

PACS: 71.20.Nr, 72.20.Ee, 72.20.Fr, 72.20.Jv, 72.30.+q

## INFLUENCE OF $\gamma$ -RADIATION ON DIRECT AND INDIRECT OPTICAL TRANSITIONS IN $(\text{TlGaSe}_2)_{1-x}(\text{TlInS}_2)_x$ MIXED CRYSTAL

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**Abstract:** The optical properties of  $(\text{TlGaSe}_2)_{1-x}(\text{TlInS}_2)_x$  solid solutions were performed through transmission and reflection measurements in the wavelength range of 400 - 1100 nm. Optical indirect and direct band gap energies of  $(\text{TlGaSe}_2)_{1-x}(\text{TlInS}_2)_x$  were found by analyzing the absorption data at room temperature, after  $\gamma$ -irradiated 0 - 25 Mrad. Band-gap energies of the studied crystals were estimated by means of the derivative spectra of transmittance and photon energy dependence of absorption coefficient. The compositional dependence of direct band-gap energy at room temperature revealed that  $\gamma$ -irradiation increased in the  $(\text{TlGaSe}_2)_{1-x}(\text{TlInS}_2)_x$  solid solutions, the direct band-gap energy increases approximately on ~0.04 eV, from D=0 Mrad to D=25 Mrad, the indirect band-gap energy increases approximately on ~0.03-0.1 eV from D=0 Mrad to D=25 Mrad. The observed bands were assigned to the transitions of electrons from conduction band to the shallow acceptor levels in the band gap.

**Key words:** Semiconductors, band-gap energy, direct and indirect band gap,  $\gamma$ -irradiation.

### 1. Introduction

$\text{TlGaSe}_2$  and  $\text{TlInS}_2$  is a semiconductor with promising optical and electrical properties, especially for applications in electronics and optoelectronics. Due to the high mass density, thallium-containing chalcogenides are promising sources of materials for the detection of hard radiation. By combining layered chalcogenides, the band gap can be tuned in a wide energy range (0.6 – 2.4 eV) and the crystal can be prepared in complex stoichiometric and crystal structures that can be used in photovoltaic. Structures of these types of semiconductors present anisotropy on account of different bonding of intra- and interlayers. Strong ionic-covalent bonding occurs within each layer packet while weak van der Waals bonding occurs between the packets. Thallium dichalcogenides with chemical formula  $\text{TlMX}_2$  (where M = In or Ga, X = S or Se) are members of layered crystals and have been previously investigated with regard to optical, electrical and structural properties. They can be good candidates for application in devices such as emission modulators, memory switching elements and nonlinear optical transducers [1–7]. Modification of the physical features of these crystals is possible and practicable due to the easy formation of mixed crystals on their own base.

In  $\text{TlGaSe}_2$  and  $\text{TlInS}_2$  crystals discovering low temperature ferroelectricity, it was found the incommensurability phase for  $\text{TlInS}_2$  between 200-220 K and 107 - 120 K for  $\text{TlGaSe}_2$ . Incommensurate phase fills the gap between the high temperature paraelectric and low temperature ferroelectric phases. Investigation of  $\text{TlGaSe}_2$  and  $\text{TlInS}_2$  contributes to better understanding of the carrier transport, recombination and optical properties.

This crystals crystallize in monoclinic system which at room-temperature belongs to symmetry group  $C2/c - C^{2h}_6$ . Crystallographic  $c$ -axis is slightly tilted from the normal to the layer plane  $c$ -axis and forms the monoclinic angle  $\beta = 100.06^\circ$ . The crystal lattice contains 16 atoms on two adjacent layers [1– 5]. Smaller units of  $\text{GaSe}_4$  form tetrahedron with Ga atoms

placed in the center and Se atoms placed in the corners. These four tetrahedral units form larger polyhedron  $\text{Ga}_4\text{Se}_{10}$  which is linked by common chalcogenide atoms at the corners connected with the next one. Four neighboring polyhedral are forming a layer plane. In each successive case two anionic layers are stacked along the [001] with  $\text{Tl}^+$  ions placed between them. Structurally every succeeding layer is twisted by  $90^\circ$  to each other and forming trigonal prismatic cavities where Tl atoms lay in straight lines  $a[110]$  and  $b[\bar{1}\bar{1}0]$  that are parallel to the edges of the  $\text{Ga}_4\text{Se}_{10}$  groups.

Due to close proximity of the direct and the indirect bandgaps the crystal is often referred as a mixed direct/indirect bandgap semiconductors. It was found experimentally that direct bandgap optical transitions are allowed slightly due to low oscillator strength constant. Theoretical calculations of the  $\text{TlGaSe}_2$  band structure have shown that the top of the valence bands is composed of Se:4p and Tl:6s wave functions, while the bottom of the conduction bands is composed of Tl:6p, Ga:4s and Se:4s states which showed the slight separation of indirect bandgap [8,9]. The valence band maximum lies in the  $\Gamma$ -point in the Brillouin zone diagram while the positions of the indirect conduction band valleys have shown controversy. Indirect minima of the conduction band were found theoretically in various directions between ( $\Gamma$ -Y) or (L-Z) lines depending on the calculation approach. According to [9], the indirect and direct bandgaps are separated energetically only by 90 meV ( $\Gamma$ -Y); in [10] estimated a value 100 meV ( $\Gamma$ -Y) separation; in [11] – 50 meV ( $\Gamma$ -Y) and Kashida et al. [12] found only 10 meV (L-Z) separation. Only in the method of Ref. [9] the spin orbit coupling was included in the analysis. Nevertheless, ( $\Gamma$ -Y) and (L-Z) indirect conduction valleys are energetically close to one another. It is well known that theoretical calculations estimate smaller bandgap value  $E_g$  comparing to experimental results. Theoretical mismatch with experiment is of about 200 – 300 meV.

A lot of optical spectroscopy studies have been performed under normal light direction perpendicularly to the layer plane. It was revealed predominant enhancement of optical transitions above the indirect bandgap edge. Different simplified approaches were used to extract the bandgap values where direct bandgap varied  $E_g^d=2.08\text{--}2.23$  eV and indirect bandgap varied  $E_g^i=1.83\text{--}2.13$  eV [2 - 12]. However, more likely, it has to do something with involvement of disorder parameter or with simplified band gap extraction approach in a narrow energy range.

This study presents the results of transmission measurements at room temperature, after  $\gamma$ - irradiated 0–25 Mrad dose, an insight to optical properties of  $(\text{TlGaSe}_2)_{1-x}(\text{TlInS}_2)_x$  solid solutions. The aimed of this work to obtain new knowledge about optical properties, in the band gap semiconductors  $(\text{TlGaSe}_2)_{1-x}(\text{TlInS}_2)_x$  solid solutions after  $\gamma$ - irradiated.

## 2. Experimental details

$(\text{TlGaSe}_2)_{1-x}(\text{TlInS}_2)_x$  solid solutions were grown by using the Bridgman-Stogbarger method from a stoichiometric compositions of a melt of starting materials. The quartz tube with reagents is inserted into a thin quartz tube, evacuated and sealed ( $10^{-5}$  Torr). The tube is introduced into perpendicular two zone furnace and temperature is increased in careful controlled manner up to melting temperature of  $950^\circ\text{C}$ . Temperature gradient is about 20 K/cm and hot zone is maintained at  $970^\circ\text{C}$ . Melt homogenized for 6–7 hours in the furnace and then translation initiated at a speed of 1.5mm/hour. When solidification is complete the top and bottom ends of the slab are removed to dispose segregated impurities. Our samples were selected from the most pure regions of bulk crystals. Obtained crystals were yellow and dark brown-red color and had cleavage normal to the  $c$ -axis.

The resulting in gots of  $(\text{TlGaSe}_2)_{1-x}(\text{TlInS}_2)_x$  solid solutions no cracks and voids on the surface. The chemical compositions of the  $(\text{TlGaSe}_2)_{1-x}(\text{TlInS}_2)_x$  solid solutions were determined

by using energy dispersive spectroscopic analyses with a JSM-6400 electron microscope. Thicknesses of the samples used for transmission experiments were in the range of 10–15 mkm.

Optical absorption obtained by unpolarized light transmission in the direction normal to the layer plane for  $(\text{TlGaSe}_2)_{1-x}(\text{TlInS}_2)_x$  solid solutions.

The transmission and the reflection measurements were carried out in the 400 - 1100 nm wavelength region with a “Shimadzu” UV-1201 model spectrophotometer. The transmission measurements were done under the normal incidence of light, which is perpendicular to the c-axis of the crystal. The measured reflectivities were compared with those for a protected silver mirror. The resolution of the spectro photometer was 5 nm. Researches are executed before and after  $\gamma$ -radiating by quanta energy  $\approx 1$  MeV (1.17 and 1.33 MeV) from  $^{60}\text{Co}$ , at room temperature.

### 3. Results and discussion

The transmittance spectra of the  $\text{TlGaSe}_2$  and  $\text{TlInS}_2$  crystals presents in Figure 1. The absorption coefficient index  $\alpha$  were calculated using the following relations:

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

where  $d$  is the sample thickness.

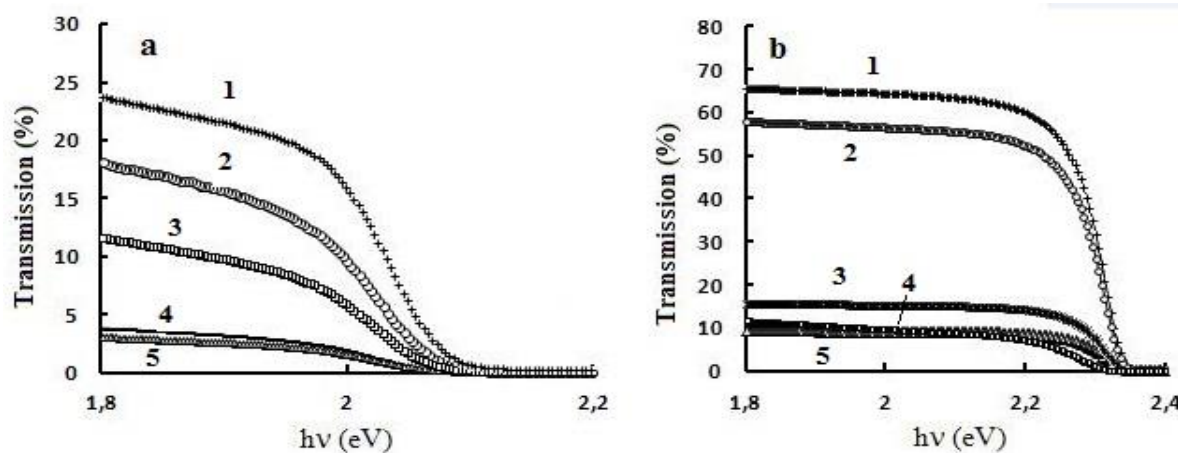


Fig. 1. Spectral dependencies of the transmittance for the  $\text{TlGaSe}_2$  and  $\text{TlInS}_2$  crystals at  $T = 300$  K for various doze of  $\gamma$  - radiation, the curve 1- 0, 2 - 1, 3 - 2, 4 - 5 and 5 - 25 Mrad.

Spectral dependencies of the transmittance for the  $\text{TlGaSe}_2$  and  $\text{TlInS}_2$  crystals at  $T = 300$  K for various doze of  $\gamma$  - radiation are represente don fig. 1. On fig. 2 are presented doze dependences of transparency at 1.8 eV. It seems in the field of a transparency of crystals (1.8 eV) at doses of irradiation 1 and 2 Mrad 5 times decreases (Fig. 2). The further growth of a dose irradiation to 25 Mrad leads to small restoration transparency of samples.

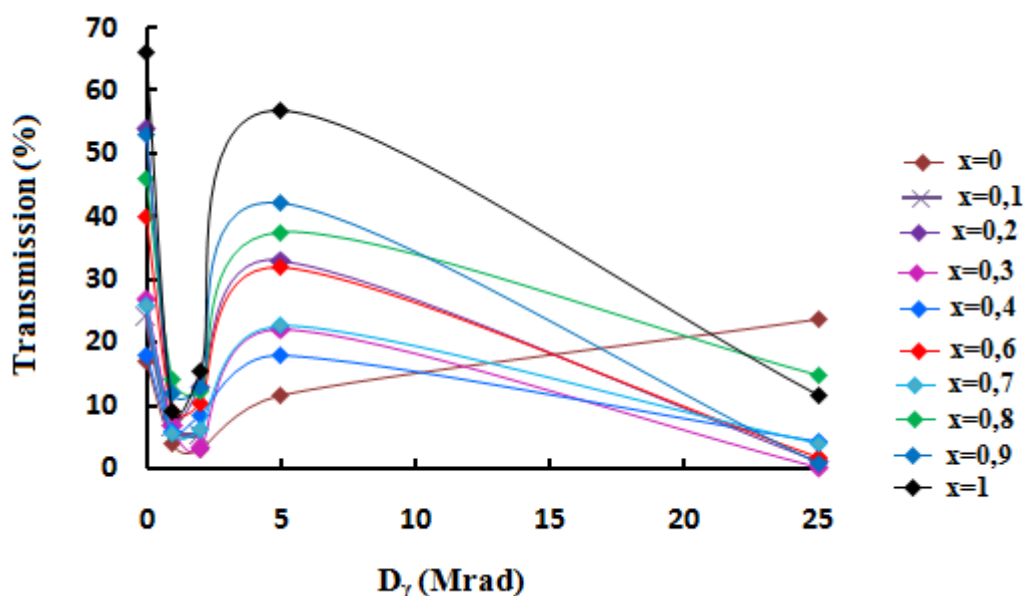


Fig. 2. Doze dependence of transmission spectra of  $(TlGaSe_2)_{1-x}(TlInS_2)_x$  mixed crystals in the field of a transparency 1.8 eV at  $T=300$  K.

The reflection measurements were carried out using specimens with natural cleavage planes and the thicknesses such that  $\alpha d \gg 1$ . Thickness of the samples was reduced until it was convenient for measuring the transmission spectra and determined through the transmission interference. We evaluated the thickness of the sample by measuring the wavelengths at which two adjacent transmission maxima occur

$$D = \frac{\lambda_1 \lambda_2}{2n(\lambda_2 - \lambda_1)}$$

The long-wavelength values of the refractive index  $n = 2.79$  for  $TlGaSe_2$ , and  $n = 2.60$  for  $TlInS_2$  found from the reflection measurements.

An analysis of the experimental data revealed that the absorption coefficient  $\alpha$  was proportional to  $(h\nu - E_g)^n$  with  $n = 2$  or  $1/2$  in two different energy regions. The dependencies of  $(\alpha h\nu)^{1/2}$  and  $(\alpha h\nu)^2$  on the photon energy  $h\nu$  for  $(TlGaSe_2)_{1-x}(TlInS_2)_x$  solid solutions at  $T = 300$  K and  $\gamma$  – irradiated are presented in Fig. 3 and Fig 4. The experimental data were fitted to a linear equation (the dashed lines) to find the energy band gaps. Linear dependencies were observed for the relations  $(\alpha h\nu)^{1/2}$  and  $(\alpha h\nu)^2$  versus  $h\nu$ . This implies the realization of the direct and indirect allowed transitions according to over the ranges 2.03–2.38 and 1.87 - 2.32 eV for  $(TlGaSe_2)_{1-x}(TlInS_2)_x$  mixed crystals, in the range of dozes 0-25 Mrad (Table 1).

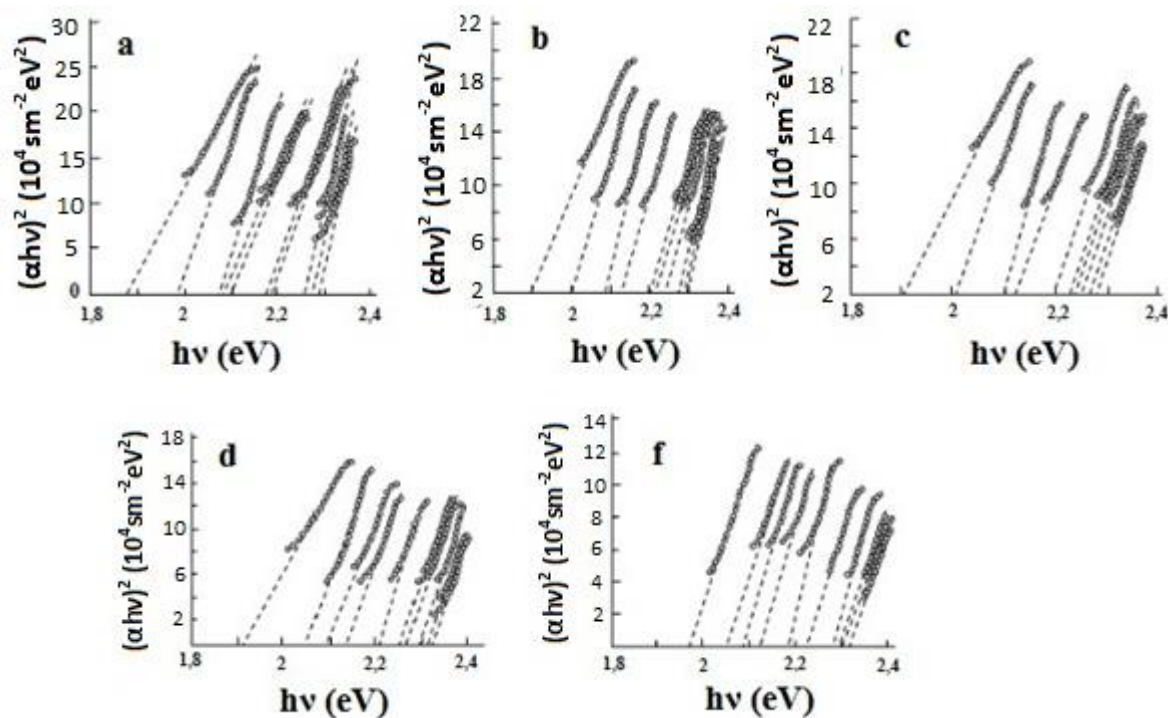


Fig. 3. The direct absorption spectra for of  $(\alpha hv)^2$  versus photon energy for the  $(TlGaSe_2)_{1-x}(TlInS_2)_x$  solid solutions at  $T = 300\text{ K}$  and  $\gamma$  – irradiated the curve 1–  $x=0$ ; 2– $0,1$ ; 3– $0,2$ ;4– $0,3$ ;5– $0,4$ ;6– $0,6$ ;7– $0,7$ ;8– $0,8$ ;9– $0,9$ ;10–  $1,0$ .Fig.a– 0; b – 1; c – 2; d – 5; f– 25Mrad.

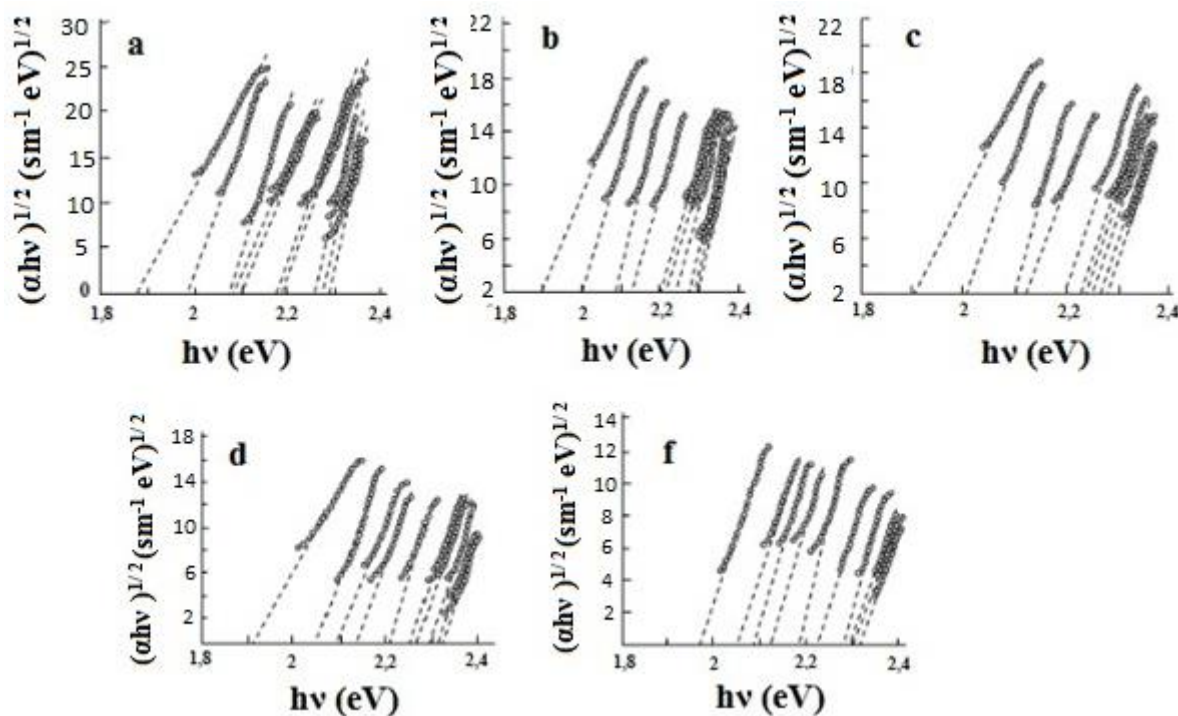


Fig. 4. The indirect absorption spectra for of  $(\alpha hv)^{1/2}$  versus photon energy for for the  $(TlGaSe_2)_{1-x}(TlInS_2)_x$  mixed crystals at  $T = 300\text{ K}$  and  $\gamma$ -irradiated the curve 1 –  $x=0$ ; 2 –  $0,1$ ; 3 –  $0,2$ ;4 –  $0,3$ ;5 –  $0,4$ ;6 –  $0,6$ ;7 –  $0,7$ ;8 –  $0,8$ ;9 –  $0,9$ ;10 –  $1,0$ . Fig.a– 0; b – 1; c – 2; d – 5; f– 25 Mrad.



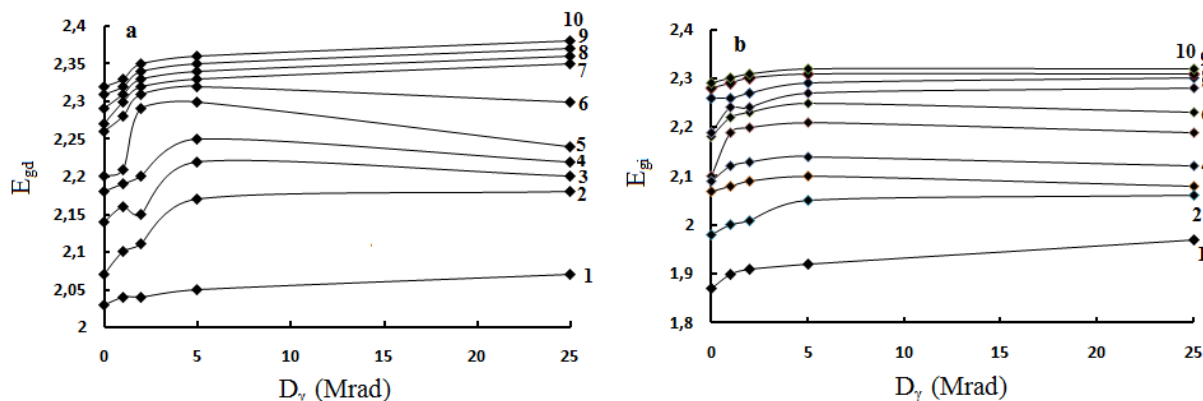


Fig. 5. The dependences of the direct (a) and indirect (b) band gap versus dose radiation for  $(TiGaSe_2)_{1-x}(TlInS_2)_x$  mixed crystals: curve 1–  $x=0$ ; 2–  $x=0,1$ ; 3–  $x=0,2$ ; 4–  $x=0,3$ ; 5–  $x=0,4$ ; 6–  $x=0,6$ ; 7–  $x=0,7$ ; 8–  $x=0,8$ ; 9–  $x=0,9$ ; 10–  $x=1,0$ .

Figure 5 presents the variations of direct energy band gaps of  $(TiGaSe_2)_{1-x}(TlInS_2)_x$  mixed crystals. As seen from this figure, the energy band gaps increase with the increasing dose radiation.

The compositional dependence of direct band gap energy at room temperature revealed that  $\gamma$ -irradiation increased in the  $(TiGaSe_2)_{1-x}(TlInS_2)_x$  solid solutions, the direct band-gap energy increases approximately on  $\sim 0.04$  eV, from  $D=0$  Mrad to  $D=25$  Mrad, the indirect band gap energy increases approximately on  $\sim 0.03-0.1$  eV from  $D=0$  Mrad to  $D=25$  Mrad (Table 1).

Table 1. Quantities of direct and indirect band-gap energy versus dose radiation and concentration (x) for  $(TiGaSe_2)_{1-x}(TlInS_2)_x$  mixed crystals.

	$E_{gd}$	$E_{gi}$	$E_{gd}$	$E_{gi}$	$E_{gd}$	$E_{gi}$	$E_{gd}$	$E_{gi}$	$E_{gd}$	$E_{gi}$
	0 Mrad		1 Mrad		2 Mrad		5 Mrad		25 Mrad	
$TiGaSe_2$	2,03	1,87	2,04	1,9	2,04	1,91	2,05	1,92	2,07	1,97
$(TiGaSe_2)_{0,9}(TlInS_2)_{0,1}$	2,07	1,98	2,1	2	2,11	2,01	2,17	2,05	2,18	2,06
$(TiGaSe_2)_{0,8}(TlInS_2)_{0,2}$	2,14	2,07	2,16	2,08	2,15	2,09	2,22	2,1	2,2	2,08
$(TiGaSe_2)_{0,7}(TlInS_2)_{0,3}$	2,18	2,09	2,19	2,12	2,2	2,13	2,25	2,14	2,22	2,12
$(TiGaSe_2)_{0,6}(TlInS_2)_{0,4}$	2,2	2,1	2,21	2,19	2,29	2,2	2,3	2,21	2,24	2,19
$(TiGaSe_2)_{0,4}(TlInS_2)_{0,6}$	2,26	2,18	2,28	2,22	2,31	2,23	2,32	2,25	2,3	2,23
$(TiGaSe_2)_{0,3}(TlInS_2)_{0,7}$	2,27	2,19	2,3	2,24	2,32	2,24	2,33	2,27	2,35	2,28
$(TiGaSe_2)_{0,2}(TlInS_2)_{0,8}$	2,29	2,26	2,31	2,26	2,33	2,27	2,34	2,29	2,36	2,3
$(TiGaSe_2)_{0,1}(TlInS_2)_{0,9}$	2,31	2,28	2,32	2,29	2,34	2,3	2,35	2,31	2,37	2,31
$TlInS_2$	2,32	2,29	2,33	2,3	2,35	2,31	2,36	2,32	2,38	2,32

#### 4. Conclusions

The transmission and the reflection spectra of  $(TiGaSe_2)_{1-x}(TlInS_2)_x$  crystals were measured over the spectral region of 400 - 1100 nm to derive the absorption coefficient. The analysis of the room temperature absorption data revealed the coexistence of indirect and direct transitions with energy band gaps of  $E_{gd} = 2.03$  and  $E_{gi} = 1.87$  eV for  $TiGaSe_2$  and  $E_{gd} = 2.32$  and  $E_{gi} = 2.29$  eV for  $TlInS_2$  for  $D=0$  Mrad. This data for  $D=25$  Mrad according to  $E_{gd} = 2.07$  and  $E_{gi} = 1.897$  eV for  $TiGaSe_2$  and  $E_{gd} = 2.38$  and  $E_{gi} = 2.32$  eV for  $TlInS_2$ .

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## ВЛИЯНИЕ $\gamma$ – ОБЛУЧЕНИЯ НА ЭНЕРГИИ ПРЯМЫХ И НЕПРЯМЫХ ОПТИЧЕСКИХ ПЕРЕХОДОВ В ТВЕРДЫХ РАСТВОРАХ $(TlGaSe_2)_{1-x}(TlInS_2)_x$

Ф.Т. Салманов

**Резюме:** Оптические свойства твердых растворов  $(TlGaSe_2)_{1-x}(TlInS_2)_x$  были исследованы в спектральной области 400 - 1100 нм посредством измерений спектров пропускания и отражения. Из анализа кривых поглощения были определены энергии прямых и непрямых оптических переходов для кристаллов твердых растворов  $(TlGaSe_2)_{1-x}(TlInS_2)_x$  при комнатной температуре. Измерения проведены до и после  $\gamma$  – облучения дозами 0 – 25 Мрад. Дозовая зависимость энергии прямых межзонных оптических переходов при комнатной температуре показал незначительный рост – приблизительно на  $\sim 0.04$  эВ, при  $\gamma$  – облучении дозами от 0 до 25 Мрад. Энергии непрямых оптических переходов кристаллов исследованных твердых растворов выросли приблизительно на  $\sim 0.03-0.1$  эВ при облучении дозами от 0 до 25 Мрад. Наблюдаемые оптические переходы связываются с переходами электронов из зоны проводимости на мелкие акцепторные уровни в запрещенной зоне.

**Ключевые слова:** Полупроводники, энергия запрещенной зоны, прямая и косвенная запрещенная зона,  $\gamma$ -облучение.

**(TlGaSe<sub>2</sub>)<sub>1-x</sub>(TlInS<sub>2</sub>)<sub>x</sub> BƏRK MƏHLULLARIN DÜZÜNƏ VƏ ÇƏPİNƏ OPTİK KEÇİDLƏRİNİN ENERJİLƏRİNƏ  $\gamma$  - ŞÜALARIN TƏSİRİ**

**F.T. Salmanov**

**Xülasə:** (TlGaSe<sub>2</sub>)<sub>1-x</sub>(TlInS<sub>2</sub>)<sub>x</sub> bərk məhlullarının optik xassələri 400-1100 nm spektral oblastda buraxma və əks olunma spektrlərinin ölçmələri ilə tədqiq edilmişdir. (TlGaSe<sub>2</sub>)<sub>1-x</sub>(TlInS<sub>2</sub>)<sub>x</sub> bərk məhlullarının udma spektrlərinin analizindən otaq temperaturunda düzünə və çəpinə optik keçidlərin enerjiləri təyin olunmuşdur. Ölçmələr  $\gamma$ -radiasiyanın 0-25 Mrad doza intervalında aparılmışdır.  $\gamma$ -radiasiyanın 0-25 Mrad intervalında artması otaq temperaturunda düzünə optik keçidlərin enerjilərinin qiymətlərində 0,04 eV-a qədər, çəpinə optik keçidlərin enerjilərinin qiymətlərində isə ~ 0,03-0,1 eV-a qədər zəif artım müşahidə olunmuşdur. Müşahidə olunan optik keçidlər elektronlarən keçirici zonadan akseptor səviyyələrinə keçməsi ilə əlaqələndirilir.

**Açar sözlər:** Yarımkəçiricilər, qadağan olunmuş zona, düzünə və çəpinə optik keçidlər,  $\gamma$ -şüalanma