

Letters to Editor

Simultaneous determination of optical activity and birefringence of TGS crystals in the polar direction

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1. Introduction

Optical activity of crystals is the result of a small contribution to the overall permittivity, due to the spatial derivatives of the polarization, taken into account when the dimensions of the unit cells are not negligible if compared with the wavelengths of the light [1]. The general requirement for a substance to be optically active is that the symmetry group of the unit structure contains no improper rotations, which include reflection planes, rotation-reflection axes and a centre of inversion. This phenomenon provides particularly valuable information in the study of molecular structure, i.e., the bonding nature of constituent atoms, the shape of the intermolecular force field and its dependence on distance. So far, because of the extremely difficult measurements, most investigations have been carried out for the directions coinciding with the optic axes, only a few attempts being made for other directions [2, 3]. In general, optical activity turns out to be small compared with the ordinary birefringence.

2. Optical activity of TGS $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$

Optical activity of TGS, when the light runs along the optic axes, was studied by several authors [4, 5]. Above the Curie temperature ($T_c = 49^\circ\text{C}$), the crystal is not optically active as it belongs to the centrosymmetric point group $2/m$ of the monoclinic system. At the Curie temperature the mirror plane disappears, and below T_c the crystal symmetry is the polar point group 2 of the monoclinic system, where the crystal is optically active. The gyration tensor g_{ij} of class 2 has the form [6]

$$(g_{ij}) = \begin{pmatrix} g_{11} & 0 & g_{31} \\ & g_{22} & 0 \\ & & g_{33} \end{pmatrix},$$

if the dyad axis is the ferroelectric axis b and (g_{ij}) is symmetric about the leading diagonal.

For studying the optical activity of this crystal we have used a recently developed method [3], based on accurate measurements of the intensity of light emerging from both parallel and crossed polarizers between which the crystal is located with proper orientation. The fractional intensity transmitted by the analyser is given by the equation

$$I = \left(\frac{(G/\bar{n})^2}{(n' - n'')^2 + (G/\bar{n})^2} + 4\Theta^2 \right) \sin^2 \left\{ \left(\frac{\pi d}{\lambda} \right) [(n' - n'')^2 + (G/\bar{n})^2]^{1/2} \right\} \quad (1)$$

where Θ is the angle between the incident polarized light and the a - or c -axis of the crystal, G is the gyration of the crystal, n' and n'' are the principal refractive indices of the crystal plate, $\bar{n} = \sqrt{n'n''}$, and d is the crystal thickness. Formula (1) is valid only for small Θ .

Equation (1) is manifested in a fringe curve as the wavelength of the incident light varies. The points of the maximum intensity satisfy the condition

$$(d/\lambda_{\max}) [(n' - n'')^2 + (G/\bar{n})^2]^{1/2} = \frac{1}{2} + N_m \quad (2)$$

and

$$I = I_0 = \frac{(G/\bar{n})^2}{(n' - n'')^2 + (G/\bar{n})^2}, \quad (3)$$

while $I = 0$, when $(d/\lambda_{\min}) [(n' - n'')^2 + (G/\bar{n})^2]^{1/2} = N_n$. Here N_m and N_n are integers. From Eqs. (2) and (3) we derive

$$n' - n'' = \sqrt{1 - I_0} \left(\frac{1}{2} + N_m \right) (\lambda_{\max}/d) \quad (4)$$

and

$$(G/\bar{n}) = \sqrt{I_0} \left(\frac{1}{2} + N_m \right) (\lambda_{\max}/d). \quad (5)$$

The gyration G is related to the specific rotation ρ by the expression $\rho = \pi G/\lambda\bar{n}$.

As the experiment involves a continuous change of the wavelength of light, and the position of the optic axes and the indicatrix depend on the wavelength and temperature, we have decided to use a cut perpendicular to b (ferroelectric) axis, since it is a bisector of the optic axes and does not change its position when the above conditions become different.

3. Experimental results

The set-up used is shown in Fig. 1. Unlike many other methods, white linearly polarized light passes through the crystal. The specimen is placed between crossed polarizer and analyser, which are followed by a monochromator. For

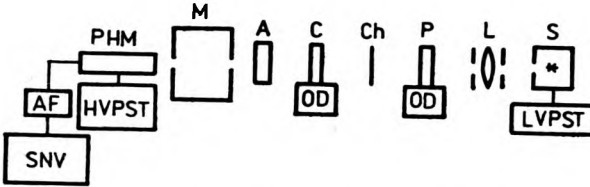


Fig. 1. The measuring set-up. S – source of light, L – collimator tube, P – polarizer, Ch – chopper, C – crystal, OD – orientation device, A – analyser, M – monochromator, PHM – photo-multiplier, AF – amplifier, SNV – selective nanovoltmeter, HVPST, LVPST – high and low voltage stabilizers

the right work of this set-up the slit of the monochromator SPM2 should be less than 0.06 mm, i.e., the width of the spectral band should not exceed 0.2–0.3 nm. For wider bands the maxima and minima of the curve have not well marked sites. The plate of TGS crystal, of the thickness $d = 0.29$ mm, was properly oriented by an apparatus allowing the crystal to rotate in three mutually perpendicular directions. From Eq. (1) it is seen that the amplitude of the fringe curve highly depends on the value of the angle θ between the plane of the incident polarized light and one of the main axes of the crystal (a or c in our case). When the angle θ is set equal to zero the amplitude of the fringe curve has its minimum at a given λ_{\max} . We used this condition for setting the angle $\theta = 0$. As mentioned above, the position of the indicatrix depends on the wavelength, for this reason the angle $\theta = 0$ was set at every λ_{\max} ; the combined curve, after taking account of the absorption effects of polarizer is shown in Fig. 2. The values 477.5 nm, 501 nm and 530 nm were assigned to the maxim, wavelengths for this curve and 490 nm and 515 nm to those of minimas.

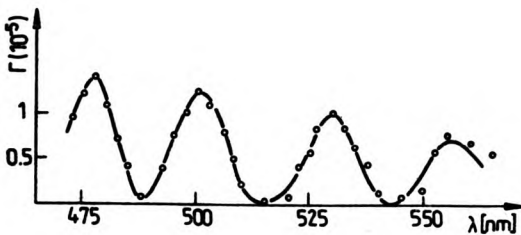


Fig. 2. Change of Γ for TGS at room temperature with respect to the wavelength

Their reciprocals are plotted in Fig. 3, the extrapolation of the straight line determines the zero point of the index N_m . Table 1 contains λ_{\max} , $1/\lambda_{\max}$ and the corresponding $1/2 + N_m$. Using these values for λ_{\max} and $1/2 + N_m$, the

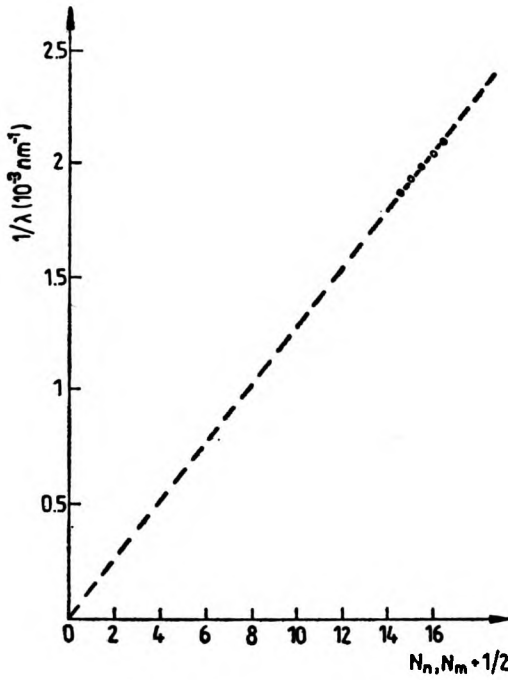


Fig. 3. $1/\lambda_{\min}$ (○) and $1/\lambda_{\max}$ (●) plotted against N_n and $N_m + 1/2$

values for G/\bar{n} and $\Delta n = n' - n''$, obtained from Eqs. (4) and (5) are given in Table 2. The birefringence is in a good agreement with the results reported by other authors [7, 8].

Table 1

λ_{\max} [nm]	$10^3/\lambda_{\max}$ [nm ⁻¹]	$1/2 + N_m$	λ_{\min} [nm]	$10^3/\lambda_{\min}$ [nm ⁻¹]	N_n
477.5	2.094	16.5	490	2.041	16
501	1.996	15.5	515	1.942	15
530	1.886	14.5	—	—	—

Table 2

λ_{\max} [nm]	$(G/\bar{n}) \cdot 10^{-5}$	Δn
477.5	10.16	0.02716
501	9.46	0.02677
530	8.38	0.02649

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