Manifestations of the polytype structure of $\beta$-TlInS$_2$ crystals in their optical anisotropy parameters

1 Adamenko D., 2 Pogodin A., 1 Vyslukiv Yu., 1 Martynyuk-Lototska I. and 1 Vlokh R.

1Vlokh Institute of Physical Optics, 23 Dragomanov Street, 79005 Lviv, Ukraine
2Department for Inorganic Chemistry, Uzhgorod National University, 46 Pidhirna Street, 88000 Uzhgorod, Ukraine, artempogodin88@gmail.com

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Abstract. We present the results of experimental studies of the temperature dependences of optical birefringence and optical indicatrix (OI) orientation increments for $\beta$-TlInS$_2$ crystals. Anomalous behaviours of the above characteristics are revealed at the two temperature points, $T_{C1} \approx 228$ K and $T_{C2} = 197$ K, which correspond to ferroelectric phase transitions in the polytypes with $c = 16c^*$ and $c = c^*$. The maps of increments of OI orientation angle and phase difference are obtained in the range from the room temperature to 100 K. It is found that the spatial distribution of increment of the OI orientation angle in $ab$ plane is homogeneous in the whole temperature range under study. The increment of the phase difference is homogeneously distributed in the $ab$ plane only at $197 K < T < 290$ K. Below $T_{C2} = 197$ K, two regions are revealed in our sample, which differ by their phase difference. Most probably, these regions correspond to two different polytypes of $\beta$-TlInS$_2$.

Keywords: TlInS$_2$ crystals, optical anisotropy, polytype structure, phase transitions

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1. Introduction

Beta-thallium-indium disulphide, or $\beta$-TlInS$_2$, is a ternary thallium halogenide that belongs to the group A$^{III}$B$^{III}$C$^{VI}$ of semiconductors ($A = Tl$, $B = Ga$ and $In$, and $C = S$, $Se$ and $Te$) [1]. The crystals of this group are characterized by low-dimensional layered or chain-like structures [1]. For instance, monoclinic TlGaS$_2$, TlInS$_2$ and TlGaSe$_2$ crystals reveal a layered structure [2–4], while tetragonal TlGaTe$_2$, TlInTe$_2$ and TlInSe$_2$ compounds crystallize in a chain structure [5]. $\beta$-TlInS$_2$ crystals represent a wide-band semiconductor having the bandgap 2.33 eV [6–8] and a layered structure that undergoes a ferroelectric phase transition (PT). According to Ref. [9], the PTs take place at the temperatures $T_C = 197$ K [2] and 204 K. According to the work [10], the PT temperatures are located in the region 195–202 K. The ferroelectric state is achieved through an intermediate incommensurate phase ($T_i = 214$ K [2] or $T_i = 216$ K [9, 10]). At $T = 293 K$, the crystals belong to the point symmetry group 2/m (the space group C2/c and $Z = 16$). The symmetry becomes lowered down to the point group 2 at $T < T_C$, with the two-fold symmetry axis being parallel to crystallographic axis $c$ [2]. The unit-cell parameters obtained from X-ray diffraction studies are equal to $a = 10.90$ Å, $b = 10.94$ Å, $c^* = 15.18$ Å and $\beta = 100.21$ deg in a rhombic setting [2] (or $\beta = 90.17$ deg [11] in a standard setting). The cleavage plane in $\beta$-TlInS$_2$ is perpendicular to the $c$ axis, while a small difference between the lattice parameters $a$ and $b$ makes the unit cell of $\beta$-TlInS$_2$ close to tetragonal [2].

High anisotropy caused by the layered structure implies that the $\beta$-TlInS$_2$ crystals can be interesting as a low-dimensional semiconductor. This has led to extensive studies of their
electronic structure [1], conductivity [8, 13] and optical properties [8, 14]. Note that the crystals are brownish yellow and transparent in the spectral range 0.5–12.5 μm [15]. Recently we have shown that β-TIInS₂ is an efficient acousto-optic and magneto-optic material [16, 17]. In particular, it has been demonstrated that the velocities of some of quasi-transverse waves are very low (~725 m/s), thus leading to extremely high acousto-optic figures of merit (~(2200–9000)×10⁻¹⁵ s²/kg).

However, the availability of cleavage planes can hinder acousto-optic applications of β-TIInS₂ in the optimized interaction geometry which is characterized by the highest figure of merit due to acousto-optic anisotropy (see, e.g., Ref. [18]). On the other hand, the crystals can also be used as an acousto-optic material for integrated-optical or waveguide applications [19].

As already mentioned above, the β-TIInS₂ crystals are interesting from the viewpoint of their structural PTs. The main peculiarity of those PTs consists in the fact that beta-thalium-indium disulphide can belong to different polytypes [20, 21], of which lattice parameters are equal to \(c = 2c^*, 4c^*, 8c^*\) and \(16c^*\), with \(c^* = 15.18\) Å. This leads to a number of anomalies observed for different physical characteristics at different temperatures [22]. These anomalies correspond to PTs among various polytypes. As a result, a controversy concerned with the sequence of PTs in β-TIInS₂ still takes place. One of the reasons is that some physical anomalies have often been accepted as marks of some PTs [23]. Later on, it has been found that the incommensurate phase appears between the normal and ordered phases only in the polytypes with \(c = c^*\), though it does not manifest itself in the crystals with \(c = 2c^*\) [24]. Moreover, the recent work [21] has testified that the polytype with \(c = c^*\) is the most unstable, while annealing of samples in air or sulphur atmosphere leads to reaching of almost homogeneous samples with a certain polytype [21]. On the contrary, aging of samples for some time, their thermal cycling and irradiation with the visible light or the X-rays convert the samples to a mixed state.

The authors of the works [21, 25] have found that the β-TIInS₂ crystals belonging to different polytypes differ by their PT sequences. For example, the temperature behaviour of dielectric permittivity in the single-layer polytypic β-TIInS₂ characterized with the parameter \(c = c^*\) testifies a PT located at \(T_c = 203–205\) K. On the other hand, the double-layer polytypic modification with \(c = 2c^*\) shows an intense dielectric peak at \(T = 212\) K, while for the four-layer polytype one can observe an intense peak at 217–220 K. For the eight-layer polytype, a broad anomaly at 209–212 K has been detected. Finally, the sixteen-layer polytype reveals a broad anomaly at \(T = 238–240\) K.

The interferometric experiments [21] have revealed that the depth of interference fringes is also sensitive to the polytype structure. This means that the sizes of homogeneous spatial regions are close to or larger than the wavelength of optical radiation. Then reasonable questions appear: (i) is it possible to detect the polytype structure by polarimetric mapping of TIInS₂ crystals and (ii) what is the size of the regions occupied by the polytypes? In order to solve these problems and elucidate the behaviour of optical anisotropy parameters in the course of PTs, we study the temperature evolution of optical birefringence and optical indicatrix (OI) orientation in the β-TIInS₂ crystals.

2. Experimental procedures and results

β-TIInS₂ was grown with a Bridgman–Stockbarger technique. Our crystals had a stoichiometric composition and were brownish yellow. Their diameters were equal to ~ 30 mm and the heights ~ 45 mm [16]. All of our crystalline samples had been kept for two years after the growth procedure was finished. A plate with the thickness 0.38 mm and the faces perpendicular to \(c\) axis
was prepared for our polarimetric measurements. This plate was placed into a temperature-regulating setup CS202-X1.AL (Advanced Research Systems, Inc.) that enabled optical measurements.

Studies of the optical birefringence and the orientation of OI for the $\beta$-TlInS$_2$ crystals are not trivial. The crystals are layered and so their lateral surfaces parallel to the crystallographic axis $c$ can be polished with great difficulties. This is because the layers are cleaved during this processing. Hence, any optical measurements can be successfully carried out only when the light propagates along the $c$ direction. On the other hand, the $\beta$-TlInS$_2$ crystals have a pseudo-tetragonal unit cell, which should imply a small birefringence along the $c$ axis. According to Ref. [9], the birefringence under normal conditions is of the order of $10^{-4}$. In fact, the conoscopic pattern obtained by us in the case when light propagates along the $c$ axis is typical for ‘almost uniaxial’ crystals (see Fig. 1).

![Fig. 1. Conoscopic pattern obtained for $\beta$-TlInS$_2$ in case when the light propagates along the $c$ axis (the wavelength is equal to $\lambda = 632.8$ nm).](image)

The next problem appearing in the studies of birefringence for the $\beta$-TlInS$_2$ crystals is concerned with a possibility of OI rotation around the $c$ axis with changing temperature. A temperature dependence of the appropriate rotation angle is a priori unknown. This implies that it is impossible to use standard methods for measuring birefringence increment, which are based on compensating phase difference. For instance, despite of extremely high measuring precision of a known Senarmont method, one cannot use it because the fast and slow axes of a quarter-wave compensator cannot keep their constant orientation with respect to the OI axes during the whole cycle of temperature measurements. The same is true of the orientation of incident linear polarization. For the same reasons, one cannot employ also a standard half-wave phase difference. To avoid the difficulties mentioned above, one has to make the incident light insensitive to the orientation of OI axes, i.e. the incident light must be polarized circularly.

An experimental setup for the studies of optical phase difference and OI orientation is shown in Fig. 2. It can be also used for obtaining polarimetric maps. To measure the phase difference and the orientation of OI, we make the probing laser beam expanded and circularly polarized. A quarter-wave plate 9 is oriented in a so-called diagonal position. The angle between the principal axes of the quarter-wave plate and the transmission direction of a polarizer 8 is equal to 45 deg. Then the sample can be treated as a linear phase retarder, for which the dependence of the output intensity $I$ on the analyzer azimuth $\alpha$ is expressed as

$$I = \frac{I_0}{2} \left[1 + \sin \Delta \Gamma \sin \left[2(\alpha - \varphi)\right]\right] = C_l + C_s \sin \left[2(\alpha - C_1)\right], \quad (1)$$

where $\varphi$ is the angle of OI orientation and $\Delta \Gamma = 2\pi d n / \lambda$ the optical phase difference (with $\Delta n$ being the linear birefringence, $d$ the sample thickness and $\lambda$ the wavelength of optical radiation).
After recording and filtering an optical image, azimuthal dependences of the intensity $I$ are fitted by the sine function for several central pixels of the beam cross-section (or for all of the pixels in case when the polarimetric maps are recorded). The fitting coefficients are as follows:

$$C_1 = \frac{I_0}{2}, \quad C_2 = \frac{I_0}{2} \sin \Delta \Gamma, \quad C_3 = \phi.$$  \hspace{1cm} (2)

Then the optical phase difference $\Delta \Gamma$ is determined by the coefficients $C_1$ and $C_2$:

$$\sin \Delta \Gamma = C_2 / C_1,$$  \hspace{1cm} (3)

while the angular orientation of the intensity minimum is given by the orientation of the principal OI axis $\phi$ and the coefficient $C_3$. Hence, fitting of dependences of the intensity of light emergent from the analyzer upon the azimuth for each pixel of the sample image enables one to construct spatial 2D maps of the optical anisotropy parameters, the optical phase difference and the OI orientation.

Under normal conditions, the absolute birefringence value for the $\beta$-TlInS$_2$ crystals is of the order of $\sim 4 \times 10^{-4}$, which agrees satisfactorily with the data [9]. As seen from Fig. 3, two anomalies are present on the temperature dependence of the birefringence increment. The first one appears in the region $T_{C1} \approx 228-248$ K. Note that, although the breaks in the temperature dependences of the birefringence increment and the angle of OI orientation are available at 228 K, the deviation of the birefringence increment from its linear extrapolation from the temperature region of paraelectric phase into the region of low-temperature phases appears at a somewhat higher temperature, $\sim 248$ K. This can be caused by a diffuse character of the normal-to-ferroelectric phase PT. As follows from the literature data [21], this anomaly corresponds, most probably, to the PT found in the crystals with the polytype $c = 16c^*$. One observes the anomaly in the increment of OI orientation angle at the same temperature, 228 K. The angle of OI orientation changes significantly with decreasing temperature. This change is equal to $\delta(\Delta \phi) \sim 30$ deg if one passes from the room temperature down to $T_{C1} \approx 228$ K. In fact, the above angle is defined by the relation:

$$\tan 2\phi = 2 R_{S3} P_{S3}^2 / (B_i - B_f) \approx n_0^2 R_{S3} P_{S3}^2 / \Delta n,$$

where $n_0$ implies the refractive index given by the
relation \( n_{c} = n_{0} \pm \Delta n / 2 \), \( R_{0}\) is the Kerr coefficient for the paraelectric phase, \( P_{3}\), the component of spontaneous polarization, and \( B\) the impermeability tensor components. Since \( \Delta n \) is quite small, the angle \( \phi \) can become high enough.

![Temperature dependences of the increment \( \Delta \phi \) of OI orientation angle and the birefringence increment \( \delta(\Delta n) \) measured for \( \beta\)-TlInS\(_2\). A dashed line corresponds to linear extrapolation of the birefringence increment from the high-temperature region of paraelectric phase into the region of low-temperature phases.](image)

The increment of optical birefringence manifests an additional anomaly at \( T_{C2} \approx 197 \) K. This anomaly corresponds to the PT from the incommensurate phase into the ordered phase for the polytype \( c = c^{*}\). Notice that this conclusion agrees well with the results of our recent work [22]. However, we have revealed no anomalous behaviour of the birefringence increment or the increment of OI orientation angle at \( T_{I} \approx 214 \) K. According to our data [23] obtained on the same crystalline boule, this temperature point corresponds to the paraelectric-to-incommensurate PT for the polytype with \( c = c^{*}\). In fact, the crystal in the temperature region \( 197 \) K \( < T < 214 \) K stays in a mixed state where the incommensurate phase of the polytype \( c = c^{*}\) is ‘mixed’ with the ferroelectric phase of the polytype \( c = 16c^{*}\). The ferroelectric phases of those polytypes are mixed below \( 197 \) K.

As seen from Fig. 4a, b, the increment of OI orientation angle under normal conditions is equal to \((84.16 \pm 14.60)\) deg over the whole map presented in Fig. 4b. The phase difference increment at the same conditions is equal to \((18.64 \pm 7.61)\) deg. The corresponding values detected at \( T = 219 \) K amount to \((98.86 \pm 13.35)\) deg and \((33.72 \pm 9.73)\) deg, respectively. It is worthwhile that the mean-square deviations for the both parameters at these temperatures are close to each other. This means that we have no reason to assume that there exist some inhomogeneities of the birefringence and the OI orientation angle as manifestations of the polytype states. The spatial distributions of the above parameters are also quite uniform at lower temperatures above \( T_{C2}\). However, in the ferroelectric phase below \( T_{C2}\) (see Fig. 4e), the distribution of phase difference increment can be clearly separated into two regions, with the corresponding phase differences equal to \((35.52 \pm 8.69)\) deg and \((60.79 \pm 8.82)\) deg. The mean values of the phase difference increment in these regions differ almost twice. Moreover, the mean-square deviations are sufficiently small, so that the values of the both parameters do not overlap. Note that the increment of the OI orientation angle remains the same in these regions. As seen from Fig. 4f, it is equal to \((91.85 \pm 7.17)\) deg.
Fig. 4. Maps of increments of the phase difference (a, c, e) and the OI orientation angle (b, d, f) measured for \( \beta \)-TlInS\(_2\) at \( T = 290 \) K (a, b), 219 K (c, d) and 169 K (e, f) in the crystallographic plane \( \text{ab} \). \( X \) and \( Y \) are axes of the laboratory coordinate system.

Since the paraelectric phase is centrosymmetric, the changes in the linear birefringence and the angle of OI orientation can be ascribed only to the squared spontaneous polarization. In other words, these changes are the same in the domains with the opposite signs of spontaneous polarization, and the domains cannot be distinguished polarimetrically. On the other hand, the domains are enantiomorphous and should have the opposite signs of their optical activity. In spite of the fact that the linear birefringence is quite small (e.g., \( 4 \times 10^{-4} \)), it is enough for masking the optical rotation caused by gyration, which has the order of magnitude \( 10^{-5} \rightarrow 10^{-4} \) for the circular birefringence in an ‘average material’. Hence, it is unlikely that the difference of the phase difference increments in different regions of the sample (see Fig. 4e) is caused by the enantiomorphous domain structure. Moreover, the OI orientation angle (see Fig. 4f) is quite homogeneously distributed over the sample area. As a consequence, we are inclined to consider these regions as those corresponding to different polytypes, namely the polytypes with \( c = c^* \) and \( c = 16c^* \). They become clearly distinguishable by the polarimetric methods only at lower temperatures, where the order parameters for the both polytypes become high enough.
3. Conclusions
In the present work we have studied experimentally the temperature dependences of increments of the optical birefringence and the OI orientation angle for the β-TlInS₂ crystals. The anomalies of those parameters have been revealed at the two temperature points, \( T_{C1} = 228 \text{ K} \) and \( T_{C2} = 197 \text{ K} \). Comparing our results with the data of earlier studies, one can conclude that the \( T_{C1} \) point corresponds to the temperature of diffused ferroelectric PT from the normal phase into the ordered phase in the polytype with \( c = 16c^* \), while \( T_{C2} \) is the temperature of PT from the incommensurate phase into the ferroelectric phase for the polytype with \( c = c^* \).

The maps of increment of the OI orientation angle and the maps of phase difference increment have been obtained in the range from the room temperature down to 100 K. It has been found that the spatial distribution of the increment of OI orientation angle in the \( ab \) plane is homogeneous in all the temperature range. On the other hand, the distribution of phase difference increment is homogeneous only at \( 197 \text{ K} < T < 290 \text{ K} \). Below the temperature point \( T_{C2} = 197 \text{ K} \), where the ferroelectric phases for the polytypes \( c = c^* \) and \( c = 16c^* \) coexist, we have revealed two regions in the sample, which differ by their phase differences. Most probably, these regions belong to the two different polytypes of the β-TlInS₂ crystals.

References


Анотація. Наведено результати експериментальних досліджень температурних залежностей приростів подвійного оптичного заломлення та орієнтації оптичної індикатриси (OI) для кристалів β-TlInS₂. Виявлено аномальну поведінку цих характеристик у двох температурних точках, T₁C ≈ 228 К і T₂C ≈ 197 K, які відповідають сегнетоелектричним фазовим переходам у політіпах із c = 16c* і c = c*. Одержано карту приростів кута орієнтації ОI і різниці фаз у діапазоні від кімнатної температури до 100 K. Встановлено, що просторовий розподіл приросту кута орієнтації ОI в плоскіні аб відповідає діапазону температур. Приріст же різниці фаз однорідно розподілений у плоскіні ab лише при 197 K < T < 290 K. Нижче T₂C ≈ 197 K у зразку виявлено дві області, які відірізуються за різницею фаз. Швидше за все, ці області відповідають двом різним політіпам у кристалах β-TlInS₂.