

Relaxation processes in hard piezoelectric ceramics

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The results of the relaxation processes investigation in polycrystalline piezoelectric elements after exiting them from the state of the thermodynamic balance under action of AC voltage of the resonance frequency, heating and uniaxial mechanical stresses are presented. The long-time reconstruction of elastic parameters takes place when elements are returned into the initial thermodynamic condition. Observed relaxation is described by the logarithmic function of time. The model, taking into account the polycrystalline structure of ceramics and presence of noncompensated mechanical stresses on crystalline boundaries, is offered for explanation of the observed results.

Представлены результаты исследования релаксационных процессов в поликристаллических пьезоэлектрических элементах после их возбуждения переменным током резонансной частоты, нагрева и одноосного механического сжатия. При возврате элементов к исходному термодинамическому состоянию происходит длительное восстановление их упругих параметров. Наблюдаемая релаксация описывается логарифмической функцией времени. Для объяснения наблюдаемых результатов предложена модель, учитывающая поликристаллическую структуру керамики и присутствие нескомпенсированных механических напряжений на границах кристаллов.

The piezoelectric ferroelectric (FE) ceramics is among the most important classes of functional materials [1, 2]. A wide variety of converters for different purpose is produced basing thereon. The converters of resonance and nonresonance types [3] are distinguished. In the first case, the piezoelectric elements work in the mode of high intensity acoustic and electrical actions. The "overexcitation" of elements and failures thereof take often place [4]. Therefore, the investigation of the influence of the driving stress level (electrical and mechanical) on the parametric stability of working piezoelectric ceramic elements (PCE) is a topical task. There are two main approaches to such studies. In the first case, the material behavior is studied immediately in the

course of external actions [5, 6]. In the second case, the aftereffect (the behavior of the piezoelectric material parameters after external actions) is investigated [7].

The purpose of this work was to study the relaxation behavior of the piezoelectric (and elastic) PCE characteristics after the element was taken out of the thermodynamic equilibrium state. The ferroelectric ceramics of the lead zirconate-titanate (PZT) solid solutions $[\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3]$ was selected as the study object. It has been shown that the relaxation is a long-term one. The reasons for the prolonged restoration of properties (even after a comparatively short-time action) are discussed.

The disk-shaped PCE of standard size ($d = 10$ mm, $h = 1$ mm) according to [8, 9] were

used in this study. The elements were made from the engineering grade piezoelectric material TsTCSt-3 [(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O₃] [8]. For control measurements, the piezoelectric elements were prepared from Pb(Zr_{0.52}Ti_{0.48})O₃ with 0.7 mol.% of MnO₂ model solid solution. In the "composition (Zr/Ti) – temperature" phase state diagram both materials are at the center of morphotropic region (MPR) of rhombohedral (Rh) and tetragonal (T) phases co-existence in the sample volume. For comparison of results, the samples from T and Rh regions of diagram were prepared and studied also.

The ceramics samples were obtained by the traditional ceramic technology via two-stage sintering at 850°C and 1200°C. The single-phase nature of ceramics was controlled by the X-ray diffractometer DRON-2 using filtered CuK_α emission. The quality of the sintered samples was characterized by the residual porosity value (not exceeding 0.2 %). Silver electrodes were used for dielectric and piezoelectric measurements. The quality of electrode burning-in was controlled by measuring the tangent of the dielectric losses tgδ. The sample polarization was carried out at 120°C in liquid silicon PES-5 in a DC field of 3 kV/mm for 1 h followed by cooling in the field down to room temperature.

As the external ambient conditions for PCE turning out of thermodynamic equilibrium state, the AC sinusoidal electric field of the resonance frequency and different amplitude (from 50 to 7500 mV/mm at 100 mV/mm step) were used as well as heating of samples, and uniaxial mechanical loading. The resonance f_r and antiresonance f_a frequencies as well as the 3rd harmonic f_{r3} of the fundamental frequency and the temperature change in the course of excitation were controlled. Temperature was measured with differential chromel-alumel (ChA) microthermocouple to within $\pm 0.05^\circ\text{C}$.

The samples were heated in a low-inertia electric furnace with the thermocouple ChA. The heating temperature was varied from 80 to 170°C, the holding time was 10 min and followed by rapid cooling to room temperature. The PCE samples were heated both in the "electrically short-circuited" and "nonshorted" states. The uniaxial mechanical load (35, 150, and 334 kg/cm² pressure) was created using a spring press with the force up to 1000 kg. The holding time under the load was 30 min.

When studying the relaxation behavior of piezoelectric materials, the resonance

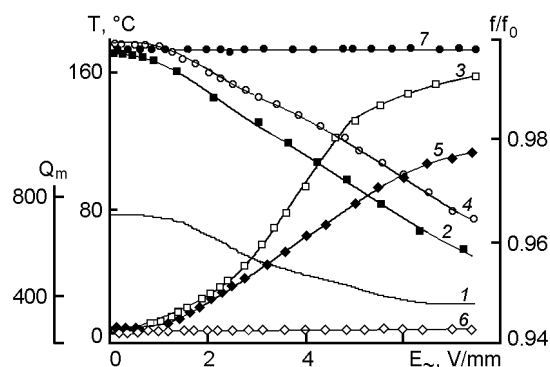


Fig. 1. Influence of the exciting voltage amplitude on the PCE heating and PCE characteristics: 1, mechanical quality; 2, resonance frequency; 3, heating at the resonance frequency; 4, 3rd harmonic frequency; 5, heating at the 3rd harmonic frequency; 6, heating at the antiresonance frequency; 7, antiresonance frequency.

characteristics of elements were measured through the specified time intervals (5 min). To reduce the error at the measurements, the following sequence was always retained: at first, the resonance frequency f_r was determined, then the antiresonance frequency f_a and at last the third harmonic frequency f_{r3} . The Poisson ratio σ , radial electromechanical force factor k_r , mechanical quality Q_m were found using known formulas [8, 9]. After plotting of time dependences $\sigma(\tau)$, $\delta_r(\sigma)$, $f_r(\sigma)$, $k_r(\sigma)$, $Q_m(\sigma)$, the most reliable logarithmic functions were found by the logarithmic approximation taking into account the values of validity.

The behavior of resonance frequency, antiresonance frequency, and the third harmonic frequency at varying strength of the AC field were studied. As the amplitude of the exciting AC field of the resonance frequency increases from 50 mV/mm to 7500 mV/mm, the following phenomena take place: a reduction in the mechanical quality Q_m (approximately by 3 times) (curve 1 in Fig. 1), a decrease of the resonance frequency (to 3–5 %) (curve 2 in Fig. 1), a decrease of the elastic compliance s_{11} (by 3–5 %), a decrease of the Poisson ratio σ (by 20–25 %), an increase in the relative resonance space δf (by 3–5 %), an increase in the electromechanical force factor k_r (by 10 %), a decrease in the real component of the PCE impedance at the resonance frequency R_r (≈ 5 times) take place, and heating of the PCE occurs (curve 3 in Fig. 1). The measurements at the first harmonic frequency reveal a similar reduction in the

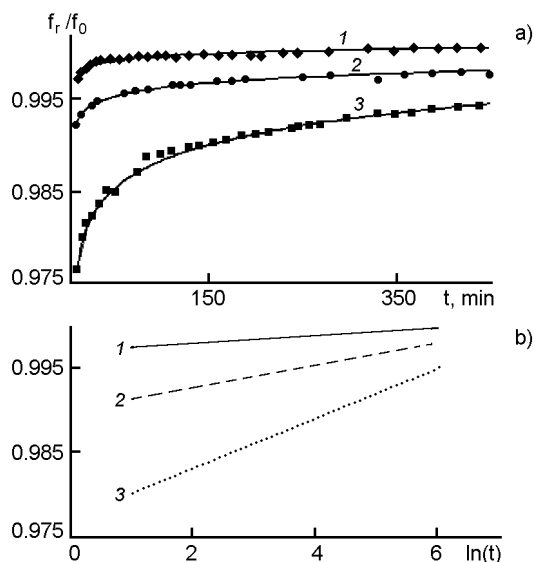


Fig. 2. Dependences of relative resonance frequency on the time after the PCE excitation at the resonance frequency. U_{exc} , mV/mm: 2500 (1), 5000 (2), 7500 (3). Time scale: (a) linear, (b), logarithmic.

resonance frequency (curve 4 in Fig. 1) and the sample heating (curve 5 in Fig. 1), but the PCE maximum temperature was lower (120°C against 170°C).

In contrast to the PCE excitation at the resonance frequency, that at the antiresonance one practically does not result in the sample heating (curve 6 in Fig. 1). The antiresonance frequency also is not changed, when the exciting field strength increases (curve 7 in Fig. 1).

After the excitation voltage is switched off, the PCE temperature is reduced down to room one during 1 min. The measurement of piezoresonance characteristics after the excitation (and after cooling to room temperature) shows that the parameters of piezoelectric elements are restored to the initial values. For all excitation field intensities, the curves are described by the functions: $f_r = A \cdot \ln(t) + C$, where A , C are the constant values. Fig. 2 shows the f_r relaxation dependences after the PCE excitation at the resonance frequency with the different field intensities. It is seen that an increase in the excitation amplitude results in higher relaxation rates.

The effect of the isothermal annealing on the PCE parameter relaxation was studied in a similar manner: holding at a temperature (80–170)°C during 10 min followed by cooling down to room temperature. From the dependences shown in Fig. 3, the PCE parameters are seen to relax to the values

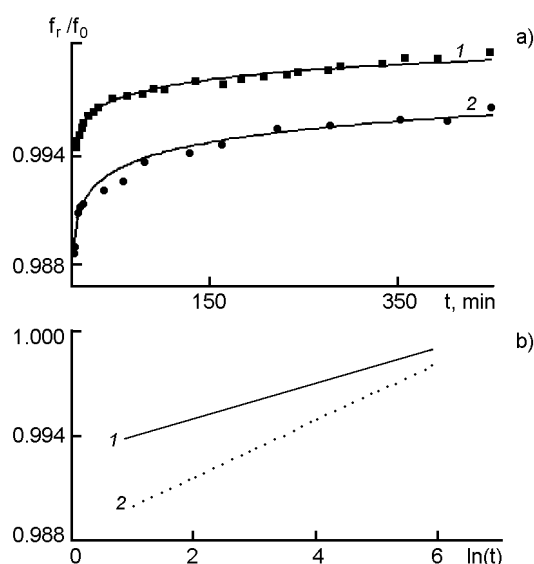


Fig. 3. Dependences of relative resonance frequency on the time after the PCE heating. T , °C: 80 (1), 170 (2). Time scale: (a) linear, (b), logarithmic.

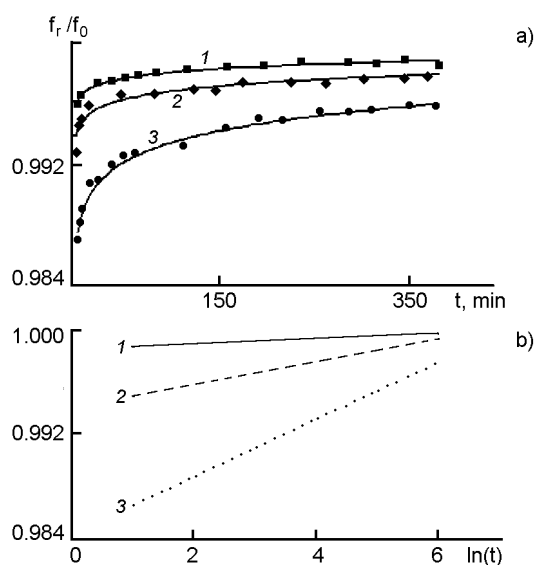


Fig. 4. Dependences of relative resonance frequency on the time after the mechanical compression of PCE. P , kg/cm²: 35 (1), 150 (2), 334 (3). Time scale: (a) linear, (b), logarithmic.

close to the initial ones. The relaxation curves (as in the preceding case) are described by dependence $f_r = A' \cdot \ln(t) + C'$, (A' , C' are constants). The relaxation is long-term. An increase in the annealing temperature results in increased relaxation rates. There are no noticeable differences after heating of elements in the "electrically short-circuited" and "non-short-circuited" state.

The uniaxial mechanical load, (pressure of 35, 150, and 334 kg/cm², the action du-

ration 30 min) causes a reduction in the frequency and subsequent relaxation (Fig. 4) according to the law: $f_r = A'' \cdot \ln(t) + C''$. An increase in the pressure accelerates the relaxation.

When studying PCE from the morphotropic, tetragonal or rhombohedral regions of the PZT phase diagram, no essential differences in the relaxation behavior of the piezoelectric parameters have been observed. Within the measurement accuracy limits, the relaxation curves in these three cases coincide, therefore, these graphs are not present in the article.

At present, the PZT based solid solutions from the so-called morphotropic region of the phase state diagram are used for the practical applications. In this case, the domains of FE phases with Rh and T types of the crystal lattice distortions coexist in the PCE volume. Therefore, in the most cases, the experimental results obtained for such solid solutions are explained just by the physical processes caused by the said co-existence, in particular, by the motion (including vibrations) of interphase boundaries. Such a situation is connected with the fact that electric field may cause the phase transition between Rh and T phases [10, 11]. However, the results obtained in this study show that the relaxation processes do not depend on the solid solution position in the phase state diagram, practically essentially identical results being obtained for both the single-phase and two-phase PCE. This indicates unambiguously that the discussed effects are not connected with the morphotropic region of the state diagram. Therefore, other mechanisms, which define long-time relaxation in the investigated piezoelectric materials should be searched. The PCE temperature change when the resonance voltage is increased (Fig. 1, curves 3 and 5) is worth to note. The relaxation effect is the more pronounced, the higher is the sample heating in the course of excitation. The PCE heating is explained rather simply. It is accepted to work with the piezoelectric elements in the so-called linear mode, when amplitudes of driving AC electric voltage and of elastic vibrations are small and the Hooke's law is met. As the vibration amplitude increases, the elastic energy anharmonicity degree of the piezoelectric element rises and as a result deviation from Hooke's law arises. In such conditions, the so-called internal friction must be considered. In this case, the terms describing the energy dissipation appear in the differential equation,

$(\rho \cdot \ddot{x} + (\eta + \eta_o) \cdot \dot{x} + s^{-1} \cdot x^2 = 0$, where ρ is the PCE density, s is the elastic compliance, η and η_o are the viscosities caused by losses on the electric load and intrinsic losses of PCE, respectively). In our experimental conditions, the viscosity η is small. The viscosity η_o increases with the AC resonance field amplitude.

As it was shown in experiment, the increasing exciting field amplitude causes a decrease in the real component of the PCE impedance at the mechanical resonance frequency. This is just the main factor causing the heating of elements. This is clearly confirmed by curve 5 in Fig. 1 which represents the element temperature in the course of heating at the third harmonic frequency of mechanical oscillations. In this case, the same strength of the exciting electric field results in a smaller amplitude of piezoelectric oscillations and the heating of element is lower.

Relaxation is the returning process of the object under investigation to the equilibrium state after leaving therefrom under external actions. The results obtained testify that a change in PCE temperature (with an increase in the driving voltage) can be a main driving force of the process which drives piezoelectric elements out of the equilibrium thermodynamic state. For this reason, we have studied the relaxation process after the thermal heating of PCE. The results are shown in Fig. 3. As is seen, completely identical physical results for relaxation are obtained both investigated processes (the resonance field excitation and the thermal heating). This allowed us to propose a simple model making it possible to explain the obtained results.

The polycrystalline structure of piezoelectric ceramics shown schematically in Fig. 5a forms the basis for our model. At temperatures lower than the Curie point, the spontaneous polarization P_s , directed along one of the crystallographic axes of crystallite arises in each grain. In the non-polarized state of PCE, the polarization directions in all crystallites are not correlated and are directed in the space randomly. The remanent polarization of element is equal to zero. The PCE does not possess any piezoelectric properties. After the polarization of elements by an external DC electric field, in each crystallite the spontaneous polarization is directed along the crystallographic axis having the most close direction to that of the polarizing field. This situation is sche-

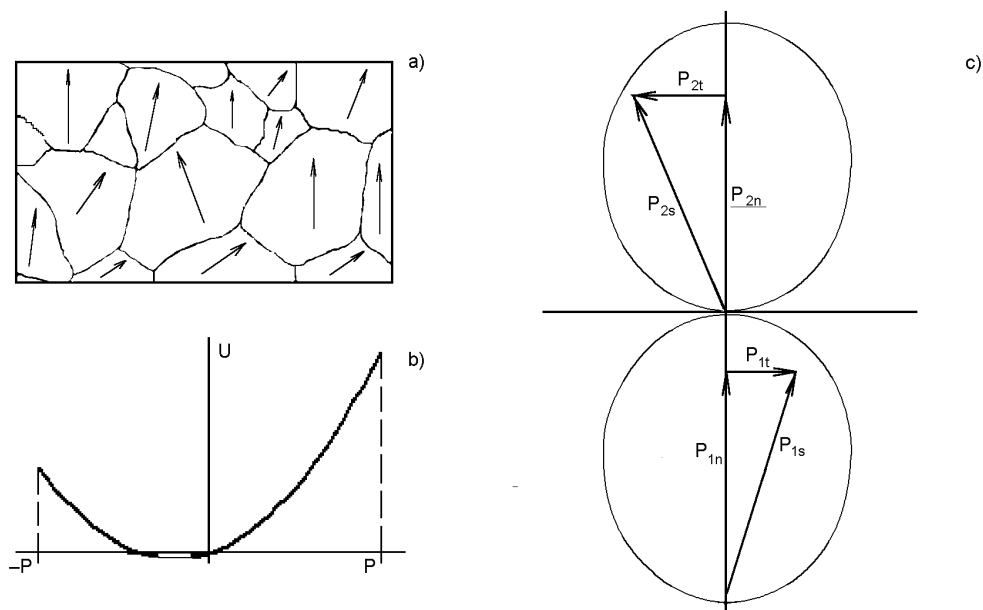


Fig. 5. Schematic representation of crystallite structure of polarized piezoceramics (a); dependence of the crystallite strain the polarization (the values d and Q are characteristic for the hard piezoelectric materials) (b); tangential and normal components of polarization vector of in the adjacent grains (c).

matically illustrated in Fig. 5a (right). The main thing of interest in what follows is the noncoincidence of the spontaneous polarization directions in neighboring crystallites. This noncoincidence results in mechanical stresses along the grain boundaries. The appearance mechanism of such stresses is illustrated in Fig. 5b and 5c. Fig. 5b shows schematically the dependence of strain on the spontaneous polarization value: $u = d \cdot P + Q \cdot P^2$, where d and Q are the piezo coefficient and the electrostriction coefficient, respectively. Within limits of each crystallite, the spontaneous deformation is uniform, but within the entire piezoelectric element such uniformity is not retained. This is illustrated in Fig. 5c which shows the projections of spontaneous polarization on the tangent plane for two adjacent crystallites. It is seen that the projections are unequal for the adjacent grains ($P_{1s} = P_{2s}$, $P_{1t} \neq P_{2t}$, P_s is the spontaneous polarization), which means the inequality of spontaneous strains in the vicinity of grain boundaries. Since no cracks are appeared on the grain boundaries after cooling lower than Curie point and after the polarization of elements (otherwise, the element could not work as the resonator), elastic strains (in this case tangential) appear along the grain boundaries. In the same way, normal elastic strains appear (since $P_{1n} \neq P_{2n}$). The IEEE Standard on Piezoelectricity requires

to hold the PCE during 5 days after the polarization of the elements prior to their controlling and use. Relaxation of internal stresses in the piezoelectric element occurs in this period, and the element itself is stabilized in the working equilibrium state.

At in our experiments, the increasing temperature causes a decrease of spontaneous polarization within each grain (crystallite). This causes a change in the spontaneous strains and, as a result, to a value change and redistribution of elastic strains. Thus, a new equilibrium state is realized at each specific temperature. However, after rapid cooling down to room temperature, the new state becomes already nonequilibrium, and its relaxation to the equilibrium one for 20°C occurs. The higher is the heating temperature, the greater is the deviation of "heated" state from the equilibrium low-temperature one. All said effects are observed under the experimental conditions used in the present work.

To confirm the proposed model, the experiments were carried out with the inclusion of mechanical stresses (Fig. 4). In this case, it is possible to assert unambiguously that a change in the internal thermodynamic state of the elements is connected with mechanical stresses inside them. The relaxation process of recovery into the initial equilibrium state after the removal of mechanical loads is identical to that following

the heating and cooling of elements, what is evident from the comparison of the experimental results shown in Figs. 3 and 4.

To conclude, much attention is given recently to the behavior of piezoelectric working elements under high loadings (electrical, mechanical, thermal). In this work, the aftereffect (relaxation to the initial state after the termination of such actions) has been studied. We have show that the processes under investigation are not connected with the so-called morphotropic region of the PZT solid solutions being the materials of the ceramic elements. A model based on the appearance of internal mechanical stresses localized near the boundaries of crystalline grains is proposed. Within the framework of the model, noncontradictory explanation of the effects of external actions and the restoration of the initial working state of elements after the termination of actions are found. In this work, we do not examine the mechanisms which determine the long-term relaxation. This is the object of another article. Here we will point out to the fact that this relaxation is the consequence of diffusion processes near the grain boundaries under the mechanical stresses. In general case for solids, such processes were considered in [12, 13], and for the PZT based solid solutions where, the FE or AFE state is realized, in [14, 15].

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Релаксаційні процеси у сегнетожорсткій кераміці

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Подано результати дослідження релаксаційних процесів у полікристалічних п'єзоелектричних елементах після їх збудження змінним струмом резонансної частоти, нагріву та одновісного механічного стиску. При поверненні елементів у вихідний термодинамічний стан відбувається довготривале відновлення їх пружних параметрів. Релаксація, що спостерігається, описується логарифмічною функцією часу. Для пояснення одержаних результатів запропоновано модель, яка бере до уваги полікристалічну структуру кераміки та наявність некомпенсованих механічних напруг на межах кристалів.