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PHYSICAL PROPERTIES OF L-α-ALANINE DISORDERED REGIONS IN TGS CRYSTALS. I. DIELECTRIC PROPERTIES

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Changes in dielectric constant and spontaneous polarization of L-α-alanine admixtured in comparison with pure TGS crystals are determined in temperature region comprising the phase transition point. A decrease in maximal value of dielectric constant and the absence of a shift in phase transition temperature are observed. Moreover, a decrease in spontaneous polarization value and a "diffluent" of the phase transition are found. For L-α-alanine admixtured crystals the hysteresis loop shows a displacement along both polarization axis and electric field axis. Next, on applying the phenomenological Okada's theory, the polarization and dielectric susceptibility of disordered regions are calculated.

1. Introduction

Admixtures essentially affect the physical properties of ferroelectric crystals, especially in the vicinity of the phase transition temperature. Hitherto, work on admixtured ferroelectrics concentrated first of all on the determination, by radiospectroscopic methods, of the properties of regions disordered by the insertion of paramagnetic ions. However, it is of interest to consider the case when the regions with a permanent dipole moment, identically oriented, are present in the crystal lattice of a ferroelectric. Such a "polar centre" can be constituted e.g. by a lattice region perturbed by X-irradiation, if the crystal was simultaneously influenced by a strong electric field. Crystals of Rochelle salt irradiated in an electric field have been studied by Okada [1], and crystals of triglycine sulphate — by Bye and Keve [2] as well as Flether et al. [3]. Ferroelectric TGS crystals with molecules of L-α-alanine introduced in the process of growth have properties similar to those of crystals irradiated in a DC electric field. Accordingly, the regions perturbed by L-α-alanine can be presumed to have the properties of polar centres i.e. to be endowed with an unswitchable dipole moment.

Hitherto, in TGS crystals admixtured with L-α-alanine (LATGS) the following properties have been investigated: the thermal diffusivity [4], dielectric permittivity, sponta-

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neous polarization, and pyroelectric coefficient [5], as well as some piezoelectric and elastic coefficients [6]. In all cases a strong internal electric field, biasing the hysteresis loop, was found to exist. From the variations of these parameters compared to pure TGS crystals, the diameter of the regions disordered by L-α-alanine was determined [4]. Hitherto, however, the physical properties of these regions have not been dealt with comprehensively. It is the aim of the present work to determine the dielectric constant and polarization of the regions disordered by L-α-alanine in TGS crystals, on the basis of theory of permanent dipole moments wedged into a ferroelectric lattice.

2. *Experimental results*

Single crystals of triglycine sulphate $(NH_3CH_2COOH)_3 \cdot H_2SO_4$ (TGS) as well as TGS crystals admixtured with L-α-alanine (LATGS) were grown by isothermal method in Institute of Physics A. Mickiewicz University. Temperature of solution was 317 K. LATGS crystals were grown under identical conditions from solution containing 3% weight of L-α-alanine. The admixture content in the samples, determined by paper chromatography, amounted to $2 \cdot 10^{-4}\%$ weight, corresponding to a concentration of $3.05 \cdot 10^{18}$ cm^{-3}.

Cubic samples were prepared with edges 1 cm or 1.5 cm in length parallel to crystallographical axes [100], [010] and [001], in order to determine later the propagation of ultrasonic waves in LATGS crystals. The system of axes was in accordance with the system proposed by Konstantinova [7]. On the surfaces perpendicular to the ferroelectric axis, silver electrodes were deposited by evaporation in vacuum. The samples were then placed in a holder filled with dry hydrogen. The temperature within the holder was controlled with an ultrathermostat in the range from 290 K to 350 K, at a stability of ±0.01 deg.

Spontaneous polarization of crystals was determined with the use of a DDP bridge with the value of measuring field of 3 kV/cm and the frequency of 50 Hz. Dielectric constant was appointed using Thompson bridge, measuring field was 10 kHz and 0.1 V/cm.

While performing the dielectric and spontaneous polarization measurement, the temperature of the crystals was increased from 290 K to 350 K. Subsequent to annealing at 370 K during 10–20 hrs, all measurements were repeated at cooling to room temperature. To eliminate the domain wall effects, all crystals were subjected to permanent polarization prior to the measurements.

No measurable differences in dielectric constant and spontaneous polarization between increase and decrease of temperature were observed.

The spontaneous polarization values obtained for the L-α-alanine admixtured TGS crystals are shown in Fig. 1, where the results for pure annealed TGS crystals (thus free of mechanical stress) are also given — dashed line. A characteristic feature of the hysteresis loop for LATGS samples consists in the presence of an internal electric field, causing a displacement of the loop. This biasing field can be compensated by applying an external electric field of appropriate strength and direction. Similar results have been reported by Lock [8]. The internal electric field, determined directly from the loop displacement and indirectly with an external compensating field, amounts to 2.2 kV/cm, irrespective of the

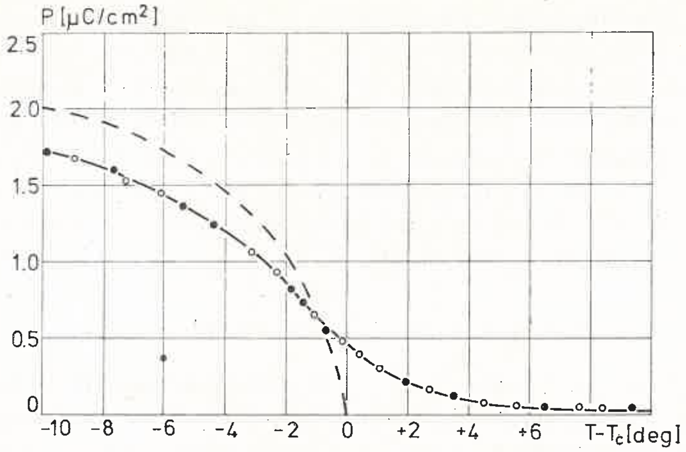

Fig. 1. Temperature-dependence of spontaneous polarization in LATGS crystal. ● — aged crystal, heating, ○ — stress-freed crystal, cooling. Dashed line — spontaneous polarization of pure TGS

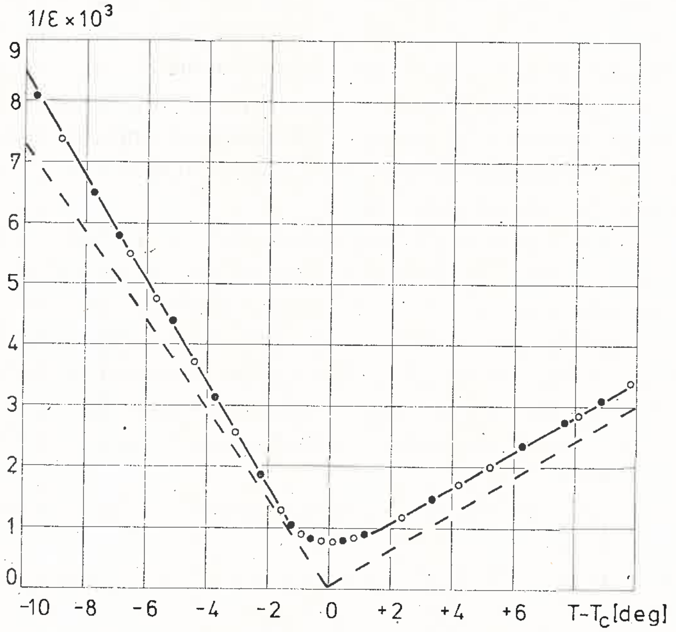

Fig. 2. Temperature-dependence of inverse dielectric constant in LATGS crystal. ● — aged crystal, heating, ○ — stress-freed crystal, cooling. Dashed line — inverse dielectric constant of pure TGS

temperature. Simultaneously, a displacement of the loop along the polarization direction was observed. Below the phase transition temperature, this displacement is proportional to the polarization value determined, and their ratio amounts to 0.12. Contrary to the results reported by Keve et al. [9, 10], the spontaneous polarization determined at present in *L*-α-alanine admixtured TGS crystals is lower than in pure TGS.

Fig. 2 shows the inverse dielectric constant ε_{22}^{-1} measured by us as a function of temperature for LATGS, together with our results for pure TGS (dashed line). One notes the strong decrease in this constant down to $\varepsilon_{\max} = 1300$, due to the presence of the internal field. It is essential that the phase transition temperature, defined by the dielectric constant maximum, has unchanged at $T_c = 322.5$ K for LATGS. This result is at variance with data of Keve et al. [9, 10], who reported an increase in T_c for LATGS, but corroborates the result of Loiacono [11] who studying the phase transition of LATGS by difference thermal analysis, found no change in T_c.

3. Dielectric properties of the disordered regions

The molecule of L-α-alanine, having a non-zero dipole moment of its own, is built into the TGS lattice presumably in place of glycine I [9]. Since, compared with glycine, the molecule of α-alanine contains a CH_3^+ groups instead of a proton, the latter molecule cannot go over into its mirror reflection unless chemical bonds are disrupted. Hence, in an elementary cell where glycine I is replaced by α-alanine, ferroelectric polarization switching is impossible. If only one optically active form of the admixture is introduced into the crystal, e.g. L-α-alanine, all the molecules replacing glycines have to be directed identically with respect to the b-axis, so that the stoichiometry and hydrogen bonds shall be conserved. Accordingly, all permanent L-α-alanine dipoles, introduced into the TGS lattice, have the same direction, whereas the other regions are under the influence of a local electric field, leading to a shifted hysteresis loop, similar to the loop observed for crystals immersed in an external electric field [9].

Since the internal field biasing the loop exceeds the coercive force, one should expect the LATGS crystals to be single domain ones. This, in fact, has been confirmed by domain structure studies, which failed to reveal oppositely oriented domains in LATGS. Hence, one is justified in omitting domain wall energy in the free energy expansion.

To describe the physical properties of the regions disordered by L-α-alanine in TGS crystals, one can apply the simple phenomenological Sawaguchi-Charter's [12] model of permanent ordered dipoles, wedged into a ferroelectric lattice, in conjunction with the above cited experimental results.

After Okada [1], the free energy per unit volume of a single-domain crystal is:

$$\phi = \left(\tfrac{1}{2}\,xP_f^2+\tfrac{1}{4}\,\xi P_f^4\right)+\tfrac{1}{2}(1-\lambda)\frac{1}{a}(P_a-P_0)^2+\tfrac{1}{2}\,\lambda(1-\lambda)k(P_f-P_a)^2, \tag{1}$$

where λ — the per cent volume of ferroelectric region, P_f — its polarization, P_a — that of the volume occupied by the polar centres, P_0 — that of the latter volume without electric field, k — the constant of interaction between the polarization P_f and P_0, and a — the dielectric susceptibility of the non-ferroelectric region.

However, the functional relation between electric field and polarization is described by the equations:

$$P = P_f+\frac{1-\lambda}{1+ak}P_0+\frac{(1-\lambda)a}{1+ak}\left[\left(x-\frac{1}{a}\right)P_f+\xi P_f^3\right], \tag{2}$$

and

$$E = -\frac{(1-\lambda)k}{1+ak}P_0 + \frac{(1-\lambda)k}{1+ak}P_f + \frac{1+\lambda ak}{1+ak}(xP_f+\xi P_f^3). \tag{3}$$

The shift of hysteresis loop along the electric field direction is presented by the 1-st term of Eq. (3),

$$E_b = -\frac{(1-\lambda)k}{1+ak}P_0. \tag{4}$$

Experimentally determined value of this field is 2200 V/cm.

The maximal value of dielectric constant

In crystal containing polar centres the inverse dielectric susceptibility is [1]:

$$\frac{1}{\chi} = \frac{\partial E}{\partial P} = \frac{(1+\lambda ak)(x+3\xi P_f^2)+(1-\lambda)k}{(1-\lambda)a(x+3\xi P_f^2)+\lambda+ak}. \tag{5}$$

Since in our experiment no external electric field was applied, this relation taking into account Eq. (3) becomes:

$$\frac{1}{\chi} = \left\{\lambda\left(\frac{1+ak}{1+\lambda ak}\right)^2\left[\frac{(1-\lambda)k}{1+\lambda ak}\frac{P_0}{P_f}+2\xi P_f^2\right]^{-1} + \frac{(1-\lambda)a}{1+\lambda ak}\right\}^{-1}. \tag{6}$$

The dielectric susceptibility becomes maximal when the condition is fulfilled

$$P_f = \left[\frac{(1-\lambda)k}{4\xi(1+\lambda ak)}P_0\right]^{1/3}. \tag{7}$$

Taking into consideration the above condition and relation (4), we obtain the expression for the maximal value of dielectric constant:

$$\varepsilon_{\max}-1 = \frac{(1-\lambda)a}{1+\lambda ak} + \frac{2}{3}\lambda\left(\frac{1+ak}{1+\lambda ak}\right)^{4/3}(4\xi E_b^2)^{-1/3}. \tag{8}$$

Our experimentally determined maximal value of the dielectric constant is:

$$\varepsilon_{\max} = 1300.$$

The phase transition temperature

The magnitude of the shift in transition temperature of LATGS as compared with pure TGS can be calculated by inserting the condition (7) into (5) and taking into account the relation (4). We thus arrive at the equation:

$$x = \frac{3}{4}\left[4\xi\left(\frac{1+ak}{1+\lambda ak}E_b\right)^2\right]^{1/3} + \frac{1+ak}{1+\lambda ak}\frac{E_b}{P_0}. \tag{9}$$

Experimentally, no shift in the Curie temperature of L-α-alanine admixtured TGS crystal was observed in comparison with pure TGS. Thus, $x = 0$ and

$$P_0 = -\tfrac{2}{3}\left(\frac{2}{\xi}\,\frac{1+ak}{1+\lambda ak}\right)^{1/3} E_b^{4/3}. \tag{10}$$

Assuming $\left(\dfrac{1+ak}{1+\lambda ak}\right)^{1/3} \approx 1$ and with regard to the experimentally observed hysteresis loop displacement of $E_b = 2.2$ kV/cm, we obtain the polarization of the disordered regions:

$$P_0 = -0.60\ \mu\text{C/cm}^2.$$

This result shows that the permanent dipole moment present in a region disordered by a molecule of L-α-alanine is directed oppositely to the field which it produces and which acts on the switchable dipole moments of the glycines lying in the ferroelectric region.

The change in slope of the function $\varepsilon^{-1}(T)$ in the paraelectric phase

In the paraelectric phase, far from T_c when $P_f = 0$, the slope of the reciprocal dielectric susceptibility for LATGS is:

$$\frac{d(\chi^{-1})_{\text{para}}}{dT} = \frac{\lambda}{C}\left[\frac{1+ak}{(1-\lambda)a\,\dfrac{\Delta T}{C}+\lambda+ak}\right]^2, \tag{11}$$

where C — Curie–Weiss constant. On the other hand, the slope of $\varepsilon^{-1}(T)$ for pure TGS is $2.81 \cdot 10^{-4}\ \text{deg}^{-1}$. Thus, their ratio amounts to:

$$\frac{[d(\chi^{-1})/dT]_{\text{LATGS}}}{[d(\chi^{-1})/dT]_{\text{TGS}}} = \frac{\lambda}{\left[1+\dfrac{1-\lambda}{1+ak}(ax-1)\right]^2}. \tag{12}$$

The ratio, experimentally determined at the temperature $T-T_c = 10$ deg, amounts to 0.88.

By having recourse to Eqs. (4), (8), (12) and our experimental data, we calculated the parameters λ, a, and k assuming, in accordance with the Okada theory, that they do not depend on temperature. The values thus obtained are:

$$\lambda = 0.80, \quad a = 210, \quad k = 7.5 \cdot 10^7\ \text{Vm/C}.$$

The susceptibility, calculated for the disordered region, is equal to that of the pure TGS crystal at the temperature 317 K i.e. at the temperature in which the LATGS crystals were grown. This fact suggests that the dielectric susceptibility value of the crystal in the process of growth was "memorized" in the disordered region.

Displacement of the hysteresis loop along the polarization axis

The displacement of the loop along the polarization axis is given by the second and the third term of Eq. (2). Temperature-independent displacement due to the polarization P_0 of disordered regions could not be observed in experiment because of losses in the condensors constituting the measuring bridge leading to discharge of the permanent polarization charges. Hence, the experimentally measured shift in hysteresis loop along the axis of polarization is defined by the third term of Eq. (2). Below T_c, where the influence of the electric field produced by the disordered regions on the polarization of the ferroelectric regions can be neglected, we can write $P_f^2 \approx -x/\xi$ i.e.

$$\frac{P_b'}{P_f} = -\frac{1-\lambda}{1+ak}. \tag{13}$$

This value, calculated with the results obtained above, amounts to 0.124, in excellent agreement with our experimentally measured value, which is 0.12. Hence, this fact attests the correctness of the results which were obtained previously.

4. *Conclusions*

When studying the dielectric properties of TGS crystals admixtured with L-α-alanine we observed, in comparison with pure TGS crystals, a decrease of maximal value of dielectric permittivity, a change in slope of the function ε^{-1} vs T in the paraelectric phase, and the absence of a shift in phase transition temperature. Moreover, we found a decrease in spontaneous polarization value, a "diffluent" phase transition, and a displacement of the hysteresis loop along both the polarization axis and the electric field axis. Assuming the crystal lattice disordering, due to the introduction of a permanently dipolar L-α-alanine molecule, as being a polar nature, we applied Okada's theory to determine the polarization of the disordered regions as $P_0 = -0.60 \cdot 10^{-2}$ C/m^2.

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