Influence of domain structure on relaxation phenomena in the PZT ceramic

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The temperature dependences of internal friction in PZT ceramics have been obtained in a wide temperature range from the room temperature to that exceeding the phase transition point from ferroelectric to paraelectric phase. The aim of the study was to describe the influence of domain structure on relaxation phenomena in samples of undoped PZT ceramics and multicomponent ceramics doped with Cd and W–Pb(W,Cd)O$_3$–PbZrO$_3$–PbTiO$_3$, prepared by the sol-gel method and by solid state reaction, respectively, followed by sintering. Basing on the internal friction measurements, the relaxation phenomena observed in examined ceramics have been described. The relaxation peaks connected with interaction point defects and domain walls and viscoelastic motion of domain walls have been observed in the temperature dependences of internal friction. For all relaxation peaks, the values of activation energy H and pre-exponential factor τ_0 have been calculated.

Исследованы температурные зависимости внутреннего трения для керамики типа ЦТС в широком диапазоне температур — от комнатной до превышающей температуру фазового перехода от ферроэлектрической фазы к параэлектрической. Целью исследования было определение влияния доменной структуры на релаксационные явления в образцах нелегированной керамики и керамики с добавками Cd и W–Pb(W,Cd)O$_3$–PbZrO$_3$–PbTiO$_3$, полученных соответственно методом золь-гель синтеза и твердофазного синтеза с последующим спеканием. На основании измерений внутреннего трения описаны релаксационные явления в исследованной керамике. На температурных зависимостях внутреннего трения наблюдались релаксационные пики, связанные с взаимодействием точечных дефектов с доменными границами и с вязко-упругим движением доменных границ. Для всех релаксационных пиков определены значения энергий активации H и предэкспоненциального множителя τ_0.

The PZT ceramics (PbTiO$_3$–PbZrO$_3$) is used for electromechanical transducers, sensors (vibration, pressure), actuators, piezoelectric transformers, ultrasound generators, filters, etc. Properties of undoped ceramics are not adequate for many applications; therefore, admixtures (dopants) are added to obtain materials with preset parameters. The dopants cause formation of defects in the ceramics structure, which influence significantly the electromechanical coupling coefficient, dielectric loss, coercive force field, mechanical quality, and internal friction. The properties of the PZT ceramic can be also influenced by varying the concentrations of main components in the solid solution resulting in changes of the ceramics structure [1–6]. The aim of this work was to determine the influence of the domain structure changes on the relaxation phenomena taking place in the undoped and doped PZT ceramics.

Samples of undoped PbZrO$_3$–PbTiO$_3$:PZT 35/65 (tetragonal structure), PZT 46/54 (morphotropic area), PZT 65/35 (rhombohedral structure), and those of Pb(W$_{0.5}$Cd$_{0.5}$)O$_3$–PbZrO$_3$–PbTiO$_3$ multicomponent ceramics PZT doped with W and Cd:PZT 2/33/65 (tetragonal structure), PZT 2/43/55 (morphotropic area), PZT 2/51/47 (rhombohedral structure), were studied. The samples were obtained by the sol-gel synthe-

sis (undoped PZT) and by the solid phase synthesis (doped PZT). Then the materials were sintered by a classical method. The internal friction (IF) was measured using a RAK-3 radio frequency relaxator controlled by a computer.

The internal friction measurements carried out at 3 K/min heating rate on the undoped PZT ceramics (Fig. 1) present two IF peaks for PZT 35/65 and PZT 46/54 ceramics and three peaks for PZT 65/35 ceramics in the $Q^{-1} = f(T)$ relationships. Basing on measured temperature dependence of electric permittivity and determined Curie temperatures (Table 1) for the tested samples, it can be stated that it is just the phase transition from the ferroelectric phase to the paraelecric one at $T_C \approx T_F$ (T_F being the maximum temperature for the P_F peak) that is responsible for the P_F peak formation for all tested samples. The fact that the P_F peak is due to the phase transition is confirmed also by the $Q^{-1}(T)$ measurements carried out at different measurement frequencies (Table 1). The unchanged temperature position of the P_F peak and its lowering height with the frequency decrease proves the origination mechanism of this peak [7–9]. Consideration of the phase diagram for the PZT ceramic allowed to assume that the phase transition from the rhombohedral phase I to rhombohedral phase II is also responsible for the P_F peak formation for PZT 65/35 [10].

A shift of the P_{RI} peak maximum towards higher temperatures with increasing measurement frequency (Table 1) evidences the relaxation character of this peak [8, 9]. In relaxation processes, the activation energy H and the relaxation time τ are de-
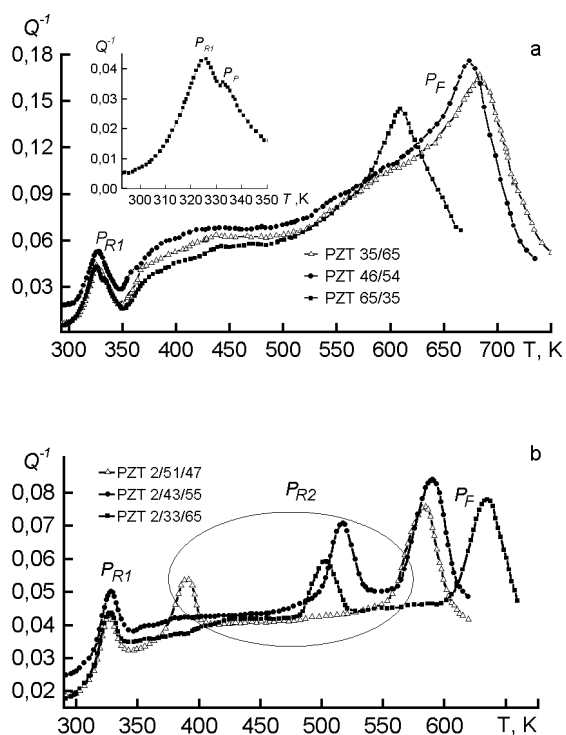

Fig. 1. Temperature dependences of internal friction for the undoped ceramics PZT 35/65, PZT 46/54, PZT 65/35 (a) and doped ones PZT 2/33/65, PZT 2/43/55, PZT 2/51/47 (b).

scribed by the Arrhenius law $\tau = \tau_0 \exp(H/kT)$, where τ_0 is a pre-exponential factor; T, temperature in K; and k, the Boltzmann constant. Using the Arrhenius law and a condition of the internal friction peak maximum $\omega\tau = 1$, it is possible to define the mechanism responsible for its formation by determining the τ_0 and H values characterizing height of potential barriers, which atoms overcome while migrating in

Table 1. Curie temperatures T_c, temperatures of the P_F peak maximum at different measurement frequencies ($f_1 < f_2$), and temperatures of relaxation peaks T_{R1}, T_{R2}.

Sample	T_c, K	T_F, K for f_1	T_F, K for f_2	T_P, K for f_1	T_P, K for f_2	T_{R1}, K [K] for f_1	T_{R1}, K for f_2	T_{R2}, K for f_1	T_{R2}, K for f_2
PZT 35/65	678	681	681	–	–	325	333	–	–
PZT 46/54	671	673	673	–	–	328	337	–	–
PZT 65/35	607	609	609	332	332	325	332	–	–
PZT 2/33/65	630	635	635	–	–	327	334	503	511
PZT 2/43/55	586	591	590	–	–	328	335	517	527
PZT 2/51/47	578	582	582	–	–	327	335	389	397

the course of relaxation [11]. The activation energy value was determined basing on the $Q^{-1}(T)$ curve half-width. The calculated values of the activation energy and pre-exponential factor (Table 2) show that point defects are responsible for the formation of the peak in question. The point defects introduced during a technological process anchor the domain walls. Therefore, the P_{RI} peak preceding the phase transition is connected with energy dissipation of mechanical vibrations due to the presence of the point defects and the domain structure in the ferroelectric material. In the PZT ceramics, oxygen vacancies are predominating point defects, therefore, the interaction of oxygen vacancies with the domain walls is responsible for the P_{RI} peak formation. This fact is proved by analysis of the obtained activation energy and pre-exponential factor values for the undoped PZT ceramics. The obtained values (Table 2) are typical of a relaxation process, namely, interaction of oxygen vacancies with domain walls [8, 12].

Three internal friction maxima (Fig. 1b) was observed for the tested multi-component PZT type ceramics doped with cadmium and tungsten. Like to the undoped ceramics, a ferroelectric-paraelectric phase transition is responsible for the P_F peak (Table 1). The relaxation process and the interaction of point defects (oxygen vacancies) with domain walls are responsible for the P_{RI} peak formation, what is confirmed by the determined values of H and τ_0 (Table 2).

With increasing $PbTiO_3$ concentration in the PZT ceramic resulting in the ceramics structure change from the rhombohedral phase tetragonal one via a phase coexistence area (rhombohedral and tetragonal), the domain structure also undergoes a change [13–15]. It can be stated that the change in the $PbTiO_3$ concentration causing a change in the domain structure does not have an influence on the height and temperature po-

sition of the peak originating from the interaction of point defects with the domain walls. The P_{RI} height is 0.035 to 0.036 for the undoped ceramics and 0.021 to 0.023 for doped one and it depends on the concentration of defects introduced to the material during a technological process (insignificant differences in the activation energy value of this process).

Consideration of the $Q^{-1} = f(T)$ relationships for the ceramics in question evidences a visible difference between the dependences obtained for doped and undoped materials. An additional internal friction peak P_{R2} preceding the phase change is observed. As the measurement frequency increases, its temperature position is shifted toward higher temperatures; this indicates its relaxation character [8, 9]. The calculated H and τ_0 values show that the relaxation process described by a single relaxation time (Table 2) cannot be responsible for the P_{R2} formation. The temperature position of the P_{R2} peak and its distance from the phase change peak influences the character of interactions responsible for the P_{R2} maximum formation. For the rhombohedral 2/51/47 PZT ceramics, the interaction of the domain walls is mainly responsible for the P_{R2} peak formation (Table 2). However, judging from a short temperature distance between P_{RI} and P_{R2}, point defects may also share in its formation. On the other hand, the calculated H and τ_0 values for the P_{R2} peak in the PZT 2/43/55 and PZT 2/33/65 ceramics (Table 2) indicate complex relaxation processes, which cannot be described by a single relaxation time. For that reason, an explanation of mechanisms responsible for their formation should be sought in the complex relaxation processes.

Since the P_{R2} peak is in the temperature range preceding the phase change, the processes responsible for its formation can be considered basing on the Wang model, characterizing the IF in the area preceding the ferroelectric-paraelectric phase change. A

Table 2. Activation energy values H and pre-exponential factors τ_0 for the IF relaxation peaks.

Sample	H, eV for P_{RI}	τ_0, s for P_{RI}	H, eV for P_{R2}	τ_0, s for P_{R2}
PZT 35/65	1.02±0.02	$(2.46\pm0.04)\cdot10^{-15}$	–	–
PZT 46/54	1.10±0.02	$(1.54\pm0.04)\cdot10^{-15}$	–	–
PZT 65/35	0.97±0.02	$(1.80\pm0.04)\cdot10^{-15}$	–	–
PZT 2/33/65	1.19±0.02	$(3.98\pm0.04)\cdot10^{-15}$	1.904±0.02	$(6.28\pm0.04)\cdot10^{-19}$
PZT 2/43/55	1.21±0.02	$(3.58\pm0.04)\cdot10^{-15}$	2.668±0.02	$(8.13\pm0.04)\cdot10^{-23}$
PZT 2/51/47	1.18±0.02	$(4.38\pm0.04)\cdot10^{-15}$	1.503±0.02	$(8.05\pm0.04)\cdot10^{-16}$

lot of mechanisms are responsible for the internal friction in this area. First, in the temperature range preceding the phase change, the domain wall density N increases with temperature and it is approximately proportional to $1/(T_c - T)$ (where T is a temperature near the Curie temperature T_c), what causes an increase in the Q^{-1} value. However, on the other hand, an increase in domain wall density results in shortened distance between them, thus, a decrease in mobility of the domain walls is caused by their mutual interaction. This results in a decrease of Q^{-1} value, when the domain wall density is too high. For that reason, the internal friction value in the area preceding a ferroelectric-paraelectric phase depends on a compromise between those factors [8]. Thus, a viscoelastic movement of the domain walls is responsible for the P_{R2} peak formation.

The absence of this maximum in the $Q^{-1} = f(T)$ relationships for the undoped PZT ceramic should be explained by differences in the ceramics microstructure. The domain size in the ferroelectric ceramics is connected with the grain size. Height of the internal friction peak is directly proportional to the square of the domain width. If the grain size decreases, the domain size decreases more sharply. Therefore, the domain influences significantly the course of the IF temperature dependence. The grain size decrease results in a decreased height of the peak originating from the mutual interaction of the domain walls; whereas at a grain size being a few μm, this relaxation peak is not observed, because the internal friction value connected with this process corresponds to a size of the internal friction background [16−19]. The domain structure, its type and mobility of the domain walls influences significantly not only the presence or absence of the P_{R2} peak, but its temperature position as well.

In the range of the PZT composition from the dual phase ($R + T$) morphotropic structure, a great number of domain walls (Fig. 2) with great mobility is observed, as well as a great number of phase boundaries (R/T) [20]. The great number of the domain walls is a cause of an increase in possible domain reorientations taking place under external actions. A great number of domain walls with sufficiently high mobility and phase boundaries cause that the specimens PZT 46/54 and PZT 2/43/55 show the internal friction maximum values as piezomodules. In the rhombohedral phase (PZT
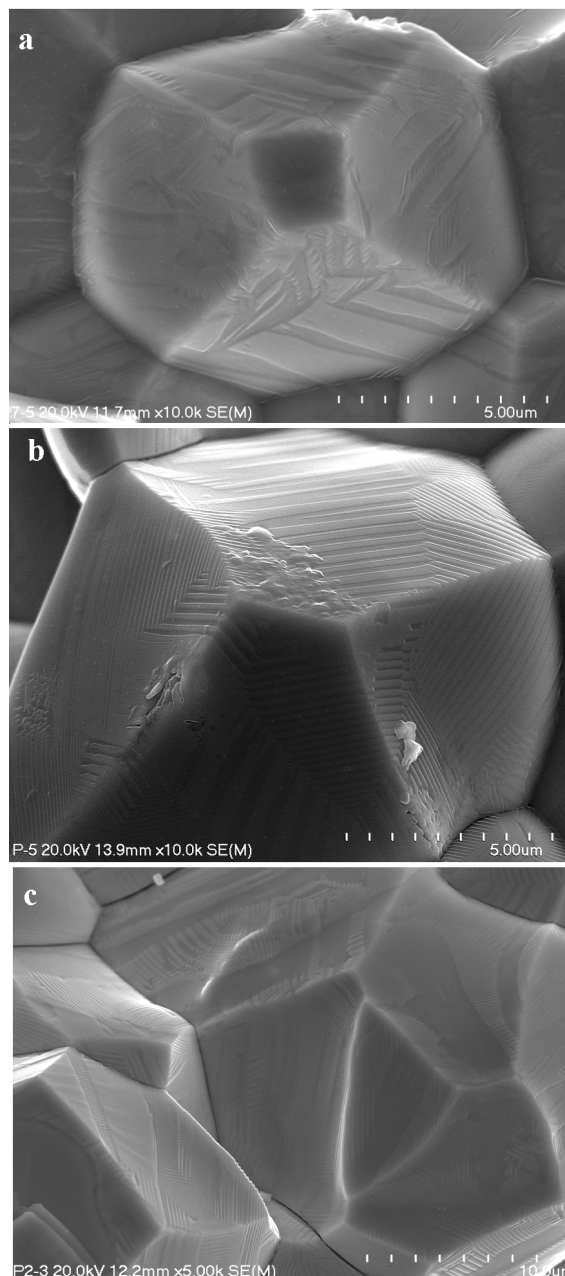

Fig. 2. Domain structure of ceramics with rhombohedral structure (a), tetragonal (b), rhomboherdal and tetragonal coexistent phases (c).

65/35, PZT 2/51/47), it is just the 180° domain structure that prevails (Fig. 2), resulting in a visible reduced number of the domain walls. This type of the domain structure causes a decreased internal friction value and piezoelectric parameters [20]. In the $PbTiO_3$ concentration range corresponding to the tetragonal phase (PZT 35/65, PZT 2/33/65), there is a complex 90° domain structure with a great number of 90° domain structures characterized by

low mobility. Such a stabilized domain structure causes a decreased IF value (as the titanium and lead concentrations increase and move away from the morphotropic area).

To conclude, a change in the domain structure of the PZT ceramics (caused by increasing $PbTiO_3$ concentration) does not result in changes of height and the temperature position of the internal friction relaxation maximum connected with the interaction of oxygen vacancies with domain walls. Its height depends on the concentration of defects introduced in the technological process of the ceramic material preparation. The domain structure type influences the temperature position of the peak connected with the mutual interaction of the domain walls or visco-elastic movement of domain walls, and the internal friction value. The highest IF value is observed for the ceramics from the morphotropic area. When moving away from this area toward both lower and higher $PbTiO_3$ concentrations, a decrease of the internal friction value is observed. The domain structure type (domain width) defines also the presence of the peak originating from the mutual interaction of the domain walls.

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Вплив доменної структури на релаксаційні явища у кераміці ЦТС

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Досліджено температурні залежності внутрішнього тертя для кераміки типу ЦТС у широкому діапазоні температур — від кімнатної до температури, що перевищує температуру фазового переходу від фероелектричної фази до параелектричної. Метою дослідження було визначення впливу доменної структури на релаксаційні явища у зразках нелегованої кераміки та кераміки з домішками Cd та W–Pb(W,Cd)O$_3$–PbZrO$_3$–PbTiO$_3$, одержаних відповідно методом золь-гель синтезу та твердофазового синтезу з наступним спіканням. На основі вимірювань внутрішнього тертя описано релаксаційні явища у досліджений кераміці. На температурних залежностях внутрішнього тертя спостерігалися релаксаційні піки, пов'язані зі взаємодією точкових дефектів з доменними межами та з в'язко-пружним рухом доменних меж. Для всіх релаксаційних піків визначено значення енергії активації H та передекспоненційного множника τ_0.