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INVESTIGATION OF THE DEPENDENCE OF DIELECTRIC PROPERTIES OF D-SERINE ADMIXTURED TGS CRYSTALS ON THE DISTANCE FROM THE SEED OF THE CRYSTAL GROWTH

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Dielectric properties of a D-serine admixtured triglycine sulphate (TGS) crystal were studied on samples cut out from different sites in the crystal. The value of spontaneous polarization P_s measured on b-cuts was found to be independent of the site. Whereas the coercive field E_c values were higher for the samples cut out closer to the seed than for those cut out at the ends of the crystal along b axis. After rejuvenation the values of the bias field E_b increased in contrary to the effect observed in the pure TGS crystals. An exponentially decreasing dependence of the maximum permittivity $\varepsilon_{\max}$ on the site of the samples (b-plates) cut out along b axis from $-b$ to $+b$ positions, was obtained.

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1. Introduction

An effective way of stabilization of one sense of the polarization vector in triglycine sulphate (TGS) crystals is introduction of an chiral organic (e.g. serine, alanine) [1–12] or inorganic (metal ion, e.g. chromium, iron, copper) [13–16] admixture to the solution from which the TGS crystals are grown. The influence of serine admixture on dielectric properties of the TGS crystals has been studied in [8, 9, 15]. The chemical formula difference between serine and glycine is that the hydrogen atom at the α-carbon in serine is replaced by the group CH_2OH in glycine. TGS crystals with D-serine admixture grow asymmetrically with respect to the seed along "b" axis similarly as it was observed for L-serine TGS crystal, though the asymmetry was now found to develop in the opposite direction. Asymmetry of the same kind was also observed for TGS crystals admixtured with L-α-alanine [4, 6, 10, 11] as well as D-α-alanine [11].

It is known [8, 9] that with increasing concentration of serine admixture in the crystal:

— the maximum permittivity $\varepsilon_{\max}$ decreases,
— the values of the coercive field E_c and bias field E_b increase,
— the value of spontaneous polarization P_s decreases,
— the domain structure becomes more refined.

Nakatani [5, 6] has studied the distribution of the bias field in the TGS crystals admixtured with L-α-alanine and DL-α-alanine and has reported that E_b is not homogeneous within a growth pyramid and its values are higher on the $-b$ side than on the $+b$ side in accordance with Refs. [10, 12]. The changes in the E_b values correspond to the changes in the alanine admixture concentration in the crystal.

The aim of this paper is to check the dependence of dielectric properties of the D-serine admixtured TGS (DSTGS) crystals on the site of the sample cut-out as well as to determine the distribution of the admixture in the crystal.

2. Experimental

The raw material of pure TGS crystals was subject to triple recrystallization [17] and the D-serine admixtured TGS crystals were grown from the solution containing 5 wt.% of D-serine admixture relative to dry mass of TGS.

The samples whose properties were measured were cut out from the pure TGS crystal grown in the ferroelectric phase at 318 K and from the DSTGS crystal grown at 316 K. The samples of both kinds of crystals were cut out at different distances from the seeds which is shown schematically in Fig. 1. All (b-cuts) samples of 0.25–0.5 cm^2 in area and of 0.1–0.2 cm thick were polished preserving the natural (001) wall of crystal (Fig. 1).

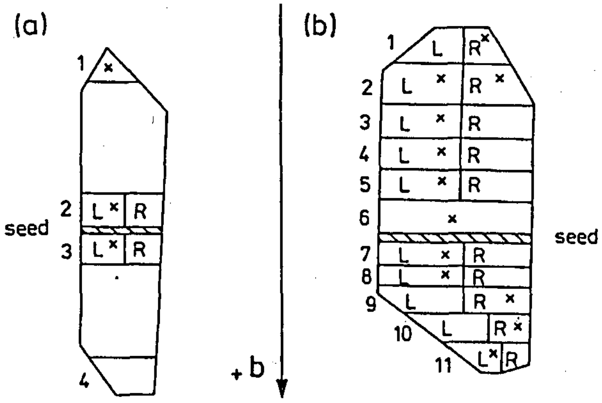

Fig. 1. A scheme of the crystal division into samples: (a) pure TGS, (b) D-serine admixtured TGS. L — left, R — right sites of a crystal. × — the measured samples.

Silver electrodes were evaporated on the surface perpendicular to the b axis. For each sample we measured spontaneous polarization P_s, coercive field E_c, bias field E_b and permittivity as a function of temperature $\varepsilon(T)$. Dielectric hysteresis loop measurements were carried out at room temperature by the Diamanta–Dvencka–Pepinsky (DDP) method applying an electric field of 290 kV/m. Temperature measurements of permittivity $\varepsilon(T)$ were performed using an E-317 type RLC bridge operating at a frequency of 1 kHz and a measuring field of 0.7 V/m. In the vicinity of the Curie point the rate of temperature changes was 0.1–0.2 K/min both on heating and on cooling.

The error of measurement was 5% for permittivity determination, 6% for spontaneous polarization, 7% for coercive field and bias field. We measured old (aged) and rejuvenated (young) samples. The samples of the DSTGS crystal were rejuvenated by annealing at about 348–368 K for 48 hours while the samples of the pure TGS crystal were rejuvenated by annealing at about 338 K for 24 hours.

3. Results

3.1. Permittivity measurements

Tables I and II present the measured values of dielectric parameters obtained for the pure TGS crystal (Tab. I) and the TGS+D-serine crystal (Tab. II).

TABLE I

The values of the Curie temperatures T_C, ΔT_C and maximum permittivity ε_{max}, $\Delta\varepsilon_{max}$ obtained for the pure TGS crystals for aged samples on heating and for rejuvenated samples on cooling, L means left sites of a crystal.

No	T_C [K]		ΔT_C [K]	$\varepsilon_{max}(10^3)$		$\Delta\varepsilon_{max}$ (10^3)
	Aged	Young		Aged	Young	
1	322.60	322.16	0.44	34.9	275.3	239.2
2 L	322.00	321.65	0.65	33.5	121.2	87.7
			Seed			
3 L	321.28	321.13	0.15	23.8	141.5	117.7
4	322.28	322.15	0.13	7.4	210.8	203.4

Figure 2 presents the temperature dependence of permittivity for three rejuvenated samples cut out from three different sites (numbered 1, 6, 11) in a TGS crystal admixtured with 5% of D-serine. The values of the maximum permittivity, ε_{max}, decrease when passing from the extreme site of "$-b$" (sample no. 1) to "$+b$" (sample no. 11). We use the setting of crystallographic axes adopted by Březina, Havránková [11] and Nakatani [6].

Figures 3a and 3b present the maximum permittivity values against the sites of the b-cuts samples, cut out in the sequence along the b axis (Fig. 1) for aged and rejuvenated samples of the pure TGS (Fig. 3a) and DSTGS crystals (Fig. 3b) on cooling. The maximum permittivity values are found to decrease exponentially

TABLE II

The values of the Curie temperatures T_C, ΔT_C, and the values of maximum permittivity $\varepsilon_{\max}$, $\Delta\varepsilon_{\max}$ as well as the values of permittivity at room temperature ε_r (rejuvenated samples) obtained for D-serine admixtured TGS crystal for aged samples on heating and for rejuvenated on cooling, L — left, R — right sites of a crystal.

No	T_C [K]		ΔT_C [K]	$\varepsilon_{\max}(10^3)$		$\Delta\varepsilon_{\max}$ (10^3)	ε_r
	Aged	Young		Aged	Young		
1 R	322.21	322.60	−0.39	13.0	28.25	15.5	60
2 R	322.86	323.02	−0.16	11.7	22.2	10.5	44
2 L	323.21	322.80	−0.41	11.5	17.7	6.2	–
3 L	321.86	323.12	−1.26	15.9	26.1	10.2	48
4 L	323.34	–	–	8.9	17.5	8.6	44
5 L	323.45	323.25	0.20	8.5	19.7	11.2	52
6	321.58	322.82	−1.24	8.9	14.7	5.8	42
Seed							
7 L	323.01	323.00	0.01	10.3	16.4	6.1	47
8 L	323.03	322.71	0.34	5.2	8.3	3.2	36
9 R	322.32	323.23	−0.91	12.3	16.5	4.2	–
10 R	321.82	322.32	−0.50	6.6	15.3	8.7	42
11 L	323.02	323.23	−0.21	8.3	9.3	1.0	42

when passing from $-b$ to $+b$ along the b axis for all samples except those of the rejuvenated pure TGS crystal.

Figure 4 presents the dependence of the maximum permittivity on the bias field for the rejuvenated D-serine admixtured TGS crystal. The samples characterized by the high bias field reveal low values of the maximum permittivity.

3.2. Measurements of dielectric histeresis loop

Tables III and IV present the results of measurements of spontaneous polarization, coercive field and bias field for aged and rejuvenated samples of the pure TGS (Table III) and DSTGS (Table IV) crystals cut out from different sites in the crystal.

Figures 5a and 5b present the dependence of coercive field on the site of the samples for the aged and rejuvenated pure TGS (Fig. 5a) and DSTGS crystal (Fig. 5b). For the pure TGS crystal we find that the samples cut out close to the seed reveal lower values of coercive field than the samples cut out from the crystal ends. The situation is reversed for the DSTGS crystals whose samples cut out close to the seed show higher coercive field values than those cut out from the crystal

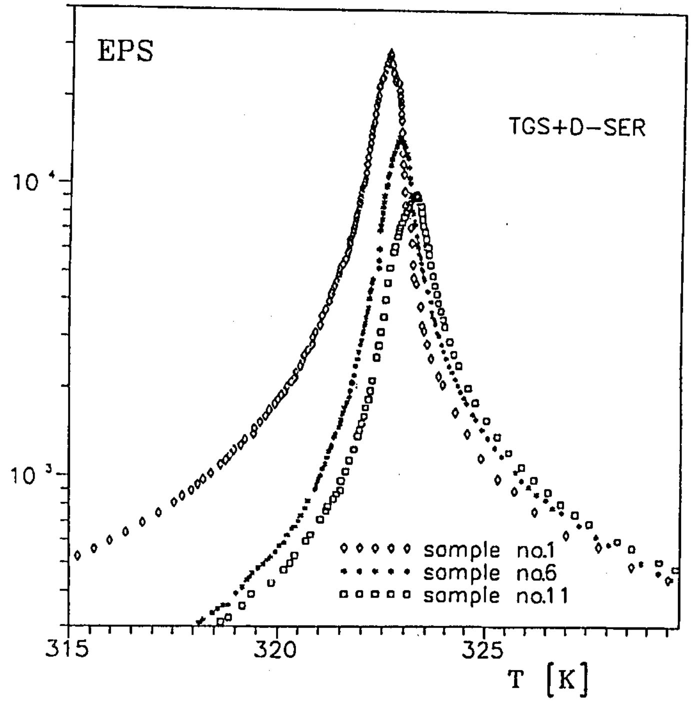

Fig. 2. Temperature dependence of permittivity for rejuvenated D-serine admixtured samples no. 1, 6, 11.

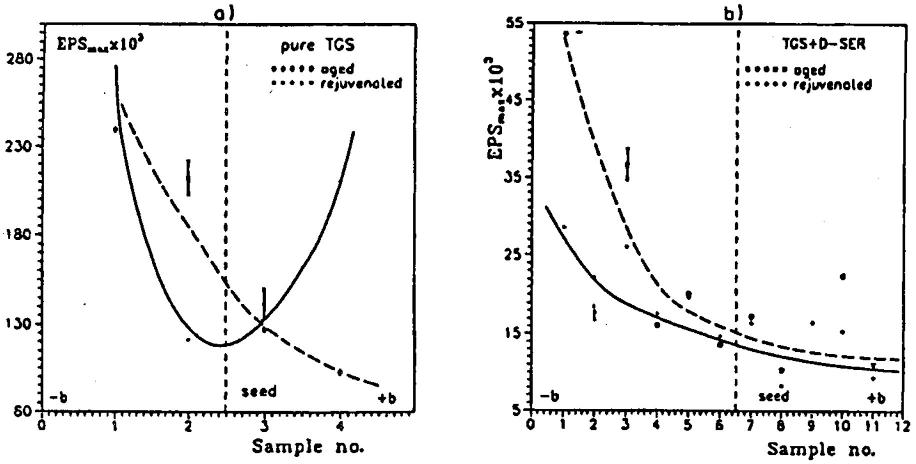

Fig. 3. The maximum permittivity values vs. the site of the samples for aged and rejuvenated samples of the pure TGS crystal (a) and D-serine admixtured TGS crystal (b), both obtained on cooling.

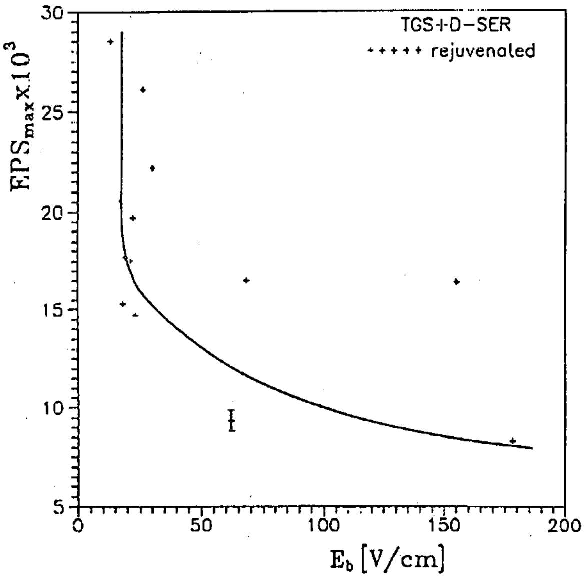

Fig. 4. The values of the maximum permittivity ε_{max} versus the bias field E_b for the rejuvenated D-serine admixtured crystal.

TABLE III

The values of the dielectric hysteresis loop parameters for the aged and rejuvenated samples of pure TGS cut out from different sites in the crystal, L — left sites of a crystal.

Samples number	P_s [μC/cm^2] Old	P_s [μC/cm^2] Young	E_c [V/cm] Old	E_c [V/cm] Young	E_b [V/cm] Old	E_b [V/cm] Young
1	2.6	2.6	560	530	60	40
2 L	2.8	2.7	500	490	32	23
Seed						
3 L	2.8	2.8	500	460	30	21
4	2.2	2.7	540	590	10	29

ends along the *b* axis. After rejuvenation, in the pure TGS crystal the coercive field decreases whereas in the DSTGS crystal it increases.

Figure 6 illustrates the results of the bias field measurements for different sites of the sample cut out from the rejuvenated DSTGS crystal. The samples cut out on the $+b$ side show higher values of the bias field than those cut out on the $-b$ side. Similar results were obtained for the aged samples of the DSTGS crystals.

In Fig. 7 we illustrate the relationship between the coercive field and the bias field. As can be seen the coercive field increases with increasing bias field.

TABLE IV

The values of the dielectric hysteresis loop parameters for the aged and rejuvenated D-serine admixtured TGS crystal cut out from different sites in the crystal, L — left, R — right sites of a crystal.

Sample number	P_s [μC/cm^2] Old	P_s [μC/cm^2] Young	P_c [V/cm] Old	P_c [V/cm] Young	P_b [V/cm] Old	P_b [V/cm] Young
1R	2.7	3.0	520	534	30	13
2R	3.0	2.9	487	455	2	30
2L	2.9	3.0	493	599	13	19
3L	2.7	2.5	540	538	22	26
4L	2.4	2.8	487	566	6	21
5L	2.8	2.9	531	693	67	22
6	2.7	3.2	592	595	8	23
			Seed			
7L	2.2	3.1	514	642	44	155
8L	2.4	2.8	533	618	209	178
9R	2.7	2.9	544	543	107	68
10R	2.7	3.2	490	469	25	18
11L	2.8	3.0	542	615	13	62

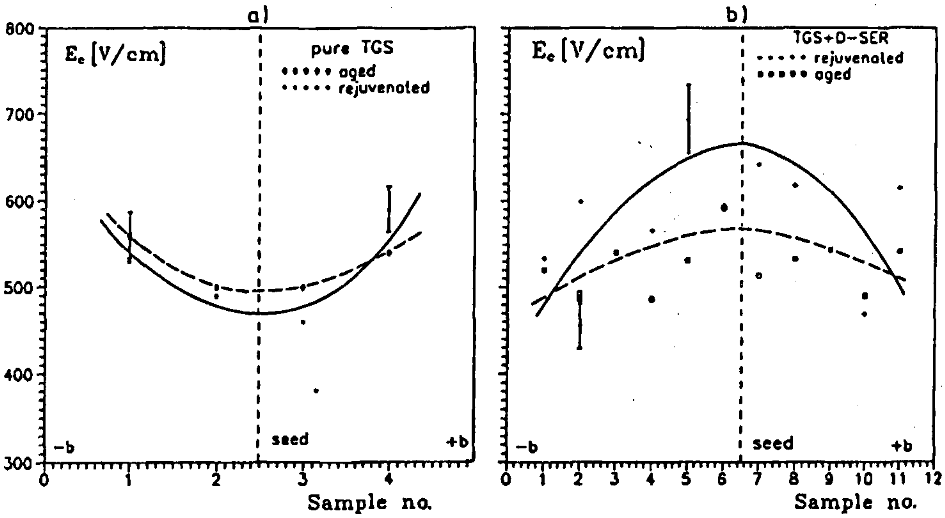

Fig. 5. The coercive field E_c versus the site of the sample cut-out from the aged and rejuvenated pure TGS crystal (a) and D-serine admixtured TGS crystal (b).

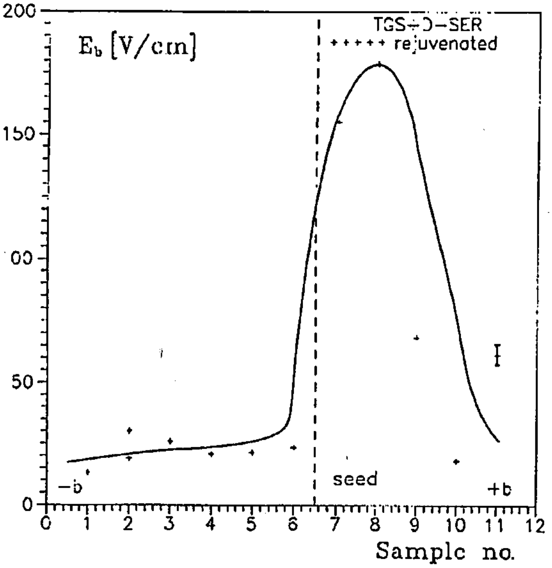

Fig. 6. The values of the bias field E_b for different sites of the sample cut-out from the rejuvenated D-serine admixtured crystals.

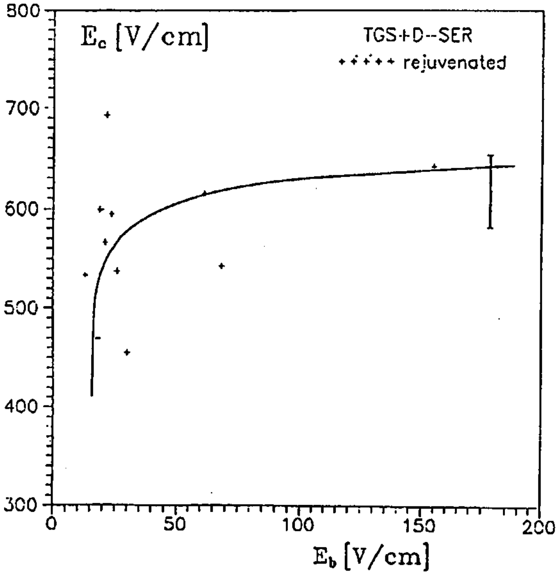

Fig. 7. The coercive field E_c versus the bias field E_b for the rejuvenated D-serine admixtured crystals.

4. Discussion of the results and conclusions

The obtained dependence of the maximum permittivity on the site of the sample cut-out, illustrated in Figs. 3a and 3b, is similar for the aged pure TGS crystal and DSTGS crystal, and can be described as a linear function decreasing from $-b$ to $+b$. After rejuvenation of the samples of pure TGS, a significant increase in the maximum permittivity, $\varepsilon_{\max}$ and $\Delta\varepsilon_{\max}$, is observed on the $+b$ side (and the obtained dependence is of the parabolic shape).

In the DSTGS crystals the dependence of the maximum permittivity on the site of the sample cut-out along the b axis from $-b$ to $+b$ decreases. For the rejuvenated pure TGS crystal this dependence is of parabolic shape with the lowest values of the maximum permittivity measured for the samples cut out in the vicinity of the nucleus and higher for the samples cut out at the ends of the crystal. The maximum permittivity values are higher by one order of magnitude for the pure TGS crystals than for the DSTGS crystals. It may be supposed that D-serine admixture stabilizes one sense of the polarization vector in a given crystal to a greater degree than it occurs in the process of spontaneous ageing.

In the pure TGS crystal the coercive field values are the lowest in the vicinity of the seed (Fig. 5a), whereas in the DSTGS crystal the coercive field values are the highest for the samples cut out close to the seed (Fig. 5b). The TGS crystals admixtured with L-serine and D-serine [8, 9] (similarly as those admixtured with L-α-alanine [4, 7] or D-α-alanine [11]) grow asymmetrically with respect to the seed. In the case of D-serine TGS on the longer side ($-b$) the maximum permittivity values are higher and the bias field values are lower than on the shorter side ($+b$). This confirms that D-serine admixture is asymmetrically built into the crystal causing an inhibition of growth along the b axis on the $+b$ side. Additional evidence supporting this conclusion is that a TGS crystal admixtured with DL-serine [18] grows symmetrically with respect to the seed. Similar results for LATGS crystals have been obtained by Březina, Havránková, Váša [19] and Nakatani [6].

The results of the measurements performed for the D-serine admixtured crystals allow us to draw the following conclusions:

1. The maximum permittivity values $\varepsilon_{\max}$ and $\Delta\varepsilon_{\max}$ decrease along the b axis from $-b$ to $+b$.
2. The values of spontaneous polarization do not depend on the site of the sample cut-out.
3. The coercive field values are greater in the vicinity of the seed than at the ends of the crystal measured along the b axis and increase after crystal rejuvenation.
4. The bias field values are greater on the $+b$ side than on the $-b$ side of the b axis.
5. The D-serine admixture is asymmetrically built into the crystal with respect to the seed with (010) planes, less admixture is build on the $-b$ side (longer part of the crystal) than on the $+b$ side (shorter one) of the b axis.

The results of the measurements performed for the pure TGS crystal lead to the following conclusions:

1. For the aged crystal the maximum permittivity values $\varepsilon_{\max}$ and $\Delta\varepsilon_{\max}$ are exponentially dependent on the site of the samples (b-cuts) cut out in various positions along the b axis from $-b$ to $+b$.
2. Spontaneous polarization does not depend on the site of the sample cut-out.
3. The coercive field E_c is higher at the ends of the crystal along the b axis than in the vicinity of the seed of growth, after rejuvenation its values decrease.

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