

## Critical temperature below the Curie temperature of ferroelectric ceramics PZT

D. V. Kuzenko

*Science & Technology Center “Reaktivelektron” of the National Academy Science  
of Ukraine Bakinskikh Komissarov Street, 83049 Donetsk, Ukraine*

danil.kuzenko@gmail.com

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The article presents the results of research the pre-transitional features of the behavior of solid solutions based on lead zirconate-titanate. The presence of a “special” critical temperature  $T_d$  on the temperature dependences of the permittivity  $\epsilon(T)$  and the remanent polarization  $P_r(T)$ , preceding the temperature of the paraelectric phase transition at the Curie temperature  $T_C$ , is noted. In the temperature range  $T < T_d$ , the  $P_r(T)$  dependence obeys a power law. In the temperature range  $T_d < T < T_C$ , this law is not fulfilled. The results of X-ray experiments make it possible to associate this behavior with reversible disordering at  $T < T_d$  of an ordered domain structure formed during the polarization of piezoelectric ceramics and with its irreversible disordering in the temperature range  $T_d < T < T_C$ . This is due to the appearance of internal mechanical stresses in a polycrystalline ferroelectric due to irreversible depolarization of the samples at temperatures  $T_d < T < T_C$ .

*Keywords:* PZT; depolarization; domain structure; critical temperature; Curie temperature.

### 1. Introduction

Ferroelectric and piezoelectric materials currently occupy an important place in the multifunctional materials market. They are used as sensors, converters, nonvolatile random access memory (FeRAM) elements, and actuators in nano/microelectromechanical systems (NEMS/MEMS).<sup>1–3</sup> Lead zirconate–titanate (PZT) is one of the most important ferroelectrics due to its remarkable piezoelectric properties. PZT piezoceramics is widely used as the main component in the production of sonars, hydrophones, high voltage generators, ultrasound generators, micropositioners.<sup>1–4</sup>

In many cases, piezoceramic materials must operate over a wide temperature range, while the surrounding space can be water, air, etc. Temperature changes result in a response of the piezoelectric coefficients, and often this response can be nonlinear. Therefore, for the practical application of piezoceramics, the temperature stability of various parameters of piezoceramics is investigated.<sup>5–9</sup>

When working in a wide temperature range, regions of reversible and irreversible changes in properties should be identified. As a rule, little attention is paid to the temperature region of irreversible changes in properties, since during the operation of piezoelectric elements they try not to bring them to such temperatures. There is no clear definition of its boundary from below, and the upper boundary is the Curie point. However, when adapting working elements to work in real operating conditions, thermal and thermoelectric treatment of elements is often carried out precisely in this

temperature range. An example is the thermal treatment of elements after polarization.

Thus, thermal depolarization in piezoelectric materials is of interest for practical applications. Various aspects of the depolarization process are considered, and the results are published in Refs. 10–14. The features of the depolarization process can be associated with the FE–PE transition (PZT solid solutions) or the FE–AFE transition ((Bi, Na)TiO<sub>3</sub> solid solutions). The influence of internal mechanical stresses and grain-crystalline structure is also often considered.<sup>15,16</sup>

In Ref. 17, when studying the aftereffect relaxation processes, it was noted that there are temperature ranges of reversible ( $T < T_d$ ) and irreversible ( $T_d < T < T_C$ ) changes in piezoelectric properties in PZT piezoceramic samples, where  $T_d$  is the critical temperature point separating these intervals.

In Ref. 11, the depolarization temperature  $T_d$  is defined as the temperature of the sharpest decrease in residual polarization.

In Ref. 18, 19 noted the presence of a temperature significantly lower than the Curie points, heating at which leads to a significant decrease in the piezoelectric properties.

The presence of the bottom limiting temperature of irreversible change in the piezoelectric properties below the Curie temperature was also noted in Ref. 20. To explain the revealed features, as a rule, one uses the concept of external and internal (domain) contributions to the properties of a ferroelectric and their temperature dependence.<sup>15–20</sup>

This paper presents the results of studying the process of temperature depolarization of piezoelectric ceramics PZT and its mechanism in the pre-transition temperature range  $T_d < T < T_C$ . The purpose of this paper is to generalize the experimental results on the determination of the nature of the critical temperature  $T_d$  for PZT-based piezoelectric ceramics, performed in Refs. 17, 21 and 22.

With all the variety of studies of the temperature dependences of the piezoelectric coefficients of the PZT system, little attention is paid in the literature to the study of the behavior of piezoelectric materials in the temperature range  $T_d < T < T_C$ . Therefore, this paper also analyzes the experimental data that take place in literature obtained in works by other authors.<sup>23,24</sup>

The obtained results are analyzed in accordance with the concept of ferroelectric polarization, to which spontaneous polarization and orientational polarization contribute in real ferroelectrics.

## 2. Materials and Methods

For the study, we used samples in the form of disks 10 mm in diameter and 1 mm thick based on ferroelectric-hard solid solutions of PZT system:

- $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.58}\text{Ti}_{0.42})\text{O}_3$  (rhombohedral symmetry);
- $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  (morphotropic region);
- $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$  (tetragonal symmetry).

The studied PZT solid solutions are in the phase diagram of the composition (Zr/Ti) — temperature both in the region of rhombohedral (Rh) at  $x = 0.58$  and tetragonal ( $T$ ) at  $x = 0.48$  distortions of the perovskite crystal lattice. We also have studied the solid solution from the morphotropic region ( $x = 0.53$ ), which is characterized by the coexistence of domains of the Rh- and  $T$ -phases in the bulk of the sample.

The conventional solid-state reaction route method with high purity ingredients was employed to prepare PZT-based ceramic samples. Samples were prepared from the oxides ( $\text{ZrO}_2$ ,  $\text{TiO}_2$ ) and carbonates ( $\text{PbCO}_3$ ,  $\text{SrCO}_3$ ). The doping chemical elements were added to the mixture of PZT-based elements in the form of oxides. The resulting oxide–carbonate mixture was mixed and attrition-milled for 3 h.

Calcination was performed at 850 °C (the first stage) for 2 h and at 1050 °C (the second stage) for 2 h in alumina crucibles. The second stage was provided in  $\text{PbO}$  atmosphere. The calcined powder was ground by ball milling for 4 h. The dried powder was mixed with polyvinyl alcohol and pressed with a pressure of 1 t/cm<sup>2</sup> into discs 15 mm in diameter and about 1 mm in thickness. The sintering of ceramic samples was provided at 1250 °C for 2 h in  $\text{PbO}$  atmosphere also.

The density of the samples is determined by hydrostatic weighing (7.6 g/cm<sup>3</sup>) and is equal to 97% of the theoretical, which determined by the X-ray method. Silver paste was

fired on the upper and lower faces of the disc as electrodes. The silver firing was performed at 700 °C during 10 min.

The polarization of the ceramic samples was carried out at a temperature of 120 °C in a DC electric field of 3 kV/mm for 1 h, followed by cooling to room temperature in the field.

Dielectric properties were measured using an LCR E7-8 meter at a frequency of 1 kHz with measured field amplitude of 4.3 V/mm. The piezoelectric coefficient  $d_{33}$  was measured by the Berlincourt method (quasi-static method). The temperature dependence of the remnant polarization  $P_r(T)$  was measured by measuring the released electric charge due to the depolarization during heating of a polarized PZT sample.

The samples were heated in the low-inertia electric furnace with the chromel–alumel thermocouple. The heating temperature of the samples was varied from 100 °C to 350 °C. To establish a uniform thermal state at each temperature (annealing temperature), the samples were kept in an isothermal state for 10 min. Isothermal annealing of the samples was carried out with an accuracy of  $\pm 0.75$  °C. After that procedure, the sample was rapid cooled (quenched) to room temperature.

The single phase nature of ceramics and structure change of the samples under the effect of DC electric field were controlled by the X-ray diffractometer DRON-3 using the filtered  $\text{Cu } K\alpha$  emission. X-ray photography was carried out 30 min after annealing (and quenching), due to the need for technological operations (chemical etching of the electrodes in nitric acid, placing the sample in the X-ray chamber).

Microstresses arising in the sample as a result of domain reorientation at annealing were estimated by the formula:

$$\frac{\Delta d}{d} = \frac{\beta}{4 \cdot \text{tg} \Theta_{hkl}}, \quad (1)$$

where  $d$  is the interplanar distance,  $\beta$  is the line broadening at half the maximum of the diffraction maximum, and  $\Theta_{hkl}$  is the angle of the diffraction maximum of the ( $hkl$ ) plane.

## 3. Experimental Results

The study of the temperature behavior of the relaxation rate of the dielectric constant after annealing, as well as the temperature dependences of the remnant polarization, dielectric constant and reverse dielectric constant, showed the presence of a special temperature point  $T_d$ , which is lower than the Curie point temperature  $T_C$  (Fig. 1).<sup>21,22</sup> The extrapolations of the reverse dielectric constant from the ferroelectric region and the paraelectric region intersect at the Curie temperature at  $\varepsilon^{-1} = 0$ .

In continuation of Refs. 17, 21 and 22, in this work, for piezoceramic samples of the composition  $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ , the temperature dependence of the remnant polarization  $P_r(T)$  was measured and the obtained dependence was numerically processed. To describe the curve  $P_r(T)$  by a power law, we plotted the dependence of the polarization  $P_r$  on the temperature difference  $T_C - T$  (Fig. 2).

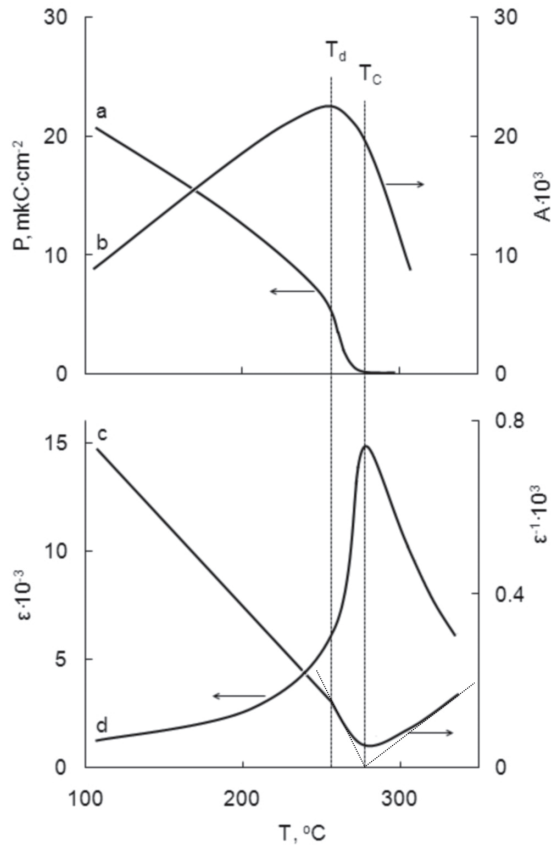


Fig. 1. Temperature dependences obtained for a sample of composition  $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ : a — remnant polarization  $P_r(T)$ ; b — relaxation rate  $A(T)$  of the dielectric constant after annealing; c — reverse dielectric constant  $\epsilon^{-1}(T)$ ; d — dielectric constant  $\epsilon(T)$ . Critical temperature  $T_d = 258^\circ\text{C}$ . Curie temperature  $T_C = 280^\circ\text{C}$ .

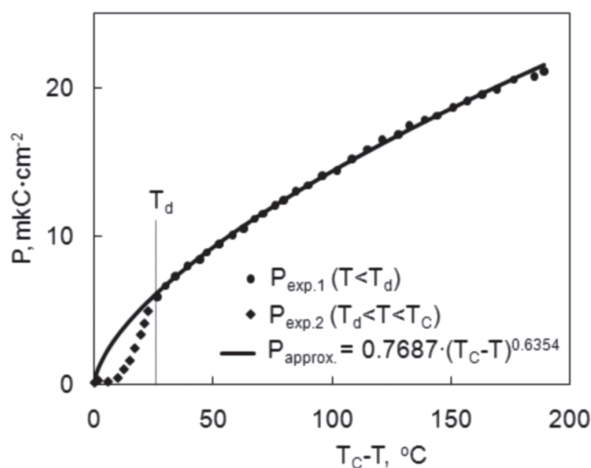


Fig. 2. Dependence of the remnant polarization  $P_r$  of the  $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  solid solution on the temperature difference  $T_C - T$ .  $P_{\text{exp.1}}$  — part of the experimental curve at  $T < T_d$ .  $P_{\text{exp.2}}$  — part of the experimental curve at  $T_d < T < T_C$ .  $P_{\text{approx.}}$  — temperature dependence of polarization obtained by approximation. Critical temperature  $T_d = 258^\circ\text{C}$ . Curie temperature  $T_C = 280^\circ\text{C}$ .

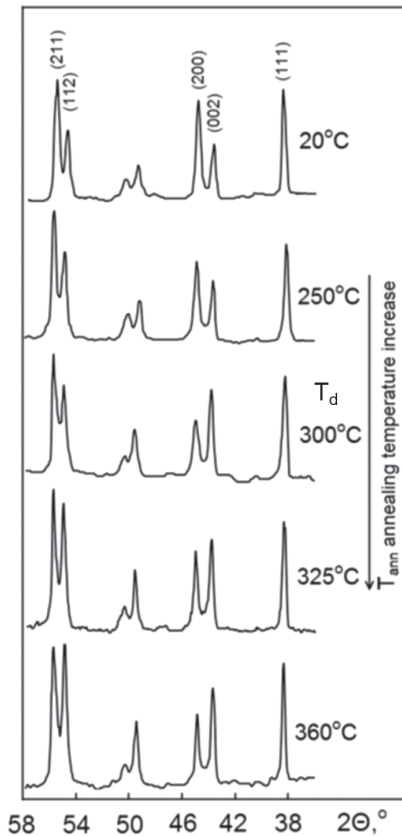


Fig. 3. Profile of diffraction lines of samples of composition  $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$  annealed at different temperatures. Critical temperature  $T_d = 300^\circ\text{C}$ , Curie temperature  $T_C = 335^\circ\text{C}$ .

As it can see, on the  $P_r(T_C - T)$  dependence (Fig. 2), two characteristic areas can be distinguished. At  $T < T_d$ , the  $P_r(T)$  dependence on the temperature difference  $T_C - T$  is fitted by a power law, which is natural for the behavior of ferroelectric polarization. In the temperature range  $T_d < T < T_C$ , this power law is not fulfilled.

In order to further study this issue, we analyzed the changes in the profiles of diffraction X-ray lines in the range of angles  $2\theta$  from  $38^\circ$  to  $58^\circ$  for solid solution  $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$  (Fig. 3).

This solid solution belongs to the tetragonal region of the phase diagram of the system of PZT solid solutions. We are interested in microstresses in the samples and their evolution with a change in the annealing temperature. This is most easily demonstrated by analyzing the change in the profile of the (200) X-ray line in solid solutions with tetragonal distortions of the crystal lattice.

X-ray diffraction patterns were obtained at room temperature ( $20^\circ\text{C}$ ) from samples that were annealed at different temperatures for 10 min. The Curie temperature is  $T_C = 335^\circ\text{C}$  and the critical temperature is  $T_d = 300^\circ\text{C}$ . X-ray diffraction patterns were obtained at room temperature. The only temperature history is different for samples.

#### 4. Discussions

Earlier, when studying the effect of the annealing temperature of polarized PZT samples, the presence of the temperature of the onset of domain disorientation was determined.<sup>22</sup> This temperature is below the Curie point temperature  $T_d < T_C$ .

The following features of the behavior of a piezoelectric ceramic sample when passing in temperature through the point  $T_d$  have been determined:

- The maximum rate of relaxation of the dielectric constant to the equilibrium value after annealing at a temperature  $T_d$ ;
- The start of the decay of the ordered state of the domain structure;
- By changing the regime of reversible disordering of domain order ( $T < T_d$ ), formed by an external electric field during the polarization of the samples, to irreversible.

The noted features of the  $T_d$  point are also manifested in the temperature dependence of polarization (Fig. 2). A deviation from the power-law dependence  $P(T)$  is clearly observed for  $T > T_d$ . The choice of the power function as an approximating function is due to the fact that, according to the theory of structural phase transitions from Ref. 25, which are described by a one-, two-, or three-component order parameter, the temperature dependence of spontaneous polarization near the Curie point temperature has the form

$$P_s \sim (T_C - T)^{0.5}. \quad (2)$$

For ceramic samples the exponent in Eq. (2) may differ from 0.5. Ferroelectric ceramics consist of many grains of various sizes and crystallographic axes orientation. As a consequence, disorientation of the spontaneous polarization of crystallite grains takes place even in polarized samples.

This leads to some difference in the exponent between the Landau theory and experiment in dependence (Eq. (2)). For a sample of composition  $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  (Fig. 2), the approximating function has the form

$$P = 0.7687 (T_C - T)^{0.6354}. \quad (3)$$

The deviation of the exponent from the theoretical is 27% and, as will be shown below, there are ferroelectrics of the PZT system with a greater deviation.

To clarify the physical essence of the deviation from the power law in the temperature range  $T_d < T < T_C$ , let us turn to the classical concepts of the electric polarization of solids.<sup>26</sup> In the general case, three types of polarization are considered for ferroelectrics: spontaneous, remanent, and orientational ones (as a rule, electronic polarization makes such a small contribution, and then only in a strong electric field that it is not considered). Spontaneous polarization is caused by mutual displacements of ions from centrosymmetrical positions. In PZT-based solid solutions, polarization occurs as a result of the displacement of the  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$  ions relative to the oxygen octahedron.

The remnant polarization  $P_r$  is due to the ordering of the ferroelectric domains, in which the polar moments of individual domains are aligned along their crystallographic directions closest to the direction of the external electric field. This ordering of domains is retained after switching off the electric field, since their turn to a disordered state is accompanied by the appearance of mechanical stresses and an increase in the energy of the system. Nevertheless, during a certain time after the polarization of the samples, mechanical relaxation of the domain structure occurs, during which there is a partial reverse domains unfolding and a decrease in polarization by the value  $\Delta P_i$ . The polarization remaining after mechanical relaxation is called remnant. In the general case, the remnant polarization is proportional to the ferroelectric spontaneous polarization:  $P_r \sim P_s$ .

Orientalional polarization appears in the process of sample polarization (or depolarization at temperatures below the Curie temperature) and is caused by a change in the degree of ordering of the domain structure.

For a polycrystalline ferroelectric PZT, spontaneous polarization  $P_s$  occurs with a decrease in temperature and a phase transition from a non-polar state to a polar state. The general polarization of ferroelectric ceramics can be represented as

$$P = P_r + \Delta P_i + P_{\text{ind}}, \quad (4)$$

where  $P_r$  is the remnant polarization,  $\Delta P_i$  is the decrease in polarization as a result of partial reverse unfolding of the domains,  $P_{\text{ind}} = \varepsilon \cdot E$  is the induced polarization. In the absence of an electric field,  $P = P_r$ .

As noted above, the remnant polarization is proportional to the spontaneous polarization ( $P_r \sim P_s$ ). Therefore, when heated at relatively low temperatures (well below the Curie point), the temperature dependence  $P_r(T)$  follows the same law that obeys the dependence  $P_s(T)$ . In the framework of Landau's theory of phase transitions, both of these dependences are described by a power law with an exponent of 1/2.

The sample heating leads to an increase in the thermal vibrations of domain walls, the energy of which at a certain temperature ( $T_d$ ) exceeds the energy of their pinning (in this work, we do not discuss the mechanisms of pinning of the directions of spontaneous polarization of domains in the polarized state) — partial disordering of the domain structure begins. On the  $P(T)$  dependence, this is manifested in the form of a sharp decrease in polarization at  $T > T_d$  and a deviation from the power-law dependence. The results of X-ray structural measurements are proof of this (Fig. 3).

Annealing at temperatures  $T > T_d$  leads to a redistribution of the components of the X-ray double line (200) — to a decrease in the intensity of the (002) line and to an increase in the intensity of the (200) line. This is a consequence of the rearrangement of the domain structure — its disordering formed upon polarization of the sample. Domain structure rearrangement can be reversible (at  $T < T_d$ ) and irreversible (at  $T > T_d$ ). Domain restructuring, in turn, must be accompanied by internal tensions.

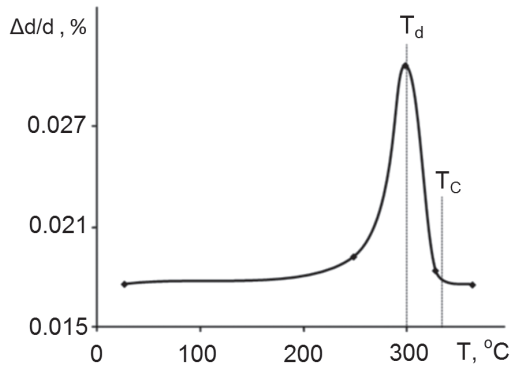


Fig. 4. Dependence of microstresses in the sample  $(\text{Pb}_{0.95}\text{Sr}_{0.05})\text{-(Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$  on the annealing temperature obtained from the analysis of diffraction lines (111).  $T_d = 300^\circ\text{C}$ ,  $T_C = 335^\circ\text{C}$ .

Figure 4 shows the dependence of microstresses in the solid solution  $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$  on the annealing temperature (obtained from the analysis of the change in the profile of the diffraction line (111)). As can be seen, an increase in temperature leads to an increase in microstresses at  $T < T_d$ , which reach a maximum at a temperature  $T_d$ . Along with this, the elastic energy of the system increases. We must note that, at these annealing temperatures, changes in the degree of domain ordering occur in a reversible manner: after heating, the domain structure returns to its initial state.

At temperature  $T_d$ , an increase in the total energy of the system reaches such a value that the ordered state of the domain structure becomes energetically less favorable than the state of partial disordering. The process of irreversible domain disordering begins, which is accompanied by a decrease in the microstress in the bulk of the sample in the temperature range  $T > T_d$ .

An additional factor leading to a decrease in the degree of domain ordering at temperatures  $T > T_d$  is the pyroelectric charge released during annealing at temperatures from this range. As noted in Refs. 17, 21 and 22, charge is released irreversibly only at these temperatures — it remains on the sample's electrodes after cooling to room temperature. Its field inside the sample is directed counter to the remnant polarization vector and is an additional factor contributing to the partial disordering of the domain structure. These factors contribute to a more rapid decay of the remnant polarization at temperatures  $T > T_d$  than it is envisaged by the power law — a sharp kink appears in the  $P_r(T)$  dependences at  $T = T_d$ .

Another manifestation of the critical behavior of the ferroelectric polarization of a piezoelectric sample at the point  $T_d$  is the minimum of the derivative  $dP/dT$  at this point (Fig. 5), which corresponds to the maximum release of the pyroelectric charge.

The reason for this behavior is the sharp change in polarization at temperature  $T_d$ .

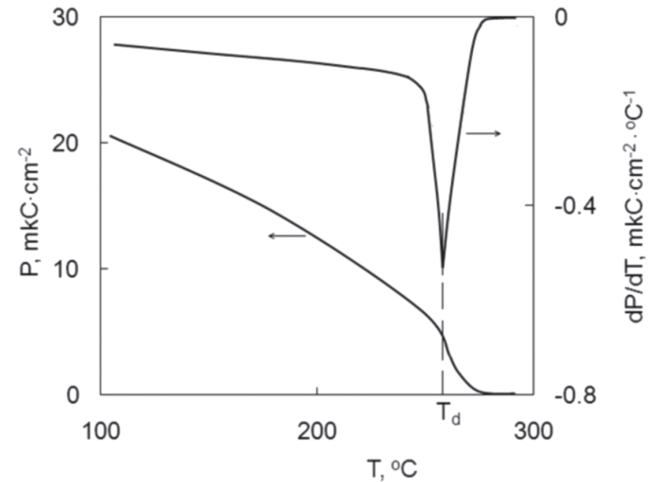


Fig. 5. Temperature dependence of the remnant polarization  $P_r$  and its temperature derivative  $dP/dT$  of the solid solution  $(\text{Pb}_{0.95}\text{Sr}_{0.05})\text{-(Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ .  $T_d = 258^\circ\text{C}$ .  $T_C = 280^\circ\text{C}$ .

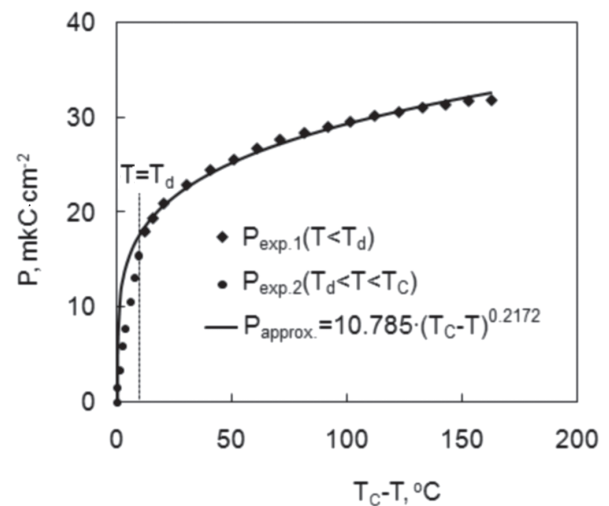


Fig. 6. Dependence of the remnant polarization  $P_r$  of the piezoceramic  $\text{Pb}(\text{Zr}_{0.66}\text{Sn}_{0.23}\text{Ti}_{0.11})\text{O}_3$  on the temperature  $T_C - T$ .  $P_{\text{exp.1}}$  — part of the experimental curve at  $T < T_d$ ;  $P_{\text{exp.2}}$  — part of the experimental curve at  $T_d < T < T_C$ ;  $P_{\text{approx.}}$  — temperature dependence of polarization obtained by approximation;  $T_d = 172^\circ\text{C}$ ;  $T_C = 184^\circ\text{C}$  (graph based on experimental data from Ref. 23).

The character of the temperature dependence of the remnant polarization obtained in our work is not a feature of only the studied samples of the composition  $(\text{Pb}_{0.95}\text{Sr}_{0.05})\text{-(Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ . After analyzing the papers of other authors, we found similar dependences in other solid solutions of the  $\text{PbZrO}_3\text{-PbTiO}_3$  system: piezoceramics of the composition  $\text{Pb}(\text{Zr}_{0.66}\text{Sn}_{0.23}\text{Ti}_{0.11})\text{O}_3$  from Ref. 23 (Fig. 6) and industrial piezoceramic material PZT-5H from Ref. 24 (Fig. 7).

In each of the dependences, one can also distinguish two characteristic temperature intervals. In the first of them a

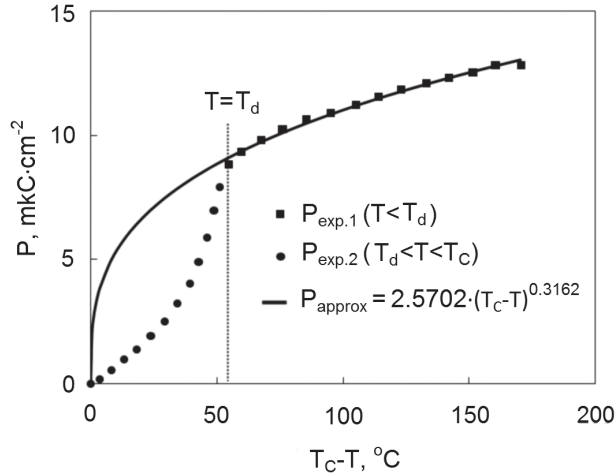


Fig. 7. Dependence of the remnant polarization  $P_r$  of industrial piezoceramic PZT-5H on the temperature  $T_C - T$ .  $P_{\text{exp.1}}$  — part of the experimental curve at  $T < T_d$ .  $P_{\text{exp.2}}$  — part of the experimental curve at  $T_d < T < T_C$ .  $P_{\text{approx.}}$  — temperature dependence of polarization obtained by approximation.  $T_d = 140^\circ\text{C}$ ,  $T_C = 195^\circ\text{C}$  (graph based on experimental data from Ref. 24).

monotonic dependence of polarization on temperature is observed, and in the second one, a sharp decrease in polarization occurs, starting from a certain temperature point.

We labeled it in Figs. 6 and 7 as  $T_d$ . The obtained approximation equations have the form

$$P = 10.785 (T_C - T)^{0.2172} \quad (5)$$

for ceramics  $\text{Pb}(\text{Zr}_{0.66}\text{Sn}_{0.23}\text{Ti}_{0.11})\text{O}_3$  and

$$P = 2.5702 (T_C - T)^{0.3162} \quad (6)$$

for industrial piezoceramic PZT-5H. The deviation from the power law also begins at temperature  $T_d$ . It is likely that in these compositions, too, an irreversible decrease in polarization occurs due to the decay of the domain structure.

## 5. Conclusions

In this paper, we continue to study the behavior of PZT-based solid solutions in the region near the critical temperature point  $T_d$ , which separates the temperature ranges of reversible and irreversible disordering of the domain structure during heating.

Based on the analysis of the relative change in the intensity of the components of diffraction X-ray lines, an explanation is proposed for this behavior by the change at temperature  $T_d$  of the regime of reversible disordering of the domain order ( $T < T_d$ ), formed by an external electric field during the polarization of the samples, to irreversible disordering ( $T > T_d$ ).

At temperatures below  $T_d$ , the  $P_r(T)$  dependence is described by a power law, which is characteristic of the temperature dependence of spontaneous polarization obtained from general considerations in the phenomenological theory of ferroelectrics. The deviation of the exponent from the

value of 0.5 is explained by the fact that the samples under study are polycrystalline. In the temperature range from  $T_d$  to  $T_C$ , the power law does not hold.

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