

THE INFLUENCE OF THE DOMAIN STRUCTURE ON PYROELECTRIC PROPERTIES IN TGS CRYSTALS*

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The results of investigations of the influence of the initial domain structure on pyroelectric properties in TGS crystals are given. The dynamic pyroelectric method is employed to investigate the problem. It has been ascertained that the domain structure of a partially polarized crystal breaks up when heated, causing a decrease in the degree of polarization. The domain structure break-up is shown as an inflexion point on the pyroelectric signal vs temperature curve. The break-up temperature depends on the extent of domain structures.

1. Introduction

There are large discrepancies between the results of measurements of pyroelectric properties of ferroelectrics obtained by dynamic and static methods. The temperature dependencies of pyroelectric coefficients, obtained (with the help of the dynamic method) were compatible with those resulting either from thermodynamic considerations or from the differentiation in the temperature dependence of spontaneous polarization. Chynoveth [1], Krajewski [2] and Krimenchugskii [3] investigated TGS pyroelectric properties using the dynamic method. Gavrilova et al. [4, 5] in the course of investigations carried out (by means of the static method) have discovered the existence of maxima on the $\gamma(T)$ curve at temperatures below the phase transition point by several and between 10 and 20 degrees centigrade. They explained the existence of these maxima by the remodelling of the domain structure. For this they used the macroscopic model of antiferroelectrics given by Kozłowski. They divided the ferroelectric phase into stable domain structure areas and the remodelling domain structure ones "accurately" located on the temperature axis. Many authors have pointed out the anomalies of other physical values characterizing ferroelectrics in the ferroelectric phase. The following anomalies in physical values in TGS crystals were investigated: 1° the coercive field anomalies by Triebwasser [6], 2° the specific heat anomalies by Strukov [7], 3° the number of domains per the unit length anomalies

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by Stankowska and Czosnowska [8], 4° light emission from the surface of the crystal anomalies by Sysło [9], 5° thermal Barkhausen noise by Rumyantsev and Rudyak [10]. The close relationship between the domain structure and the thermal hysteresis loop of the dielectric permittivity in TGS crystals has been ascertained by Jaśkiewicz and Kwoka [11].

In the present paper, the author, by means of the dynamic pyroelectric method, studied the processes of remodelling the domain structures having various sizes.

2. Principles of measurement

The macroscopic polarization P_m of a crystal divided into domains is equal to

$$P_m = P_s \frac{S^+ - S^-}{S^+ + S^-}, \quad (1)$$

where P_s is the spontaneous polarization, S^+ and S^- denote the surface area of domains parallel to the ferroelectric axis and antiparallel, respectively. The quotient

$$\frac{S^+ - S^-}{S^+ + S^-} = \varphi \quad (2)$$

is the degree to which the crystal is polarized. If in the course of measurement of the pyroelectric coefficient γ the degree of polarization changes, then

$$\gamma_m = \frac{\partial P_m}{\partial T} = \varphi \frac{P_s}{T} + P_s \frac{\partial \varphi}{\partial T}, \quad (3)$$

where γ_m is the pyroelectric coefficient of a crystal divided into domains.

If the temperature changes slowly the static method measures the current connected with the sum of both right-hand side components while the dynamic method gives only the current related to the first term of Eq. (3). The above interpretation of Eq. (3) allows one to explain the discrepancies between the results obtained by dynamic and static methods. The dynamic pyroelectric method can be employed to investigate such a change in domain structure which leads to a change of the degree of polarization. Information on remodelling can be obtained by qualitative studies. For this reason, the measurements of the pulswise changes in temperature of the sample can be neglected and "thin sample" have not to be taken into the experiment. The term "thin sample" is understood to be a sample in which the temperature gradient is much smaller than the amplitude of these pulswise changes in temperature. The form of the pyroelectric U_p temperature dependencies can differ according to the value of the pyroelectric coefficient for specific heat and thermal conductivity, depending on temperature.

In order to estimate the influence of these parameters on the course of the $\gamma(T)$ the course of $U_p(T)$ have been carried out. The measurement was made on 1.5 mm thin sample polarized by the field of 1 kV/cm during subsequent cooling from 85°C to room temperature. This measurement was carried out in the absence of the polarizing field and at the same time heated at the rate of 0.1°C/min. The curves representing measurements made on the same crystal put into a polarizing field of 400 V/cm are shown in

Fig. 1. The figure shows obviously that the temperature dependencies of specific heat and thermal conductivity do not distort the shape of the $\gamma(T)$ curve markedly. The measuring devices employed in the course of investigation has been described in paper [12].

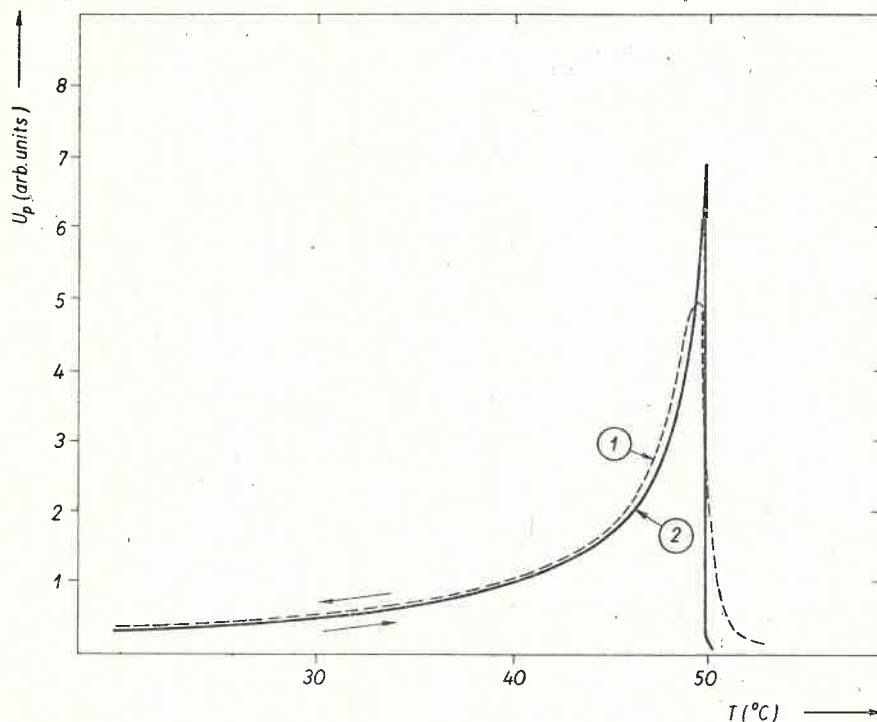


Fig. 1. Pyroelectric signal vs temperature in a 1.5 mm thick crystal. Curve 1 — the crystal polarized at the same time when cooled from 85°C to room temperature. Curve 2 — the plot has been obtained in presence of a polarizing field of 400 V/cm

3. Preparing and qualifying the samples

1 to 1.5 mm thick samples were cut from a [001] pyramid of a big TGS single crystal. For these investigations, only samples which had revealed no memory of domain structure were taken into account [13]. The samples chosen in this way were then provided with silver film electrodes, obtained by evaporation under a pressure less than 10^{-4} mm Hg. The sample was then heated at 90°C for 10 to 20 hours, then placed in room temperature. The pyroelectric signal was then obtained. This signal was similar to that obtained after the sample had been polarized until saturation. The samples having ratios of these signals lower than 0.05 were accepted.

4. Measuring mode

In previously heated samples the wide domain pattern and the narrow domain pattern was generated according to the rate of cooling i.e. respectively 0.03°C/cm and 0.5°C/min. The samples were polarized at room temperature by a field of 50 V/cm for 5 min. Evalua-

tion of the domain width has been based on the measurements referring to the thermal hysteresis loop of the dielectric permittivity. The results of these measurements are shown in Fig. 2. Comparison of these results with the conclusions drawn by Jaśkiewicz and Kwoka [11] confirms the assumptions regarding the domain structure. The results of pyroelectric measurements are shown in Fig. 3. There are inflexion points at a temperature lower

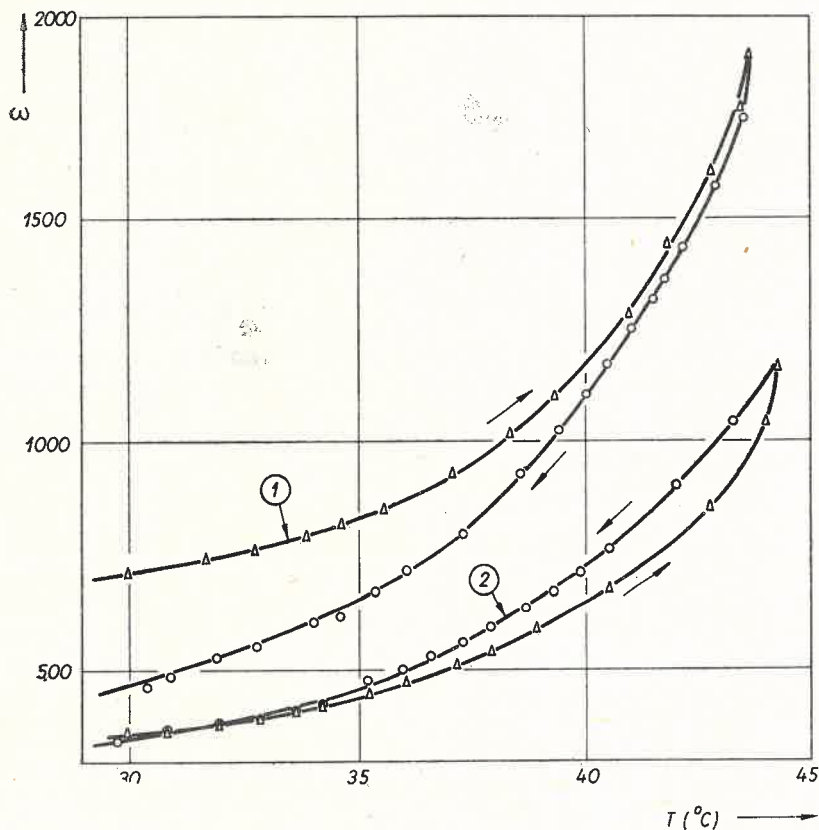


Fig. 2. Thermal hysteresis loop of dielectric permittivity. Curve 1 — narrow domains. Curve 2 — wide domains

by 7 degrees centigrade than the phase transition point on curve 1 and close to the phase transition point on curve 2, respectively. It is proper to add that in the region in which the inflexion points on $U_p(T)$ curves occur, one can notice, using the oscilloscope, that the thermal Barkhausen leaps are in the direction of the pyroelectric impulses due to the pulswise heating of the crystal.

The influence of the polarizing process on pyroelectric properties of a sample for a given initial domain structure has also been investigated. After heating, the samples were cooled to room temperature at the rate of $0.1^\circ\text{C}/\text{min}$. The samples were then exposed in succession to each of the fields of 100, 250 and 500 V/cm, for 10 min. The results of these measurements are shown in Fig. 4. Figure 4 shows that the distance between the

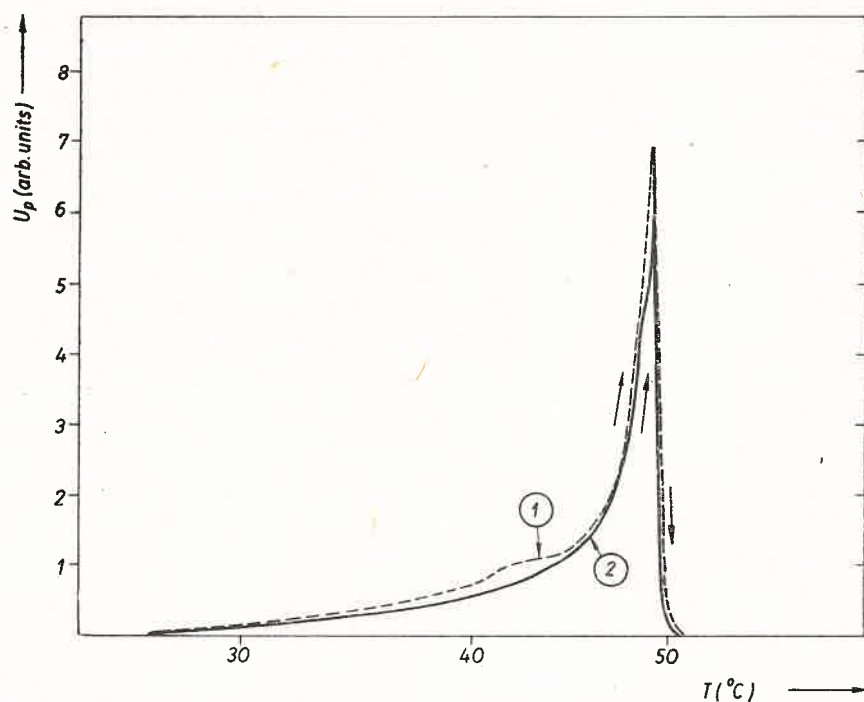


Fig. 3. Pyroelectric signal vs temperature: 1 — wide domains, 2 — narrow domains

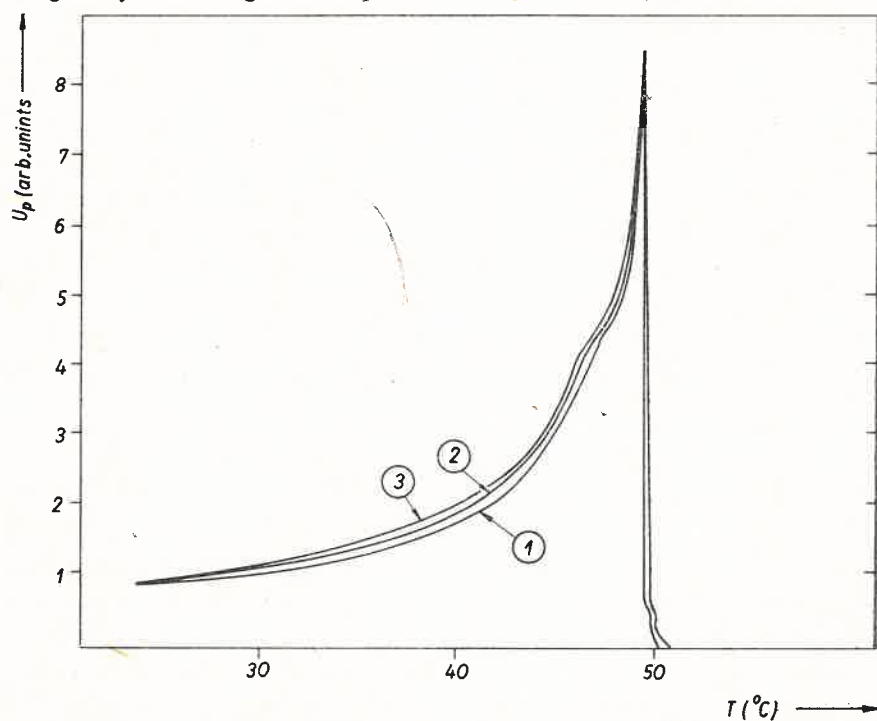


Fig. 4. Pyroelectric signal vs temperature: 1 — $E = 100$ V/cm applied for 10 minutes at room temperature; 2 — $E = 250$ V/cm, $t = 10$ min, 3 — $E = 500$ V/cm, $t = 10$ min

inflection point and the phase transition point on the $U_p(T)$ curve, increases as the value of polarizing field increases. This effect vanishes for a field of about 500 V/cm. The polarizing field of higher intensity applied to the crystal causes its permanent polarization.

5. Discussion

The presence of inflection points on the $U_p(T)$ curves can be explained by the breakage of the domain structure. According to Mazur and Jaśkiewicz [15] the maximum value of the domain depolarization factor is given by

$$N = 2A(T - T_c) - 2BP^2 - 2CP^4, \quad (4)$$

where A , B and C are the factors of free energy expansion, T_c is the temperature of the Curie point.

The relation of the depolarization factor to the domain width for the laminar domain structure is then

$$N = \frac{6.8a}{(1 + \sqrt{\epsilon_a \epsilon_b})d}, \quad (5)$$

where a is the average domain width, d is the crystal thickness, ϵ_a and ϵ_b denote the dielectric permittivities along the corresponding crystallographic axes.

Equations (4) and (5) thus show that while the crystal is heated, the wide domains achieve the permissible values of N at lower temperatures than the narrow ones, which is why they must break up sooner into numerous small domains.

During the polarizing treatment the field-oriented domains grow bigger, sponging on those of reverse orientation. These domains ought to break up into several domains of reverse orientation thus lowering the degree of polarization of the crystal, which is observed as an inflection point on the $U_p(T)$ curve. The temperature dependencies of the pyroelectric signal shown in Fig. 3 supports the above-mentioned consideration. While the polarizing field is being applied to the crystal, sideways movement of the domain occurs at the rate given by Jaśkiewicz, Dacko and Vo Duy Danh [16]. Movement of the domain wall stops when

$$E = \frac{2\pi^2 P_s}{d \sqrt{\epsilon_a \epsilon_b}} (a_1 - a_2), \quad (6)$$

where a_1 and a_2 are the widths of domains between which sideways movement takes place, E is the field intensity. The width of the domains resulting from polarization processes as the polarizing field increases. The domains created by higher polarizing fields should break up earlier than those created by means of lower intensity fields. The use of strong polarizing fields for longer periods lead to separation, in the crystal, of space charge which fastens the present domain structure. The breakage of such a structure occurs in the neighbourhood of the phase transition point.

6. Conclusions

The break-up of the domain structure with the polarization factor $\varphi \neq 0$, due to increased temperature of the crystal, occurs in such a way that the polarization factor lowers its value. The domain structure break-up can be perceived as thermal Barkhausen effect against a background of a pyroelectric signal due to pulsewise heating of the crystal. The break-up temperature is defined in terms of the initial domain structure, period of application, and magnitude of the field which is polarizing the crystal at room temperature.

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