Chapter 13
Electric Response to Bending Vibrations and Pyroelectric Effect in Unpolarized Ferroelectric Ceramic Plates with Electrodes, Differing in the Magnitude of the Coefficient of Thermal Expansion on Opposite Surfaces

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Abstract The manufacture of electrode materials by the methods of sintering and cathodic sputtering of metals with different coefficients of linear thermal expansion on opposite surfaces of unpolarized ferroelectric ceramics plates creates stationary gradients of mechanical deformations and stresses in specimens' volume. As a result, an electrical response to the three-point mechanical loading (flexural vibrations at the resonant frequency) and pyroelectric current in the dynamic mode of measurement were observed.

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13.1 Introduction

It is known that the unipolarity of the switching characteristics in ferroelectric crystals depends on the material and the method of applying of the electrodes. For example, when using liquid electrodes, the unipolarity of the repolarization of BaTiO$_3$ crystals in the fields lower than the coercive one was revealed by studying the motion of 90° boundaries [1]. A switching unipolarity can be obtained by using non-equivalent electrodes (different material or method of application) [2–6]. This unipolarity does not disappear under the long-term action of a strong alternating field as well as after heating above the Curie temperature T_C. In TGS crystals, when using In-Au electrodes, the unipolarity turned out to be greater than the natural one [7, 8]. Investigation of the pyroelectricity in a quasistatic mode revealed two types of pyroelectric current change with temperature. In the first case, the dependence of the pyroelectric current on temperature has the usual form with a maximum in the T_C region (the pyroelectric current flows in the external circuit from the face to the electrode providing the worst repolarization conditions, or the electrode is applied on the crystal face with a large number of defects). In the other case, the pyro-electric current changes its direction near T_C [9, 10]. As a rule, the explanation of the effects of unipolarity is based on the assumption of the existence of a special layer at the surface with a state of polarization that differs from the bulk part of the sample under study. A considerable number of theoretical and experimental studies have been devoted to the proof and confirmation of the relation between a unipolar state and a spatial distribution of polarization in ferroelectrics, covering practically the entire period of the development of the physics of ferroelectricity.

   The scope of the present work is an investigation of the unipolarity, caused by a stationary strain gradient in the near-surface regions of non-poled ferroelectric ceramics. This gradient was formed by applying on the opposite surfaces of the samples electrodes from the metals with different values of linear thermal expansion coefficient α^T.

13.2 The Contribution of the Temperature Dependence of the Dielectric Constant to the Pyroelectric Effect

According to thermodynamics in the absence of electric fields [11], the pyroelectric coefficient $\gamma \sim \varepsilon P$, where ε is the dielectric constant and P is the polarization, then the extremum condition of P:

$$\varepsilon\frac{dP}{dT} + P\frac{d\varepsilon}{dT} = 0, \quad \frac{d\varepsilon}{dT} = -\frac{\varepsilon\gamma}{P} > 0, \quad \text{since } \gamma < 0 \tag{13.1}$$

   Consequently, the maximum of $\gamma(T)$ is below the maximum of $\varepsilon(T)$ at the site of increase of $\varepsilon(T)$.

The presence of an electric field will lead to an additional relative shift of the maxima $\varepsilon(T)$ and $\gamma(T)$. The source of the electric field can be the external field, contact fields, the unipolarity field, and the field of free charges shielding the polarization. The contribution of the component $Ed\varepsilon/dT$ is usually considered small and is usually not taken into account in the calculations, without making any remarks about the direction of E with respect to the direction of P.

At the same time, the presence of a field of some nature that coincides in direction with P, may even lead to a sign change of $\gamma(T)$. This is due to independence of P and $\varepsilon(T)$, since, if $P(T)$ is a vector, then $\varepsilon(T)$ is the possibility of variations of this vector in magnitude.

An additional contribution to the pyroelectric response arises, since

$$D = \varepsilon\varepsilon_0 E + P, \quad \gamma = \frac{dD}{dT} = E\varepsilon_0\frac{d\varepsilon}{dT} + \frac{dP}{dT} \tag{13.2}$$

where dE/dT is assumed equal to zero, therefore we neglect changes of E.

In the capacity of E, we can consider the external field, contact fields, the unipolarity field, which manifests itself under changes of P. This contribution can, in dependrnce on the signs of E, dP/dT, $d\varepsilon/dT$ both add up to $\gamma = dP/dT$ and subtract from it. Usually $dP/dT < 0$ and $d\varepsilon/dT > 0$, then the presence of E, coinciding with P, will lead to a decrease of γ. If E is antiparallel to P, then γ will increase. The pyroelectric response can also be determined by the first term of (2), while dP/dT is small.

Not taking into account the contribution of the constituent $\sim E(d\varepsilon/dT)$ to the pyroelectric response is typical for most papers, which leads to an incorrect interpretation of the experimental data. The contribution to the pyroelectric response due to the temperature dependence of the permittivity takes place in all possible cases of investigation. Under certain conditions, this contribution may turn out to be predominant.

13.3 Samples and Experimental Techniques

To investigate responses to bending vibrations, unpolarized plates were manufactured from hot-pressed ferroelectric ceramics PZT-19 with sizes $54 \times 4 \times 0.6$ mm^3, firstly. On one surface of all the plates, the electrode was sintered by the method of reduction of silver nitrate at 730 °C for 30 min. Then 3 types of electrodes were applied to opposite surface: (i) sintering of Ag method; (2) method of cathodic sputtering of Pt and (3) thermal evaporation of monel in a vacuum. The values of linear thermal expansion coefficients α^T for Ag and Pt were 19.5×10^{-6} K^{-1} and 9.2×10^{-6} K^{-1}, respectively.

The scheme and measurement technique using the three-point scheme are given in [12]. Also in [12], studies of the effect of mechanical damage to the electrode surface from Ag prior to sintering were performed. One of the surfaces of the
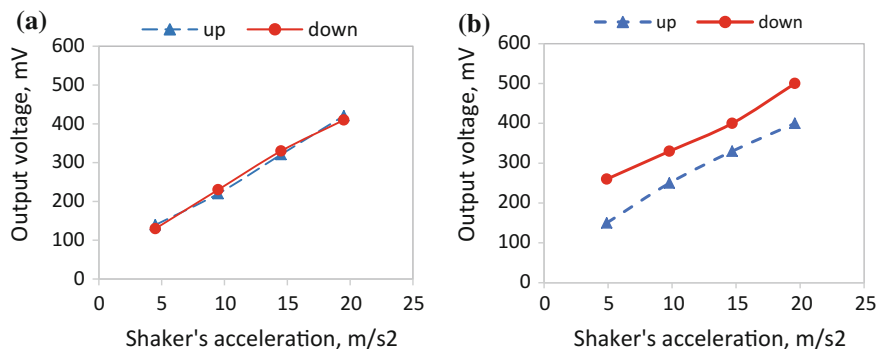
(a)

(b)

Fig. 13.1 Relationship between electrical response of samples with applied Ag electrodes on both sides to mechanical impact of proof mass 3 g at the resonance frequency and acceleration of the worktable: before (up) and after (down) rotation of the specimens on 180°: **a** equivalent electrode surfaces, **b** one of the surfaces is damaged

sample from PZT-19 with sizes $50 \times 4 \times 0.7$ mm^3 was processed with grinding powders, which had different grain sizes. At the boundary of this surface with bulk of ceramic beam, non-equivalent gradient of mechanical strain and tangential compressive stresses were applied. The results of testing the sample using a three-point loading scheme with a mass of 3.1 g with equivalent surfaces and a sample with one damaged surface are shown in Fig. 13.1.

Figure 13.1a, b show the relationships between the electrical response of specimen and acceleration of worktable. Analysis of Fig. 13.1a shows that after sintering of Ag, electrical polarization stable to cyclic mechanical load is created by static strain gradients at the boundaries of sintered layers with the bulk of ceramics and by tangential compressive stresses in the near-electrode layers.

Figure 13.1b shows a 25% increase in the electrical response (from 0.26 to 0.5 V, depending on the acceleration), when rougher face is located on the opposite side of the proof mass. The difference in the magnitude of the output voltage can account for higher values of residual polaristion of the surface.

This effect was investigated at room temperature in the ferroelectric phase of PZT-19. Most likely, it can occur in a very thin transition layer: border of cermet layer—volumetric, homogeneous bulk of ceramic. Assuming that the thickness of this layer is about 1 μm, it generates on resitive load of 360 kΩ electric potential with the electric field strength up to 50 kV/cm.

Measurements of electrical responses of plates with one Ag and one Pt electrodes to the bending at the resonance frequency, given by the shaker, according to the three-point loading scheme of the attached mass 1 g (Fig. 13.2), showed that their amplitude increased up to 100% when the plate experienced tensile stress on the side of Pt (Fig. 13.2). The measurements were carried out at normal temperature (T_{norm}). For comparison, Fig. 13.1a shows similar responses of a plate with symmetric electrodes from Ag at the fixed value of resistive load. In addition, the

Fig. 13.2 Electrical responses of samples with applied Ag and Pt electrodes to the bending at the resonance frequency
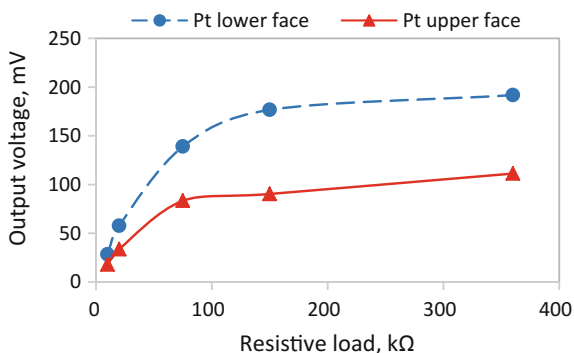
samples were examined using a YE 2730A d_{33} meter. The average d_{33} module was equal to 5×10^{-12} C/N.

The study of pyroelectric effect at the dynamic mode of measurement by sinusoidally modulated thermal radiation has important features. Such an effect leads to periodic changes in the temperature gradient in the interelectrode space of the samples under study. The maximum temperature decreases from the irradiated electrode in the volume at each modulation period. The rotation of a uniformly polarized sample in a holder at 180° should result in a mandatory change in sign of pyroelectric response.

In samples with antiparallel polarization of near-electrode regions, the sign of the pyro-response is preserved. Its amplitudes are proportional to the pyroelectric coefficient in the near-electrode region. Taking this into account, we will consider successively the experimental results for each sample. In addition, the observed unipolarity with electric displacement fields in samples with a stationary deformation gradient in the near-electrode space requires the obligatory consideration of the contribution of the temperature variations of the dielectric constant to the pyroelectric current. Let us consider this in more detail.

The study of unipolarity was carried out with a rectangular sample of the PZT-19 with dimensions $8 \times 3.5 \times 0.72$ mm^3 and electrodes from different metals, applied by technology described above. The pyroelectric effect was investigated in a dynamic mode of measurement at a thermal radiation frequency of 3 Hz. Orthogonal projections of the pyroelectric response in a dynamic mode were recorded with the help of two lock-in nanovoltmeters (Unipan). First, thermal radiation occurred from the one electrode of the sample, then from the other one electrode. According to the measured projections of the pyroelectric response, its modulus was calculated. The coefficient γ was determined by comparing the modulus of the pyroelectric response with the response of the reference sample (PZT-11).

In Figs. 13.3, 13.4 and 13.5, the unit of measurement of the pyroelectric coefficient is $[\gamma] = \text{Cl K}^{-1}\text{ m}^{-2}$, and complex component of the pyroelectric signal voltage U_p is dimensionless.

(a)

Dependence $\gamma = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the normal Ag electrode

(b)

Dependence $\gamma = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the damaged surface with Ag electrode

(c)

Dependence $U_p = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the normal Ag electrode

(d)

Dependence $U_p = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the damaged surface with *Ag* electrode
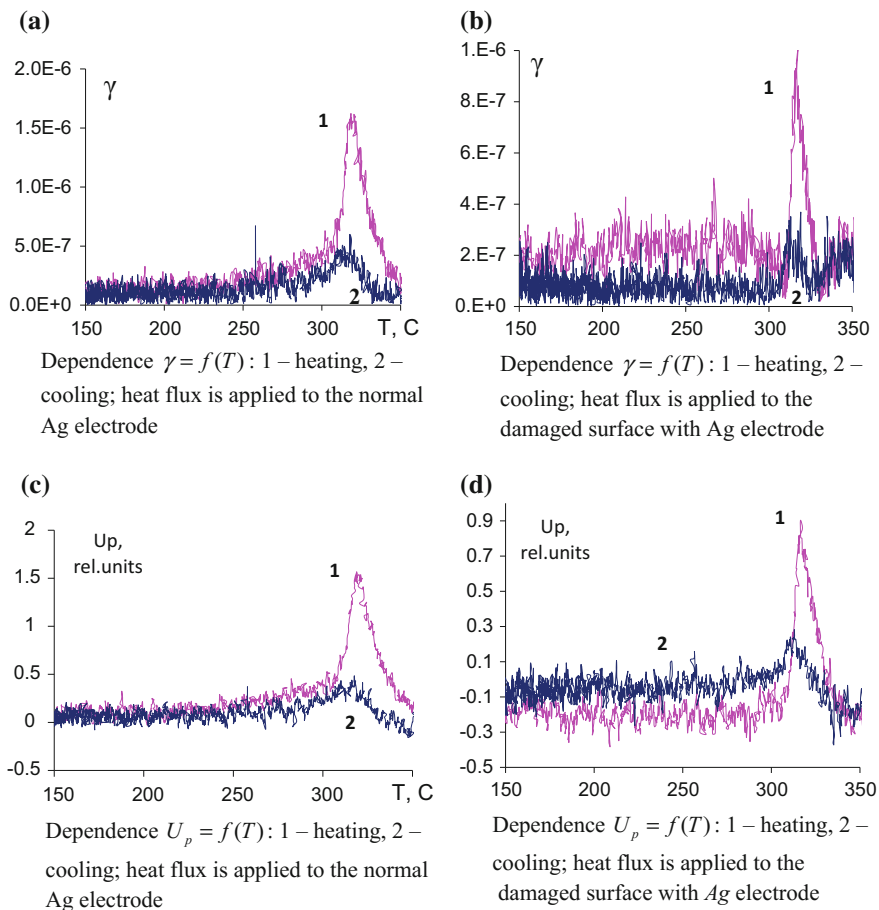
Fig. 13.3 Dependencies of pyroelectric coefficient and complex component of the pyroelectric signal voltage on temperature for sample from PZT-19; one electrode is made from Ag, the other is Ag on a damaged surface

Analysis of the results, shown in Figs. 13.3, 13.4 and 13.5, allows us to draw the following conclusions:

(i)   In all the samples studied, when the electrodes were applied, near-surface layers with stationary counter-directed gradients of deformation were formed;

(ii) investigation of the temperature dependences of pyroelectric responses showed that their amplitude is the result of the algebraic summation of signals from each layer;
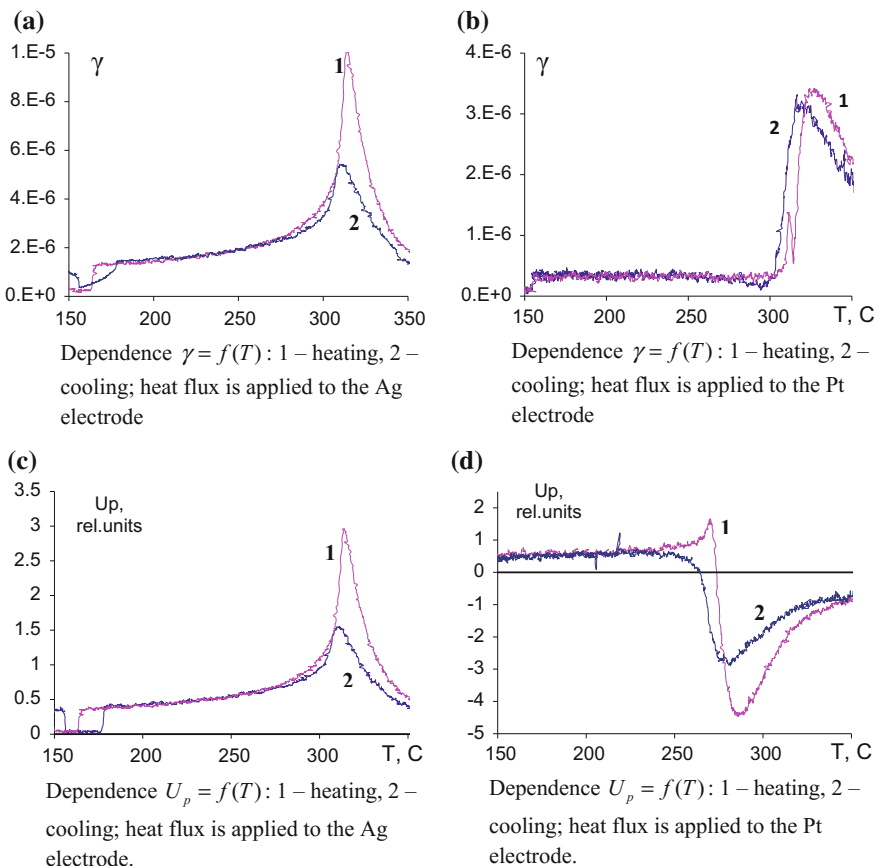
(a)

Dependence $\gamma = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the Ag electrode

(b)

Dependence $\gamma = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the Pt electrode

(c)

Dependence $U_p = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the Ag electrode.

(d)

Dependence $U_p = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the Pt electrode.

Fig. 13.4 Dependencies of pyroelectric coefficient and complex component of the pyroelectric signal voltage on temperature for sample from PZT-19; one electrode is made from Pt, the other one is Ag

(iii) in the ferroelectric phase for PZT-19 with heating and cooling from 300 °C, the resulting response corresponds to the difference in the pyroelectric coefficients of each layer; at $T > 300$ °C in the paraelectric phase, this response is due to the difference in the quantities of $d\varepsilon/dT$.
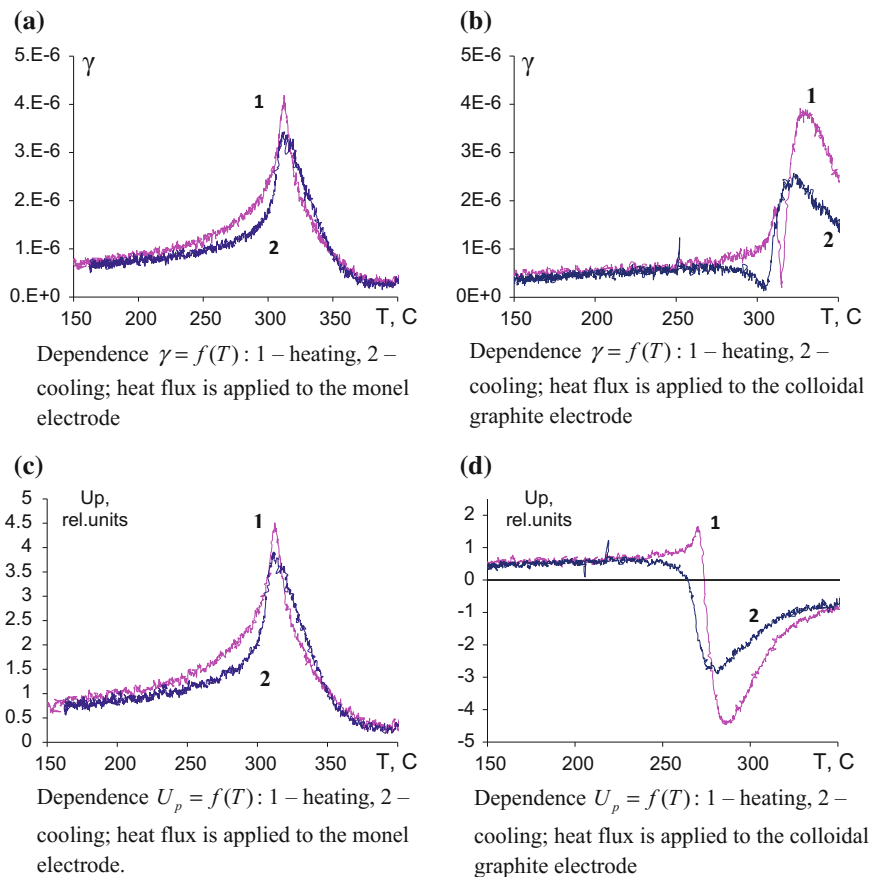
(a)

Dependence $\gamma = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the monel electrode

(b)

Dependence $\gamma = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the colloidal graphite electrode

(c)

Dependence $U_p = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the monel electrode.

(d)

Dependence $U_p = f(T)$: 1 – heating, 2 – cooling; heat flux is applied to the colloidal graphite electrode

Fig. 13.5 Dependencies of pyroelectric coefficient and complex component of the pyroelectric signal voltage on temperature for sample from PZT-19; one electrode is made from monel, the other one is colloidal graphite

13.4   Conclusion

The main results of this study are the detection of thermally stable macroscopic polarization, formed during application of electrodes, and internal electric displacement field, created by stationary strain gradients in the near-electrode layers.

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