

ANISOTROPY OF THE DIELECTRIC PROPERTIES IN DIGLYCINE NITRATE

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The anisotropy of the dielectric permittivity and spontaneous polarization for pure and α -alanine doped diglycine nitrate has been studied. The actual polar direction is considered to be the normal direction to the 60°X-cut. The deviation of the spontaneous polarization vector in the mirror plane m for the ferroelectric phase has not been observed. The mechanism of partial substitution of alanine for glycine in this crystal is shown to be the same as in triglycine sulfate.

Keywords: anisotropy, dielectric permittivity, spontaneous polarization, diglycine nitrate, phase transition, alanine doping.

INTRODUCTION

Diglycine nitrate (DGN) is very similar to widely studied ferroelectric crystals of the triglycine sulfate (TGS) family due to their physical, chemical and structural properties.¹ On the other hand, a number of features in the behaviour of physical parameters near the Curie temperature shows that the DGN occupies the specific place among another ferroelectrics which contains glycine in the structure.²⁻¹³ Unlike the crystals of TGS family, the phase transition of order-disorder type in DGN occurs with the change of symmetry from a centrosymmetric $2/m$ point group in the paraelectric phase to polar m in the ferroelectric phase and the transition itself occurs at lower temperature ($T_c = 206$ K) in contrast to the case with TGS.³ The direction of spontaneous polarization P_S is near [101] direction.¹

According to the symmetry of the ferroelectric phase of DGN there is no unique direction of the polarization vector. The symmetry limitation requires the polar vector to be in the mirror plane m and its change (turn) is possible in this plane.

For DGN the fairly large deviation of the spontaneous polarization vector from [101] direction with the lowering of the temperature has been detected by the pyroelectric method on the basis of the results of the temperature dependences of P_S and their projections on the (100) and (001) plane measurements.⁶ However, the data of the studies⁷⁻¹² are contradicted by the results and conclusions of paper.⁶

It is known¹⁴⁻¹⁶ that considerable changes of the dielectric behaviour of TGS are produced by the effect of organic substances (similar to glycine) doping. It is evident that the same visible changes of the dielectric properties should be expected for the doped DGN.

The aim of the present paper is further investigation of the behaviour of dielectric

permittivity and spontaneous polarization of the pure and alanine doped DGN crystals over a wide temperature range in order to determine the actual polar direction and re-examine the effect of the deviation of P_S direction with temperature as well. Besides, it was intended to study the mechanism of the partial substitution of the glycine molecules by alanine molecules in case of DGN.

EXPERIMENTAL

The single crystals of the pure DGN were obtained by slow evaporation of the aqueous solution which contained stoichiometric quantities of glycine and nitric acid.⁵

The amino acids exist in two optically active forms and the most important results of the dielectric properties for TGS were obtained with the alanine as dopant.¹⁴⁻¹⁶ For this reason, the *L*- α -alanine (a left-hand crystal) and *D*- α -alanine (a right-hand crystal) were chosen as the dopant of the DGN.

A series of the single crystals of alanine doped DGN were grown by similar way, as for pure DGN, for the saturated aqueous solutions containing 10, 15 and 20 per cent either *L*- α -alanine or *D*- α -alanine (LADGN-10, LADGN-15, LADGN-20, DADGN-10 and so on) by evaporation of the solvent at the constant temperature 30°C.

The external shape of the grown DGN crystals (pure and doped) is practically the same. For the measuring of the physical properties of the DGN we used a left-angles system of the coordinates¹⁷ (Figure 1). The *X*-axis and *Z*-axis lie in the mirror plane *m* and the *Y*-axis is perpendicular to its plane. The angle included between the crystallographic *c*-axis and *Z*-axis is about $\sim 7^\circ$.¹ In Figure 1 the *X'* and *Z'* axes which correspond to orientation of the optical indicatrix axes⁷ at the room temperature and [101] direction are shown as well.

In order to study the anisotropy of the dielectric properties of pure and doped DGN crystals some series of the separately grown substances (DGN, LADGN AND DADGN) were prepared. The cutting orientation was chosen in such a way that a normal to surface of the sample lay in the mirror plane and made an angle with *X*-axis. The number of the various cuts for the samples was 12 for pure DGN and 6 for each of the crystals doped by certain degrees. Besides, the samples of *Y*-cut were prepared as well. Taking into account that for the crystals grown from the same matter solutions the effect of different unipolarity is possible,⁹ each series of the samples with certain degree of doping was prepared from the same crystal.

The dielectric constant was measured with a.c. capacitance bridge at frequency 1 kHz and field stress about 0.5 V/cm. The 50-Hz ferroelectrics hysteresis loops were detected by means of the modified scheme of Sawyer-Tower which compensated the linear polarization. The magnitudes of P_S were determined by extrapolation of the induced part of polarization to the values at zero applied field. Actually, due to neglect of the kinetic process the magnitudes of P_S determined by this method are different from real ones by not more than 5-7 per cent. However, this error is constant and doesn't influence the relative changes of P_S with direction of the external field. In this case, the error occurred in the determination of the geometrical size and the accuracy of the samples orientation (3 per cent) are more

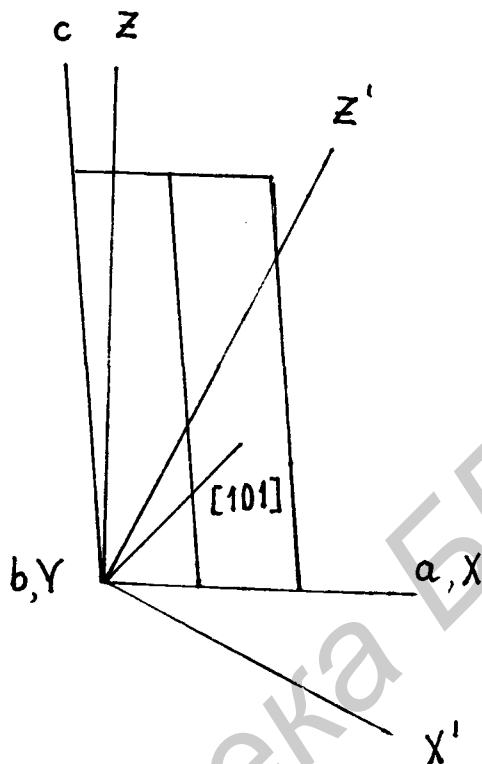


FIGURE 1 Projection of the DGN shape on the mirror plane m .

important than error connected with the extrapolation process. Taking into account the accuracy of the measurements this error could not exceed more than 2 per cent. The hysteresis loops were photographed and then projected on the screen where the value of P_S was measured.

For specifying the P_S direction and for observing the deviations of the P_S with temperature the cross-sections of indicatory surface of ϵ and P_S by mirror plane m were plotted. In accordance with this, the temperature dependences of $\epsilon = \epsilon(T)$ and $P_S = P_S(T)$ for the samples of various cuts of DGN in a certain temperature range were studied. Taking into account the existence of the self unipolarity of all studied crystals, it was found, that the temperature of the phase transition T_c for dielectric constant ϵ and polarization, P_S , can differ from sample to sample not more than 1-1.5 K as a result of diffusion of phase transition by grown defects. For dielectric constant the T_c was determined on the basis of the $\epsilon^{-1} = \epsilon^{-1}(T)$ dependence by means of extrapolation of linear part $\epsilon^{-1} = \epsilon^{-1}(T)$ of paraelectric phase till crossing with temperature axes.

RESULTS

1. Dielectric properties of the pure DGN crystals

The temperature dependences of the reciprocal dielectric constants and sponta-

neous polarization for different cuts of DGN are presented in Figure 2. It is evident from Figure 2a that the behaviour of the dielectric constant ϵ in the paraelectric phase follows the Curie-Weiss law, but the temperature range Curie law holds $\Delta T = T - T_c$ and the value of the Curie constant depends on orientation of the sample measured. For cuts close to the polar direction the temperature range is maximum and equal to 6 K while for cuts which are far away from the polar cut ΔT is about 2 K. The deviation from the Curie law in a range far from T_c can be explained by the existence of large contribution of the noncritical degrees of freedom of the dielectric permittivity.¹¹ Moreover, for DGN the experimental data (Table I) shows not only a narrow region of the Curie law, but a relatively smaller value of the Curie constant in comparison with crystals in the TGS family.

In the temperature range $\Delta T \leq 4$ K the experimental dependences of $P_s(T)$ can be approximated by the power law

$$P \sim (T_c - T)^n. \quad (1)$$

On the basis of this dependence in the plot in a double logarithmic scale (Figure 3) it was found that the value of the critical index n is about 0.5 in agreement with the Landau theory.

As it is evident from Figure 2 and Table I the value of the ϵ and P_s for [101] direction isn't the largest in DGN. In order to improve the direction along which the ϵ and P_s values are largest the cross-sections of the indicatory surfaces by mirror plane m were plotted on the basis of data in Table I (Figure 4).

In the coordinate system where the reference axes lie along the directions of proper vectors of the tensor of dielectric permittivity, the indicatory surface of $\epsilon(\theta)$ (Figure 4a) is described by the equation:

$$\epsilon(\theta) = [\epsilon_3^0 + \epsilon_3(T)] \cdot \cos^2\theta + \epsilon_2^0 \cdot \sin^2\theta, \quad (2)$$

where θ is angle included between the direction of the largest value of ϵ and the normal to surface of the sample; ϵ_3^0 and ϵ_2^0 represent the contribution of the noncritical mode to the values of the component ϵ_2 and ϵ_3 of tensor ϵ ; $\epsilon(T)$ is

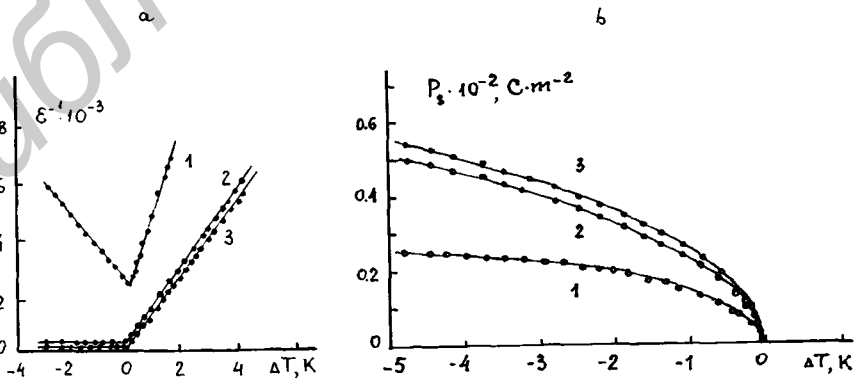


FIGURE 2 (a) The temperature dependences of the reciprocal dielectric permittivity $\epsilon^{-1} = \epsilon^{-1}(T)$ for various cuts of pure DGN 1 - $\theta = 0^\circ$; 2 - $\theta = 45^\circ$; 3 - $\theta = 60^\circ$ and (b) the temperature dependences of the $P_s = P_s(T - T_c)$ of the various cuts of pure DGN samples 1 - $\theta = 0^\circ$; 2 - $\theta = 45^\circ$; 3 - $\theta = 60^\circ$.

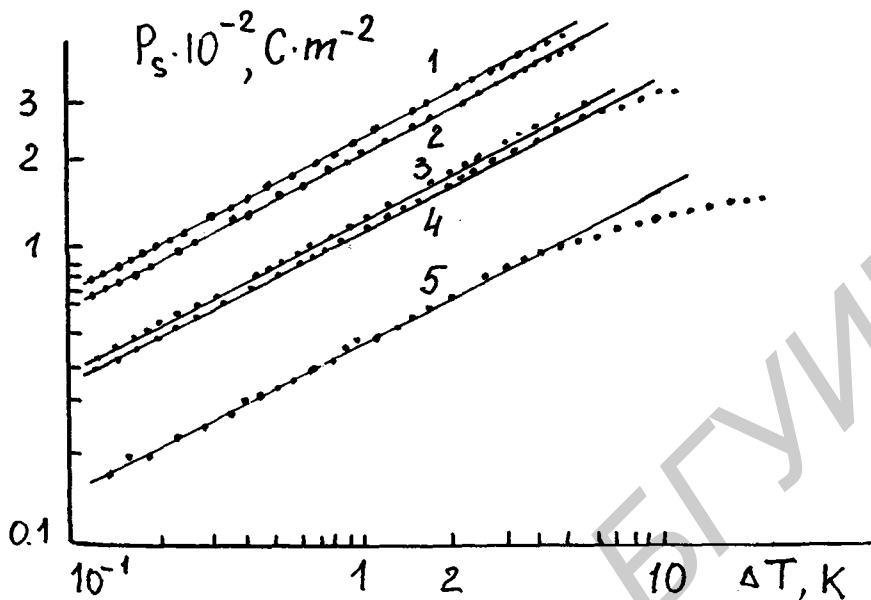


FIGURE 3 The temperature dependences of spontaneous polarization $P_s(T_c - T)$ of DGN for various directions in a double logarithmic scale: 1 - $\theta = 60^\circ$; 2 - $\theta = 45^\circ$; 3 - $\theta = 80^\circ$; 4 - $\theta = 90^\circ$; 5 - $\theta = 300^\circ$.

TABLE I

The values of the Curie-Weiss constant (C) and spontaneous polarization ($P_s \cdot 10^{-2} \text{C} \cdot \text{m}^{-2}$) of pure and doped with α -alanine DGN crystals ($\Delta T = T_c - T = 1 \text{ K}$)

Cuts (θ)	Crystal									
	DGN		LADGN-10		LADGN-15		DADGN-10		DADGN-15	
	C, K	P_s	C, K	P_s	C, K	P_s	C, K	P_s	C, K	P_s
0	260	0.130	225	0.125	210	0.110	230	0.140	260	0.160
30	600	0.215								
40	700	0.225								
45	820	0.230	800	0.220	820	0.225	810	0.225	810	0.235
60	860	0.240	900	0.240	900	0.245	833	0.250	840	0.260
70	790	0.235								
80	700	0.215								
90	620	0.195	730	0.180	730	0.205	700	0.175	714	0.195
97	460	0.185								
300	175	0.100								
315	90	0.050								
330	0	0								

contribution of the critical mode to ϵ_3 described by the Curie-Weiss law. For DGN the Curie constant $C = 850 \text{ K}$, $\epsilon_3^0 = 15$ and $\epsilon_2^0 = 10$. That is why in the vicinity of phase transition $T - T_c \leq 5 \text{ K}$, $\epsilon_3(T) \gg \epsilon_3^0 \approx \epsilon_2^0$ and equation (2) become more simple

$$\epsilon(\theta) = \epsilon_3 \cdot \cos^2\theta, \quad (3)$$

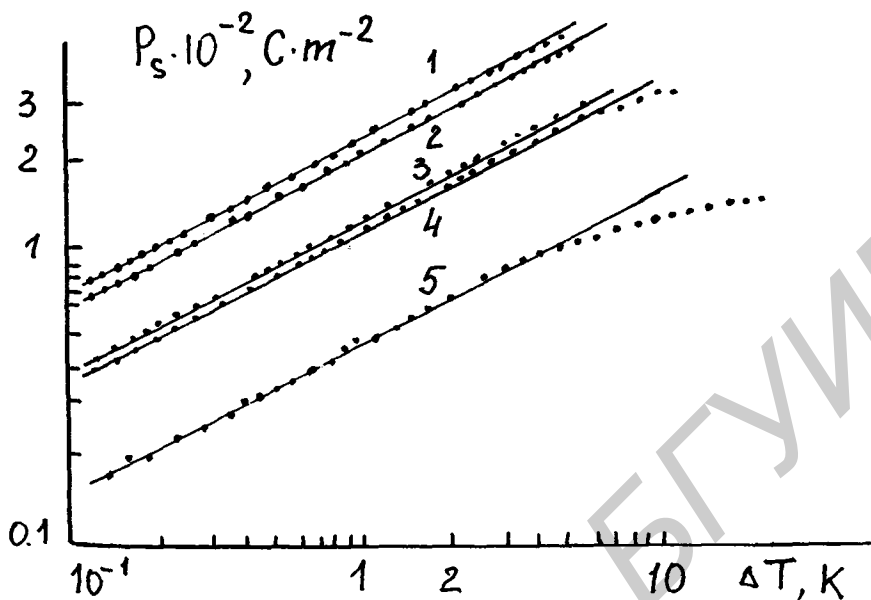


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	C, K	P_s	C, K	P_s	C, K	P_s	C, K	P_s	C, K	P_s
0	260	0.130	225	0.125	210	0.110	230	0.140	260	0.160
30	600	0.215								
40	700	0.225								
45	820	0.230	800	0.220	820	0.225	810	0.225	810	0.235
60	860	0.240	900	0.240	900	0.245	833	0.250	840	0.260
70	790	0.235								
80	700	0.215								
90	620	0.195	730	0.180	730	0.205	700	0.175	714	0.195
97	460	0.185								
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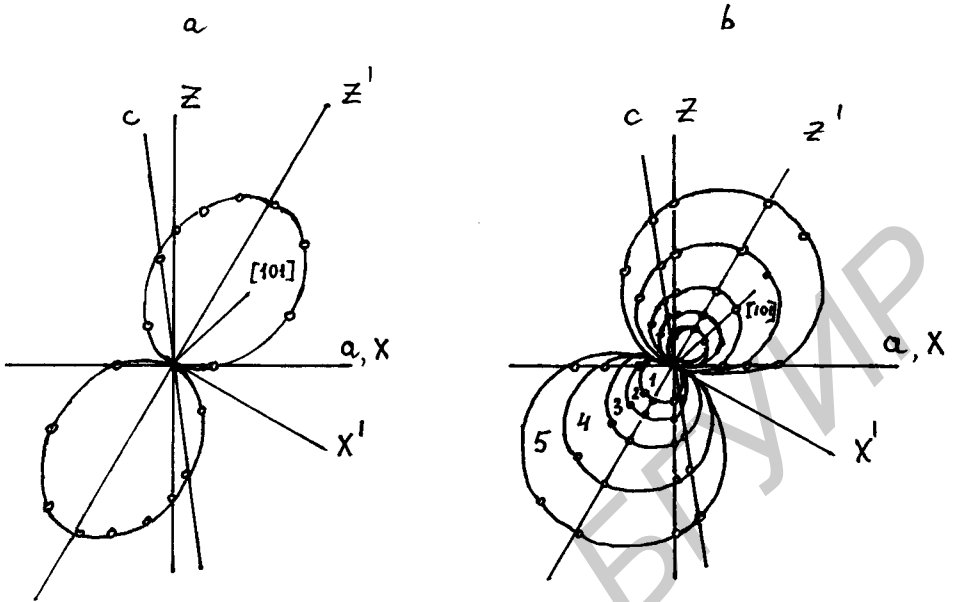


FIGURE 4 The cross-sections of indicatory surface of ϵ and P_S by mirror plane m for pure DGN. (a) $\epsilon(\theta)$, $\Delta T = 2$ K and (b) $P_S(\theta)$, 1 - $\Delta T = 0.5$ K; 2 - $\Delta T = 1.0$ K; 3 - $\Delta T = 2.0$ K; 4 - $\Delta T = 5.0$ K; 5 - $\Delta T = 10.0$ K.

where the direction of the principal axes ϵ_3 corresponds to the direction of normal to 60° -X cut with degree of accuracy $\pm 1^\circ$.

As for spontaneous polarization, the cross-section of indicatory surface by mirror plane m (Figure 4b) is quite well described by the equation of indicatory surface of the polar vector

$$P_S(\theta) = P_{60} \cdot \cos \theta, \quad (4)$$

where P_{60} is the largest value of the P_S . The differences in the polarization P_S values at $\theta < \pm 15^\circ$ is less than 10 per cent and it slightly exceeds the experimental error 5%. However, as the values of P_S were determined for cuts with large values of angle where the differences in values of polarization are essentially exceeding the error of experiment, the data analysis carried out on the basis of the Equation (4) made it possible to determine the direction of principal axes of the indicatory surface of P_S with a precision of 3° (1 per cent). The direction of the P_S which was determined in such a way as in case with ϵ , coincides with the normal of 60° -X-cut and by 2 – 4° differs from the Z' -axis direction. This difference may be connected with rotation of the characteristic surface and the optical ellipse in the temperature range 200 – 290 K.

2. Dielectric properties of the doped DGN crystals.

The obtained experimental temperature dependences $\epsilon = \epsilon(T)$ of the samples of various cuts of the doped DGN crystals with either L - α -alanine or D - α -alanine

show the decreasing of the largest values of ϵ in the vicinity of T_c and shifting the phase transition temperature T_c into the range of higher temperature with increasing alanine concentration.

The hysteresis loop shapes of the doped DGN crystals indicate an existence of the self bias field ϵ_B whose values grow with the increasing of α -alanine concentration. The addition of the alanine into the crystal changes the form of the $P_S = P_S(T)$ dependence only. For the doped DGN crystals the dependence of the temperature dependences of reversible part of polarization in the vicinity of T_c ¹¹ seems to be similar to the dependence for pure DGN observed under the external field influence.¹² The value of the saturated spontaneous polarization (at $T_c - T > 20$ K) is practically the same as for the pure DGN.

Using Equations (3) and (4) the cross-sections of the indicatory surfaces of the ϵ and P_S by mirror plane m either for L - α -alanine or D - α -alanine doped DGN crystals were plotted. In Figure 5 only the results for DADGN-15 are presented. As for other substances, the similar dependences are observed differing from each other by the values of ϵ and P_S . The form of all cross-sections of the indicatory surfaces shows that the P_S direction of DGN crystals doped with alanine coincides in the direction of the normal to $60^\circ X$ -cut.

DISCUSSION

According to Sato³ the contribution to the value of spontaneous polarization are due to three ions: glycine I, glycine II and NO_3^- . When the $[101]$ direction was

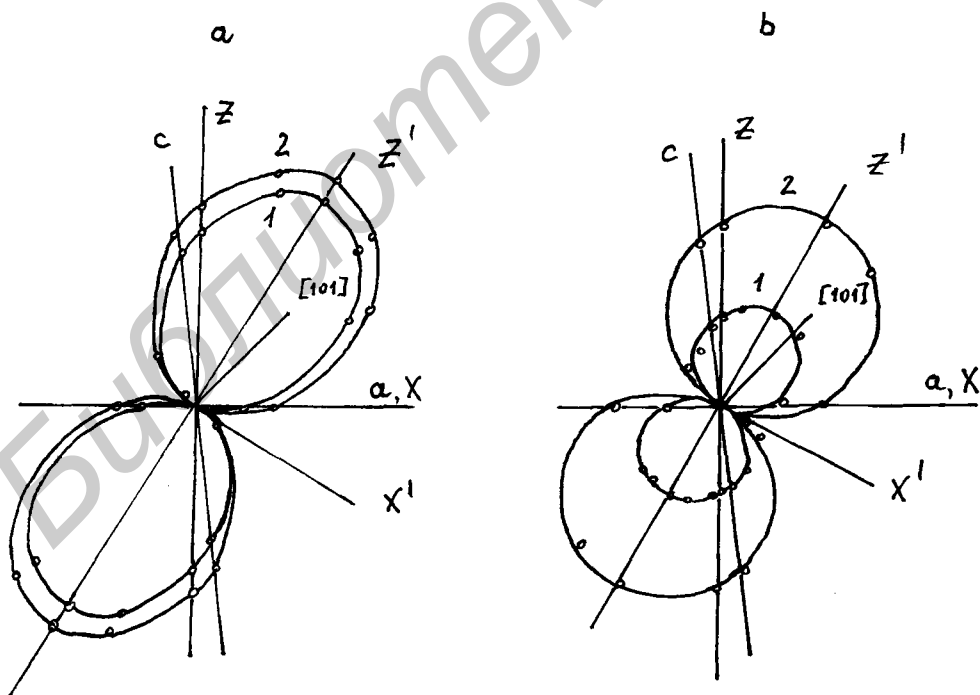


FIGURE 5 The cross-sections of indicatory surface of ϵ and P_S by mirror plane for pure and with D - α -alanine doped DGN crystals: (a) $\epsilon(\theta)$, $\Delta T = 2$ K; 1 - DGN; 2 - DADGN-15 and (b) $P_S(\theta)$; $\Delta T = 1$ K; 1 - DGN; 2 - DADGN-15.

chosen as the polar the similarity of the DGN and TGS molecule structure was taken into account.

For the ferroelectric phase of DGN the unit cell parameters are the following³: $a = 9.485 \text{ \AA}$, $b = 5.132 \text{ \AA}$, $c = 9.089 \text{ \AA}$, $\beta = 97.89^\circ$ and the angle between the [100] and [101] directions is about 48.9° . It means that the projections of P_S along the X- and Z-axes are $P_x = 0.65 \cdot P_S$ and $P_z = 0.75 \cdot P_S$ respectively, i.e. they slightly differ from each other. Then the values of the dielectric constants ϵ_{11} and ϵ_{33} in the vicinity of the Curie temperature would differ slightly from each other as well. However, the experimental results^{5,10} show that the largest value of the ϵ_{11} is much less than the ϵ_{33} value. This experimental result may be explained only if we suppose that the direction vector of the spontaneous polarization is different from [101] direction.

The results of the present work on the anisotropy of dielectric permittivity as well as spontaneous polarization and the analysis of cross-section of indicatory surfaces of ϵ and P_S by mirror plane m (Figure 2, 4; Table I) show that the largest values of ϵ and P_S are observed along the direction of the normal to 60° X-cut of pure DGN. The direction differing from [101] direction is likely to be considered as the polar one. The polar direction coincides with the direction of the normal to the 60° X-cut and is confirmed by the data of Reference 4, but in contrast to the mechanism of onset of P_S suggested by Sato³ in which the onset of the polar state in DGN is connected with the reorientation of "heavy" NH_3^+ and NO_3^- group.

Moreover, the data of Table I and Figure 4 show that in the temperature range $T_c - T \leq 10 \text{ K}$ the deviation of P_S vector from direction of the normal to 60° X-cut isn't determined in contrast with the results of Reference 6 within the observed experimental error. It should be pointed out that in accordance with Reference 5 the DGN possess the self unipolarity which is mainly dependent on the direction in the crystal. Thus, along the [101] direction it practically equals zero while along the [001] direction the value of the internal bias field is $\epsilon_B \sim 700 \text{ V/cm}$. Taking into account the complex temperature dependence of the internal bias field in DGN one may suppose that the sample used for the pyroelectric measurement⁶ was oriented in a different way and was therefore under unequal electrical conditions. That is why in the present paper the value of spontaneous polarization was determined by means of the dielectric hysteresis loop method in order to eliminate the measurement errors.

Attention should be paid to the fact that within the experiment, the determined P_S direction is consistent with the optical indicatrix axis in Reference 7. This correspondence isn't associated with crystal symmetry and isn't required. The optical indicatrix axis was found at room temperature (at paraelectric phase) and its correspondence with the P_S direction is found to be crystallographically specific. So, the Z'-axis indicates the specific direction of the crystal in paraelectric phase which with the lowering of the temperature before and after phase transition (206 K) remains specific. On the basis of the data mentioned above, we think this specific direction is unlikely to begin changing its orientation with further lowering temperature (below T_c).

As it was noted already, for the doped DGN crystals the shift of the T_c is typically towards higher temperatures. Nevertheless, in a number of cases the shift of the T_c towards the lower temperatures was observed in the range of the 1 K. Such

behaviour of T_c may be connected with the sample's monodomain degree and explained by the fact that the substitution of the glycine molecules by alanine results in the lowering of the phase transition temperature due to decreasing the concentration of the ferroelectric switching dipoles. On the other hand, the permanent self bias field E_b , which occurs as a substitution effect, increases the T_c values. Shift in T_c depends on which of the mechanisms is predominant.

The diffusion of phase transition and connected processes with it, as in case with TGS^{14,15}, can be explained by existence of large internal electric fields in doped samples of DGN resulting in appearance of polarization far above the phase transition temperature due to the local lowering of the paraelectric phase symmetry by the dopants. These and some other similar results in the glycine-containing crystal structure allow to suppose that the mechanism of partial substitution of glycine molecules by dopance of the α -alanine will be the same for all such kinds of crystals (including DGN). This suggestion may be confirmed by the experimentally determined dipole moment of α -alanine molecule together with the dipole moment of the glycine molecule in the DGN crystal structure as a result of the absence of deviation of P_S vector in doped crystals from the polarization direction in pure crystals (Figure 5).

In fact, all experimentally obtained temperature dependences of the dielectric parameters showed the more essential influence of D - α -alanine dopance in comparison with L - α -alanine dopance on the DGN physical properties. For the DADGN the larger diffusion of phase transition, wider temperature ranges of pyro- and piezoactivity of the samples⁹ (at the same alanine concentration in comparison with LADGN solutions) were observed.

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