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THE STUDY OF BIREFRINGENCE AND ORIENTATIONAL ORDER IN PLASTIC TERT-BUTYL BROMIDE

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Abstract The method of measuring birefringence in uniaxial crystals with weak anisotropy has been developed. The results are presented for plastic tert-butyl bromide investigation and determination of orientational order parameter in noncubic phase of this crystal.

INTRODUCTION

In noncubic phases a number of plastic crystals show weak birefringence,[1] whose measuring is interesting for orientational order investigation in such crystals.

There are various methods of measuring birefringence. However, the application of these methods is complicated due to some plastic crystal properties (low Δn, plasticity, absence of sharp faces etc.).

In this work we used a modification of interference method to measure weak birefringence in uniaxial crystals[2] for investigation of tert-butyl bromide noncubic plastic phase.

EXPERIMENTAL

Below melting point 256.1 K tert-butyl bromide forms plastic crystal with face-centered cubic lattice (phase I)

which, when cooled up to 231.5 K transforms into plastic phase with noncubic lattice (phase II).[3] The latter being stable up to 209 K. In this phase birefringence was found,[4] but it was not measured.

Commercial grade of tert-butyl bromide was fractionally distilled. Samples boiling temperature was 346.3 K, melting point - 256.8K. The purified substance was sealed into cylindrical glass capillary tubes with 0.5 - 0.85 mm diameters.

The growth of crystals could be followed by observation through crossed polaroids. Single crystals of the plastic phase I were easily grown from the melt. A single crystal or a group of single crystals of the low-temperature plastic phase was formed on cooling the sample 5 to 10° below the transition temperature 231.5 K. The procedure was repeated until formation of a large enough single crystal of the phase II.

To measure the difference between principal values of the refractive indices $\Delta n = n_e - n_o$ a polarizing microscope was used. The thermostat with the sample was installed on the microscope table so that the crystal could be rotated around the tube axis.

The light beam is directed normally to the tube axis. Then from Fig. 1 it follows

$$\cos\theta = \sin\beta \cos\gamma , \qquad (1)$$

where θ is the angle between the wave normal N and crystal optical axis z, β is the angle between the optical axis z and the tube axis L, γ is the angle between the wave normal and the plane passing through the tube and optical axis.

From the Fresnel equation of normals it follows:

$$\frac{1}{n^2} = \frac{1}{n_e^2}\sin^2\theta + \frac{1}{n_o^2}\cos^2\theta \ , \qquad (2)$$

neglecting the terms of order of $(\Delta n)^2$, we get:

$$|\Delta n| = \frac{(k-1)\,\lambda}{d\,\sin^2\beta\,(\cos^2\gamma_1 - \cos^2\gamma_k)} \ , \qquad (3)$$

where $k = 2,3,4,\ldots$, d is the crystal diameter, λ is the wavelength, γ_1 is the lowest value of the angle γ, at which intensity minimum of monochromatic light having passed through the crystal is observed; γ_k are the next value of the angle γ, at which minima are observed.

The angle β was easily measured with the help of observation in the white light.

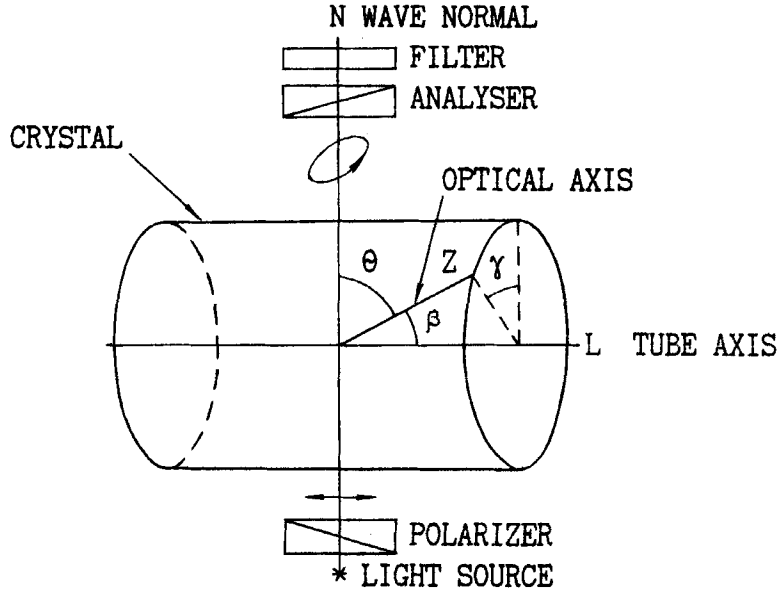

FIGURE 1 Schematic drawing of the optical system.

Formula (3) gives the absolute value Δn. To determine the sign of this difference it is enough to use a quartz wedge as a compensator.

RESULTS AND DISCUSSION

In Table I the results of the investigation of three crystals with different diameters at the wavelength 602 nm in the temperature range 210-231 K are given. The error of Δn value determination was 3%. Measurements at the wavelengths 491 and 666 nm gave identical results. We have found that $\Delta n > 0$.

TABLE I Birefringence of plastic phase II of tert-butyl bromide. $\lambda = 602$ nm.

d=0.50mm, β=82.5°				d=0.62mm, β=66.5°				d=0.85mm, β = 61.0°				
T,K	γ_1	γ_2	$\Delta n \cdot 10^3$	T,K	γ_1	γ_2	$\Delta n \cdot 10^3$	T,K	γ_1	γ_2	γ_3	$\Delta n \cdot 10^3$
231	37	59	3.28	231	21.5	44	3.31	230	30	47	65	3.25
227	36	58	3.28	228	21	43	3.43	228	30	46	63.5	3.41
223	34	53	3.76	225	20	42	3.49	225	27	43	58	3.59
218	32	50	4.00	223	19	40	3.75	219	24	40	53	3.83
213	30	47	4.30	217	16.5	37	4.10	215	21.5	37	49.5	4.12
211	29.5	45.5	4.60	210	14	34.5	4.40	211	18.5	34	46	4.40

The orientational order of axially symmetric molecules in uniaxial noncubic plastic crystals may be characterized by the same order parameter as in liquid crystals: $S = 1/2 \langle 3\cos \theta_{az} - 1 \rangle$, where θ_{az} is the angle between the symmetry axis of molecule and crystal optical axis.

The orientational order parameter defines the ratio of differences of average polarizabilities of a molecule in the directions parallel and perpendicular to the optical crystal axis and the principal molecule polarizabilities $S = (\alpha_e - \alpha_o)/(\alpha_{\parallel} - \alpha_{\perp})$.

The value of Δn may be connected with the difference $(\alpha_e - \alpha_o)$:[5]

$$\frac{2n \cdot \Delta n}{n^2 + 2} \cdot \frac{M}{\rho} = \frac{4}{3} \pi N_A (\alpha_e - \alpha_o) , \qquad (4)$$

where M is molecular weight, n is the refractive index, ρ is the density. Using the data of Table I we obtained that $S = 0.038$ at $T = 231$ K. With the temperature decrease the orientational order increases, at 210 K $S = 0.052$. According to nuclear magnetic resonance data[6] the orientational order parameter in perdeuterated tert-butyl bromide changes from 0.028 up to 0.040 in the same temperature range. Such agreeement may be considered satisfactory.

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