

Optical properties of D-serine doped TGS crystals for pyroelectric sensors*

V.YU. KURLYAK¹, V.YO. STADNYK¹, B.V. ANDRIYEVSKY^{2†}, M.O. ROMANYUK¹, Z.O. KOHUT³,
V.M. GABA³

¹The Ivan Franko National University of Lviv, 8 Kyrylo-and-Mefodii St., UA-79005 Lviv, Ukraine

²Faculty of Electronics and Computer Sciences, Koszalin University of Technology,
2 Śniadeckich St., PL-75-453, Koszalin, Poland

³National University "Lviv Politechnic", 12 Bandera St., UA-79013 Lviv, Ukraine

Refractive and birefringence indices in the range of transparency of 300 to 700 nm for triglycine sulphate crystals doped with D-serine molecules have been measured in the temperature range of 290 K to 340 K. The obtained optical properties are discussed together with characteristic electrical features of these materials used as pyroelectric sensors for measurement of temperature. The experimental results obtained in this study will be necessary as the reference data for comparison with the calculated refractive indices of TGS + D-serine on the basis of density functional theory. Determination of the proper position of D-serine, will reveal the features of TGS + D-serine crystal structure necessary to achieve stable unipolarity.

Keywords: *pyroelectric sensors; ferroelectrics; triglycine sulphate; optical properties*

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1. Introduction

Sensors that can convert optical radiation into the electric energy are known as pyroelectric sensors. A capacitor-like device with a dielectric layer in the form of crystalline plate is a sensitive part of the pyroelectric sensor. Thin layer of the light absorbing substance is deposited on one of the electrodes. As a result, the optical energy absorbed by this substance is converted into the thermal one which consequently increases temperature of the crystal. This leads to the change in the pyroelectric polarization of the crystal plate which can be recorded and used for the measurement of sensor temperature. Commonly, several such pyroelectric sensors are connected in series to create one measuring device. This may guarantee the insensitivity of the measuring sensor to ambient temperature changes and enable the alternating output voltage

when moving the focused image of an object on the sensitive surface of the sensor.

The spectral sensitivity of the sensor is determined by the absorption capacity of the pyroelectric coating plate in a certain frequency range of electromagnetic radiation. It is also influenced by optical filters installed in the front of the sensitive element.

The main parameters of pyrosensors are dependent on the material constants of the sensitive crystalline plate of the device. Relations for the figure of merit of a pyroelectric sensor acting in the mode of impulse radiation and empty circle were presented in the literature [1–3]:

$$M_1 = \frac{\gamma}{c_1} \quad (1)$$

In the mode of empty circle and low flux:

$$M_2 = \frac{\gamma}{c_1} \varepsilon \text{ and } M_3 = \frac{\gamma}{c_1} (\varepsilon \cdot t g \delta)^{0.5} \quad (2)$$

where ε is dielectric permittivity, γ is pyroelectric coefficient, c_1 is thermal capacity of a unit volume.

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†E-mail: bohdan.andriyevskyy@tu.koszalin.pl

The figure of merit M_1 is a transforming coefficient at low load resistance, M_2 is the same but at high resistance, and M_3 characterizes the detecting ability of the sensor.

Materials for pyroelectric sensors should have the values M_1 , M_2 and M_3 as high as possible. The choice of pyroelectric material for the sensor depends not only on the figure of merit but is influenced by other factors. The crucial ones are:

1. temperature of ferroelectric phase transition T_C , which determines the temperature and dynamic range of the sensor;
2. mechanical strength and hydrophobicity;
3. magnitude of acoustic losses, which corresponds to the attenuation of elastic vibrations;
4. stability of single domain state;
5. level of additional noises;
6. time stability of parameters;
7. simplicity of technology of the sensitive element;
8. possibility of manufacturing thin layers, while preserving the characteristics of the bulk material;
9. possibility of manufacturing sensitive elements of sensors with large dimensions.

TGS crystals are among the most widely used pyro-active materials [4–12]. Despite the fact that almost every year tens of thousands of new synthesized pyroactive crystals, ceramics and polymers are synthesized, TGS is currently the material with the highest figure of merit M_3 , which characterizes the detecting ability of sensors. Efforts to remove the drawbacks inherent to TGS are constantly undertaken. The main aims of these efforts are to obtain a stable single domain structure of TGS, insensitive to temperature, climate and radiation changes, and able to extend the temperature range of the pyroelectric sensor sensitivity.

Since pure TGS and isomorphous crystals are “soft” ferroelectric materials with low coercive fields, they have a domain structure with unstable unipolarity. In order to obtain stronger ferroelectric activity they are doped during the crystal growth

by ions of chromium, copper, nickel or the glycine molecules of TGS are replaced by the structurally similar ones, such as L- α -alanine [13].

Presently, pure TGS are practically not used for pyroelectric sensors and the TGS doped crystal is one of the most often used for the fabrication of highly sensitive pyroelectric devices operating at low frequency modulation.

The introduction of structurally similar organic impurities into TGS crystal causes fixation of one of the polarizations $+P_c$ or $-P_c$ and appearance of a bias field E_b in the crystal. As a result, the dielectric parameters of the doped crystals undergo minor changes during spontaneous aging that is essential in practical use of these crystals.

It is known that the molecular serine ($C_3O_3NH_7$) exists in two stereoisomeric forms, L and D, which differ in the sign of optical activity. Stereoisomers are isomeric molecules that have the same molecular formula and sequence of bonded atoms, but that differ only in the three-dimensional orientation of their atoms in space (L- and D-serine molecules may be converted one to another by applying the symmetry operation of mirror reflection) [14–18]. In crystals, L- or D-serine may exist in the monoprotonated, $CH_2(OH)CH(NH_3)COOH^+$, and zwitterion, $CH_2(OH)CH(NH_3)COO^-$, forms [15–18]. For example, in one of the serine containing crystal ($C_3O_3NH_7$) $_2$ H $_3$ PO $_4$ H $_2$ O [17, 18], the corresponding lengths of the bonds C–C and C–N in both forms of serine molecule (monoprotonated and zwitterion) are similar and are equal to $d_{C-C} = 1.514 \text{ \AA}$ and 1.527 \AA and $d_{C-N} = 1.486 \text{ \AA}$ and 1.497 \AA , respectively. However, due to deprotonation of the carboxyl group in zwitterion, two C–O bonds become close to each other, i.e. 1.250 \AA and 1.254 \AA . The later magnitudes are close to the averaged C–O distances in the carboxyl group COOH of the monoprotonated ion $CH_2(OH)CH(NH_3)COOH^+$, 1.205 \AA and 1.316 \AA .

In a TGS crystal with admixture of L-serine, these two forms of serine are connected one to another by hydrogen bonds. It was revealed that a relatively small amount of L-serine in the freshly prepared TGS + L-serine crystal increases

substantially its spontaneous polarization [16, 19]. Further increase of the concentration of serine admixture leads to a decrease of spontaneous polarization and increase of the coercive and bias electric fields. TGS + L-serine crystals grow asymmetrically along the b-axis when compared to their initial form. It was suggested in [19] that distribution of L-serine admixture is inhomogeneous. The admixture inhibits the growth of the crystal in b-axis direction, so that more impurities are embedded into the crystal in its less developed side. It was found that the internal electric field leads to the same effect as the external field applied to the crystal. Since the bias electric field E_b is higher for the growth of (0 0 1) pyramid than that of (1 1 0), the conclusion was derived that more impurities are embedded in the (0 0 1) pyramid during the crystal growth.

It was also found that for crystals with a low impurity concentration, maximum dielectric permittivity ϵ_{\max} is smaller than for the pure TGS crystal and the value of ϵ_{\max} decreases with increasing concentration of serine in the solution. The Curie temperature T_C of TGS + L-serine crystal is lower than that for pure TGS crystal. The temperature dependences of spontaneous polarization $P_s(T)$ and coercive field $E_c(T)$ of TGS + L-serine crystal show that spontaneous polarization decreases and coercive field increases with an increase of the L-serine concentration in the growth solution.

We have not found similar reference information on TGS + D-serine crystal, but one should expect similar effects to those observed in TGS + L-serine, described above. This suggestion is based on the fact that TGS + D-serine crystals grow asymmetrically with respect to the seed along b-axis, similarly to that observed for TGS + L-serine crystal, though the asymmetry in case of TGS + D-serine was found to be developed in the opposite direction of b-axis [20].

Optical and refractive methods are known to be a sensitive instrument for studying of the ferroelectric properties of crystals [21]. In the present study, the characteristics of optical refractive properties of TGS crystals doped with D-serine molecules in the

temperature range of 290 K to 340 K have been obtained and discussed in view of their application as pyroelectric sensors.

2. Experimental

For optical measurements, the parallel plate samples of TGS crystal doped with 5 % D-serine were cut from a (0 0 1) pyramid in the most developed part of the single crystal grown close to its seed region. Three kinds of the plates orientations, i.e. (1 0 0), (0 1 0), and (0 0 1), were cut for the measurements of the birefringence Δn_i of the material in three directions, $I = x, y, z$. For the study of refractive indices n , the plates of 0.1 mm to 0.2 mm thickness were used, whereas for the measurements of birefringence Δn , the plates of 2 mm to 3 mm thickness were employed. The crystal orientation of the plates was checked by conoscopic observation with He–Ne laser beam and additionally using a polarization microscope.

Dispersion of refractive index $n(\lambda)$ of a crystal were measured using the spectral interferometric Obreimov method [22]. In the method, a plane optical wave incident on the edge of a parallel plate crystal is splitting into two beams. Along the edge of geometrical shadow, the light beams passing through the crystals and environment are overlapping due to diffraction and they interfere. The corresponding difference of optical paths Δ depends on the refractive index n of a crystal and its geometric thickness d [22]:

$$\Delta = d(n - 1) \quad (3)$$

The refractive index n of a crystal may be presented as:

$$n(\lambda, T) = 1 + k\lambda/d(T) \quad (4)$$

The crystal sample thickness d is usually measured using a quartz dilatometer. The interference order k is obtained from the same relation 4 using results of separate measurements of n by the immersion Obreimov method at one wavelength λ [22]. Measurements of refractive indices using this method can be performed in the spectral range

of crystal transparency 290 to 750 nm and temperature range 77 K to 950 K with an accuracy near $\delta n \approx 2 \times 10^{-4}$.

3. Results and discussion

We have found that the TGS grown with addition of D-serine are characterized by smaller refractive indices n_x and n_z and larger n_y one in comparison with pure TGS, where x, y, and z are directions of the crystal and physical axes of the crystal (Fig. 1). The relations between refractive indices, $n_x > n_z > n_y$, and their corresponding dispersions, $dn_x/d\lambda > dn_y/d\lambda > dn_z/d\lambda$, for the TGS + D-serine crystals remain the same as those for pure TGS. Differences of refractive indices of TGS + D-serine and TGS crystals for the wavelength $\lambda = 300$ nm and 700 nm are as follows: $n_x^{(TGS+D-serine)} - n_x^{(TGS)} = -2.9 \times 10^{-3}$ and -2.0×10^{-3} , $n_y^{(TGS+D-serine)} - n_y^{(TGS)} = 3.6 \times 10^{-3}$ and 2.8×10^{-3} , $n_z^{(TGS+D-serine)} - n_z^{(TGS)} = -2.8 \times 10^{-3}$ and -1.8×10^{-3} . These results indicate that the degree of anisotropy of optical indicatrix of TGS + D-serine, determined as the value of maximum refractive indices difference, is smaller than for the pure TGS (Fig. 1). One of possible explanations of this result could be, in principle, the random positions of D-serine molecules in TGS + D-serine crystal. This, however, is only one explanation among many others. Other probable suggestion proposed earlier for TGS + L-serine crystals is location of D-serine in the place of glycine-I unit in pure TGS [19].

Analysis of the dependences $n_i(\lambda)$ for TGS + D-serine by the model of effective ultraviolet oscillators has been performed and the increase in $\Delta\lambda_{0y} = 8.5$ nm and decrease in $\Delta\lambda_{0x} = -5.2$ nm and $\Delta\lambda_{0z} = -4.3$ nm have been obtained in relation to the pure TGS. These results are in qualitative accordance with the changes of refractive index anisotropy discussed above.

It is known that the molecular refraction:

$$R = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{4}{3} \pi N_A \alpha_E \quad (5)$$

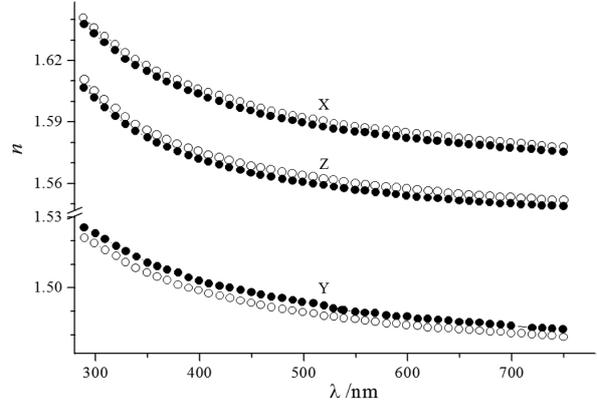


Fig. 1. Dispersion of refractive indices $n_i(\lambda)$ ($i = x, y, z$) of pure TGS (open circles) and TGS + D-serine (closed circles) crystals at ambient temperature, $T = 293$ K.

of TGS, being an additive value, is composed of approximately equal contributions of four molecular groups: (1) NH_3 ion, (2) glycine core, (3) carboxyl ion and (4) SO_4 ion with hydrogen bonds. Addition of D-serine $\text{CH}_2(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}$ into the TGS crystal or substitution of the glycine $\text{CH}_2\text{NH}_2\text{COOH}$ by D-serine should increase the molecular refraction R of TGS + D-serine. If, however, one takes into account corresponding increase in the molecular weight M , the averaged refractive index n of TGS + D-serine may be expected unchanged or changed only slightly, according to the relation 5. The latter conclusion is generally supported by the experimental results obtained (Fig. 1).

Temperature changes of the refractive indices n_i ($i = x, y, z$) of TGS + D-serine are linear in the paraelectric phase and nonlinear in the ferroelectric one (Fig. 2). The largest temperature changes of refractive indices in the polar phase are observed for the x-polarization. The relation $\partial n_x / \partial T > |\partial n_z / \partial T| > |\partial n_y / \partial T|$ takes place for TGS + D-serine, which is the same as for pure TGS. The only difference is in the magnitudes of $\partial n_i / \partial T$, which are much smaller than those for pure TGS. In other words, insertion of the D-serine admixture leads to a decrease in the temperature sensitivity of refractive indices $n_i(T)$. On the phenomenological level, this result is obtained due to the influence

of internal stresses and decrease in spontaneous electrical polarization of the doped crystals [23–25]. On the microscopic level, the results observed may be associated with the fact that all glycine molecular groups in TGS are almost plane and are oriented perpendicularly to the polar y -axis, what determines the anisotropy of refractive indices of TGS, $n_x > n_z > n_y$. If the D-serine molecular group is oriented along the polar axis in TGS + D-serine, this may result in a change in the corresponding optical anisotropy due to the relative increase of n_y and decrease of n_x and n_z , which is really observed.

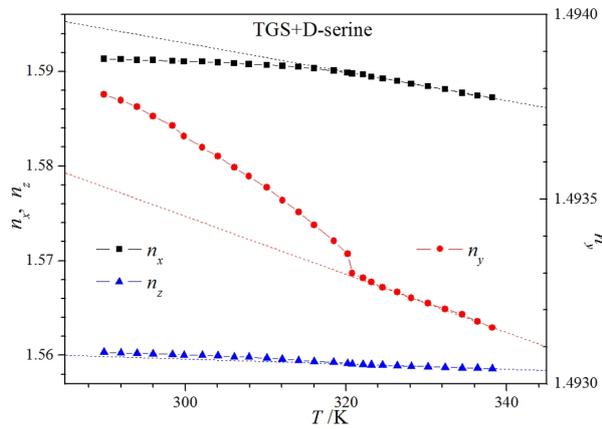


Fig. 2. Temperature dependences of refractive indices $n_i(T)$ ($i = x, y, z$) of TGS + D-serine at the wavelength $\lambda = 500$ nm.

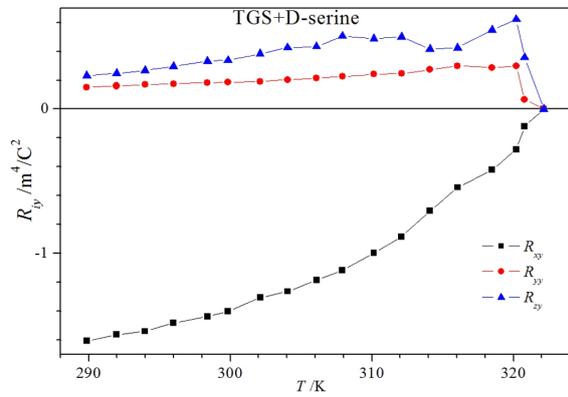


Fig. 3. Temperature dependences of coefficients of quadratic EOE R_{iy} ($i = x, y, z$) of TGS + D-serine at the wavelength $\lambda = 500$ nm.

Changes in the dependences $n_i(T)$ observed at the Curie temperature, $T_C = 322$ K (Fig. 2) may be associated with the ferroelectric phase transition resulting in the spontaneous electrooptic effect (EOE) in the crystal. Because of the presence of the inversion symmetry operation in the structure of paraelectric phase of TGS, the linear EOE is impossible [26]. For this reason, the spontaneous increments of refractive index of TGS may be presented at first approximation in the form:

$$\delta n_i = \frac{1}{2} n_i^3 R_{iy} P_y^2, i = x, y, z \quad (6)$$

where R_{iy} are coefficients of the quadratic EOE, P_y is the spontaneous polarization, P_s along y -axis of TGS and n_i are refractive indices. The coefficients of quadratic EOE, R_{iy} were calculated using the relation 6 in the temperature range of 290 K to 322 K (Fig. 3). For the calculations of R_{iy} , the temperature dependence of square of spontaneous polarization has been taken as $P_y^2 = a(T - T_C)$, where the coefficient a is equal to $3 \times 10^{-5} \text{ C}^2/(\text{m}^4 \cdot \text{K})$ [27, 28].

Although the relation between principal refractive indices of TGS + D-serine is the same as for TGS, $n_x > n_z > n_y$, the temperature dependences of spontaneous temperature changes $\delta n_i^{(s)}$ (differences between experimental points and corresponding dashed lines in Fig. 2 and Fig. 4) and corresponding coefficients of quadratic EOE, R_{iy} are different (Fig. 2 – 5).

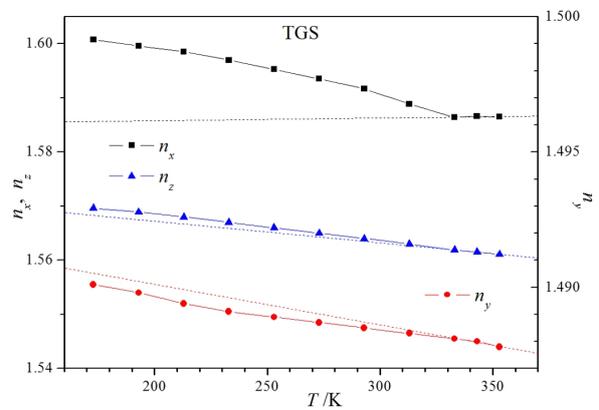


Fig. 4. Temperature dependences of refractive indices $n_i(T)$ ($i = x, y, z$) of TGS at the wavelength $\lambda = 500$ nm.

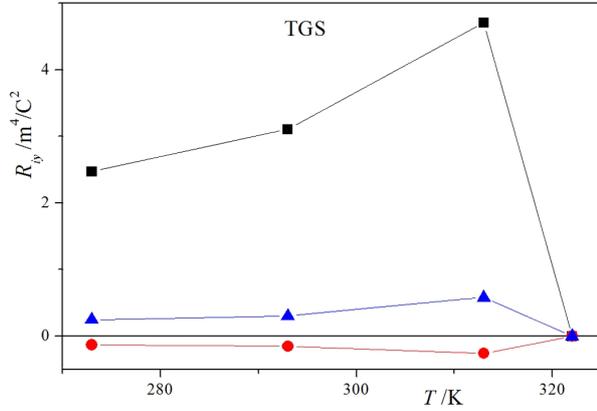


Fig. 5. Temperature dependences of coefficients of quadratic EOE R_{iy} ($i = x, y, z$) of TGS at the wavelength $\lambda = 500$ nm.

The values of birefringence $\Delta n_i = n_j - n_k$ ($i, j, k = x, y, z$) of TGS + D-serine are different from those for the pure TGS (Fig. 1). At the same time, the relations between the dispersions of principal birefringence remain the same as those for pure TGS, $|\partial\Delta n_z/\partial\lambda| > |\partial\Delta n_x/\partial\lambda| > |\partial\Delta n_y/\partial\lambda|$. It is seen from Fig. 1 that the relations $\Delta n_x^{(\text{TGS}+\text{D-serine})} < \Delta n_x^{(\text{TGS})}$ and $\Delta n_z^{(\text{TGS}+\text{D-serine})} < \Delta n_z^{(\text{TGS})}$ take place. The difference between the birefringences $\Delta n_y^{(\text{TGS}+\text{D-serine})} - \Delta n_y^{(\text{TGS})}$ changes between positive 5.59×10^{-4} (at $\lambda = 300$ nm) and negative -7.32×10^{-4} (at $\lambda = 750$ nm) value, depending on the wavelength region. In the wavelength region of $\lambda \approx 365$ nm, the equality of birefringences $\Delta n_y^{(\text{TGS}+\text{D-serine})} = \Delta n_y^{(\text{TGS})} = 0.03089$ takes place. We have found that the absolute value of temperature change of birefringence $|d(\Delta n_y)/dT|$ for TGS + D-serine is much smaller than that for pure TGS. This results in a displacement of the spectral point, where $\Delta n_y^{(\text{TGS}+\text{D-serine})} = \Delta n_y^{(\text{TGS})}$, to the shorter wavelengths when temperature decreases to room temperature ($T = 293$ K).

One can expect that different amounts of D-serine admixture will lead to monotonous changes in refractive indices and birefringence of TGS + D-serine, that would be rather a common result. However, the presence of the spectral point, where the difference between the birefringence of pure and D-serine doped TGS changes its sign, is a

special result, which may be used for the study of the admixture distribution by the optical method.

Decrease in temperature leads to an increase in the birefringence Δn_i ($i = x, y, z$) in three crystallographic directions (Fig. 6).

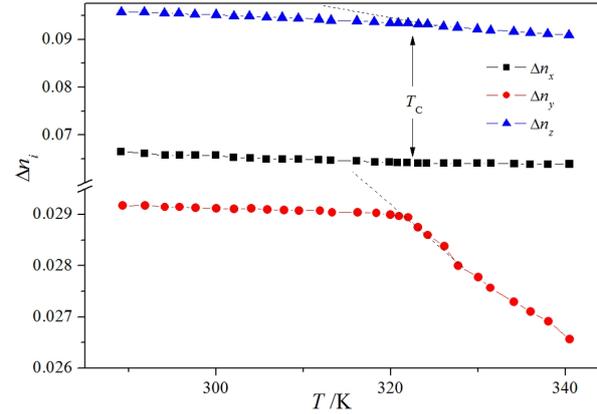


Fig. 6. Temperature dependences of birefringence $\Delta n_i(T)$ ($i = x, y, z$) of TGS + D-serine at the wavelength $\lambda = 500$ nm.

The dependences $\Delta n_i(T)$ ($i = x, y, z$) are linear in the paraelectric phase and are characterized by small nonlinearities in the polar one. The main parameters of pyroelectric sensors obtained on the basis of TGS and TGS + D-serine crystals are presented in Table 1. Here, ϵ is dielectric permittivity of a crystal in the paraelectric phase, γ is pyroelectric coefficient, c is heat capacity, $\text{tg}\delta$ is a measure of dielectric losses, $M_1 = \frac{\gamma}{c}$, $M_2 = \frac{\gamma}{c}\epsilon$ and $M_3 = \frac{\gamma}{c}(\epsilon \cdot \text{tg}\delta)$ are figures of merit related to the pyroelectric effect. The larger are the coefficients M_1 , M_2 and M_3 , the better the crystal is as a pyroelectric material.

The main advantage of TGS + D-serine as a material for pyroelectric sensor in comparison to pure TGS is the high coercive field. This leads to a decrease of the relative instability of pyroelectric material what is seen in Table 1. Also, TGS + D-serine is similar to linear pyroelectrics. An increase in the coercive field of TGS + D-serine in comparison to pure TGS may be associated with the corresponding decrease of the optical anisotropy observed in the present study upon the transition from TGS to TGS + D-serine.

Table 1. Influence of D-serine admixture on the pyroelectric parameters of TGS at room temperature.

| Material | ϵ | $\text{tg}\delta$ | $\gamma \times 10^4$ | $M_1 \times 10^{10}$ C/(m ² ·K) | $M_2 \times 10^{10}$ C·m/J | $M_3 \times 10^{10}$ C·m/J | Relative instability, % C·m/J |
|-------------------|------------|-------------------|----------------------|---|-------------------------------|-------------------------------|----------------------------------|
| TGS | 40 | 0.1 | 3.5 | 1.4 | 3.5 | 0.7 | 60 |
| TGS + 5% D-serine | 47 | 0.085 | 1.6 | 0.64 | 1.4 | 0.3 | 8 |

4. Conclusions

Magnitudes of the principal refractive indices of TGS + D-serine crystals, n_x , n_y , and n_z , were found to be close to those for pure TGS. This may be explained by the close chemical compositions of these substances. However, the temperature dependences of refractive indices and birefringence of TGS + D-serine differ from the analogous values of TGS more substantially. This may be related to different stability of the unipolar state of these materials.

The experimental results obtained in this study will be necessary as the reference data for the comparison with the calculated refractive indices of TGS + D-serine. These refractive indices will be obtained by using the density functional theory (DFT) based calculation codes. The corresponding computer simulation runs will be done for different positions of D-serine molecules within the TGS unit cell. Determination of the proper position of D-serine, should reveal the features of TGS + D-serine crystal structure necessary to achieve stable unipolarity.

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