Thermophysical Properties of Piezoelectric PZT Ceramics

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Abstract. The anomalous behaviour of thermal conductivity and thermal expansion of PZT-19, PZT-22 and PCR -8 ceramics below the ferroelectric transition temperature is found.

Keywords: ferroelectrics; thermal conductivity, thermal expansion

The ferroelectrics ceramic on the basis solid solutions of PbZrO$_3$ – PbTiO$_3$ of a perovskite – type structure finds a wide applications owing to its excellent properties and possibility to vary with a change of the chemical compound. These materials have high piezoelectric and dielectric parameters. Wide isomorphism and the presence of morphotropist region (MR) – a region of structural tetragonal - rhombohedral transition are distinctive peculiarities of the materials [1].

At the same time considered piezoceramics belongs to an interesting class of ferroelectric systems with disordered structures are realized. In ceramic materials are diffusion as against usual homogeneous ferroelectrics the phase transition in the polar state and anomalies of physical properties in wide temperatures range [2]. The mechanism of phase transition in such inhomogeneous polycomponent systems is complex and till now insufficiently clear.

The present work is devoted to research of thermophysical properties (thermal conductivity and thermal expansion) in the ferroelectric transition region in PZT-19, PZT-22 and PCR-8, which are needed to understand a nature of observed phase transitions and in contrast to the electro physical properties of these materials are insufficiently explored.

Studied samples have been prepared by a hot pressing technology in SII of physics of Rostov State University. It is know that in ceramics PZT-19, PZT-22 and PCR-8 at the transition from cubic phase into ferroelectric one there is a temperature range with tetragonal-rhombohedral structure – morphotrope region (MR). The PZT-19 belongs to the MR on a phase diagram of concentration state, PRT-22 and PCR -8 relate o tetragonal region adjoining to the MR [1]. The structure transitions from cubic phase into ferroelectric one in PZT-19, PZT-22 and PCR -8 are occured at 570, 590, 600 T correspondingly.

A coefficient of the thermal conductivity are measured with disks-shape samples of diameter 25 mm and height 6 mm. To measure a coefficient of the thermal expansion are used the samples of diameter 10 mm and height 10 mm. The measurements of thermophysical properties are carried out on the non-polarized ceramics along a pressing axis.
The thermal conductivity is measured by an absolute compensated method in the argon atmosphere. A purified argon is delivered into the autoclave after pumping out up to $10^{-3}$ mm. The temperature gradient is 5 K and in a region of structural transition is 2 K. A temperature maintenance precision is 0.2 K. An error of the thermal conductivity measurement is 4% at 500 K.

To measure a coefficient of thermal expansion is used a quartz capacitance dilatometer. The dilatometer with a sample is placed into the autoclave degassed up to $10^{-2}$ mm and supported. A sensitivity of the apparatus to the shift is $10^{-9}$ m, an error of measurements is 3%. Velocity of temperature changing is 0.8 K/m. The process of measurements and analysis of experimental results is carried out by means of a program for automation of thermophysical investigations.

In figure 1a is represented the thermal conductivity temperature dependence of PZT-19 in a wide interval of temperatures 290-800 K including a region of phase transition. As it is shown in fig. 1 the thermal conductivity changes with the temperature change and has character peculiar to disordered and glass materials, i.e. the thermal conductivity rises at an increase of temperature. The same temperature dependence $\lambda$ is observed for PZT-22 and PCR-8 (see Fig. 2, 3).

According to [3], this behavior may be caused by that an interaction of longitudinal acoustic phonons with a soft mode may lead to decrease of an average length of the free rundown at a decrease of temperature. According to the dynamic theory the interaction of soft mode phonons with acoustic lattice oscillations considerably grows in the neighborhood of the phase transition $T_c$ due to their approach. The proximity of two types oscillations energies allows increasing a number of scattering acts in participation of optic phonons. It may lead to noticeable decrease of the thermal conductivity at the phase transition to the ferroelectric state [4,5]. Such scattering process is confirmed by researches carried out on crystals SrTiO$_3$ [3].

It should be noted that higher the $T_c$ is observed the same dependence for phosphate crystals KH$_2$PO$_4$, KH$_2$AsO$_4$ [6]. To explain this behavior it supposed to be a formal analogy on the structure between disordered phases of some crystals and glasses where length of the phonon free rundown is limited by sizes of a crystallite. Also it is probable that glassdipole state is realized in a region of structure transition.

Figure 1b represents a temperature dependence of thermal expansion coefficient $\alpha$ ceramics PZT-19. There is observed an anomaly on the temperature dependence of $\alpha$ in a region of ferroelectric phase transition in cooling and heating regimes. The coefficient $\alpha$ increases with decrease of temperature below $T_c$ in region of ferroelectric phase, and then smoothly passes on usual temperature reduction. Magnitude $\alpha$ assumes small values in temperature interval $T < T_c$ (in the MR), but noticeably increases at high temperatures $T > T_c$. The $\alpha$ change below $T_c$ points not only at considerable changes in a local surrounding of atoms, but also at essential change in their interaction.
The temperature hysteresis (Fig. 1a,b) characterizes this transition as first order phase transition. A distinctive feature of this hysteresis is its global character in the MR, i.e. it is keeping in a wide temperature interval below $T_c$. This hysteresis is usually characteristic for incommensurate modulated structures and is caused by an attachment of domain walls and phase of boundaries on the structure inhomogeneity and the crystal boundaries ("pinning-effect").

The temperature dependence of thermal conductivity and coefficient of thermal expansion of PZT-22 is given in fig. 2. The coefficient of thermal expansion is decreased monotonously close to 530K. In the morphotrope region of this ceramics coexist two phase: rhombohedral and tetragonal and up to 530 K prevails the first phase. Upper this temperature up to $T_c$ there is observed, a gradual transition from rhombohedral phase into tetragonal one, i.e. a region of diffuse phase transition appears.

There the coefficient of thermal expansion $\alpha$ begins decreasing intensively taking a negative value (-0.47·10^{-6}K^{-1}). Upper the $T_c$ the coefficient of thermal expansion increases with temperature more sharply.

Figure 3 present a temperature dependence of coefficient of thermal expansion and thermal conductivity of PCR-8. In contrast to PZT-19 and PZT-22 this piezoceramics in the MP belong two tetragonal structure [7], located closer to $T_c$ point (525-590K). The coefficient $\alpha$ decreases with temperature almost linearly approximately up to 525K. Upper this point up to $T_c$ there is observed an intensive decrease of coefficient $\alpha$, and $\alpha$ takes a negative value in Curie point (at $T_c$ = 598K coefficient $\alpha$ =-1,2·10^{-6}K^{-1})

A negative value of coefficient $\alpha$ in both piezoceramics in a region of размытый phase transition (PZT-22) and two tetragonal phase (PCR-8) in observed in many the metals and semiconductors. In thermodynamics point of view the negative value of coefficient $\alpha$ in a region of structure phase transition is explained by the effective value of unharmonic coefficient of Grüneizen ($\gamma_{\text{eff}}$), which is estimated by experimental data of coefficient $\alpha$ of a comprehensive compression modulus (B), molar volume (V) and specific heat capacity (C_p) $\gamma_{\text{eff}}=3\alpha BV/C_p$.

A contribution into effective $\gamma_{\text{eff}}$ in unharmony of thermal oscillations make the longitudinal - $\gamma_l$ and trasversal - $\gamma_s$ components. It is appear such a situation when the contribution of negative transversal component prevails over positive longitudinal one. Then $\gamma_{\text{eff}}$ and $\alpha$ have a negative sign.

It should be noted that recently [8] anomalous behavior of $\alpha$ and global hysteresis below the ferroelectric transition temperature are found in crystals (NH$_4$)$_2$SO$_4$ and (Rb$_{0.1}$ (NH$_4$)$_{0.9}$) SO$_4$ by methods x-ray diffractometry. As shown in [8], such situation can be realized if the atoms form connected nonequivalent sublattices. These sublattices can move apart with temperature decreasing not owing to the inharmonism of atom oscillations but their interactions, for example, owing to the strong dipole-dipole interaction of the structural elements in a region of transition into ferroelectric state.
Below $T_c$ in the ceramics PZT-19, PZT-22 and PCR-8 there is formed a region of structure tetragonal – rhombohedral transition, where an appearance of the ferroelectric phase occurs gradually by means of nucleation’s of the polar phase at $T_c$ and their expansion all over the volume when temperature falls. Thus, as it is clear in fig.3 the anomaly of thermal physical properties has diffuse character.

As one can see, a quantitative character of the temperature behavior $\alpha$ studied systems is almost indifferent. The thermal expansion of PZT-19, PZT-22 and PCR-8 may be quantitatively considered as average between usual thermal expansion of polycrystals PbZrO$_3$ [9] and a substantial thermal compression PbTiO$_3$ [10]. It should be noted that below the $T_c$ the $\alpha$ anomaly is positive in PbZrO$_3$ in a region of antiferromagnetic phase at the temperature increasing, while the $\alpha$ anomaly for PbTiO$_3$ is negative in a region of tetragonal ferrophase. So when temperature falls in a narrow temperature range of $T_c$ transition from cubic phase into tetragonal rhombohedral phase of ceramics on the basis of Pb(Ti, Zr)O$_3$ we observe a sharp decrease of $\alpha$ as for PbZrO$_3$. Then there is observed an normal behavior of $\alpha$, in a wide temperature interval below the $T_c$, featured for tetragonal ferrophase PbTiO$_3$.

Thus, the results demonstrate complex character of the thermophysical properties for ferroelectric ceramics PZT, which consists in the anomalous behavior of thermal conductivity and thermal expansion in a region the ferroelectric phase transition with tetragonal rhombohedral for more completed understanding of the results there are needed further investigations of ferroceramic materials on the bases of solid solutions of Pb(Ti,Zr)O$_3$ with different composition.

**References**

Fig.1a Temperature dependence of the thermal conductivity of PZT-19 ceramics

Fig.1b Temperature dependence of the thermal expansion coefficient of PZT-19 ceramics
Fig. 2 Temperature dependence of the thermal conductivity and thermal expansion coefficient of PZT-22 ceramics

Fig. 3 Temperature dependence of the thermal conductivity and thermal expansion coefficient of PCR-8 ceramics