be emphasized that at the room temperature, the E values increase to about 150 GPa. The presence of the characteristic P_F maximum in the $Q^{-1}(T)$ curve, correlating with the presence of the distinct A_F minimum in the $E(T)$ dependence, is connected with a phase transition, taking place for the ceramics of the PZT type with the composition in question. This phenomenon is connected with the transition from the ferroelectric phase to the paraelectric phase (Curie temperature T_C) and

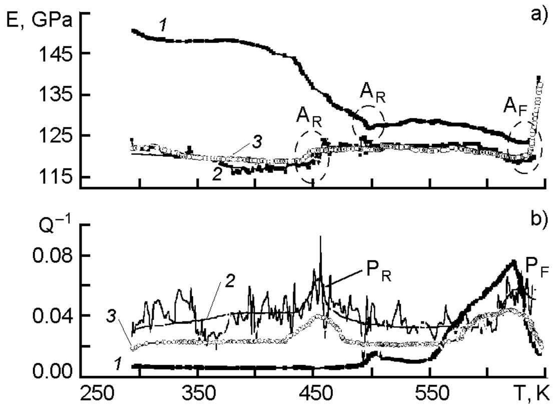

Fig. 2. Temperature dependences $Q^{-1} = f(T)$ and $E = f(T)$ for the tested PZT ceramics after irradiation at 200 kGy dose obtained in 3 successive heating cycles: *1* — 1st process of heating; *2* — 2nd process of heating; *3* — 3rd process of heating .

the simultaneous change of the tetragonal structure into the regular one [5, 8, 9].

In order to obtain more information on changes in the ceramics structure during its heating, and in particular to define the phenomena responsible for the P_R maxima formation in the $Q^{-1}(T)$ dependences and correlate the A_R minima in the $E(T)$ dependences with P_R maxima, $Q^{-1}(T)$ and $E(T)$ dependences were determined in the successive heating cycles for the samples irradiated at 200 kGy dose. The test results are presented in Fig. 2. As in the previous measurements on the $Q^{-1} = f(T)$ curve during the first heating performed immediately after the irradiation, the P_R and P_F maxima were observed. In the $E = f(T)$ dependences, characteristic minima were observed at the temperature positions correlated with the peaks in the $Q^{-1} = f(T)$ curve. After the 2nd and 3rd heating cycles of the sample, a distinct increase in the internal friction value for the $Q^{-1} = f(T)$ curve to the point nearing a phase transition was revealed as well as the P_R maximum displacement toward lower temperatures, namely, to T_{PR} = 455 K for the 2nd heating cycle and then to T_{PR} = 450 K for 3rd heating cycle. The P_R peak height increased distinctly in comparison with that before irradiation.

As to the P_F maximum connected with the phase change, a distinct decrease in its height after 2nd and 3rd heating cycles was observed and a gradual displacement of the P_F peak toward higher temperatures: T_{PF} = 626 K for 2nd heating cycle and T_{PF} = 635 K for 3rd one. As to $E = f(T)$, a sharp decrease in the Young's modulus value was observed in the successive 2 heating cycles (at room temperature, 122 GPa).

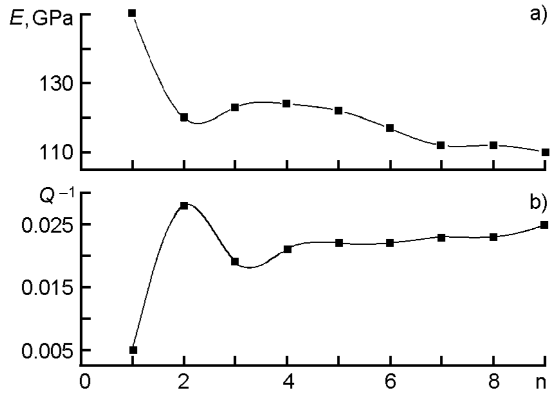

Fig. 3. Young's modulus values E (a) and internal friction Q^{-1} (b) for the tested PZT ceramics after irradiation at 200 kGy dose obtained in 9 successive heating cycles.

The behavior of the Young's modulus values E and internal friction values Q^{-1} during all 9 heating cycles of the irradiated sample are presented in Fig. 3. The E values are seen to decrease from 150 GPa for the irradiated sample to about 110 GPa for the sample heated above the Curie temperature for 9 cycles. As to internal friction, we observe rapid changes during 3 first heating cycles, that suggests considerable changes taking place in the sample. In the subsequent heating cycles, there is a slow stable increase in the Q^{-1} value to the value close to that for non-irradiated sample.

The P_R maximum formation in the $Q^{-1} = f(T)$ curves was the reason for determining characteristic parameters of this peak. Basing on the tests conducted for several years, it has been found that height and the temperature position of the P_R maximum depend on numerous factors, such as the sample heating and cooling rates, introduced additional defects due to heating in vacuum atmosphere or irradiation of the PZT ceramic samples [9, 10–12]. As to the ceramic ssample irradiated with any kind of the radiation, we deal with (besides of generating defects in the structure) with formation of additional local stresses, which affect also the behavior of the Young's modulus together with the temperature changes according to the relationship [13, 14]:

$$3\sigma = \left(\frac{c}{a} - 1\right)E, \tag{2}$$

where σ is the mechanical stress formed in the sample; c, a are lattice constants.

It can be seen that the Young's modulus increases together with an increase in mechanical stresses, what proves the character of changes obtained in the $E = f(T)$ dependences before and after the irradiation (Fig. 1). The sample heating after the irradiation in the successive cycles results in gradual disappearance of the formed stresses and an increase in the Young's modulus as well as in the internal friction Q^{-1} (Fig. 3).

The P_R maximum displacement toward higher temperatures during the subsequent cycles of the sample heating and changes in its height for the irradiated sample as compared to the non-irradiated one show its thermally activated relaxation character [15]. For the relaxation processes, the activation energy H and the relaxation time τ are described by Arrhenius law:

$$\tau = \tau_0 \exp\left(\frac{H}{kT}\right), \tag{3}$$

where τ_0 is the pre-exponential factor; T, temperature [K]; k, the Boltzmann constant. Using the Arrhenius law and the condition for the maximum of the internal friction peak $\omega\tau = 1$, a mechanism responsible for its formation can be defined by determining the values τ_0 and H characterizing height of the potential barrier which atoms overcome while migrating in the relaxation process [16].

The activation energy values were determined basing on the $Q^{-1}(T)$ curve half-width. The calculated values of the activation energy and pre-exponential factor are presented in Table. The variations in the P_R relaxation peak height and its temperature position during 9 heating cycles are presented in Fig. 4. The P_R peak activation parameters obtained by measurements during the heating cycle for the non-irradiated sample evidence clearly the relaxation processes connected with the interaction of the point defects (oxygen vacancies) and the domain walls. The determined values of the activation energy and the pre-exponential factor: $H = 0.86$ eV and $\tau_0 = 1.43 \cdot 10^{-15}$ s (Table) are consistent with the results obtained by other authors, such as [5, 6, 11]. Basing on the tests results for the ferroelectric ceramics obtained for several years, it has been found that different types of point

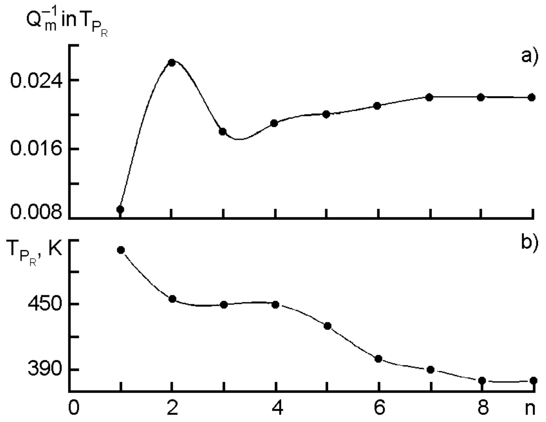

Fig. 4. Changes in the Q_m^{-1} relaxation peak height and its temperature position for the tested PZT ceramics after the irradiation at 200 kGy dose obtained in 9 successive heating cycles.

Table. Activation energy H and pre-exponential factor τ_0 for the P_R maximum of the non-irradiated sample and in the successive heating cycles of the sample irradiated at 200 kGy dose.

Heating cycle number	H [eV]	τ_0 [s]	T_C [K]
The sample before irradiation			
1	(0.86±0.02)	$(1.43\pm0.04)\cdot10^{-15}$	640
The sample after irradiation at 200 kGy dose			
1	(0.70±0.02)	$(1.26\pm0.04)\cdot10^{-11}$	620
2	(1.15±0.02)	$(1.18\pm0.04)\cdot10^{-16}$	626
3	(0.86±0.02)	$(3.82\pm0.04)\cdot10^{-14}$	635
4	(0.85±0.02)	$(2.73\pm0.04)\cdot10^{-14}$	637
5	(0.84±0.02)	$(1.35\pm0.04)\cdot10^{-14}$	638
6	(0.84±0.02)	$(6.35\pm0.04)\cdot10^{-15}$	638
7	(0.84±0.02)	$(1.25\pm0.04)\cdot10^{-15}$	640
8	(0.84±0.02)	$(1.18\pm0.04)\cdot10^{-15}$	640
9	(0.84±0.02)	$(1.62\pm0.04)\cdot10^{-15}$	640

defects have different activation energy values. For example, the migration activation energy for Ti^{4+} is about 1.5 eV, for Ba^{2+}, about 3.4 eV [17]. The activation energy of the oxygen vacancy migration in $BaTiO_3$ is within limits of 0.42 to 0.66 eV, whereas in the the multi-component PZT type ceramic, it amounts from about 0.59 to 1.17 eV and it depends, among others factors, on the chemical composition, production method and amount and type of the introduced admixtures in the tested samples [18, 19].

High γ radiation dose used (200 kGy) provide additional point defects in the structure of the PZT type ceramics. In the $Q^{-1} = f(T)$ curves determined in the successive 9 heating cycles, the following phenomena were observed: (1) the shift of the P_R peak toward higher temperature for 1st heating cycle followed by gradual return to the temperature characteristic for the sample before irradiation (Fig. 4); (2) a sharp decrease in the P_R peak height for 1st heating cycle and its increase in the successive cycles to the value characteristic for the sample before irradiation (Fig. 4). The activation parameters of the P_R peak determined in the first heating cycle: $H = 0.70$ eV and $\tau_0 = 1.26 \cdot 10^{-11}$ s (Table) confirm the phenomenon observed, namely, a decrease in the activation energy and an increase in the pre-exponential factor value for the irradiated sample; this is connected with lower energy dissipation by the domain walls fastened strongly by a greater number of point defects. The successive heating cycles cause an increase of the H value and the decrease of the τ_0 value, what is proved by a gradual increase in the P_R peak height and its temperature displacement toward lower temperatures, as a result of gradual disappearance of point defects (heating out).

Thus, γ irradiation of the PZT type ferroelectric ceramics with the perovskite structure at high doses (e.g. 200 kGy) results in changes of its mechanical properties due to introduced additional structural defects. This irradiation plays an important part in the migration of point defects and their interaction with the domain walls, thus affecting considerably the relaxation processes and changing their activation parameters. As it has been proved in this work, the irradiation of PZT ceramic samples followed by several repeated heating cycles has a significant influence both on the internal friction Q^{-1} values and the Young's modulus E. Those changes are observed within the whole temperature ranges of the determined $Q^{-1} = f(T)$ and $E = f(T)$ dependences. From the practical point of view, this is very important for the use of those materials in industry due to influence on the stability of parameters of transducers obtained on PZT base. An influence of any external factors (such as e.g. radiation, temperature) may cause permanent disturbances in operating of this equipment.

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Релаксаційні явища в опроміненій п'єзокераміці типу ЦТС

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Досліджено зразки багатокомпонентної кераміки типу ЦТС складу $Pb_{0,975}Ba_{0,01}Ca_{0,01}Sr_{0,005}(Zr_{0,52}Ti_{0,48})O_3$ + 1,4 мас.% Bi_2O_3 + 0,3 мас.t% GeO, одержаної методом гарячого пресування. Деякі зразки були поляризовані низькотемпературним методом (T = 423 К, напруга електричного поля E_p = 30 кВ/см, час τ = 30 хв), інші опромінені γ-променями (Co-60, 200 кГй). Для всіх зразків одержано температурні залежності внутрішнього тертя Q^{-1} та динамічного модуля Юнга E при нагріванні зі швидкістю 3 К/хв. На кривих $Q^{-1}(T)$ для неопроміненого зразка спостерігаються два максимуми P_R та P_F при T_R = 380 К та T_F = 640 К. Після опромінення дозою 200 кГй пік P_R зміщується у напрямі до вищих температур, а пік P_F — у напрямі до нижчих температур. В області температур максимумів P_R и P_F динамічний модуль Юнга знижується. При кімнатній температурі значення E становить 133 ГПа для неопроміненого зразка та 150 ГПа для опроміненого. Показано, що релаксаційний пік P_R обумовлений взаємодією доменних меж з кисневими вакансіями, а пік P_F пов'язаний з фазовим переходом при температурі Кюрі.