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Optical features of novel semiconducting crystals $Tl_{1-x}Ga_{1-x}Sn_xSe_2$ ($x = 0.05; 0.1$)

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ABSTRACT

The results of the novel $Tl_{1-x}Ga_{1-x}Sn_xSe_2$ single crystals ($x = 0.05; 0.1$) growth together with complex studies of their optical, electric and photoelectric properties are presented. Semiconductor crystalline alloys Tl_2Se , $Ga(In)_2Se_3$, $SnSe_2$ possessing congruent melting features has been served as components for the quasi-ternary systems. The $Tl_2Se-Ga_2Se_3$ was melted congruently at temperature 1073 K. Two compounds existed for the $Tl_2Se-In_2Se_3$ system: $TlInSe_2$ melting congruently at 1023 K, and $Tl_2Se-In_2Se_3$ within congruent melting nature at 1029 K. Isothermal section of the $Tl_2Se-Ga_2Se_3-SnSe_2$ system at 520 K have been constructed from X-ray phase and formation of the ternary compounds Tl_4SnSe_4 , Tl_2SnSe_3 , $TlGaSe_2$ was confirmed. The spectral dependences of the absorption coefficients near the fundamental absorption have been studied with respect to direct as indirect dipole allowed inter-band transitions realized in the $(TlGaSe_2)_{1-x}(SnSe_2)_x$ crystals for the studied temperature range. Following the Urbach's energy the role of electron-phonon interaction and structural disorder was analyzed.

1. Introduction

Recently one can observe an increasing interest for study of layered semiconductors for optoelectronics [1–3] due to their promising electronic and nanophotonic features. Particular interest present infrared materials based on thallium chalcogenides [4,5]. Main direction of the further improvement of these materials is a design of correspond solid state alloys [4–6]. Our earlier studies of the $TlInSe_2-SnSe_2$ system [7] indicate a possibility of formation single phase compounds in a wide solid content range (up to 28 mol.

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Table 1Principal structural parameters of the compounds. $\text{Tl}_2\text{Se}-\text{C}_{2}^{\text{III}}\text{Se}_3$ and $\text{Tl}_2\text{Se}-\text{SnSe}_2$ systems.

Compound	S.G.	Lattice periods, nm			Ref.
		<i>a</i>	<i>b</i>	<i>c</i>	
TlGaSe_2	<i>C2/c</i>	1.0779 $\beta = 99.993^\circ$	1.0776	1.5663	[11]
	<i>I4/mcm</i>	0.7620 $\alpha = 90.15^\circ$	– $\beta = 90.15^\circ$	3.0500 $\gamma = 90.15^\circ$	[12]
TlInSe_2	<i>I4/mcm</i>	0.8075	–	0.6847	[13]
Tl_2SnSe_3	<i>Pnam</i>	0.8051	0.8169	2.124	[14]
Tl_4SnSe_4	<i>P2₁/c</i>	0.8481	0.8411	1.5800	[15]
		$\beta = 102.39$			

% SnSe_2). Particular interest presents a possibility of their application as third order non-linear optical materials which may be promising for the use in mid-IR spectral range effective materials for the non-linear frequency transformation in the IR region of the spectrum which is crucial for IR optical riggers and IR lidar systems. As a fundamental basis for the further search are sued $\text{Tl}_2\text{Se}-\text{Ga}(\text{In})_2\text{Se}_3-\text{SnSe}_2$. Of particular interest may be their application in photonic crystals [7].

In the present work we present the results of the $\text{Tl}_{1-x}\text{Ga}_{1-x}\text{Sn}_x\text{Se}_2$ single crystals ($x = 0.05; 0.1$) growth together with complex studies of their optical, electric and photoelectric properties. The semiconductor alloys Tl_2Se , $\text{Ga}(\text{In})_2\text{Se}_3$, SnSe_2 possess congruent melting features which can serve as components for the quasi-ternary systems. The $\text{Tl}_2\text{Se}-\text{Ga}_2\text{Se}_3$ system is melted congruently at temperature 1073 K [8]. There are two compounds existing for the $\text{Tl}_2\text{Se}-\text{In}_2\text{Se}_3$ system: TlInSe_2 that melts congruently at 1023 K, and $\text{Tl}_2\text{Se}-\text{In}_2\text{Se}_3$ within congruent melting nature at 1029 K [9]. At the same time three compounds are formed in the $\text{Tl}_2\text{Se}-\text{SnSe}_2$ system, Tl_4SnSe_4 and Tl_2SnSe_3 that melt congruently at 718 and 735 K, respectively, and $\text{Tl}_2\text{Sn}_2\text{Se}_5$ that exists within a narrow temperature range (it is formed at 732 K in the peritectic reaction $\text{L} + \text{SnSe}_2 \leftrightarrow \text{Tl}_2\text{Sn}_2\text{Se}_5$ and is decomposed below 655 K) [10].

The basic data on the principal structural parameters of the titled compounds of $\text{Tl}_2\text{Se}-\text{C}_{2}^{\text{III}}\text{Se}_3$ and $\text{Tl}_2\text{Se}-\text{SnSe}_2$ systems are given in Table 1.

All the $\text{Ga}_2\text{Se}_3-\text{SnSe}_2$ and $\text{In}_2\text{Se}_3-\text{SnSe}_2$ systems are of the eutectic type [16–18].

Phase equilibria for the $\text{TlGaSe}_2-\text{SnSe}_2$ alloy system have been investigated in [19]. Three quaternary compounds have been formed by peritectic reactions $\text{L} + \alpha \leftrightarrow \text{Tl}_3\text{Ga}_3\text{SnSe}_8$ at 952 K, $\text{L} + \text{Tl}_3\text{Ga}_3\text{SnSe}_8 \leftrightarrow \text{TlGaSnSe}_4$ at 851 K, and $\text{L} + \text{SnSe}_2 \leftrightarrow \text{TlGaSn}_2\text{Se}_6$ at 833 K. The solid solution range of TlGaSe_2 is extended up to 18 mol.% SnSe_2 at 670 K. It was found that $\text{TlGaSn}_2\text{Se}_6$ crystallizes in the $\text{TlInGe}_2\text{Se}_6$ structure type (S.G. $R\bar{3}$, $a = 1.03289$, $c = 0.94340$ nm) [20].

The solid solution range of the ternary compound TlInSe_2 is extended within 72–100 mol.% TlInSe_2 [7].

2. Experimental

Phase equilibrium diagrams for the $\text{Tl}_2\text{Se}-\text{Ga}(\text{In})_2\text{Se}_3-\text{SnSe}_2$ systems were studied for 94 samples. The batches were composed from high-purity elements Tl, Sn, Ga, In, Se (purity better than 99.99 wt.%). The samples were synthesized by melting in evacuated quartz ampoules in a shaft-type furnace. The alloys were heated to the maximal temperature equal to about 700 K and have been kept for 5 h. Then the melts were cooled at a rate of 10–20 K/h to 520 K and after they have been annealed to establish equilibrium state for 500 h. Finally, the samples were quenched to ambient temperature in air.

The samples were explored by X-ray diffraction (XRD) and differential thermal (DTA) analysis. Powder diffraction patterns were recorded using a DRON -4 13 X-ray diffractometer with $\text{CuK}\alpha$ source in the 2θ range varying within 10–80° with 0.05° scan increment and 5 s exposure for each point. DTA utilized a Paulik-Paulik-Erdey system derivatograph that was equipped by a Pt/Pt-Rh thermocouple.

Single crystals from the solid solutions range containing 5 and 10 mol.% SnSe_2 were grown by Bridgman-Stokbarger method in a two-zone vertical furnace. Calculated amounts of elements with 10 g total weight were loaded in quartz containers with conical bottoms, evacuated and soldered. Preliminary synthesis of the alloys was held in a shaft-type furnace where the containers with the batches were placed upside down and heated to 1220 K. After keeping at the maximum temperature for 10 h the containers with the melts were transferred to the pre-heated growth furnaces (cone down). The maximum temperature of the grown zone (upper furnace) was selected from the phase diagram of the $\text{TlGaSe}_2-\text{SnSe}_2$ system at 70–80 K above the liquidus temperature, and the temperature of the annealing zone (bottom furnace) was varied within 720–770 K. The temperature gradient at the solid-melt interface was equal to about 3–3.5 K/mm. The rate of lowering of the containers with the melts was equal to 7 mm/day. After reaching the isothermal zone, the crystals were annealed for 100 h. Cooling to ambient temperature drafted additional 100 h. The maximal size of the single crystals was limited by the batch weight and the sizes of the container and did not exceed 20–25 mm in length and up to 13 mm in diameter.

The samples for optical studies were cleaved from the middle part of the single crystalline in got. The layered structure of the investigated crystals allowed to do optical measurements on parallel-plane surfaces of optical quality without additional polishing. An MDR-206 monochromator with spectra resolution 0.37 nm was used for studies of optimal transmittance/absorption. The light beam was incident perpendicularly to the layers (parallelly to the crystallographic axis *c*). A nitrogen cryostat with a Utrecs K41-3 thermostat was employed within the temperature range of 100–300 K (temperature stabilization accuracy ± 0.2 K).

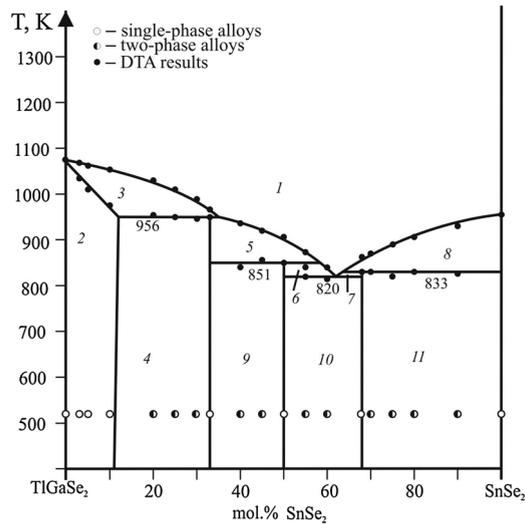


Fig. 1. Phase diagram of the TlGaSe₂-SnSe₂ system (1 - L, 2 - α, 3 - L + α, 4 - α + Tl₂Ga₂SnSe₆, 5 - L + Tl₂Ga₂SnSe₆, 6 - L + TlGaSnSe₄, 7 - L + TlGaSn₂Se₆, 8 - L + SnSe₂, 9 - Tl₂Ga₂SnSe₆ + TlGaSnSe₄, 10 - TlGaSnSe₄ + TlGaSn₂Se₆, 11 - TlGaSn₂Se₆ + SnSe₂).

3. Results and discussion

The results of the exploration for the TlGaSe₂-SnSe₂ system (Fig. 1) confirmed the formation of compounds with SnSe₂ content of 50 and 66.7 mol. % [19].

XRD and DTA data indicate the formation of the phase of the Tl₂Ga₂SnSe₆ composition, rather than Tl₃Ga₃SnSe₈ as reported in [19]. The compound is formed in the peritectic reaction L + α ↔ Tl₂Ga₂SnSe₆ at 956 K. The boundary composition of the solid solution range of thallium gallium diselenide is equal to about 11 mol. % SnSe₂ which is less than in the work [19].

Isothermal section of the Tl₂Se-Ga₂Se₃-SnSe₂ system at 520 K was constructed from X-ray phase analysis results as shown in Fig. 2. The formation of the ternary compounds Tl₄SnSe₄, Tl₂SnSe₃, TlGaSe₂ was confirmed. Three quaternary phases are seen at the TlGaSe₂-SnSe₂ section. Nine single-phase fields and 14 two-phase equilibria split the concentration triangle into 10 three-phase regions. The largest solid solution ranges are based on the compounds TlGaSe₂ and Ga₂Se₃.

Using the literature data on the boundary systems and the quasi-binary TlInSe₂-SnSe₂ section as well as our XRD investigation of alloys, isothermal section of the quasi-ternary system Tl₂Se-In₂Se₃-SnSe₂ at 520 K was build. The results are presented in Fig. 3.

No quaternary compounds were detected in this system. The location of 5 three-phase fields was determined, and 11 two-phase equilibria of binary and ternary compounds were observed. The solid solubility based on TlInSe₂ is equal to 28 mol.% along the TlInSe₂-SnSe₂ section which is consistent with the existed data [7].

The field of application of semiconductors in optoelectronics is related to the value of optical band gap energy. The spectral distribution of the transmission coefficient was studied to estimate optical band gap energy. Absorption coefficient near the fundamental absorption edge was calculated by an equation (1) [21]:

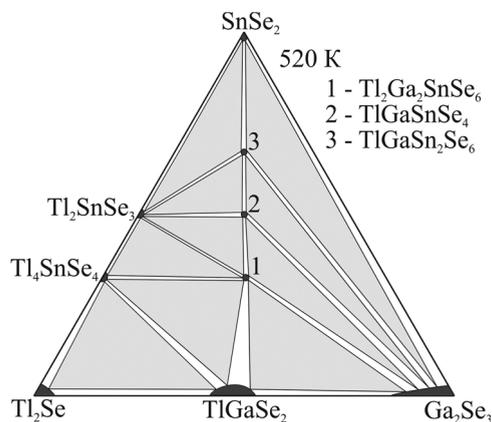


Fig. 2. Isothermal section of the Tl₂Se-Ga₂Se₃-SnSe₂ system at 520 K.

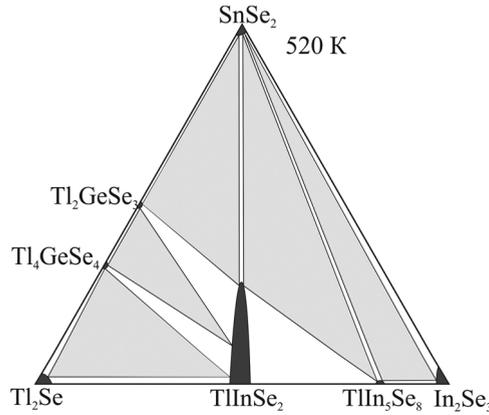


Fig. 3. Isothermal section of the Tl_2Se - In_2Se_3 - $SnSe_2$ system at 520 K.

$$\alpha = \frac{1}{d} \ln \left[\frac{(1 - R)^2}{2T} + \left(\frac{(1 - R)^4}{4T^2} + R^2 \right)^{1/2} \right] \tag{1}$$

where I is the intensity of the light transmitted through the sample; I_0 is the incident light intensity; R is the reflectance coefficient for normal incidence; α is the absorption coefficient; d is the sample thickness; $T = I/I_0$ is the transmission coefficient. The calculation results are presented in Fig. 4.

(Fig. 5) which agrees well with the data of [22,23].

To determine the band gap energy for direct (E_g^d) and indirect (E_g^i) permitted transitions, the dependences $(ah\nu)^2 = f(h\nu)$ and $(ah\nu)^{1/2} = f(h\nu)$ were extrapolated to $(ah\nu)^2 = 0$ and $(ah\nu)^{1/2} = 0$ (Fig. 5, Table 2).

One can see that the edge of the fundamental absorption band is spectrally red shifted with increasing x , i.e. increasing the content of $SnSe_2$ (see Fig. 5, Table 2). The decrease of the band gap energy may be caused by formation of solid solutions due to statistical substitution of Ga atoms ($r(Ga^{3+}) = 0.062$ nm) by Sn atoms ($r(Sn^{4+}) = 0.067$ nm) and the increase of Tl vacancy concentration. The obtained results confirm that the band gap energy decreases with increasing temperature for all the investigated samples. The authors of [24] explain the variation of the band gap energy with temperature by changes in the frequency of phonons that favor various effects like thermal expansion of the lattice, increase in the electron-phonon bonding, and consequently mutual repulsion of intra-band electronic states. Numerical simulation of the temperature dependence for the band gap energy taking into account the thermal expansion of the energy states for the allowed inter-band transitions of the titled semiconductor was performed in [25]. It was determined that with increasing temperature, the boundaries of the conduction and the valence bands begin to penetrate noticeably deep into the for Tl_2Se - $Ga(In)_2Se_3$ - $SnSe_2$ forbidden band gap which leads to its contraction. The temperature

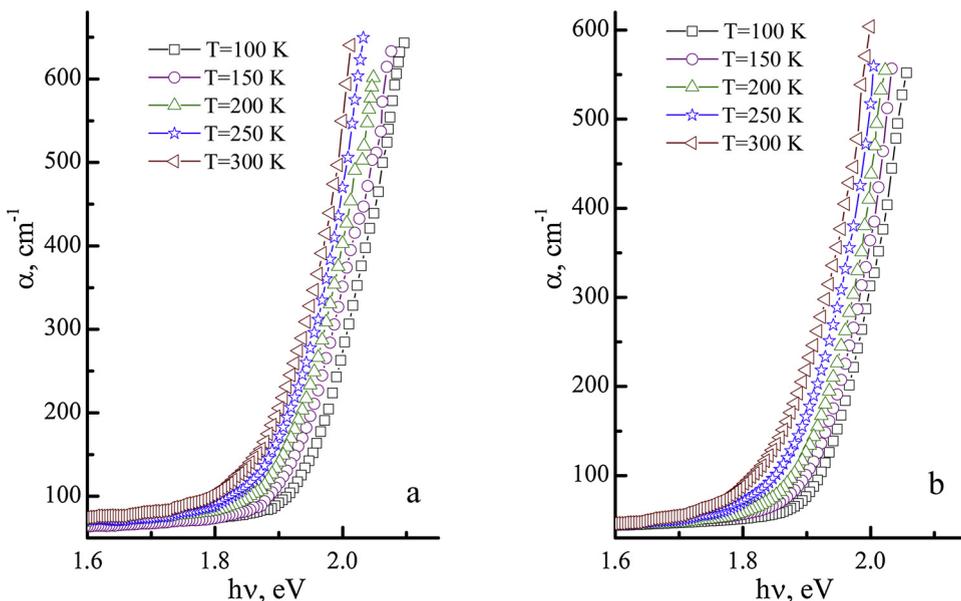


Fig. 4. Typical absorption spectra obtained at temperatures 100, 150, 200 and 300 K for $(TlGaSe_2)_{1-x}(SnSe_2)_x$ samples: a) $x = 0.05$; b) $x = 0.1$.

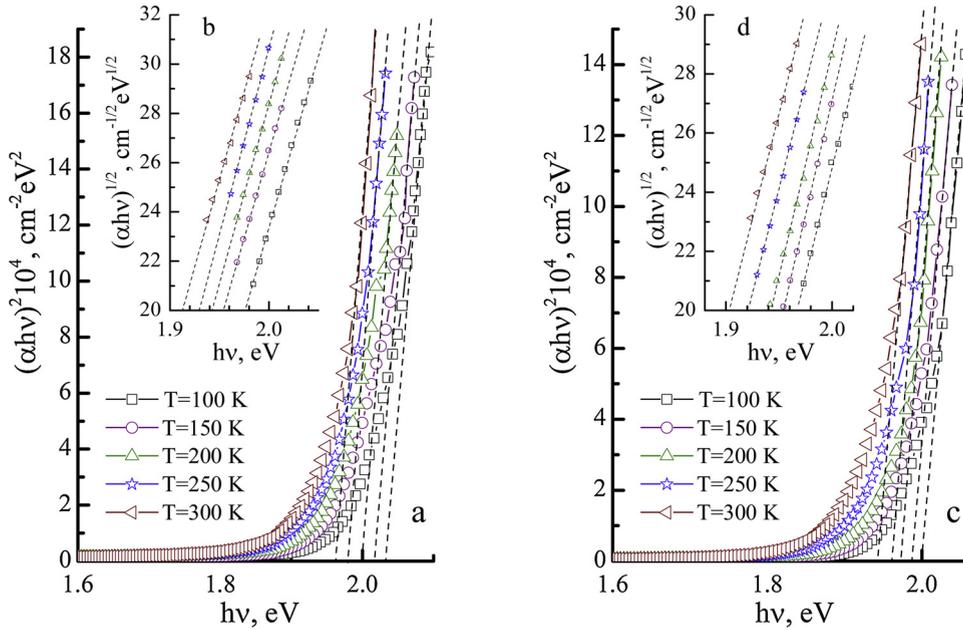


Fig. 5. Direct (a, c) and indirect (b, d) absorption spectra versus photon energy for the $(\text{TlGaSe}_2)_{1-x}(\text{SnSe}_2)_x$ samples: a, b) $x = 0.05$; c, d) $x = 0.1$.

Table 2

The dependence of the band gap energy versus temperature in for the $(\text{TlGaSe}_2)_{1-x}(\text{SnSe}_2)_x$ crystals.

Sample	Sample temp.(K)	E_g^d , eV	E_g^i , eV	Sample	Sample temp.(K)	E_g^d , eV	E_g^i , eV
7x = 0.05	100	2.02	1.82	x=0.10	100	1.99	1.81
	150	2.00	1.80		150	1.98	1.80
	200	1.98	1.79		200	1.97	1.77
	250	1.96	1.77		250	1.95	1.75
	300	1.95	1.75		300	1.93	1.72

coefficient of the band gap energy variation was calculated from the results presented in Table 2. The value of $3.3\text{--}4.5 \cdot 10^{-4}$ eV/K agrees well with the data of [26,27].

Exponential dependence of α on $h\nu$ is observed below the region of strong absorption (Fig.6) in the whole range of available compositions and temperatures.

The exponential portions of the $\alpha(h\nu)$ dependence follow Urbach's rule [28]:

$$\alpha(h\nu, T) = \alpha_0 \exp\left[\frac{h\nu - E_0}{E_u(T)}\right] \tag{2}$$

where α is the absorption coefficient, α_0 is a constant that depends on the sample quality, E_0 is a parameter close to the band gap energy at $T = 0$ K, E_u is Urbach's energy ($E_u = k_B T / \sigma(T)$, where k_B is Boltzmann constant, $\sigma(T)$ is the steepness parameter of the absorption edge that is equal to the energy width of the region of the absorption edge and is a measure of disordering of the material. From the experimental results, E_u was determined as $E_u = \Delta(h\nu) / \Delta(\ln \alpha)$, and α_0 and E_0 are the coordinates of the convergence point of $\ln \alpha = f(h\nu, T)$.

The fitting of the absorption spectra by Urbach's formula yielded the values of E_u , α_0 , and E_0 which are presented in Table 3 and in Fig. 7.

The temperature dependences of Urbach's energy determined from the experimental data as $E_u = \Delta(h\nu) / \Delta(\ln \alpha)$ are presented in Fig. 7 by open points. One can see an increase in E_u with the temperature increasing from 100 to 300 K for both compositions. We consider this fact to be caused by an increase in the concentration of charged defects that were neutral at low temperatures due to their thermionisation.

Additional ionization of defect centers in the sample gives some contribution to E_u increase with temperature. This one causes the distortion of the potential periodicity by random electric field due to the fluctuations of the concentration of charged defects [24].

The temperature dependence of E_u is sufficiently well consistent with the empirical model proposed by Z. Yang et al. [29] which takes into account the influence of electron/exciton-phonon interaction and structural and compositional distortion on of phonons that are associated with Urbach's tail. Temperature dependence of Urbach's energy was analyzed to estimate the dominant mechanisms that contribute to behavior of the fundamental absorption edge. It was determined that E_u can be modeled as an Einstein

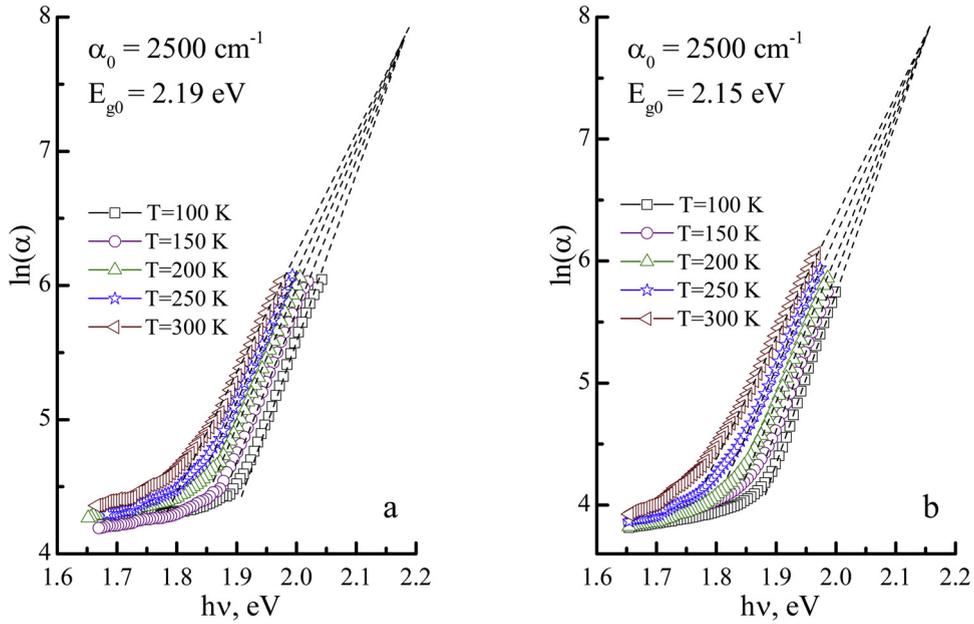


Fig. 6. Absorption coefficient vs photon energy for the (TlGaSe₂)_{1-x}(SnSe₂)_x samples: a) x = 0.05; b) x = 0.1.

Table 3
Urbach's Rule Parameters.

Samples	Sample temp.(K)	Urbach energy, (meV)	Steepness parameter	Samples	Sample temp.(K)	Urbach energy, (meV)	Steepness parameter
x = 0.05	100	66	0.13	x=0.10	100	79	0.11
	150	75	0.17		150	87	0.15
	200	85	0.20		200	96	0.18
	250	90	0.23		250	102	0.21
	300	103	0.25		300	111	0.23

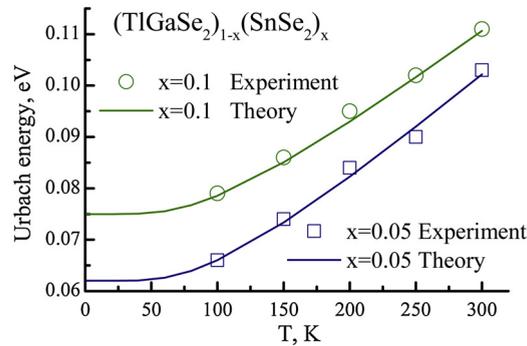


Fig. 7. Urbach's energy as a function of temperature for the (TlGaSe₂)_{1-x}(SnSe₂)_x samples.

oscillator [30] which takes into account the contributions of dynamic (thermal) and static (structural and compositional) disorder. According to this model, Urbach's energy can be expressed by the following expression:

$$E_U = A \left(\frac{1}{e^{\theta/T} - 1} \right) + B \tag{3}$$

where A and B are constants associated with thermal, structural and compositional disorders; θ is the Einstein temperature corresponding to the average frequency of phonon excitations of non-interacting oscillators.

Eq. (3) means that Urbach's energy significantly depends on the electron-phonon interaction and structural disorder and may be presented as a sum of the two terms. The first term of Eq. (3) is the contribution of the electron-phonon interaction in a form of the Debye-Waller factor, and the second one is due to the mean-square deviation of the atoms from equilibrium positions which is caused by structural disordering of a perfect crystalline lattice. The best fit for experimental results (open points) and Eq. 3 with adjustable

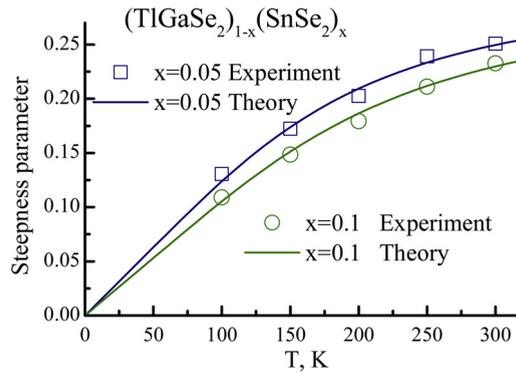


Fig. 8. Steepness parameter vs temperature for the $(\text{TlGaSe}_2)_{1-x}(\text{SnSe}_2)_x$ samples.

parameters A and B (continuous line) is plotted in Fig. 7. The adjustable parameters A and B for the $(\text{TlGaSe}_2)_{1-x}(\text{SnSe}_2)_x$ crystals with $x = 0.05$ are equal to 62 and 62 meV; for $x = 0.1$ these parameters are equal to 55 and 75 meV, respectively.

From the A and B , the contribution to Urbach's energy for both terms is commensurable for $x = 0.05$. The increase in the parameter B with the concentration of SnSe_2 ($x = 0.1$) is evidently due to the increase in the concentration of structural defects as confirmed by X-ray diffraction studies.

The steepness parameter $\sigma(T) = kT\Delta(\ln\alpha)/\Delta(h\nu)$ calculated from the experimental data concerning the absorption tails in the region of the fundamental edge is shown in Fig. 8 as open points.

The $\sigma(T)$ dependence is approximated in the whole range of temperatures by the expression for the absorption edge which involves the contribution of electron-phonon interaction [31,32]:

$$\sigma(T) = \sigma_0(2kT/h\nu_0) \text{th}(h\nu_0/2kT), \quad (4)$$

where $h\nu_0$ is an effective phonon energy which prevalingly coincides with the energy of the phonons involved in the formation of the long-wave side of the absorption edge; σ_0 is a temperature-independent but material-dependent parameter that is inversely proportional to the constant g of the interaction between electrons / excitons and phonons according to the formula $\sigma_0 = (2/3)g^{-1}$.

Experimental data were expressed according to Eq. (4) with σ_0 and $h\nu_0$ as adjustable parameters to estimating the value of phonon energies associated with Urbach's tails. The best fit of the experimental data to Eq. 4 is plotted in Fig. 8 and is indicated by solid lines. The approximation parameters were equal to $\sigma_0 = 0.30$ and 0.29 ; $h\nu_0 = 41$ and 47 meV for $x = 0.05$ and 0.1 , respectively, which is in a good agreement with the results of [33]. The effective phonon energy $h\nu_0$ is higher than the highest optical mode in the TlGaSe_2 crystals [34]. The higher $h\nu_0$ value in ternary chalcopyrites and mixed chalcogenides is associated with structure disorders caused by cation defects (interstitial atoms, cation vacancies) and deviations from perfect stoichiometry [35]. The decrease of σ_0 at higher SnSe_2 content can be related to the increase of Sn^{4+} ions in Ga^{3+} sites and of silver vacancies since they, as charged impurities, affect the electron-phonon interaction. A similar behavior was also observed for the TlInSe_2 crystals when In ions were substituted by Si or Ge [30,34,35].

4. Conclusions

The existence of two new compounds, $\text{Tl}_2\text{Ga}_2\text{SnSe}_6$ and $\text{Tl}_{5.6}\text{InSn}_{6.7}\text{S}_{17.6}$, were established following quasi-ternary systems $\text{Tl}_2\text{Se}-\text{Ga}(\text{In})_2\text{Se}_3-\text{SnSe}_2$ applying physical-chemical analysis methods. Their isothermal sections at 520 K in the entire concentration range were constructed. The titled systems are characterized by the solid solubility in the ternary compounds $\text{TlC}^{\text{III}}\text{Se}_2$. The homogeneity regions are stretched along the $\text{TlC}^{\text{III}}\text{Se}_2-\text{SnSe}_2$ sections. Optical absorption in the region of the fundamental absorption edge was investigated. Band gap energy and Urbach's rule parameters were estimated. The edge of the fundamental absorption band is spectrally red shifted with increasing x , i.e. increasing the content of SnSe_2 . The decrease of the band gap energy may be caused by formation of solid solutions due to statistical substitution of Ga atoms ($r(\text{Ga}^{3+}) = 0.062$ nm) by Sn atoms ($r(\text{Sn}^{4+}) = 0.067$ nm) and the increase of Tl vacancy concentration. The higher Urbach parameter $h\nu_0$ value is associated with enhancement of structural disordering caused by cation defects (interstitial atoms, cation vacancies) and deviations from perfect stoichiometry. The decrease of σ_0 at higher SnSe_2 content can be related to the increase of Sn^{4+} ions in Ga^{3+} site positions and of silver vacancies since they are charged impurities and affect the electron-phonon interaction.

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