

Relaxation processes in lead zirconate-titanate based piezoelectric ceramics.

2. Influence of thermal treatment

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The study results of thermal annealing effect on relaxation processes in lead zirconate-titanate based piezoelectric ceramics quenched to room temperature are presented. The relaxation is long-term. Two temperature intervals of thermal annealing are established characterized by reversible and irreversible changes of dielectric parameters. The temperature T_d separating these intervals manifests itself in temperature dependences of the polarization and the inverse dielectric constant, and is defined by destruction of dipole ordering below Curie point. The mechanism of the long-time relaxation caused by capture of a charge released at the sample annealing by vacancies in crystal lattice of lead zirconate-titanate solid solutions.

Представлены результаты изучения влияния температуры отжига на релаксационные процессы в пьезокерамике цирконата-титаната свинца после закалки образцов до комнатной температуры. Релаксация является долговременной. Установлено наличие двух температурных интервалов отжига, характеризующихся обратимыми и необратимыми изменениями диэлектрических параметров. Температура T_d , разделяющая эти интервалы, проявляется на температурных зависимостях поляризации и обратной диэлектрической проницаемости и определяется разрушением дипольного упорядочения ниже точки Кюри. Предлагается механизм долговременной релаксации, обусловленной захватом заряда, выделившегося при отжиге образцов, вакансиями кристаллической решетки твердых растворов цирконата-титаната свинца.

1. Introduction

Piezoelectric ferroelectric (FE) ceramics are an important class of functional materials [1, 2]. In recent years, different kinds of sensors are used due to the hardening of worldwide requirements for safe work of devices with moving working parts, in industry and all modes of transport. Exploitation of ceramic elements showed that the relaxation properties of materials after the removal of external physical actions have been insufficiently studied till this date [3–6].

In the mentioned works (as in most others) the behavior of piezoelectric ceramic elements (PCE) during the application of external influences is studied. Our previous paper [7] presents the study results of the PCE behavior after termination of external actions. It was shown that the relaxation processes after any kind of action (temperature, electric field, mechanical effects) are described by the same law, although the change of properties in the process of each action kind are described by their individual

laws. At the small action amplitudes, the considered processes were reversible.

The aim of the present study is to investigate the relaxation behavior of the dielectric constant of piezoceramic elements after short heating (during 10 min) and fast cooling (quenching) to room temperature. Piezoelectric ceramics of the lead zirconate-titanate (PZT-Pb(Zr_{1-x}Ti_x)O₃) based solid solutions was selected as the object of our investigations. It is shown that relaxation is a long-time, the mechanisms of this relaxation are discussed.

2. Experimental

The disk-shaped piezoceramic elements of standard sizes $d = 10$ mm, $h = 1$ mm (in accordance with [8]) were used in the present studies. The elements were made of the engineering grade (Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O₃ based piezoelectric material. The said solid solution is located at the center of morphotropic region (MPR) in the "composition (Zr/Ti) — temperature" phase diagram where rhombohedral (Rh) and tetragonal (T) phases are co-existing in the sample volume.

The 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-3 using the filtered CuK_α emission. The residual porosity of samples was not more than 0.2 %. Silver electrodes were used for dielectric and piezoelectric measurements. The polarization was carried out at 120°C in PES-5 silicon liquid in DC electric field with intensity 3 kV/mm during 1 h with the subsequent cooling down to room temperature in the field.

Temperature dependences of dielectric constant ε were carried out in AC electric field with intensity 0.3 V/mm and frequency 1 kHz. Temperature dependences of residual polarization were obtained by integration of electric charge released under heating and thermal depolarization of the samples.

The samples were prepared for measurements of the relaxation parameters (ageing) as follows. The samples were heated in a low-inertia electric furnace provided with the chromel-alumel (XA) thermocouple. The temperature of isothermal exposure was from 80 to 350°C, exposure time at each temperature was 10 min, with the subsequent fast cooling to room temperature. Temperature was measured at $\pm 0.5^\circ\text{C}$ accuracy using a differential XA thermocouple.

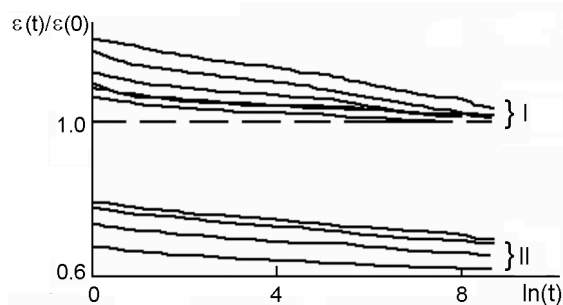


Fig. 1. Dependences of the relative dielectric constant on the holding duration after isothermal annealing (10 min) into different temperature regions and quenching of the sample. Temperature region: I — (100–260)°C, II — (260–350)°C.

After isothermal heating at each temperature followed by fast cooling to room temperature, the samples were aged at this temperature during 100 h and dielectric constant was measured during that time.

The piezoelectric elements were aged both in external electric field with intensity up to 700 V/mm and without application of the field. In our experiments, the DC field direction was along and against the direction of the sample polarization.

3. Results and discussion

Dependences of dielectric constant on the ageing time in the linear and logarithmic time scale are shown in Fig. 1. All experimentally measured values of the dielectric constant ε follow the law:

$$\frac{\varepsilon(t)}{\varepsilon_0} = -A \cdot \ln t + B, \quad (1)$$

where t is the ageing time (the time after quenching the sample); $\varepsilon(t)$, the ε value at time t ; ε_0 , the initial dielectric constant value (before annealing). This expression can be rewritten in a form which is adopted in the study of relaxation processes:

$$\varepsilon(t)/\varepsilon(0) = -A \cdot \ln(t/\tau), \quad (2)$$

where $\tau = \exp(B/A)$. The presence of the logarithmic dependence in equation (2) points to the wide range of relaxation times [9].

As is seen from Fig. 1, we can distinguish the characteristic temperature $T_d = 260^\circ\text{C}$, and the temperature interval of the sample annealing before quenching can be divided into two parts: $T_{ann} < T_d$ and $T_{ann} > T_d$. The temperature T_d is characterized by two distinctive features. First,

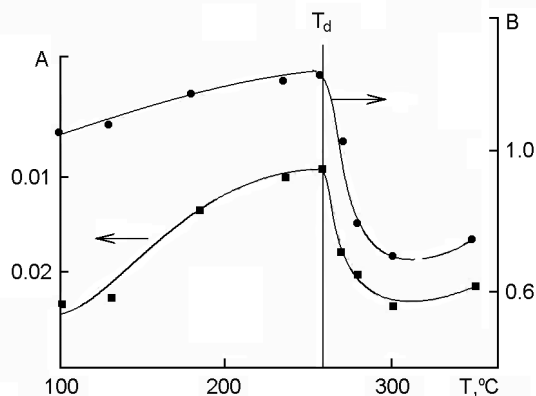


Fig. 2. Dependences of the coefficients A and B from Eq.(2) on the annealing temperature.

the dielectric constant of the investigated solid solution after annealing at temperatures $T_{ann} < T_d$ increases, while it decreases after annealing at temperatures above T_d . Second, if $T_{ann} < T_d$, in the process of heating and subsequent ageing the changes in the sample properties are reversible. In the case of $T_{ann} > T_d$ a irreversible changes in the sample properties take place. The temperature dependences of the coefficients A and B have the maxima at $T_{ann} = T_d$ (Fig. 2).

The temperature dependences of the dielectric constant and residual polarization were measured to clarify the physical nature of the characteristic temperature T_d . Fig. 3 shows the temperature dependences of the dielectric constant, residual polarization and the inverse dielectric constant. The totality of these dependences clears up completely the nature of the temperature T_d . Despite the fact that the temperature T_d is much below the Curie point T_c of the investigated solid solution, the depolarization of the sample begins at $T = T_d$. At the same time, the maximum of the temperature dependence $\varepsilon(t)$ corresponds to the Curie point T_c . At the point T_d , the dependence of the inverse dielectric constant $\varepsilon^{-1}(t)$ on the temperature deviates from the classical linear law.

The external DC electric field affects the position of the point T_d . Fig. 4 shows the dependences of A coefficient in (2) on the strength and direction of the applied field. As is seen, the field causes a significant shift of the initial dependence $A(T_{ann})$ along the temperature axis. The direction of the said shift depends on the direction of the applied field.

Before to discuss the mechanism of relaxation studied in this work, we recall results of [7], where we studied the relaxation processes in ceramic samples of the same

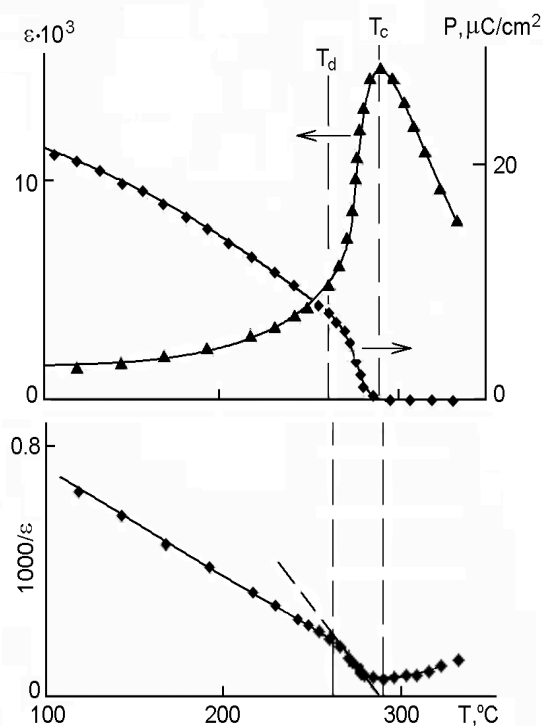


Fig. 3. Temperature dependences of dielectric constant, remanent polarization and inverse dielectric constant.

solid solution that was investigated in this study. As external factors destroying the equilibrium state at short-term action, temperature, uniaxial pressure, electric field of the same and opposite direction relative to the remnant polarization were involved. In all cases, independent on physical nature of the external actions, the ageing process of the samples was submitted to the general relaxation law (1).

In all noticed examples (in the present paper, too), the external actions cause a partial (reversible or irreversible) depolarization of the samples. As a consequence, a surface electric charge uncompensated by the polarization field (pyrocharge) is released on the sample surfaces. At the cancellation of the external actions, the residual polarization is returned to its original state reversibly (if the action was relatively weak) or irreversibly. Along with this, the electric charge released earlier is bound by the restored sample polarization. Temperature T_d separates the temperature ranges of reversible and irreversible changes in the residual polarization. Theoretical results given in [10] show that the ordered state of a unipolar domain structure in a ferroelectric plate is broken down during heating before reaching the Curie point. The differ-

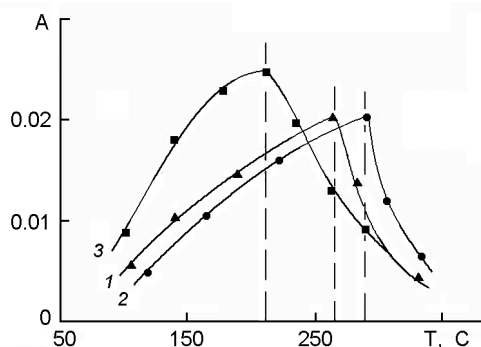


Fig. 4. Temperature dependences of A coefficient (2): 1, without the action of DC electric field; 2, with DC electric field (300 V/mm) directed along to the sample polarization vector; 3, with DC electric field (300 V/mm) directed against the sample polarization vector.

ence between the destruction temperatures of the single-domain and a polydomain states can attain 10°C (and even more) in a perfect single crystal. In polycrystalline samples, due to additional mechanical stresses on the grain boundaries caused by mismatch of crystallographic planes and directions of the spontaneous polarization in the neighboring crystallites, this interval may be much wider. Such a mechanism is fully agrees with the results of temperature measurements shown in Fig. 3. The interval $\Delta = (T_c - T_d)$ is equal to 30°C .

The electric field enhances the stability of single-domain state of the sample if the field direction and the polarization vector coincide, and lowers the stability for opposite directions thereof (in the second case, we can draw an analogy with the process of polarization reversal near the coercive field). Such situation is seen in Fig. 4. The maximum of $A(T_{ann})$ dependence corresponding to the temperature T_d is shifted to higher temperatures when the directions of the external field and polarization coincide and to the lower ones in opposite case.

Together with the above process, the electric charge released under external actions onto the ferroelectric sample is captured by crystal lattice defects. In the PZT solid solutions, such lattice defects are predominantly oxygen vacancies in the anion sublattice and lead vacancies in the A sublattice of the perovskite crystal structure [11–14]. As a result, F^+ or F^0 centers are formed. Said excited centers are separated from the ground-state by a potential barrier [13, 15]. As noted in [16, 17] the defects under discussion are concentrated on the sample surface and, to a lesser ex-

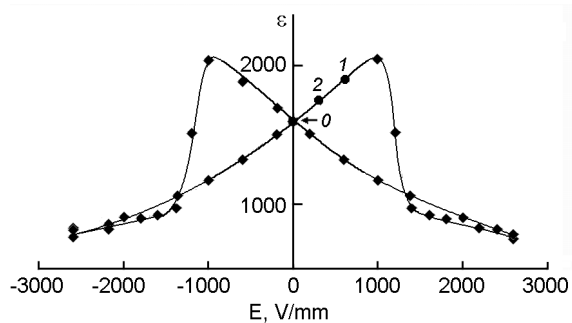


Fig. 5. Hysteretic loop of the dielectric constant.

tent, on heterogeneities of the samples. As an example, grain boundaries can be such heterogeneities.

The potential barrier height is from 0.3 to 1.5 eV for different centers. After the sample quenching, return of the remanent polarization to the initial state and binding of the charge released before, the relaxation of charged vacancies (F -centers) to the ground state begins. The charge released during the relaxation of F -centers, is bound by the electric field of remanent polarization. For the above heights of potential barriers, the time required to restitution of the original state, is ranged from several tens to several hundreds of hours. It is these relaxation times we observed in this work and in [7] for external actions of different nature.

We estimated the potential barrier heights, which determine the relaxation process (1), basing on the results of our experiments. These values are in the range of 0.5–1.0 eV. These estimations confirm that it is just the vacancies of the crystal lattice that are physical factor determining the relaxation process in our experiments.

4. Conclusion

Thus proposed model of relaxation can explain why in all cases the dielectric constant decreases after switching off external actions. Let us turn to Fig. 5 which shows the dielectric constant hysteretic loop of a piezoelectric element. The release of electric charge during the partial depolarization of the polarized sample (under external action of any nature) results in the appearance of an electric field directed along the polarization direction. The transition from point 0 to point 1 in the hysteretic loop occurs. After removing the external action and quenching of the sample, most of the released charge is bound, the field generated by it is weakened, and a fast transition

along the loop from point 1 to the point 2 occurs. As a fraction of the charge is bound by the crystal lattice vacancies, the sample is subjected to an "external" electric field, that is why the dielectric constant exceeds the initial value. Therefore, the dielectric constant after cooling from temperatures $T_{ann} < T_d$ exceeds its initial value. The field is zeroed and dielectric constant returns to the initial value only due to the charged centers (F^+ and F^0) relaxation process.

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Релаксаційні процеси у п'єзоелектричній кераміці на основі цирконату-титанату свинцю.

2. Вплив термічної обробки

Д.В.Кузенко, В.М.Іщук, А.І.Бажин, Н.А.Спирідонов

Представлено результати дослідження впливу температури відпалу на релаксаційні процеси у п'єзокераміці титанату-цирконату свинцю після загартовування зразків до кімнатної температури. Релаксація є довготривалою. Виявлено наявність двох температурних інтервалів відпалу, які характеризуються оборотними та необоротними змінами діелектричних параметрів. Температура T_d , яка розділяє ці інтервали, виявляється на температурних залежностях поляризації та зворотній діелектричній проникності та визначається руйнуванням дипольного впорядкування нижче точки Кюрі. Пропонується механізм довготривалої релаксації, обумовленої захопленням заряду, що вивільняється при відпалі зразків, вакансіями кристалічної ґратки твердих розчинів цирконату-титанату.