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PHOTOINDUCED OPTICAL PROPERTIES OF $Tl_{1−x}In_{1−x}Si_xSe_2$ SINGLE CRYSTALS

INDUKOWANE ŚWIATŁEM WŁAŚCIWOŚCI OPTYCZNE MONOKRYSZTAŁÓW $Tl_{1−x}In_{1−x}Si_xSe_2$

The influence of temperature on electroconductivity and photoinduced changes of the absorption at 0.15 eV under influence of the second harmonic generation of CO_2 laser for the two type of single crystals were investigated. The single crystals $Tl_{1−x}In_{1−x}Si_xSe_2$ (x=0.1 and 0.2) have been grown by the two-zone Bridgaman-Stockbarger method. The temperature studies of electroconductivity were done in cryostat with thermoregulation in the temperature 77 - 300 K, with stabilization ±0.1 K. Photoinduced treatment of the investigated single crystals were performed using the 180 ns pulses second harmonic generation of the CO_2 laser operating at 5.3 μm. Experimental studies have shown that for the $Tl_{1−x}In_{1−x}Si_xSe_2$ single crystals with decreasing temperature from 300 up to 240 K and from 315 up to 270 K the conductivity is realized by thermally excited impurities with activation energies equal to about 0.24 eV and 0.22 eV for x= 0.1 and 0.2, respectively. Photoinduced absorption achieves its maximum at a power density below 100 mJ/cm². Has been shown that the samples with x=0.2 demonstrated higher changes of the photoinduced absorption with respect to the x=0.1.With further decreasing temperature is observed monotonic decrease in the activation energy of conductivity. The origin of these effects is caused by the excitations of both the electronic as well as phonon subsystem. At some power densities the anharmonic excitations become dominant and as a consequence the photoinduced absorption dependence is saturated what were observed. Additionally, we were evaluated at given temperature the average jump length of R for localized states near Fermi level.

Keywords: $Tl_{1−x}In_{1−x}Si_xSe_2$ single crystal, chalcogenide crystals, optical properties, photoinduced absorption, dark electroconductivity, electroconductivity mechanisms

W pracy badano wpływ temperatury na przewodnictwo elektryczne oraz indukowane światłem zmiany absorpcji optycznej przy 0.15 eV, pod działaniem drugiej harmonicznej lasera CO_2 dla dwóch typów monokryształów. Monokryształy $Tl_{1−x}In_{1−x}Si_xSe_2$ (x=0.1 i 0.2) otrzymano w pionowym dwustrefowym piecu metodą Bridgamana-Stockbargera. Badania temperaturowe przewodności elektrycznej przeprowadzono w kriostacie z termoregulacją, w temperaturze 77-300 K, przy stabilizacji ±0,1 K. Fotoindukowaną obróbkę laserową monokryształów wykonano przy użyciu 180 ns impulsów drugiej harmonicznej lasera CO_2 o długości fali 5,3 μm. Eksperymentalnie wykazano, że z obniżaniem temperatury od 300 do 240 K i od 315 do 270 K przewodnictwo elektryczne monokryształów $Tl_{1−x}In_{1−x}Si_xSe_2$ jest wywołane przez wzbudzenia termicznie domieszek z energią aktywacji równą około 0,24 eV i 0,22 eV dla õ = 0,1 i 0,2, odpowiednio. Indukowana optycznie absorpcja osiąga maksimum przy gęstości mocy poniżej 100 mJ/cm². Stwierdzono, że próbka z x = 0,2 wykazuje większe zmiany absorpcji indukowanej światłem w porównaniu do próbki z x = 0.1. Z dalszym spadkiem temperatury obserwowano monotoniczny spadek energii aktywacji przewodnictwa. Pochodzenie tych efektów jest spowodowane przez wzbudzanie zarówno podsystemu elektronowego jak i fononowego. Przy niektórych gęściach mocy wzbudzenia anharmoniczne zaczynają dominować, co w konsekwencji prowadzi do nasycenia indukowanej światłem zależności absorpcji optycznej. Dodatkowo w pracy wyznaczono dla danej temperatury średnią długość skoku R dla stanów zlokalizowanych w pobliżu poziomu Fermiego.

1. Introduction

The group of novel thallous-containing ternary compounds with general formulae $TlB^{III}C_2^{VI}$ (B=In, Ga, C=S, Se, Te) possesses substantial anisotropy due to presence of layered-chain structure. These materials have an anisotropy due to high mobility intra the layers and low mobility inter the layers. As a consequence they show different effective

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masses determined by corresponding anisotropy of chemical bonds. The inter-layer chemical bonds are week Van-der-Waals chemical forces characterized by low degree of wave functions overlap. One of the most studies representatives for the such kind of crystal for this series is TlInSe$_2$ [1-3]. Interest to these Tl-containing type of compounds is caused by possible their applications for manufacturing of optoelectronic devices in the visible and infrared spectral range [4-7]. Based on TlInSe$_2$ there are created low-inertial photoresistors, detectors of X-ray irradiation and acoustooptical modulaotrs. For the crystals TlInSe$_2$ there are studied electrical, photoelectron features as well as the properties which may be applied for radiation dosimeters and optically operated triggers [8]. In the references [9] there is explored an influence of Ag, Cu, Au Eu, Sm, Yb impurities on electrical features of TlInSe$_2$. Additionally there were explored temperature dependences of dielectric susceptibility and conductivity for the TlInSe$_2$ in the electrical fields.

For extension of the titled class the changes and operation by their optoelectronic features would be important to explore a possibility of cationic substitution for the TlInSe$_2$ and of the related solid state alloys. The principal goal of the present work is to study of changes of optical constants for the titled compounds using external laser light n the infrared spectral range. The studies will be performed for TlInSe$_2$-SiSe$_2$ compounds. The discussion of the observed phenomena will be given within a framework of quantum chemical simulations.
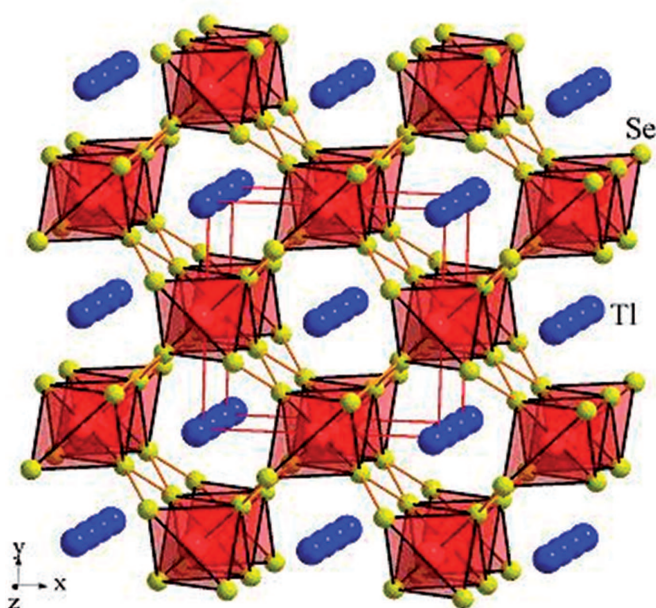

Fig. 1. Laying of InSe$_4$ tetrahedra for the crystals TlInSe$_2$

For extension of operation opportunities for the titled crystals and their derivatives very promising seems to be cationic substitution for the crystals TlInSe$_2$ and exploration of their solid state alloys. The main goal of this work is to study their electronic parameters, particularly for the solid state alloys TlInSe$_2$-SiSe$_2$ and exploration of the conductivity transport mechanisms. Generally the structure may be presented as tetrahedral formed by the Se atoms and surrounded by In cations (see Fig.1). The such formed tetrahedra linked by the edges form the columns along the principal crystal axis. The

inter-atomic distances for the Se atoms situated in the neighbor columns do not exceed the sum of ionic radiuses of Se. For the solid state alloy there occurs some isovalent substitution of the atoms. The Tl atoms are situated in the channels between these columns which are formed by isovalnet substitution of two atoms (Tl and In) by one atom. Following the ref. 10 for the solid state alloys Si atoms statistically occupy positions of In atoms. As a consequence there occurr vacancies in the positions of Tl atoms. Finally for the solid state alloys Tl$_{1-x}$In$_{1-x}$Si$_x$Se$_2$ one can occur additionally hole conductivity due to defects formed by Tl atoms.

2. Experimental

The crystal growth was performed by Bridgman-Stockbarger method in vertical two-zone furnaces. The process was carried out by slow movement of the crucible along the fixed gradient field of the furnaces. The such obtained crystals (similar to the ref. 10) possessed high homogeneouity and had very close principal parameters. For performance of optical measurements the crystals were cleaved along the cleavage plane. The studied samples possessed a form of parallelepipeds. The Ohmic contacts were deposited on the fresh cleaved surfaces of indium on the opposite faces of plates.

The crystalline surfaces were mirror-like which allows using them for studies without any additional treatment. The temperature studies were done in cryostat with thermoregulation in the temperature 77 - 300 K, with stabilization ±0.1 K.

3. Results and discussion

The single crystals Tl$_{1-x}$In$_{1-x}$Si$_x$Se$_2$ (x =0.1; 0.2) are high Ohmic p-type semiconductors. The hole types of conductivity is caused by shallow type vacancies which are situated in the bottom of the forbidden gap. The latter are of acceptor type. They cause a hole type of conductivity which is typical for different kind of chalcogen materials. With increasing x the conductive type remains the same. The concentration of the Si dopnts is less than the concentration of the stoichiometric vacancies and other structural defects. The high concentration of V_{Tl}, is caused by partial occupation by Tl atoms of the crystallographic local site positions *4a*. Additionally its reflects a statistical replacement of In atoms by Si atoms in the site positions *4b* as well as presence of other defects. And it is one of reason of disturbance of the long-range ordering [11]. This one leads to appearance of additional trapping levels intra the forbidden energy gap. This is more close to the solid state alloys. The optoelectronic properties of the disordered materials possess a couple of specific features which are clearly manifested by Urbach rule. It is shown as an Urbach edge for proper inter-band transitions. There occurs some temperature dependence of electroconductivity $\sigma(T)$, which may be fitted in the coordinate system $\ln \sigma - 100/T$ by straights with different activation energies (E_A), which correspond to different transport mechanisms [12].
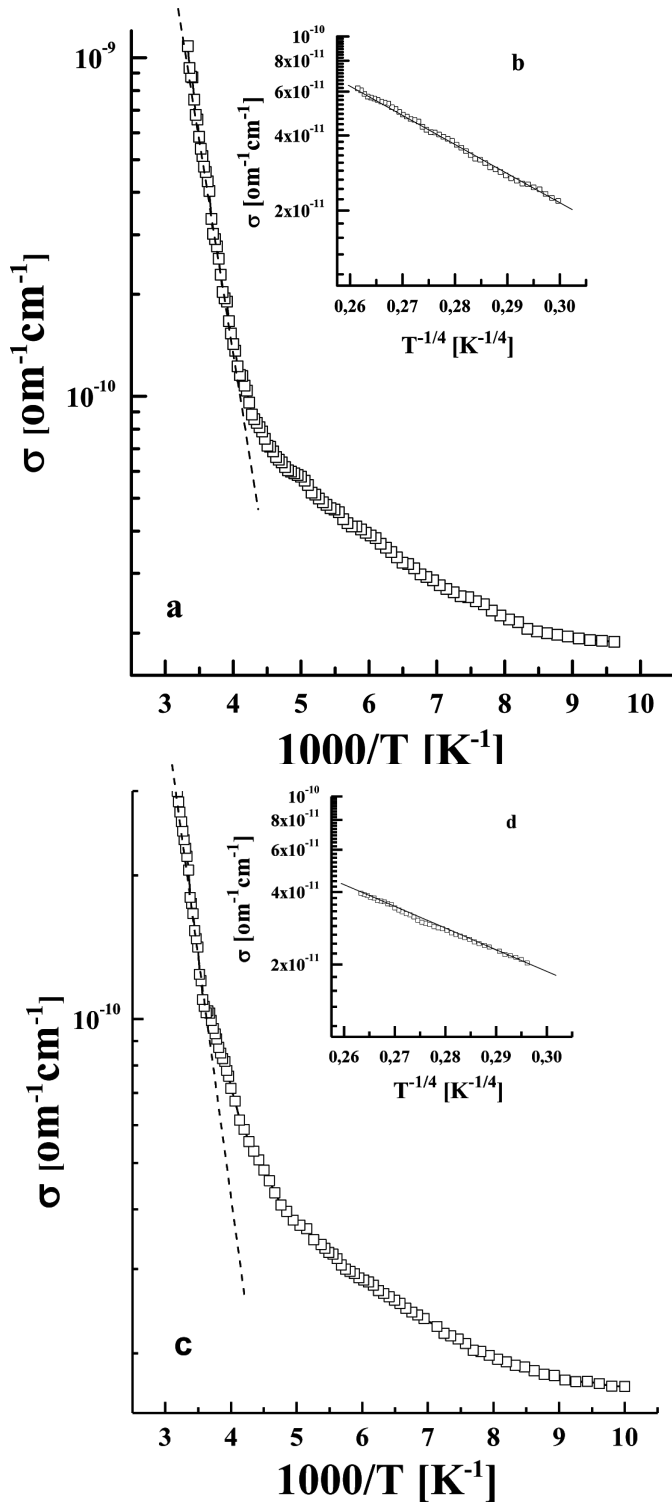
Fig. 2. Temperature dependence of specific electroconductivity for the single crystals $Tl_{1-x}In_{1-x}Si_xSe_2$: a, b $x = 0.1$; c, d $x = 0.2$

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_A}{kT}\right) \qquad (1)$$

where σ_0 is dependent on type of conductive mechanisms for disordered compounds.

The energy of activation calculated following an Eq. (1) was equal to ~0.24 ÍV, 0.22 eV, for $x = 0.1$ and 0.2; respectively. The coefficient σ_0 for this range following the Mott criterion [13] corresponds to electroconductivity mechanisms caused by excitation of carriers from the levels near E_F, which are situated in the tails of the valence band (for p-type semiconductors). For the alloys with defect donors (Si_{In}) and acceptors (V_{Tl}) the Fermi level is situated in the defective sub-bands within the forbidden gap. The latter from the maximal charge density of the acceptors levels for the studied crystals. Because the defective sub-bands is increased due to increasing defect content [10], the activation energy will be decreased. This is a consequence of decrease of the energy distances between the impurity and the proper band.

The existence of different energy levels within the energy gap of crystals $Tl_{1-x}In_{1-x}Si_xSe_2$ also may be caused by intrinsic structural defects, such as V_{Tl}, V_{In}, V_{Se} and defects, occurring during crystal growth, which is typical for layered crystals. During temperature decrease of the thermoactivated conductivity there is absent some permanent inclination, the continuously decreases with decreasing temperature to ~120 K.

Conductivity values in this field were rebuilt in the appropriate coordinates. As shown in (Fig. 2. b, d) depending on the given straightening we have obtained different magnitudes. This suggests that the temperature favours a charge transfer by means of hopping conduction carriers by localized states that lie in a narrow band of energies near the Fermi level. In this case, the conductivity is described by the known Mott ratio [13]:

$$\sigma \sim \exp\left[-(T_0/T)^{1/4}\right] \qquad (2)$$

Obviously, the rapid freezing of doped carriers in the permitted area at low temperatures leads to the fact that there comes in a time when the largest contribution to the conductivity jumps which are initiated by carriers for localized impurity states. Of course, hopping conduction mechanism is characterized by extremely low mobility of charge carriers and may be considered as jumps carried out through a weak overlap tail part of the wave functions of neighbouring acceptors. But hopping conduction band may be considered as a hopping conduction participating for every hole located on the acceptor.

Following the steepness $\ln(\sigma) - T^{-1/4}$ it was defined the magnitude of T_0 for electroconductivity along the chaines of $Tl_{1-x}In_{1-x}Si_xSe_2$, which was equal to 7.2×10^5 K and 4.6×10^5 K for $x = 0.1$; and 0.2, respectively.

$$T_0 = \frac{16}{N_F k a^3} \qquad (3)$$

where k – is Boltzmann constant, a – radius of localization, N_F – is the density of states near the Fermi energy level.

Assuming that the localization radius is equal to radius of the first coulombic excitons [14] for the crystals $A^{III}B^{III}C_2^{VI}$ (a = 20 Å) one can estimate the density of localized states near Fermi levels: $N_F = 3.2\times10^{19}$ eV^{-1}cm^{-1} and 5.02×10^{19} eV^{-1}cm^{-1} for $x = 0.1$; and 0.2; respectively.

In the Fig. 2 (a, c) are presented temperature dependences of specific dark electroconductivity for the $Tl_{1-x}In_{1-x}Si_xSe_2$ at $x = 0.1$; 0.2 in the Arrhenius coordinates ($\ln(\sigma) - 10^3/T$). Following the analysis of the experimental results concerning the temperature dependences of dark electroconductivity it was established that within the temperature range 300-240 K and 315- 270 K for the samples with $x = 0.1$ and $x = 0.2$, respectively, there is a good fitting by expression of disordered semiconductors:

As a consequence we have performed additional photoinduced treatment of the studied crystal using the 180 ns pulses second harmonic generation of the CO_2 laser operating at wavelength 5.3 μm.

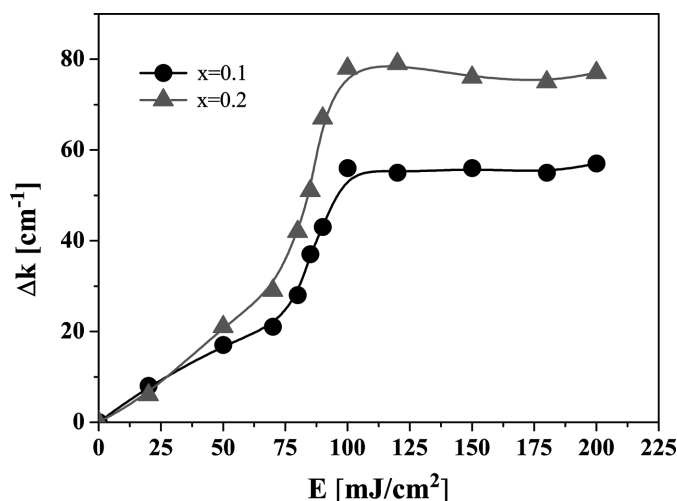
Fig. 3. Photoinduced changes of the absorption at 0.15 eV for the two types of the samples under influence of the second harmonic generation of CO_2 laser

Following the presented dependences in the Fig. 3 one can see that the photoinduced absorption achieves its maximum at power densities below 100 mJ/cm^2. With higher power densities the output signal is saturated. The samples with x=0.2 demonstrate higher changes of the photoinduced absorption with respect to the x=0.1. The origin of the effects is caused by the excitations of both the electronic as well as phonon subsystem. At some power densities the anharmonic excitations become dominate. As a consequence the dependence is saturated.

The high value of N_F for the studied single crystals may confirm a fact that we deal with the single crystals with high degree of disorder. The highly deformed and breaken chemical bonds are typical for amorphous phase and lead to occurrence of observed acceptor properties. Such defects play a crucial role for the crystals with layered and chain-like structures. The anisotropy of the chemical bonds for layered crystals favors a formation of huge number of defects in the range close to the inter-layers voids. This fact disturbs partially the long-range crystalline order and formation of the localized trapping levels within the energy gap. The availability of such defects is explained by high density near the Fermi level.

Following the presented data one can expect a possibility to decrease the effective energy gap during illumination. Using an equation:

$$R = \frac{3}{8}aT_0^{1/4}T^{-1/4} \qquad (4)$$

one can evaluate at given temperature the average jump length of R for localized states near Fermi level. At T = 125 K, R = 65 $\overset{\circ}{A}$, and at T = 215 T R = 57 $\overset{\circ}{A}$. So the average lengths of the jumps within the temperature range 125-215 K for x =0.1 is equal to R_{av} =61 $\overset{\circ}{A}$. The magnitude of R_{av} for this case 3 times exceeds the average distance between the carrier localized centers, i.e. $R_{av/a}$ ≈3. For x =0.2 R=58 $\overset{\circ}{A}$ at T=130 K and R=51 $\overset{\circ}{A}$ at T=210 K. The average jump distance

for the titled crystals within the temperature range 130-210 K is equal to R_{av} =55 $\overset{\circ}{A}$. The magnitude R_{av} is approximately 2.7 times higher with respect to average distances between the localized carrier centers (a=20$\overset{\circ}{A}$).

Following the Eq. (4) with decreasing temperature the average length of carrier's jumps is increased. This is a consequence of enhanced probability of carrier jumps with decreasing temperature. This probability increases for the higher distances, however energetically it is more close localization centers. The jumps as a rule are observed between the states with minimal activation energy ∆E. Following the presented reasons the energy may be considered as a width of the optimal band for energies near the Fermi levels:

$$\frac{4\pi}{3}R^3N_F\frac{\Delta E}{2} = 1 \qquad (5)$$

Following the equations (4) and (5) at different temperatures we have evaluated the following magnitudes: the average length of carrier jumps and distribution of the localized states for the titled crystals (see TABLE 1).

TABLE 1

The average length of the jump and spread of energy carriers localized states of crystals $Tl_{1-x}In_{1-x}Si_xSe_2$

$Tl_{1-x}In_{1-x}Si_xSe_2$	T [K]	R [$\overset{\circ}{A}$]	∆E [meV]
x =0.1	125	65	53
	213	57	79
x =0.2	130	58	49
	210	51	70

The concentration of deep traps (N_t = $N_F\Delta E$) for the studied crystals is equal to ~2.08×10¹⁸cm^{-3} and ~2.93×10¹⁸cm^{-3}, respectively. Following the obtained results the doping influences on the degree of disordering and leads to enhanced concentration of localized electronic states. So the titled crystals may be considered like disordered array of the near ordered ranges. High conductivity in localized states in the band gap is due to the existence of a high concentration of defect centres. Thus, in the temperature range 125-215 K ~ in the studied solid solutions there exists a hopping conductivity with variable-length jump over states localized near the Fermi level. In the temperature range T <125 K the conductivity of single crystals is independent on temperature. This suggests that the layers along the crystal in this temperature range are caused by a hopping conduction and are activation-free.

4. Conclusions

Following the performed experimental results one can see that for the studied $Tl_{1-x}In_{1-x}Si_xSe_2$ single crystals with decreasing temperature from 300 up to 240 K and from 315 up to 270 K the conductivity is formed by thermally excited impurities with activation energies equal to about 0.24 eV and 0.22 eV for x = 0.1 and 0.2, respectively. With further decreasing temperature it is observed monotonic decrease in the activation energy of conductivity. In the temperature range 125 <T <215 K the conductivity in crystals may be presented by

means of jumping carriers by localized states near the Fermi level. In this temperature range observed hopping conduction with variable jump length that with further decreasing temperature is activation-free. Photoinduced absorption achieves its maximum at a power density below 100 mJ/cm^2. With higher power densities the signal is saturated. The samples with $x = 0.2$ demonstrate higher changes of the photoinduced absorption with respect to the $x = 0.1$. The origin of the effects is caused by the excitations of both the electronic as well as phonon subsystem. At some power densities the anharmonic excitations become dominant. As a consequence the dependence is saturated.

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REFERENCES

[1] N.A. Abdullaev, K.R. Allakhverdiev, G.L. Belenkii, T.G. Mamedov, R.A. Suleimanov, Ya.N. Sharifov, Phase transition and anisotropy of thermal expansion in $TlInS_2$, Solid State Commun. **53** (7), 601-602 (1985).

[2] V.M. Burlakov, M.R. Yakheev, Raman scattering in ferroelectric $TlGaSe_2$. Soft Mode and Order Parameter, Phys. Status Solidi B **151** (1), 337-346 (1989).

[3] Sh. Nurov, V.M. Burlakov, E.A. Vinogradov, N.M. Gasanly, B.M. Dzhavadov, Vibrational Spectra of $TlInS_2$, $TlIn_{0.95}Ga_{0.05}S_2$, and $TlIn(S_{0.8}Se_{0.2})_2$ Crystals in the Vicinity of Phase Transitions, Phys. Status Solidi B **137** (1), 21-32 (1986).

[4] Ya.O. Dovgii, I.V. Kityk, M.I. Kolinko, A.S. Krochuk, A.V. Franiv, M.K. Zamorskii, Band structure and charge density distribution of cubic face-centred TlI single crystals, Phys. Status Solidi B **167** (2), 637-646 (1991).

[5] Ya.O. Dovgii, I.V. Kityk, I.G. Man'kovskaya, L.N. Evstigneeva, Polarized light spectrum of Tl_3SbS_3 single crystals. Sov. Phys. Semicond. **24** (9), 1004-1005 (1990).

[6] Ya.O. Dovgii, I.V. Kityk, M.I. Kolin'ko, A.S. Krochuk, A.V. Franiv. Band-structure and electron-density distribution of FCC TLI, Phys. Solid State. **33** (1) 225-233 (1991).

[7] Ya.O. Dovgii, I.V. Kityk. Photokinetic effects in Tl_3SbS_3 single crystals. Sov. Phys. Semicond. **25** (10), 1108-1111 (1991).

[8] S.N. Mustafaeva, V.A. Ramazanzade, M.M. Asadov, Influence of intercalation on electrical and photoelectrical properties of ternary chain and layer semiconductors, Mater. Chem. Phys. **40** (2), 142-145 (1995).

[9] E.M. Godzzhaev, E.A. Allakhyarov, Kh.S. Khalilova, A.M. Suleimanova, Transport properties of $TlInSe_2$ <Ln >(Ln = Eu, Sm, Yb), Inorg. Mater. **39** (7), 676-679 (2003).

[10] G.E. Davydyuk, O.Y. Khyzhun, A.H. Reshak, H. Kamarudin, G.L. Myronchuk, S.P. Danylchuk, A.O. Fedorchuk, L.V. Piskach, M.Yu. Mozolyuk, O.V. Parasyuk, Photoelectrical properties and the electronic structure of $Tl(1-x)In(1-x)Sn(x)Se_2$ (x = 0, 0.1, 0.2, 0.25) single crystalline alloys, Phys. Chem. Chem. Phys. **15** (18), 6965-72 (2013).

[11] G.L. Myronchuk, O.V. Zamurueva, O.V. Parasyuk, L.V. Piskach, A.O. Fedorchuk, N.S. AlZayed, A.M. El-Naggar, J. Ebothe, M. Lis, I.V. Kityk, Structural and optical properties of novel optoelectronic $Tl_{1-x}In_{1-x}Si_xSe_2$ single crystals. J. Mater. Sci. - Mater. Electron. **25**, 3226-3232 (2014).

[12] M. Makowska-Janusik, I.V. Kityk, G. Myronchuk, O. Zamuraeva, O.V. Parasyuk, Manifestation of intrinsic defects in the band structures of quaternary chalcogenide $Ag_2In_2SiSe_6$ and $Ag_2In_2GeSe_6$ crystals. Cryst. Eng. Comm. **16**, 9534-9544 (2014).

[13] N. Mott, EA Davis, Электронные процессы в некристаллических веществах, Moskow, 1974.

[14] Ya.O. Dovgii, I.V. Kityk, Light Dispersion in CdJ_2 crystals, Izvestiya Vysshikh Uchebnykh Zavedenii Fizika **28** (6), 101-104 (1985).