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On the Pyroelectricity of DKDP Single Crystals and PZT-40 Ceramics at 1.5–30 K

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Abstract—By analyzing experimental data, the lowest modes that are responsible for pyroelectricity in DKDP single crystals (87.3 and 201.6 cm^{-1}) and in PZT-40 ferroelectric ceramics (20.7, 54.75, and 171.3 cm^{-1}) are determined. A set of physical mechanisms that occur in real polar dielectrics that are piroelectrically active in the temperature range 0–30 K is discussed; and methods of their identification, separation, and determination of quantitative characteristics for each component of spontaneous polarization are shown.

Keywords: pyroelectricity, cryogenic temperature, ferroelectric.

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The investigation of cryogenic pyroelectricity clarifies the fundamental issues of polar state peculiarities. The physical mechanisms that occur in cryogenic pyroelectrical processes have been determined at temperatures of more than 4 K. As has been shown, in this temperature range the temperature dependences of the pyroelectric coefficient at constant mechanical stress $\gamma^{\sigma}(T)$ is described in terms of Debye specific heat functions for linear pyroelectrics and Einstein functions for segnetoelectrics. These theories were developed by C. Boguslavskii and, independently, by K. Czukor with the assistance of A. Einstein [1]. The agreement of these classical theories with experimental data is evidence of the existence of two, fundamentally different mechanisms for a temperature variation of spontaneous polarization in two classes of polar dielectrics [2].

The purpose of the present paper is a description of the method for the determination of pyroelectrically active lattice vibrations and for finding other pyroelectricity mechanisms, which is peculiar to samples with different kinds of defects and temperatures that are less than 5 K. The experimental results and their analysis are represented below. The determination of the pyroelectric coefficients was carried out by the statistical method, described in detail in [2], with the graphic recording [3] of pyroelectric signals.

For the purpose of determining the general causes of pyroactivity at $T < 5$ K, samples of polar dielectrics with different qualities were selected for analysis, viz., a DKDP sample, which is an isotopic analogue of the classical hydrogenous KDP ferroelectric (the deuterium content is about 90%, Curie point $T_c \cong 207$ K, a first-order phase transition occurs close to a second-order phase transition) and a sample of multicomponent ferrohard PZT-40 ceramic (composition: $0.98(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O_3 + 0.02Cd(BiMn_{1/8}Cr_{1/6})O_3 + MnO_2$(0.26 wt %); $T_c \cong$ 613 K, a first-order phase transition occurs close to a second-order phase transition).

In Fig. 1 the temperature dependences on the pyrocoefficient $\gamma^{\sigma}(T)$ of a DKDP single crystal (a) and a PZT-40 ceramic (b) are shown. The experimental data for $\gamma^{\sigma}_{\exp}(T)$ (marked with circles) are clearly approximated by summation of Einstein functions:

$$\gamma^{\sigma}(T) = \Sigma\gamma^{\sigma}_{Ei}(T)$$
$$= \Sigma A_i\{(\Theta_{Ei}/T)^2 \exp[\Theta_{Ei}/T]/(\exp[\Theta_{Ei}/T] - 1)^2\},$$

where A_i is a coefficient; $\Theta_{Ei} = h\nu_i/k$ is the Einstein temperature of the active pyroelectric i-mode; ν_i is the frequency of the mode; and h and k are the Planck and Boltzmann constants, respectively.

The determination of the components of the general dependence on $\gamma^{\sigma}(T)$ starts at low temperatures, it is the $\gamma^{\sigma}_{E1}(T)$ component (see Fig. 2). Using the well-known χ^2 criteria the most probable fitting function is chosen, in this case, it is the Einstein function. The set of experimental points must be described as a sum of functions that are appropriate for the physical mechanism of the model of the phenomenon. In this case, we have a sum of Einstein functions. This step is extremely important, since it prevents many unproductive theoretical approaches. Using "OriginPro 8" software, the values of two parameters (A_1 and Θ_{E1}) for

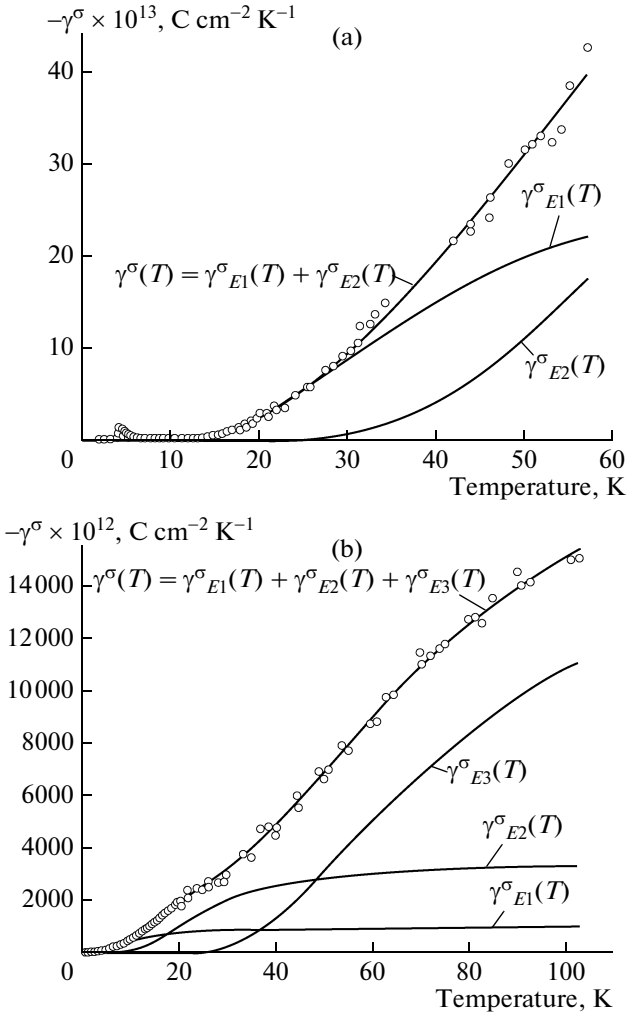

Fig. 1. Experimental dependences of the $\gamma^\sigma_{\text{exp}}(T)$ pyroelectric coefficient (circles) for DKDP single crystals (a) and for PZT-40 ferroelectric ceramic (b). The $\gamma^\sigma_{E1}(T)$, $\gamma^\sigma_{E2}(T)$, $\gamma^\sigma_{E3}(T)$ and $\gamma^\sigma(T)$ curves show the temperature dependence on the contribution of corresponding modes and their total values.

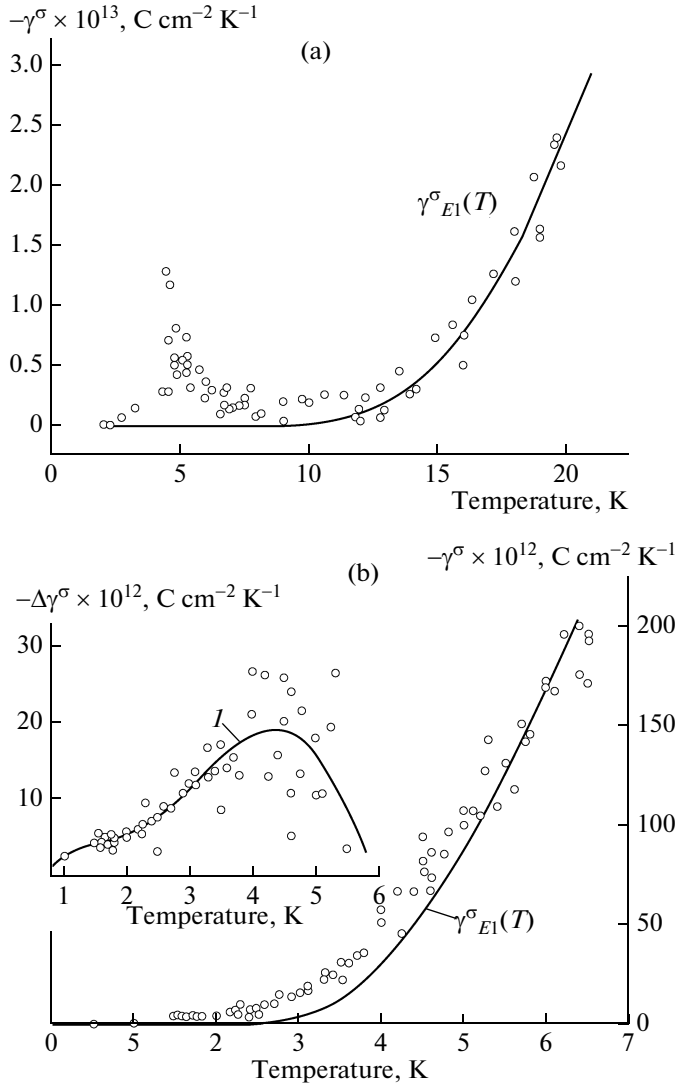

Fig. 2. The low-temperature part of the experimental dependences of $\gamma^\sigma_{\text{exp}}(T)$ pyroelectric coefficient (circles) for DKDP single crystals (a) and PZT-40 ferroelectric ceramic (b). The $\gamma^\sigma_{E1}(T)$ curves represent the temperature dependence of the lowest mode contribution. In (a) one can easily see the presence of a proton component as a set of points above the $\gamma^\sigma_{E1}(T)$ curve. In the inset of (b), this component is represented as the difference $\Delta\gamma^\sigma = \gamma^\sigma_{\text{exp}}(T) - \gamma^\sigma_{E1}(T)$. Curve 1 shows the approximation of the experimental points using the least squares method.

given nonlinear function are calculated and the error of experimental point approximation is minimized. The $\gamma^\sigma_{E2}(T)$ component is estimated using the same procedure from the difference between dependences of $\gamma^\sigma_{\text{exp}}(T)$ experimental data and $\gamma^\sigma_{E1}(T)$ curves respectively (Fig. 3).

The $\gamma^\sigma_{E3}(T)$ component for the PZT-40 sample, in turn is determined from the difference dependence by subtraction of the $\gamma^\sigma_{E1}(T)$ and $\gamma^\sigma_{E2}(T)$ curves from the experimental points $\gamma^\sigma_{\text{exp}}(T)$.

Analysis allows determination of the frequencies of the mode, which are responsible for the pyroelectricity of samples:

DKDP

$A_1 = -33.05 \times 10^{-13}$ C cm^{-2} K^{-1};

$\Theta_{E1} = 126.1$ K; $\nu_1 = 87.3$ cm^{-1};

$A_2 = -111.4 \times 10^{-13}$ C cm^{-2} K^{-1};

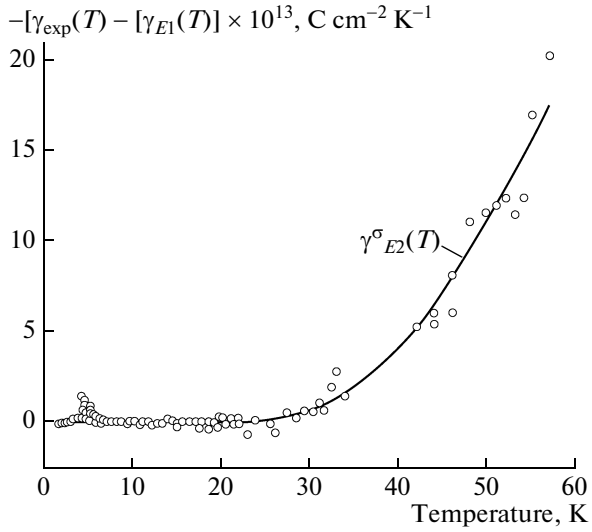

Fig. 3. The $\gamma^{\sigma}_{E2}(T)$ pyrocoefficient component for a DKDP single crystal is defined as a set of points from the $[\gamma^{\sigma}_{exp}(T) - \gamma^{\sigma}_{E1}(T)]$ difference.

$\Theta_{E2} = 291.3$ K; $\nu_2 = 201.6$ cm^{-1};
PZT-40
$A_1 = -983 \times 10^{-12}$ C cm^{-2} K^{-1};
$\Theta_{E1} = 29.94$ K; $\nu_1 = 20.7$ cm^{-1};
$A_2 = -3522 \times 10^{-12}$ C cm^{-2} K^{-1};
$\Theta_{E2} = 79.11$ K; $\nu_2 = 54.75$ cm^{-1};
$A_3 = -17\,590 \times 10^{-12}$ C cm^{-2} K^{-1};
$\Theta_{E3} = 247.5$ K; $\nu_2 = 171.3$ cm^{-1}.

The low-frequency oscillation spectrum is known only for DKDP. It has been studied in the range of 75–366 cm^{-1}. The curve in this interval can be referred to external vibrations, i.e., the vibrations of a crystal lattice consisting of K^+ and $D_2PO_4^-$ ions [4]. Their values are identical to the same vibrations of KDP [5], which allows the assumption that they are equal to the refined data for KDP according to the reference data [6]. The two values of 86 and 206 cm^{-1} out of six allowed vibrations are similar to our results.

The frequency values of the PZT-40 ceramics clarified the spectrums of these non-transparent samples for the first time. It is obvious that the spectrum must be shifted to the low-frequency region and filled more amply, which is qualitatively observed. One typical feature is a small (units) number of pyroelectrically active modes, even for ceramics with complex chemical compositions.

For these samples, as well as for the impurity $LiNbO_3$, $LiTaO_3$ [7] and triglycine sulfate (TGS) [8] samples, the presence of a low-temperature component contribution prior to the appearance of the lowest mode is typical. This component for DKDP (Fig. 2a) is represented by a peak in the experimental points at 5 K; for PZT-40 (approximated curve *1* on the inset of Fig. 2b), it corresponds to a peak at ≈4.5 K. According to the data shown in Fig. 2, this feature can be characterized as being a general property of hydrogenous and oxygen octahedral single- and polycrystalline ferroelectrics, which is due to the same cause. In [7, 8] the cause for the appearance of such a low-temperature component was shown. This is the presence in the structure of a delocalized proton with impurities, which is localized in an orderly manner at $T \longrightarrow 0$. In [7] the process of localization and formation of the corresponding spontaneous polarization component is based on theory [9], which comes from the localization of a slightly linked dipole element of a structure (or a charged ion) to a skeleton of the lattice in the deeper well of a double-well potential upon decreasing temperature, no matter how small the difference of energies in these two minimums is. At temperatures much higher than the helium temperature a similar process is known for molecular groups [10]. At $T \leq 5$ K only protons can be the migratory elements of a structure. In the DKDP structure, when the deuteration is incomplete, the proton is an impurity itself. In the PZT-40 structure such protons appear because of the unavoidable capture of hydroxyl groups from atmospheric moisture by structural defects, following the formation of a polar medium. A similar process was experimentally confirmed for $LiTaO_3 + Rh^{3+}$ [7]. In this data there are not enough experimental points for quantitative analysis, but the position of the pyrocoefficient anomaly on the temperature scale, and configuration of peaks indicate the discussed localization mechanism.

The present research allows the formulation of general conclusions about the occurrence of the physical mechanisms that are responsible for temperature changes in spontaneous polarization at low-temperature scales.

Highly perfect samples of ferroelectrics and linear pyroelectrics show the fulfillment of canonical laws: for ferroelectrics, $\gamma^{\sigma}(T) = -A_1 E(\Theta_{E1}/T)$ and the lowest, pyroelectrically active, polar optic mode occurs (see the TGS case in [2]); for linear pyroelectrics, $\gamma^{\sigma}(T) = -T^3$ and the initial part of Debye function $\gamma^{\sigma}(T) = -BD(\Theta_D/T)$ appears (see the $Li_2SO_4 \cdot H_2O$ case in [11]).

Samples with polar, in particular, growth, impurity defects form additives to the matrix, polar system, in the general case, consisting of several multidirectional components. The value of spontaneous polarization for this kind of additive system is lower by orders of magnitude than that of spontaneous polarization of the matrix and it decreases to zero at $T \sim 15$ K. Its contribution to pyroelectricity (the components of total pyrocoefficient $\gamma^{\sigma}_{dop}(T)$) is usually appreciable in the temperature range that is bounded below by the region of 2–4 K and above, depending on the type and impurity concentration, for $LiNbO_3 + Fe^{3+}$ 5 wt % and

$LiTaO_3$ + Rh^{3+} 1.5 wt % [7] by 4–12 K; for TGS + Cr^{3+} 0.03 wt % [2] by 2–8 K; and for natural mineral samples of tourmaline [12] by 4–28 K. The $\gamma^{\sigma}_{dop}(T)$ component is also described by theory [9] and, in most cases, is opposite in sign to $\gamma^{\sigma}(T)$.

Usually the proton component coincides in sign with $\gamma^{\sigma}(T)$, and since it is notable for a low excitation energy, the characteristic interval of its occurrence is 1–6 K. A proton is equiprobably in local minimums at temperatures higher than 6 K. Normally, the proton and impurity components overlap [7]. The listed components of spontaneous polarization are in thermodynamic equilibrium, and the total pyrocoefficient tends to zero, when $T \longrightarrow 0$.

The incorporation of metastable centers into a matrix, for instance, by γ-irradiation, turns it into a thermodynamically nonequilibrium state for a long period of time. In this case, due to the damping of other mechanisms, another component, namely $\gamma^{\sigma}_{rad}(T) \sim T^{0-1}$ becomes noticeable in the cryogenic temperature region ($T < 2$ K). Such a pyrocoefficient component has been observed for TGS single crystals with L,α-alanine (≈0.01 wt %) and phosphorus (≈0.1 wt %) impurities, irradiated at a dose of 35 Mrad [13].

The mechanism of the formation and temperature changes of this spontaneous polarization component remains unclear [14]. A number of these conditions allow the observation of the temperature dependence on the effective charge of a dipole while keeping their positions relative to each other. A similar model of pyroelectricity has been discussed several times [15] and the phenomenon of charge changes has been observed in a $LiNbO_3$ single crystal [16].

In addition, since a thermodynamically nonequilibrium state is more or less inherent for some part of the sample volume as a result of electrical, mechanical, and other effects, this pyroelectric component must be appropriate for all samples that open sequences of activated pyroelectricity mechanisms with increasing temperatures from 0 K.

CONCLUSIONS

The interval of 0–30 K is a region where there are a large number of physical processes caused by temperature changes in the corresponding spontaneous polarization components of real crystals. The analysis of the $\gamma^{\sigma}(T)$ dependence in this region should be carried out with the identification, separation, and determination of the individual qualitative characteristics for each component.

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