DIELECTRIC PROPERTIES OF TRIGLYCINE SULPHATE CRYSTALS ADMIXTURED

WITH D- AND DL-PHENYLALANINE

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The paper reports studies on the effect of D-phenylalanine and DL-phenylalanine admixtures on dielectric properties and domain structure of triglycine sulphate crystals. Permittivity ε and loss tangent tg δ were measured in a wide range of temperatures (10-340 K) as a function of measuring field varied from 1 to 10000 kHz, for samples cut out from two growth pyramids (001) and (110) from triglycine sulphate crystals containing different concentrations of admixtures. A comparison of the effects of D-phenylalanine and DL-phenylalanine admixtures on dielectric properties of triglycine sulphate crystals was made. With increasing concentrations of admixtures in the crystals, the values of ε_{max} decreased while E_c and E_b (bias field) increased, and P_s and T_c showed insignificant changes. Observations of the domain structure of the admixtured crystals by the liquid crystal method proved its refinement and irregularity. Changes in the domain structure of the crystals occurring in the process of spontaneous ageing were analysed.

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1. Introduction

Dielectric properties of triglycine sulphate (TGS) crystals admixtured with organic compounds have been studied by many authors [1–6]. So far the subject of interest has been the influence of such aminoacids as alanine, serine, valine and threonine [7–10]. The purpose of this work was to check the influence of D-(D-Phe) and DL-phenylalanine (DL-Phe) admixtures on dielectric properties of TGS crystals. Phenylalanine is a derivative of alanine whose one proton from the methyl group has been replaced by a phenyl group (Fig. 1). Phenylalanine is an optically active neutral aminoacid, therefore it can be either dextrorotatory (D+) or laevorotatory (L-). In this study D-phenylalanine and a 1:1 mixture of D- and L-phenylalanine were used.



Fig. 1. A schematic presentation of the structure of the alanine derivatives used as admixtures of TGS crystals.

2. Experiment

Single crystals of pure and D-phenylalanine (DPTGS) or DL-phenylalanine (DLPTGS) admixtured TGS crystals were grown from aqueous solutions of triglycine sulphate with an appropriate amount of the admixtures: 0, 1, 2, 4, 5, 10, 15, 20wt% D-, DL-Phe relative to pure TGS. These crystals were grown by the dynamic method in the ferroelectric phase at a constant temperature ($\approx 35^{\circ}$ C) by slow evaporation of water. DPTGS crystals grew asymmetrically with respect to the nucleus, along the ferroelectric axis b. DLPTGS crystals grew symmetrically but were more sensitive to touch and temperature changes. Samples to be studied were cut out from the two growth pyramids (001) and (110) (sample size: area 20 mm², thickness ≈ 1.5 mm). Gold electrodes were evaporated on their surfaces in the direction perpendicular to the ferroelectric b-axis.

Temperature measurements (100-340 K) of permittivity ε and $tg\delta$ were performed for both aged and young samples at the measuring field frequency 1-10000 kHz, using an impedance analyser HP 4192A. The amplitude of the measuring field was 1 V/cm. Temperature measurements (to \approx 10 K) were performed with the use of RCL GR 1689 M bridge and HP 4275A analyser, in the flow helium cryostat, which enabled a determination of temperature with the accuracy of 0.42 K.

Spontaneous polarization P_s , coercive field E_c and bias field E_b were determined from the dielectric hysteresis loops measured with a DDP bridge. Introduction of D-Phe or DL-Phe admixture to TGS crystals causes a shift of the dielectric hysteresis loop along the E axis by a value known as the bias field E_b . The value of E_b is proportional to the amount of the admixture and can serve as its measure [11].

The actual amount of the admixtures in the crystals was determined by UV spectroscopy using the fact that phenylalanine molecules are characterised by a specific absorption spectrum. Absorption of radiation at a certain wavelength is directly correlated with the concentration of the absorbing molecules, so the latter value can be found applying the Lambert-Beer law [12, 13]. Slices (2 g) from different sites in the crystals grown from solutions containing different concentrations of admixtures were cleft off. These slices were dissolved in water, then absorption spectra of the solutions were taken and the mean weight percent of the admixture is non-uniformly built into the crystal and its concentration in the crystal is much lower than that in the solution from which it was grown (Table I). This method cannot be used for determination of the admixtures concentrations in the samples used for dielectric measurements (≈ 0.20 g). For these samples the concentration

TABLE I

The percent contributions of D-Phe and DL-Phe in DPTGS and DLPTGS crystals versus the concentrations of these admixtures in the solutions from which the crystals were grown.

% concentrations	% contributions	% contributions				
D-Phe and DL-Phe	D-Phe in DPTGS	DL-Phe in DLPTGS				
in solutions	crystals	crystals				
1	0.05	0.06				
2	0.07	0.08				
4	0.08	0.11				
5	0.09	0.13				
10	0.12	0.18				
15	0.19	0.28				
20	0.24	0.32				

of admixtures can be estimated from the bias field which is directly proportional to the contents of the admixture.

Figure 2 presents the relation between the contribution of D-Phe and DL-Phe in admixtured TGS crystals on the concentration of the admixtures in the solution.

Figure 3 presents the values of $E_{\rm b}$ versus the concentration of the admixture in the crystals for samples cut out from the (001) and (110) growth pyramids of DPTGS and DLPTGS crystals. As follows from Fig. 3, more DL-Phe than



Fig. 2. The percent contribution of the admixtures in DPTGS and DLPTGS crystals versus the concentration of the admixtures in the solutions.

Fig. 3 Bias field E_b versus the contribution of admixtures in the crystals, measured for DPTGS and DLPTGS in the (001) and (110) growth pyramids.

D-Phe is built into TGS crystals. Moreover, for both admixtures, values of $E_{\rm b}$ are always greater for the samples cut out from the (001) growth pyramid (so a greater amount of admixture must have been built into this pyramid) than those observed for (110) growth pyramid.

The temperature dependencies of ε and $tg\delta$ for DPTGS crystals (a, b) and DLPTGS crystals (c, d) of different concentration of the admixtures in the crystals for (110) growth pyramid, are shown in Fig. 4. The curve of $\varepsilon(T)$ (4a, c) reveals three maxima: a low-temperature one at about 190 K, an intermediate one near 260 K and the highest third one at $T_c \approx 321.5$ K. The values of the maxima decrease with increasing concentration of the admixtures D-Phe and DL-Phe in TGS crystals. The maxima are more pronounced on the $tg\delta(T)$ curves (4b, d), on which they appear at somewhat lower temperatures than the corresponding maxima in $\varepsilon(T)$. With increasing concentration of the admixtures in DPTGS and DLPTGS crystals, the values of ε_{max} and $tg\delta_{max}$ increase in the range of low concentrations of the admixtures and then decrease. In DPTGS crystals of the



Fig. 4. The temperature dependencies of ε (a, c) and tg δ (b, d) for young samples cut out from the (110) pyramid from DPTGS and DLPTGS crystals grown from the solutions of different concentration of admixtures.



Fig. 5. The temperature dependencies of ε (a, c) and tg δ (b, d) for young samples cut out from the (110) pyramid from DLPTGS crystals grown from the solutions with 1% (a, b) and 20% (c, d) DL-Phe, for different frequencies.

highest concentration of D-Phe, the low-temperature maxima $\varepsilon(T)$ and $tg\delta(T)$ do not occur.

Measurements of $\varepsilon(T)$ and $tg\delta(T)$ [14-16] were performed for the measuring field frequency varied from 1 to 13000 kHz for DPTGS and DLPTGS crystals of different concentrations of the admixtures (in the ranges of temperatures: 100-340 K and 10-300 K). Figure 5 presents the plots of these dependencies for DLPTGS crystals grown from the solutions containing 1% (a, b) and 20% (c, d) of the admixture. For DPTGS crystals the dependencies are similar. The $\varepsilon(T)$ curves for different frequencies of the measuring field reveal three maxima at 160-170 K, 280-290 K and T_c . Also three maxima appear on the plots of $tg\delta(T)$, at 150-200 K, 280-300 K and 320 K. With increasing frequency of the measuring field the values of ε_{max} and $tg\delta_{max}$ decrease and shift towards higher temperatures. For frequencies higher than 1000 kHz, the low temperature maximum ε at 150-200 K and maximum ε at 280-290 K disappear, while the $tg\delta(T)$ maxima join into a single broad one.

The values of ε_{\max} and $tg\delta_{\max}$ decrease with increasing frequency of the measuring field and with increasing concentrations of the admixtures in both DPTGS and DLPTGS crystals.



Fig. 6. The low-temperature dependencies of ε' (a) and ε'' (b) for young samples cut out from (110) growth pyramid from DLPTGS crystals grown from the solutions with 20% DL-Phe, for different frequencies.

For DLPTGS crystals grown from the solution admixtured in 20% DL-Phe in low temperatures (≈ 10 K) all curves of $\varepsilon'(T)$ and $\varepsilon''(T)$ meet at one point, irrespective of the frequency of the measuring field (Fig. 6).

Figure 7 presents the values of ε_{max} (a) and T_c (b) versus contributions of D-Phe and DL-Phe admixtures in the crystals for the samples cut out from the (001) and (110) pyramids. The values of ε_{max} are higher for the samples cut out from the (110) pyramid than from (001) one for both admixtures and lower for DLPTGS crystals than DPTGS crystals. This means that a greater amount of each admixture is built into the (110) pyramid and more DL-Phe than D-Phe is built into the corresponding crystals. The Curie temperature for crystals with the two kinds of admixtures studied varies between 321.3 and 321.8 K.



Fig. 7. The values of ε_{max} (a) and T_c (b) versus the contributions of the D-Phe and DL-Phe admixtures in the DPTGS and DLPTGS crystals for the samples cut out from the (001) and (110) growth pyramids.



Fig. 8. The values P_s (a) and E_c (b) versus the percent contribution of the D-Phe and DL-Phe admixtures in the DPTGS and DLPTGS crystals for samples cut out from the (001) and (110) growth pyramids.

Figure 8 shows values of spontaneous polarization P_s and coercive field E_c (at room temperature) versus the concentration of the admixtures in the crystals for samples cut out for the (001) and (110) growth pyramids for DPTGS and DLPTGS crystals. The values of P_s do not depend on the kind of admixture, its concentration and growth pyramid, while those of E_c increase with the concentration of the admixtures and for the crystals of high concentration of admixtures they are higher for the growth pyramid (001) than for (110).

Table II gives the values of dielectric parameters for samples of aged and young DPTGS and DLPTGS crystals grown from the solution with 0, 2, 10 and 15wt% of the admixtures and cut out from the (110) growth pyramids. The samples were rejuvenated at 363 K (\approx 30 h, with electrodes). For DLPTGS crystals the values of ε_{max} , P_s and T_c are lower while E_b and E_c are higher than for DPTGS crystals, which confirms that more DL-Phe than D-Phe builds into the TGS crystals. After rejuvenation the values of ε_{max} , P_s and E_c increase, while that of E_b decreases. Rejuvenation of the samples with electrodes causes their monodomenisation, which increases the coercive field.

The domain structure of DPTGS [17] and DLPTGS crystals was studied by the liquid crystal method (in 4-*n*-butylo-*N*-(methoxybenzylidene)-aniline) [18], for aged and rejuvenated crystals. For aged crystals it is irregular and fuzzy, whereas after rejuvenation of the crystals with a low concentration of the admixtures the structure becomes strongly refined. The refinement decreases with increasing concentration of the admixtures but is still greater than for pure TGS crystals. Similar observations were made for TGS crystals admixtured with Cu^{2+} and Cr^{3+} ions [6].

The process of spontaneous ageing of domain structure was studied by observations in the time elapsed from the moment the samples reached the Curie point. Figure 9 presents the number of domains per 1 mm of the crystal length versus the logarithm of time for DPTGS (a) and DLPTGS (b) crystals of different

I ε_{max} and L_c were measured for the measuring near irequency of 1 kmz.	$\kappa = \Delta \varepsilon^* = T_c \uparrow T_c \downarrow \Delta T_c = E_b = F_s \times 10^{-2} = E_c = \%$ contribution	[K] [K] [K] [V/cm] [C/m ²] [V/cm] in the crystal	$300 \left(\frac{1}{10000000} 321.62 \right) 321.50 \left(0.12 \right) 10 \left(2.50 \right) 360 $	300 ^{1 U 30 U} 321.71 321.35 0.36 5 2.70 450 ^U	000 100000 321.75 321.71 0.04 45 2.50 400 0.066	000 10200 321.69 321.63 0.06 20 2.75 460 0.000	$300 \left \begin{array}{ccc} 0.1 \\ 0.1 \\ 0.0 \end{array} \right 321.76 \left 321.66 \\ 0.10 \\ 0.10 \\ \end{array} \right 80 \left \begin{array}{ccc} 2.20 \\ 2.20 \\ 0.075 \\ \end{array} \right 390 \left \begin{array}{ccc} 0.075 \\ 0.075 \\ 0.075 \\ \end{array} \right $	60 0100 321.72 321.69 0.03 25 2.80 470 0.019	$100 \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$200 \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$300 \begin{vmatrix} 3 & 5 & 5 & 5 \\ 3 & 5 & 5 & 5 \\ 3 & 21.82 \end{vmatrix} 321.79 \begin{vmatrix} 0.03 \\ 0.03 \end{vmatrix} 190 \begin{vmatrix} 2.10 \\ 2.10 \end{vmatrix} 420 \begin{vmatrix} 0.18 \\ 0.18 \end{vmatrix}$	000 30000 321.85 321.84 0.01 75 2.70 550 0.10	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	400 1 1000 321.72 321.60 0.12 50 2.75 430 0.13	$00 \mid_{36000} \mid 321.90 \mid 321.86 \mid 0.04 \mid 315 \mid 2.00 \mid 550 \mid_{0.98} \mid 0.98$	00 2000 391 28 391 29 0 01 05 3 55 500 0120
leasuring 1	E _b	[V/cm	10	5	45	3 20	80	3 25	7 130	1 40	3 190	1 75	2 150	2 50	1 315	1 95
the m	ΔT_{c}	[K]	0.12	0.36	0.04	0.06	0.10	0.03	0.07	0.01	0.03	0.01	0.02	0.15	0.04	0.04
surea ior	$T_{c} \downarrow$	[K]	321.50	321.35	321.71	321.63	321.66	321.69	321.53	321.69	321.79	321.84	321.58	321.60	321.86	321.82
were mea	$T_c \uparrow$	[K]	321.62	321.71	321.75	321.69	321.76	321.72	321.60	321.70	321.82	321.85	321.60	321.72	321.90	321.86
x and Ic	$\Delta \varepsilon^*$		105600		102000		81800		19600		35800		17000		26800	
ues oi ε_{ma}	$\Delta \varepsilon$		33800	102300	38000	100000	37300	7960	11100	16200	10600	33000	8000	11400	9500	28100
s. I ne val	$\varepsilon_{ m max}$	→	56200	128000	56000	120000	49500	94000	29000	37500	15000	41200	22000	31000	18500	35800
dmixture	€max		22400	25700	18000	20000	12200	14400	17900	21300	4400	7200	14000	19600	0006	7700
I the a	xture	lution	<i>ъ</i>	Y	ಹ	y	ಣ	y	ත්	Y	ಸ	y	5 D	y	ರ	Λ
0 %	dmiy	ie sol		_		Phe	5	Phe	0	he	0	Phe	5	Phe	5	Phe

A comparison of the values of ε_{max} , $\Delta \varepsilon$, T_c , ΔT_c , E_b , P_s , E_c and the percent contribution of the admixtures in the crystals for samples cut out from the (110) growth pyramid for aged (a) and young (y) DPTGS and DLPTGS crystals grown from the solutions with 0, 2, 10, 1500 of the oblighteen The values of a graph of the maximum of the max TABLE II measuring field frequency of 1 kHz and for the

 $\Delta \varepsilon^* = \varepsilon_{\max y} - \varepsilon_{\max a}$

l

concentrations of the admixture. In DPTGS and DLPTGS crystals the process of spontaneous ageing runs at two stages and the point of inflection is shifted towards longer times with increasing concentration of the admixture. The first stage (to 10 h) is quicker, the slope of the curves [the number of domains per 1 mm (nd/mm) versus the logarithm of time (lgt)] decreases with increasing concentration of the admixtures in the crystals (Table III). The domain structure of both DPTGS and DLPTGS crystals is more refined than that of pure TGS crystals.



Fig. 9. The number of domains per 1 mm (nd/mm) of the crystal length versus the logarithm of time, for DPTGS (a) and DLPTGS (b) crystals of different concentrations of the admixture in the solutions.

TABLE III

The tangent of the slope of nd/mm(lgt) in the first $(tg\alpha_1)$ and second $(tg\alpha_2)$ stage of ageing of the crystals with different amount of D-Phe and DL-Phe admixtures, h — number of hours of spontaneous ageing corresponding to the change in the slope of the dependence nd/mm(lgt).

——————————————————————————————————————]	 D-Phe	e	DL-Phe				
$\mathbf{solution}$	$tg\alpha_1$	· h	$tg\alpha_2$	$\mathrm{tg} lpha_1$	h	$tg\alpha_2$		
0	3.27	8	0.34	3.27	8	0.34		
2	1.88	8.5	0.29	1.23	8.5	0.42		
5	1.23	8.5	0.30	0.60	8.5	0.33		
10	1.43	9	0.53	0.97	10	0.34		
15	0.93	12	0.34	0.51	10	0.34		
20	0.70	12	0.30	0.50	10	0.27		

3. Discussion

Because of the symmetry of TGS elementary cell, three crystallographically inequivalent glycine groups GI, GII and GIII are distinguished [19]. As follows from the structural [20, 21] and spectroscopic [22, 23] studies, the ferroelectric properties of triglycine sulphate are determined by GI glycine, therefore, replacement of GI by D-Phe or DL-Phe changes the dielectric properties of TGS crystals. Also morphology of DPTGS and DLPTGS crystals is different than that of pure TGS. In pure TGS crystals the rate of growth in both directions along the polar axis b, measured with respect to the nucleus, is the same. In the crystals admixtured with optically active molecules of D-phenylalanine, the asymmetry of growth in this direction is observed, which depends on the concentration of a given admixture in the solution from which the crystals were grown. DPTGS crystals grow slower in the sense [010] than $[0\overline{10}]$, while DLPTGS crystals grow slower in both senses of this direction, with no asymmetry. During the crystal growth the molecules of the admixtures are replacing the molecules of glycine GI, GII and GIII. As follows from the dielectric studies of TGS crystals admixtured with alanine, grown above and below $T_{\rm c}$, the admixture causes greater changes in the dielectric properties of the crystals grown below the Curie point, as in these conditions the GI glycine molecules are replaced to a greater degree. In the crystals grown above the Curie point, the molecules of the admixture replace the GI, GII and GIII molecules at the same probability, and the dielectric changes induced are smaller [7, 24]. These conclusions were later confirmed by the results of the Raman study [25] indicating that in TGS crystals admixtured with alanine, the molecules of this compound replace all three kinds of glycine molecules, although not to the same degree, and replacement of GI is preferred. Phenylalanine structurally resembles alanine, the difference is that one of the hydrogen atoms from the CH₃ group is replaced by the phenyl C_6H_5 . Therefore the molecules of D-Phe and DL-Phe are bigger than those of alanine. For this reason, the concentration of these admixtures in the crystals is smaller than that in the alanine doped crystal. This may be responsible for a lack of monodomenisation of the title crystals. The field of stress appearing as a result of their incorporation, stabilises polarization in the crystal, which leads to the appearance of a bias field $E_{\rm b}$. The experimental data concerning the influence of these admixtures on dielectric properties of TGS crystals suggest that the asymmetric stress field in the crystal lattice is a result of the inequivalent replacement of GI by D-Phe or DL-Phe. The bias field E_b , much lower than in the crystals DPTGS and DLPTGS also testifies to the fact that a smaller amount of admixture is built into these crystals than into those admixtured with alanine.

For the measured frequency region between 1 to 10^4 kHz, the dielectric dispersion can be related to the crystal lattice defects, domain structure and piezoeffect. Two relaxation regions can be distinguished in the temperature range from 100 to 300 K. It is expected that the maxima of permittivity ε and tg δ observed in the range 150-200 K (Fig. 5) are related to hindered rotation of NH₃ group in GI glycine, while those in the range 280-300 K may be related to hindered rotation of NH₃ group in the GII and GIII glycines and the effect of the domain structure, similarly as for TGS crystals admixtured with L-treonine [16].

In low-temperatures (10-50 K) the parameters ε' and ε'' do not depend on the frequency of the measuring field and take the same value (Fig. 6).

The maxima in ε depend not only on the measuring field frequency but on the contents of admixture as well. The aminoacid molecules can replace the glycine molecules in the TGS crystals. If the GI molecules are replaced, then the number of glycines responsible for the low-temperature relaxation decreases and the maximum of ε from the region 150–200 K decreases with increasing concentration of the admixture (Fig. 4). For the TGS crystal grown from the solution of the highest concentration of D-Phe — 20%, we did not observe any low-temperature maximum. This observation can be explained by the fact that in crystals of a high concentration of admixture the domain structure is strongly fixed and, moreover, in low temperatures the rotation of NH_3 groups is inhibited. Repolarization of TGS crystals is related to reorientations of GI glycine. However, the possibility of GI reorientations depends on the rotation of NH₃ group in the double GII-GIII ion. The introduction of admixture results at first in the unipolarity of the hysteresis loop and then inhibits the reorientation of GI. This is a result of hindering the rotation of NH₃ group in GI with increasing concentration of the admixture, manifested as disappearance of the dielectric loss maximum.

Spontaneous polarization P_s does not depend linearly on the concentration of admixture in the crystal, as well as the bias field, but the coercive field E_c increases with increasing admixture content. This increase can be explained by the fact that D-Phe and DL-Phe molecules built into the crystal fix the domain structure and thus a stronger electric field is required to repolarise the crystal.

The dielectric properties of the crystal are strictly related to the domain structure of TGS crystals [26]. The domain structure was observed by the liquid crystal method [18]. For aged DPTGS and DLPTGS crystals it is irregular and without the lens type domains typical of pure TGS crystals. After rejuvenation the domain structure becomes strongly refined and dependent on the concentration of admixture in the crystal (Fig. 8). For small concentrations of the admixtures, the domain structure is most refined and the degree of refinement decreases with increasing admixture concentration. The presence of phenylalanine molecules slows down the process of spontaneous ageing of TGS crystals. This process takes place in two stages: in the first 10 hours after the phase transition it is rather fast and then it gets stabilised (Table III).

4. Conclusions

- 1. TGS crystals admixtured with D-Phe grow asymmetrically along the b axis whereas those admixtured with DL-Phe grow symmetrically.
- 2. UV spectroscopy and dielectric data indicate that admixtures are non-uniformly built into the crystals and more DL-Phe than D-Phe is built into TGS crystals.
- 3. With increasing concentrations of both admixtures D-Phe and DL-Phe, in the TGS crystals the values of $E_{\rm b}$ and $E_{\rm c}$ increase while $\varepsilon_{\rm max}$ decrease and the Curie temperature and $P_{\rm s}$ undergoes only insignificant changes.

4. Introduction of D-Phe and DL-Phe admixtures into TGS crystals causes a refinement of the domain structure and enhances the irregular shape of domains. Refinement of the domain structure decreases with increasing concentration of admixtures in the crystal.

Acknowledgments

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