Temperature dependences of optical indicatrix and thermal expansion parameters of TlIn(S$_{1-x}$Se$_x$)$_2$ solid solutions (x = 0, 0.02 and 0.06)

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Abstract. Temperature dependences of relative elongation, thermal expansion coefficient, birefringence increment and angle of optical indicatrix rotation are studied for TlIn(S$_{1-x}$Se$_x$)$_2$ crystals (x = 0, 0.02 and 0.06). We have found that all of these crystals reveal at least two diffused phase transitions (PTs), from normal phase to incommensurate phase and from incommensurate phase to ferroelectric phase. The temperature regions where these PTs take place are determined. A low-temperature PT represents a diffused PT of the first order. We have detected with our techniques that the solid solution with x = 0.02 is non-uniformly stressed. These internal stresses can be caused by a polytype structure. An additional anomaly in the temperature dependence of thermal expansion coefficient occurring at the temperature $T_1$ = 214 K in the compound with x = 0.06 also points to the existence of polytype structure.

Keywords: birefringence, optical indicatrix, thermal expansion, phase transitions, polytype structure, TlIn(S$_{1-x}$Se$_x$)$_2$ crystals

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1. Introduction

$\beta$-TlInS$_2$ and TlInSe$_2$ crystals are ternary thallium halogenides that belong to a group $A^{III}B^{III}C_{VI}$ of semiconductors, with A = Tl, B = Ga and In, and C = S, Se and Te [1]. They are characterized by low-dimensional layered or chain-like structures [1]. In particular, TlGaS$_2$, $\beta$-TlInS$_2$ and TlGaSe$_2$ crystals are monoclinal and reveal a layered structure [2–4], while tetragonal TlGaTe$_2$, TlInTe$_2$ and TlInSe$_2$ compounds crystallize in a chain-like structure [5]. Thallium-indium disulphide represents a wide-band semiconductor-ferroelectric crystal, with the bandgap equal to 2.33 eV [6–8]. At $T = 293$ K, the crystal belongs to the point symmetry group $2/m$ (the space group C2/c and $Z = 16$), with the two-fold symmetry axis being parallel to crystallographic axis c [2]. The unit-cell parameters obtained from the 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 [9] 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 close to tetragonal [2]. The crystal is characterized by a layered structure and undergoes a ferroelectric phase transition (PT). The latter takes place at the temperature $T_c = 197$ K according to Ref. [2], at 204 K according to Ref. [10] and in the temperature region 195–202 K, according to Ref. [11]. The symmetry becomes lowered down to the point group 2 at $T < T_c$. An incommensurate (IC) phase is observed at the temperatures higher than the ferroelectric PT point ($T_i = 214$ K [2] or $T_i = 216$ K [10, 11]).
The main peculiarity of the PTs in β-TlInS₂ crystals consists in the fact that different polytypes can coexist in the crystalline matrix [12, 13]. They are characterized by different lattice parameters c. The unit cell parameter c for different polytypes is equal to \( c = 2c^* \), \( 4c^* \), \( 8c^* \) and \( 16c^* \), with \( c^* = 15.18 \text{ Å} \). Each of pure polytypes is characterized by its own ferroelectric PT point. For instance, we have \( T_C = 203–205 \text{ K} \) for \( c = c^* \), \( T_C = 217–220 \text{ K} \) for \( c = 4c^* \), \( T_C = 209–212 \text{ K} \) for \( c = 8c^* \) and \( T_C = 238–240 \text{ K} \) for \( c = 16c^* \) [13]. As a result of coexistence of different polytypes in the crystalline matrix, a number of anomalies have been observed for different physical characteristics at different temperatures. These anomalies have also been detected in our recent works [14, 15]. They correspond to the PTs in different polytypes. In particular, it has been found that the IC phase appears between the normal and ordered phases only in the polytype with \( c = c^* \), though it does not manifest itself in the crystal with \( c = 2c^* \) [16]. Moreover, the recent work [13] has testified that the polytype with \( c = c^* \) is the most unstable. It has been shown in the work [17] that the IC PT occurs at \( T_i = 216 \text{ K} \). Double hysteresis loops have been observed in the temperature region 200.8–204.0 K, which testifies that an antiferroelectric ordering takes place in this region. ‘Mixed’ (or ‘triple’) dielectric hysteresis loops are seen in the temperature region 175–200 K. This implies that a heterostructure phase exists in this temperature region, i.e. the ferroelectric and antiferroelectric phases coexist. The dielectric hysteresis loops become canonical only below 175 K, which is typical for the ferroelectric PT.

The TlInSe₂ crystal crystallizes in tetragonal lattice with the space symmetry group 14/mcm (the point group 4/mmm) and its unit cell contains two formula units [5, 18]. The crystal is characterized by a chain-like structure. Its bandgap is equal to 1.35 eV [5]. According to the data of heat capacity studies, the crystal exhibits no structural PTs in the temperature range 4–300 K [19].

A morphotropic phase boundary appears at \( 0.70 < x < 0.75 \) on the phase diagram of solid solutions TlIn(S₁₋ₓSeₓ)₂ [20]. This boundary separates the monoclinic and tetragonal phases. The Raman spectra of these solid solutions have been studied for the case \( 0 \leq x \leq 0.1 \) [21]. According to the heat capacity studies (see Refs. [22, 23]), we have \( T_C = 190 \text{ K} \) and \( T_i = 213 \text{ K} \) for the solid solutions with \( x = 0.1 \). The studies [23, 24] have been devoted to the influence of isomorphic substitution on the lattice parameters, in particular for the case of TlIn(S₁₋ₓSeₓ)₂ crystals, and to the studies of real and imaginary parts of the dielectric function. The \((x,T)\)-phase diagram for polycrystalline TlIn(S₁₋ₓSeₓ)₂ solid solutions with \( 0 \leq x \leq 0.15 \) has been obtained in Ref. [25]. A broadening of the temperature region where the IC phase exists has been observed with increasing selenium concentration. However, the polycrystalline structure typical for these compounds leads to smearing of the peculiarities caused by the polytype structure in single crystals. Single TlIn(S₁₋ₓSeₓ)₂ crystals with \( x = 0.01, 0.02, 0.04, 0.05, 0.10 \) and 0.20 have been investigated in the work [26], issuing from the temperature dependences of dielectric permittivity. Nonetheless, no phase diagram has been obtained. In the present work, we study the parameters of optical indicatrix and thermal expansion for the TlIn(S₁₋ₓSeₓ)₂ solid solutions with single-crystalline structure at the concentrations \( x = 0, 0.02 \) and 0.06.

2. Experimental procedures
The TlIn(S₁₋ₓSeₓ)₂ crystals with the selenium concentrations \( x = 0, 0.02 \) and 0.06 were grown using a Bridgman–Stockbarger technique [21]. X-ray diffraction studies were performed for structural characterization, using a Bregg–Brentano method and a diffractometer DRON-3M (Cu-Kα radiation). Basing on the X-ray structural data, we established that our single
TlIn(S$_{1-x}$Se$_x$)$_2$ crystals have a monoclinic structure (the space group of symmetry C2/c and the point group 2/m). The elemental analysis of chemical composition of TlIn(S$_{1-x}$Se$_x$)$_2$ was approved by a FEM in combination with energy-dispersive X-ray fluorescence spectroscopy. A layered structure, which leads to cleavage of the crystalline plates along the direction perpendicular to the crystallographic axis $c$, hinders fabrication of bulk samples for our studies. That is why only samples with faces perpendicular to the crystallographic axes $c$ were prepared for our thermal-expansion measurements. The sample thicknesses along the $c$ axis were equal to 4.21 mm for $x = 0$, 1.52 mm for $x = 0.02$ and 1.36 mm for $x = 0.06$.

The relative thermal elongation $\Delta L_c / L_c^0 = (L_c - L_c^0) / L_c^0$ (with $L_c^0$ being the initial sample size along the $c$ axis and $L_c$ the thermally induced size) was measured with a quartz capacity dilatometer. The thermal expansion coefficient was calculated as $\alpha_c = \partial (\Delta L_c / L_c^0) / \partial T$. A detailed description of our setup was presented in Ref. [27]. The average sensitivity of our dilatometer was about 2 nm in the temperature range 155–290 K under test. The measurements were carried out in the cooling run, with the temperature scan rate 0.3 K/min. The mean-square error of the expansion coefficients did not exceed $3\times10^{-6}$ K$^{-1}$.

Finally, temperature dependences of the optical birefringence and the orientation angle of optical indicatrix were studied for the case of light propagation along the $c$ axis, using a method described in detail in our recent work [15].

3. Results and discussion

Temperature dependences of the thermal expansion coefficient $\alpha_c$ for TlIn(S$_{1-x}$Se$_x$)$_2$ with the selenium concentrations $x = 0$, 0.02 and 0.06 are calculated following from the temperature dependences of relative elongations (see Fig. 1).

The results of our studies for the pure $\beta$-TlInS$_2$ crystals (see Fig. 1a, b) agree well with the earlier results [14]. Note that the dilatometric data in the work [14] has been obtained only down to 150 K, while in the present work we reach the temperature point 100 K. As seen from Fig. 1a, b, the relative elongation and the thermal expansion coefficient in the low-temperature region behave in anomalous manner. The PT temperatures are almost the same as in Ref. [14]. They are $T_{i1} = 221$ K and $T_{c1} = 206$ K, according to the relative elongation data (see Fig. 1a), and $T_{i2} = 214$ K and $T_{c2} = 206$ K according to the data for thermal expansion coefficient (see Fig. 1b). Following from the work [15], the anomalies in the orientation angle of optical indicatrix and the birefringence increment appear at the two temperature points, $T_{c1} \approx 228$ K and $T_{c2} \approx 197$ K. Comparing the results [15] with the data by the other authors, we have concluded [15] that the $T_{c1}$ point corresponds to the temperature of diffused PT from the normal phase into the ordered phase in the polytype with $c = 16c^*$, while $T_{c2}$ is the temperature of diffused PT from the IC phase into the ferroelectric phase in the polytype with $c = c^*$. Notice that the anomaly at $T_{i} = 214$–221 K revealed in the present work is very close to $T_{c1}$ and, at the same time, to the PT point $T_{i} = 214$ K [2] (or 216 K [9, 10]) which characterizes the PT into the IC phase in the polytype with $c = c^*$. Hence, the temperature $T_{c1}$ found in Ref. [15], probably, represents the $T_i$ point for $c = c^*$ polytype. Additional anomalies of the relative elongation and the thermal expansion coefficient are observed at still lower temperatures ($T_2 = 162$ K). One can suppose that these anomalies correspond to the point where the PT from the IC to the normal ferroelectric phase becomes completed in the polytype with $c = c^*$. Notice that this structural transformation begins at $T = T_{c2} \approx 197$ K (or 206 K).
Fig. 1. Temperature dependences of relative elongation (a, c, e) and thermal expansion coefficient (b, d, f) along the crystallographic axis c, as obtained for TlIn(S$_1$–xSe$_x$)$_2$ solid solutions with selenium concentrations x = 0 (a, b), 0.02 (c, d) and 0.06 (e, f).

As seen from Fig. 2, the crystals with the selenium concentrations x = 0.02 and 0.06 are ‘almost’ optically uniaxial. However the angle between the optic axes in the crystals with x = 0.02 is larger than that for the crystals with x = 0.06. Note that the conoscopic patterns for the pure β-TlInS$_2$ crystals are also typical for ‘almost uniaxial’ crystals [15]. Moreover, the conoscopic patterns for the compound with x = 0.02 are deformed, which is peculiar for non-uniformly stressed crystals. This is the reason why the measurements of temperature dependences of the birefringence increment and the angle of optical indicatrix rotation fail for the crystals with x = 0.02.
Conoscopic patterns observed for TlIn(S$_{1-x}$Se$_x$)$_2$ crystals at light propagation along the c axis: x = 0.02 (a) and 0.06 (b) (the light wavelength $\lambda$ = 632.8 nm).

According to the dilatometric data depicted in Fig. 1c, d, the special temperature points for the crystals with x = 0.02 are $T_i$ = 201 K, $T_C$ = 180 K and $T_2$ = 160 K. Our results are close to the data for the temperature dependence of the dielectric permittivity obtained in Ref. [28] ($T_i$ = 203 K and $T_C$ = 183 K) and those reported in the works [29, 30] ($T_i$ = 204 K and $T_C$ = 190 K).

Concerning the TlIn(S$_{0.94}$Se$_{0.06}$)$_2$ crystals, smoothed anomalies in the temperature dependences of the relative elongation and the thermal expansion coefficient are present in the vicinity of $T_i$ = 185 K, $T_C$ = 166 K and $T_2$ = 157 K (see Fig. 1e, f). An additional anomaly clearly seen on the temperature dependence of thermal expansion coefficient is observed at $T_1$ = 214 K (see Fig. 1e). One can suppose that this point corresponds to the PT in some other polytype in the solid solution TlIn(S$_{0.94}$Se$_{0.06}$)$_2$. The temperature $T_i$ = 185 K seems to correspond to the PT from the paraelectric phase to the IC phase and $T_C$ = 166 K to the PT from the IC phase to the ferroelectric phase.
A scatter of data points in the temperature dependences of birefringence increment and angle of optical indicatrix rotation is high enough for TlIn(S$_{0.94}$Se$_{0.06}$)$_2$ (see Fig. 3a, b). One can detect only the $T_C$ point from these dependences. However, smoothing and taking temperature derivatives of these dependences (see Fig. 3c) enable one to detect the $T_i$ point, too. Clear jumps in the temperature derivatives of the angle of optical indicatrix rotation and the birefringence increment observed at $T_C$ testify a first-order character of this PT.

Summarizing our results, we state that the TlIn(S$_{1-x}$Se$_x$)$_2$ crystals with $x = 0, 0.02$ and $0.06$ have two diffused PTs. One of them is the PT from the normal phase into the IC phase and the other from the IC phase to the ordered phase. The temperature regions where these PTs take place are collected in Table 1. As seen from Table 1, the temperatures points $T_i$ and $T_C$ decrease with increasing selenium concentration.

| $x$  | $T_i$, K | $T_C$, K |
|------|----------|----------|
| 0    | 214–228  | 162–206  |
| 0.02 | 201      | 160–180  |
| 0.06 | 185      | 157–166  |

4. Conclusion

We have studied the temperature dependences of the relative elongation, the thermal expansion coefficient, the optical birefringence increment and the angle of optical indicatrix rotation for the single TlIn(S$_{1-x}$Se$_x$)$_2$ crystals with $x = 0, 0.02$ and $0.06$. We have found that all of these crystals reveal at least two diffused PTs. Following from the comparison of our results with the literature data, one can suppose that these phase transformations represent the normal-to-IC PT and the IC-to-ferroelectric phase PT. The lower-temperature PT is of the first order. The temperature regions where these PTs take place are determined. The temperatures of the PTs decrease with increasing selenium concentration. We have also detected that the solid solution with $x = 0.02$ is non-uniformly stressed. The corresponding internal stresses can be caused by the polypeptide structure. The existence of the polypeptide structure is also testified by the additional anomaly observed at $T_i = 214$ K in the temperature dependence of the thermal expansion coefficient for the compound with selenium concentration $x = 0.06$.

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Анотація. Досліджено температурні залежності відносного теплового видовження, коефіцієнта теплового розширення, приросту подвійного оптичного заломлення та кута повороту оптичної індикатриси для кристалів TlIn(S1−xSe2x)2 (x = 0, 0.02 і 0.06). Показано, що ці кристали виявляють щонайменше два розмиті фазові переходи (ФП) – переходи з нормальної в неспівмірну фазу та з неспівмірної в сегнетоелектричну фазу. Встановлено температурні ділянки, де відбуваються ці ФП. Ніжкотемпературний ФП представляє собою розмитий ФП першого роду. На основі наших методик виявлено, що твердий розчин із x = 0,02 неоднорідно напружений. Ці внутрішні напруження можуть бути зумовлені політипною структурою. Додаткова аномалія на температурній залежності коефіцієнта теплового розширення, яка з’являється для сполуки з x = 0.06 за температури Т1 = 214 К, також вказує на існування політипної структури.