



Contents lists available at ScienceDirect

## Materials Science in Semiconductor Processing

journal homepage: [www.elsevier.com/locate/mssp](http://www.elsevier.com/locate/mssp)Defect characterization of  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  layered single crystals by photoluminescenceN.M. Gasanly<sup>a,b,\*</sup><sup>a</sup> Department of Physics, Middle East Technical University, 06800 Ankara, Turkey<sup>b</sup> Virtual International Scientific Research Centre, Baku State University, 1148 Baku, Azerbaijan

## ARTICLE INFO

**Keywords:**  
Semiconductors  
Chalcogenides  
Photoluminescence  
Defects levels

## ABSTRACT

Photoluminescence (PL) spectra of  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  layered crystals grown by the Bridgman method have been studied in the energy region of 2.02–2.35 eV and in the temperature range of 16–45 K. A broad PL band centered at 2.20 eV was observed at  $T=16$  K. Variations of emission band has been studied as a function of excitation laser intensity in the 0.1 to 149.9  $\text{mW cm}^{-2}$  range. Radiative transitions from shallow donor level located at 10 meV below the bottom of conduction band to moderately deep acceptor level located at 180 meV above the top of the valence band were suggested to be responsible for the observed PL band. An energy level diagram showing transitions in the band gap of the crystal was plotted taking into account the results of present work and previously reported paper on thermally stimulated current measurements carried out below room temperature. Analysis of the transmission and reflection measurements performed in the wavelength range of 400–1030 nm at room temperature revealed the presence of indirect transitions with 2.22 eV band gap energy.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

The quinary  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  (TGISS) crystal belongs to the group of layered semiconductors. This compound is a structural analog of  $\text{TlGaSe}_2$  and  $\text{TlInS}_2$ , in which three quarters (a quarter) of gallium (indium) and selenium (sulfur) ions are replaced by indium (gallium) and sulfur (selenium) ions, respectively [1,2]. This substitution allows, at least in principle, the tailoring of several important physical properties. The lattice of TGISS consists of strictly periodic two-dimensional layers arranged parallel to the (001) plane. Each successive layer is rotated by a  $90^\circ$  angle with respect to the previous one. Interlayer bonding is formed between Tl and Se(S) atoms while the bonding between Ga(In) and Se(S) atoms is an intralayer type. The fundamental structural unit of a layer is

the  $\text{Ga}_4(\text{In}_4)\text{Se}_6(\text{S}_6)$  adamantane-like units linked together by bridging Se(S) atoms. The Tl atoms are in trigonal prismatic voids resulting from the combination of the  $\text{Ga}_4(\text{In}_4)\text{Se}_6(\text{S}_6)$  polyhedra into a layer.

In view of their possible applications in optoelectronic devices in the visible range, a great deal of attention has been devoted to the study of the optical and photoelectrical properties of  $\text{TlGaSe}_2$  and  $\text{TlInS}_2$  crystals [3–10]. It was revealed that the fundamental absorption edge is formed by the indirect transitions with band gap energies  $E_{\text{gi}}=1.98$  and 2.06 eV ( $\text{TlGaSe}_2$ ) and  $E_{\text{gi}}=2.27$  and 2.44 eV ( $\text{TlInS}_2$ ) at  $T=300$  and 10 K, respectively. A high photosensitivity in the visible range of spectra, high birefringence in conjunction with a wide transparency range of 0.6–16  $\mu\text{m}$  make these crystals useful for optoelectronic applications [11].

Earlier we studied the low-temperature photoluminescence (PL) spectra of  $\text{TlGaSe}_2$  and  $\text{TlInS}_2$  crystals and observed one and two broad emission bands, respectively, which were assigned to donor–acceptor pair (DAP) recombination [12,13]. Moreover, recently we have studied the low-temperature PL

\* Corresponding author at: Department of Physics, Middle East Technical University, 06800 Ankara, Turkey  
E-mail address: [nizami@metu.edu.tr](mailto:nizami@metu.edu.tr)

spectra of quaternary  $\text{Tl}_4\text{GaIn}_3\text{S}_8$ ,  $\text{Tl}_2\text{Ga}_2\text{S}_3\text{Se}$ ,  $\text{Tl}_4\text{InGa}_3\text{S}_8$  and  $\text{Tl}_2\text{In}_2\text{Se}_3\text{S}$  crystals [14–17]. The observed emission bands were attributed to the transitions from shallow donor to moderately deep acceptor levels. Analysis of the thermally stimulated current (TSC) measurements carried out on  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystal in the temperature range of 10–300 K revealed the presence of one electron trap at 12 meV [18].

The influence of defects on the performance of optoelectronic devices is a well-known subject. In optoelectronic devices such as LEDs or lasers, defects may introduce non radiative recombination centers to lower the internal quantum efficiency or even render light generation impossible, depending on defect density. In the case of electronic devices, defects introduce scattering centers lowering carrier mobility, hence hindering high-frequency operation. Thus, it is very useful to get detailed information on energetic parameters of recombination centers in semiconductor in order to obtain high-quality devices. In the present paper we report the intensity variations of the PL emission with temperature (16–45 K) and excitation laser intensity ( $0.1$ – $149.9 \text{ mW cm}^{-2}$ ) in  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystals. The analysis of the data suggests that the radiative transitions originate from recombination of charge carriers from donor to acceptor states.

## 2. Experimental details

$\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  semiconductor polycrystals were synthesized using high-purity elements taken in stoichiometric proportions. Selenium (Aldrich cat. no. 204307), gallium (Aldrich cat. no. 263273), indium (Fluka cat. No. 57077) and sulfur (Fluka cat. no. 84680) were of 99.999% purity and thallium (Fluka cat no. 88202) was of 99.99% purity. The single crystals were grown by the Bridgman method in evacuated ( $10^{-5}$  Torr) silica tubes (15 mm in diameter and about 60 cm in length) with a tip at the bottom in our crystal growth laboratory. The ampoule was moved in a vertical furnace through a thermal gradient of  $30^\circ\text{C cm}^{-1}$  at a rate of  $1.0 \text{ mm h}^{-1}$ . The resulting ingot appeared orange in color and the freshly cleaved surfaces were mirror-like. Fig. 1 shows the photograph of the grown crystal with typical size about  $35 \times 12 \times 5 \text{ mm}^3$ . The chemical composition of  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystals was determined by energy-dispersive spectroscopic analysis using JSM-6400 electron microscope (Fig. 2). The atomic composition of the studied samples (Tl: Ga: In: Se: S) was found to be 25.4: 6.3: 19.1: 12.3: 36.9, respectively.

The electrical conductivity of the studied sample was n-type as determined by the hot probe method. In the PL experiments the green line ( $\lambda=532 \text{ nm}$ ) of a continuous



Fig. 1. The photograph of the  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  grown crystal.

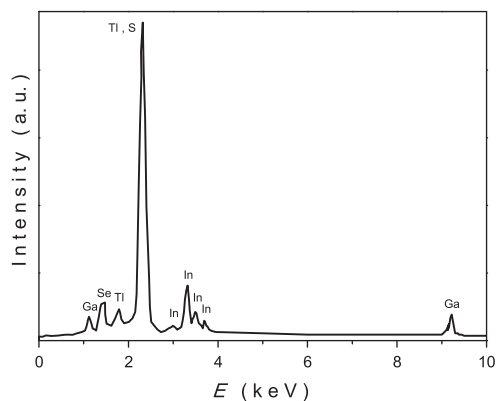


Fig. 2. Energy-dispersive spectroscopic analysis of  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystal.

frequency-doubled YAG: $\text{Nd}^{3+}$  laser was used as the excitation light source. PL spectra were registered by collecting the light from the laser-illuminated face of the sample. A “CTI-Cryogenics M-22” closed-cycle helium cryostat was used to cool the sample from room temperature down to 16 K, and the temperature was controlled within an accuracy of  $\pm 0.5 \text{ K}$ . The PL spectra of the sample in the region 2.02–2.35 eV were analyzed using a “Oriol MS-257” grating monochromator and “Hamamatsu S7031” FFT-CCD Image Sensor with single stage electric cooler. Sets of neutral density filters were used to adjust the exciting laser intensity from 0.1 to  $149.9 \text{ mW cm}^{-2}$ . All of the PL spectra have been corrected for the spectral response of the optical apparatus.

Transmission and reflection experiments were performed at room temperature in the 400–1030 nm spectral range using a Shimadzu UV 1201 model spectrophotometer which consisted of a 20 W halogen lamp, a holographic grating and a silicon photodiode. The resolution of the spectrophotometer was 5 nm. Transmission measurements were accomplished under normal incidence of light with a polarization direction along the (001) plane which is perpendicular to the *c*-axis of the crystal. The reflection experiments were carried out using a specular reflectance measurement attachment providing  $5^\circ$  incident angle.

## 3. Results and discussion

Fig. 3 shows the room temperature transmittance and reflectance spectra of  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystals in the wavelength range of 400–1030 nm. The reflection measurements were carried out using the sample with natural cleavage planes and the thickness (*d*) such that  $\alpha d \gg 1$ . Absorption coefficient ( $\alpha$ ) was calculated from the transmittance (*T*) and reflectance (*R*) spectra using expression [19]

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

The dependence of  $(\alpha h\nu)^{1/2}$  on the photon energy  $h\nu$  is presented in inset of Fig. 3. The experimental data were fitted to a linear equation (the solid line) to find the energy band gap. Using the extrapolation of the straight line down to

$(\alpha h\nu)^{1/2}=0$ , the value of the indirect band gap energy was determined as 2.22 eV.

Fig. 4 presents the PL spectra of  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystals in 16–45 K temperature range at constant laser excitation intensity  $L=149.9 \text{ mW cm}^{-2}$ . The observed emission band has asymmetrical Gaussian line shape and centered at

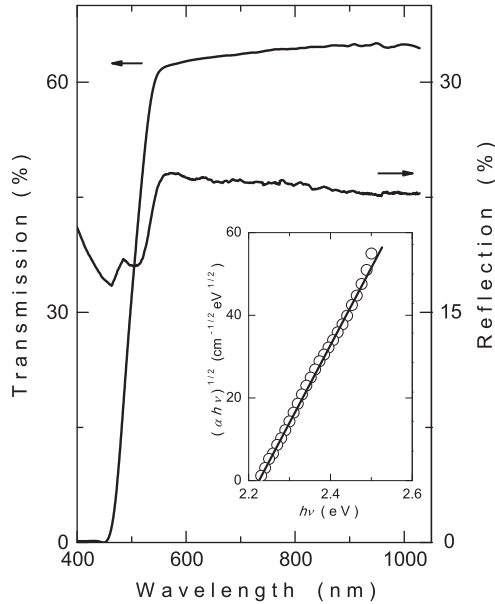


Fig. 3. The spectral dependencies of the transmittance and reflectivity for  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystal at  $T=300 \text{ K}$ . Inset: The dependence of  $(\alpha h\nu)^{1/2}$  on the photon energy  $h\nu$ .

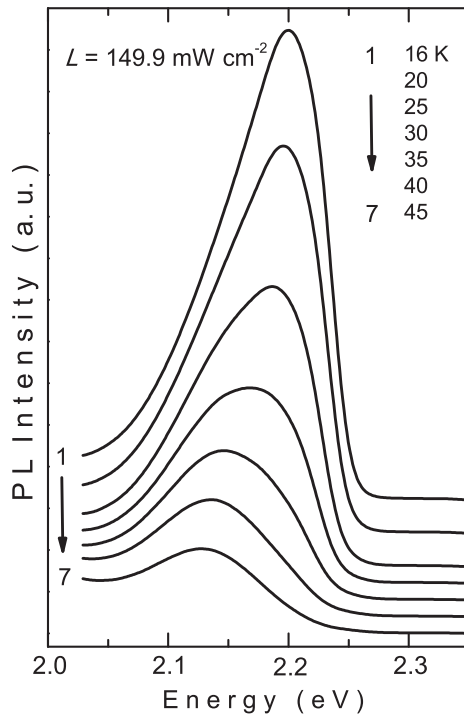


Fig. 4. Temperature dependence of PL spectra from  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystals at excitation laser intensity  $L=149.9 \text{ mW cm}^{-2}$ .

2.20 eV at  $T=16 \text{ K}$ . As seen from the Fig. 4, emission band changes its peak position and intensity as a function of the sample temperature: the peak position shows several degrees of red shift and the peak intensity decreases as temperature is increased. Inset of Fig. 5 illustrates the shift of the peak energy to lower energies with increasing temperature. It is well known that the donor–acceptor pair transition energy decreases along with the band gap energy when the temperature is increased [20].

The experimental data for the temperature dependence of PL band intensity can be fitted by the following expression [19]:

$$I(T) = \frac{I_0}{1 + \alpha \exp(-E_t/kT)} \quad (2)$$

where  $I_0$  is a proportionality constant,  $E_t$  is the thermal activation energy,  $k$  is the Boltzmann constant and  $\alpha$  is the recombination process rate parameter. Fig. 5 shows the temperature dependence of the emission band maximum intensity as a function of the reciprocal temperature in the 16–45 K range. After a nonlinear least squares fit, the quenching activation energy for emission band is found to be 10 meV. Since  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystal is an n-type semiconductor, we believe that this level is shallow donor level located at  $E_d=10 \text{ meV}$  below the bottom of the conduction band.

The laser excitation intensity dependence of PL spectra also provides valuable information about the recombination mechanism responsible for the observed luminescence. Fig. 6 (a) and (b) presents the PL spectra of the  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystals for 26 different laser intensities at  $T=30 \text{ K}$ . From analysis of the spectra, we obtained the information about the peak energy position and intensity for emission band at

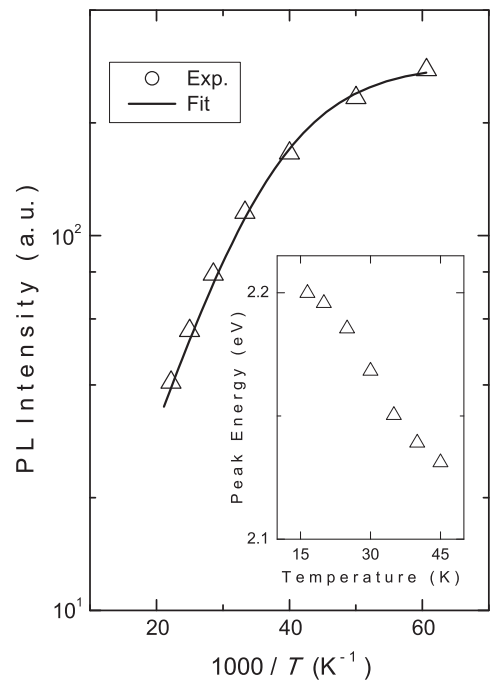


Fig. 5. Temperature dependencies of PL band intensity for  $\text{Tl}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystal. Triangles are the experimental data. Solid curve shows the theoretical fit using Eq. (2). Inset: temperature dependence of emission band peak energy.

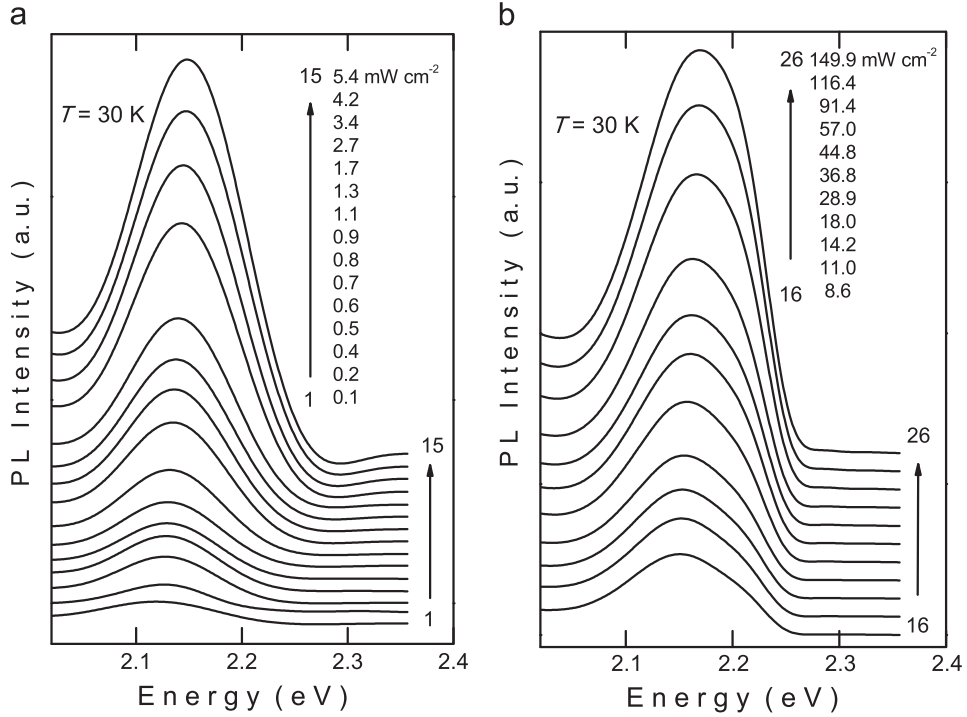


Fig. 6. (a) and (b). PL spectra of  $Tl_4GaIn_3Se_2S_6$  crystal as a function of excitation laser intensity at  $T=30$  K.

various laser excitation intensities. This analysis reveals that the peak energy position changes with laser excitation intensity (blue shift). The behavior of the emission band is in agreement with the idea of inhomogeneously distributed donor–acceptor pairs for which increasing laser excitation intensity leads to blue shift of the band by exciting more pairs that are closely spaced [20]. A careful inspection of the data shows that the emission band maximum slightly shifts towards higher energies ( $\Delta E_p=40$  meV) with increasing excitation laser intensities from 0.1 to  $149.9 \text{ mW cm}^{-2}$  (i.e., 12 meV per decade of exciting intensity). The magnitude of the observed blue shift is typical of ternary and quaternary chalcogenide compounds such as  $Tl_2InGaS_4$  [21],  $HgInGaS_4$  [22],  $CuIn_{1-x}Ga_xSe_2$  [23],  $Tl_4Ga_3InSe_8$  [24] which are 20, 20, 15, 14 meV per decade of intensity of exciting radiation, respectively.

The dependence of the emission band peak energy ( $E_p$ ) at  $T=30$  K as a function of excitation laser intensity ( $L$ ) is given in Fig. 7. The experimental data in Fig. 7 are then fitted by the following expression [25]:

$$L(E_p) = L_0 \frac{(E_p - E_\infty)^3}{(E_B + E_\infty - 2E_p)} \exp\left[-\frac{2(E_B - E_\infty)}{E_p - E_\infty}\right] \quad (3)$$

where  $L_0$  is a proportionality constant,  $E_B$  is the emitted photon energy of a close donor–acceptor pair separated by a shallow impurity Bohr radius ( $R_B$ ), and  $E_\infty$  is the emitted photon energy of an infinitely distant donor–acceptor pair. From a nonlinear least square fit to the experimental data, the photon energy values for an infinitely distant donor–acceptor pair and a close donor–acceptor pair separated by  $R_B$  are found to be  $E_\infty=2.12$  eV and  $E_B=2.24$  eV, respectively. These limiting photon energy values are in good agreement with the

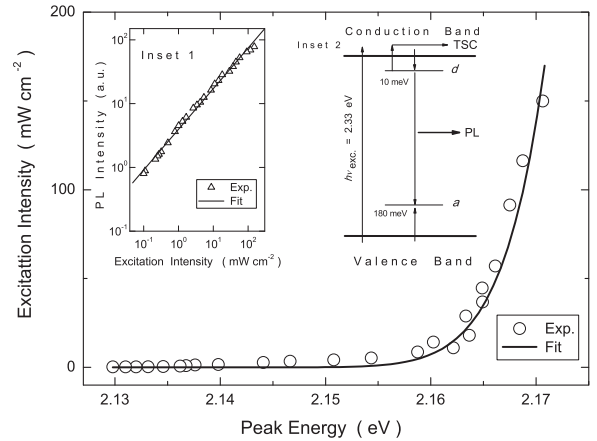


Fig. 7. Excitation laser intensity versus emission band peak energy at  $T=30$  K. The solid curve represents the theoretical fit using Eq. (3). Inset 1: dependence of PL intensity at the emission band maximums versus excitation laser intensity at  $T=30$  K. The solid line shows the theoretical fit using Eq. (4). Inset 2: energy level diagram of  $Tl_4Galn_3Se_2S_6$  crystal at  $T=30$  K.

band gap energy ( $E_g=2.31$  eV) and the observed values of the peak energy position (i.e.,  $E_\infty < 2.13 \text{ eV} < E_p < 2.17 \text{ eV} < E_B < E_g$ ) at  $T=30$  K.

In PL spectra of  $Tl_4Galn_3Se_2S_6$  crystal, the increase in the peak intensities of emission band with increase in the laser excitation intensity was also observed. The logarithmic plot of PL intensity versus laser excitation intensity is given in inset 1 of Fig. 7. Experimental data can be fitted by

a simple power law of the form

$$I \propto L^\gamma \quad (4)$$

where  $I$  is the PL intensity,  $L$  is the excitation laser intensity and  $\gamma$  is a dimensionless constant. We find that PL intensity at the emission band maximum increases sublinearly with increase of excitation laser intensity with the value of  $\gamma=0.58$ . It is well known that for excitation laser photon energy exceeding the band gap energy  $E_g$ , the exponent  $\gamma$  is generally  $1 < \gamma < 2$  for free- and bound-exciton emission, whereas  $0 < \gamma \leq 1$  is typical for free-to-bound and donor-acceptor pair recombination [26,27]. Thus, the obtained value of  $\gamma < 1$  for the observed band is further evidence that the observed emission is due to donor-acceptor pair recombination.

The analysis of the PL spectra as a function of temperature and excitation laser intensity allows one to obtain a possible scheme for the states located in the forbidden energy gap of the  $\text{Ti}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystal (inset 2 of Fig. 7). In the proposed scheme, shallow donor level  $d$  is located at 10 meV below the bottom of the conduction band. On the basis of general expression for the emission energy of donor-acceptor pair [19] and taking into account the values of  $E_g$  and  $E_\infty$ , the sum of the activation energies of the donor ( $E_d$ ) and acceptor ( $E_a$ ) levels, involved in the emission band, has been estimated as being  $E_d + E_a = E_g - E_\infty = 2.31 \text{ eV} - 2.12 \text{ eV} = 0.19 \text{ eV}$ . Considering that the donor level  $d$  is located at 10 meV below the bottom of the conduction band, this result suggests that the acceptor level  $a$ , involved in the emission band, is located at 180 meV above the top of the valence band. Taking into account the above considerations, the observed emission band in the PL spectra has been attributed to the radiative transitions from the donor level  $d$  to the acceptor level  $a$ . Since the studied crystals were not intentionally doped, these centers are thought to originate from anion vacancies caused by nonstoichiometry and/or stacking faults, quite possible to exist in layered  $\text{Ti}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  due to the weakness of the van der Waals forces between the layers [28]. The determined values of activation energies of the donor and acceptor states in  $\text{Ti}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystal (10 and 180 meV, respectively) are found of the same order as those established from reported PL studies on quaternary layered crystals  $\text{Ti}_4\text{GaIn}_3\text{S}_8$  (10 and 190 meV) [14],  $\text{Ti}_2\text{Ga}_2\text{S}_3\text{Se}$  (10 and 160 meV) [15],  $\text{Ti}_4\text{InGa}_3\text{S}_8$  (20 and 200 meV) [16] and  $\text{Ti}_2\text{In}_2\text{Se}_3\text{S}$  (30 and 230 meV) [17].

And finally, we would like to give an insight into the transitions in the forbidden band gap of  $\text{Ti}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  by combining the results of present and previously reported works. The results of thermally stimulated current (TSC) study in the 10–300 K temperature range showed the existence of one electron trap at 12 meV [18]. Taking into account the possible errors, the obtained energies of 10 and 12 meV in the PL and TSC studies, respectively, may possibly be assigned to the same level. This level is thought to be partially compensated allowing for both PL emission and thermally stimulated current.

#### 4. Conclusions

The PL spectra of  $\text{Ti}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  crystals as a function of temperature and excitation laser intensity were studied. A broad emission band centered at 2.20 eV was observed in the

PL spectra at  $T=16 \text{ K}$ . The variation of the spectra with laser excitation intensity and temperature suggest that the transitions between the donor and acceptor levels can be responsible for the observed emission band. Also, the intensity of the emission band increases sublinearly with respect to the excitation laser intensity and confirm our assignment that the observed emission band in  $\text{Ti}_4\text{GaIn}_3\text{Se}_2\text{S}_6$  is due to donor-acceptor pair recombination. As the studied crystals were not intentionally doped, these centers are thought to originate from anion vacancies caused by nonstoichiometry and/or stacking faults, created during crystal growth. From the analysis of transmission and reflection spectra measured at room temperature in the wavelength range of 400–1030 nm, the band gap energy of 2.22 eV was determined.

#### Acknowledgment

The author is grateful to Dr. A. Seyhan and Dr. A. Gencer for their assistance.

#### References

- [1] K.A. Yee, A. Albright, *J. Am. Chem. Soc.* 113 (1991) 6474–6478.
- [2] A.M. Panich, *J. Phys.: Condens. Matter* 20 (2008) 293202–01–293202–42.
- [3] P.P. Guranich, R.R. Rosul, O.O. Gommonai, A.G. Slivka, I.Y. Roman, A. V. Gommonai, *Solid State Commun.* 184 (2014) 21–24.
- [4] S. Ozdemir, S. Altindal, *J. Alloy. Compd.* 566 (2013) 108–111.
- [5] M.M. El-Nahhas, H.A.M. Ali, E.F.M. El-Zaidia, *Physica B* 431 (2013) 54–57.
- [6] A.V. Gommonai, I. Petrushynets, Y.M. Azhnuok, O.O. Gommonai, I.Y. Roman, I.I. Turok, A.M. Solomon, R.R. Rosul, D.R. Zahn, *J. Cryst. Growth* 367 (2013) 35–41.
- [7] M. Seyidov, R. Suleymanov, E. Balaban, Y. Sale, *Phys. Scr* (2015) 015805–01–015805–07.
- [8] S. Ozdemir, M. Bucurgat, *Curr. Appl. Phys.* 13 (2013) 1948–1952.
- [9] V. Grivickas, V. Bikbajevs, P. Grivickas, *Phys. Status Solidi (B)* 243 (2006) R31–R33.
- [10] R. Paucar, K. Harada, R. Masumoto, K. Wakita, Y.G. Shim, O. Alekperov, N. Mamedov, *Phys. Status Solidi (C)* 10 (2013) 1132–1135.
- [11] K.R. Allakhverdiev, *Solid State Commun.* 111 (1999) 253–257.
- [12] N.M. Gasanly, A. Serpenguzel, A. Aydinli, S.M.A. Baten, *J. Lumin.* 86 (2000) 39–43.
- [13] A. Aydinli, N.M. Gasanly, I. Yilmaz, A. Serpenguzel, *Semicond. Sci. Technol.* 14 (1999) 599–603.
- [14] K. Goksen, N.M. Gasanly, *Cryst. Res. Technol.* 43 (2008) 514–521.
- [15] N.M. Gasanly, *Physica B* 407 (2012) 4318–4322.
- [16] K. Goksen, N.M. Gasanly, *J. Phys.: Condens. Matter* 19 (2007) 10.456221.
- [17] I. Guler, K. Goksen, N.M. Gasanly, R. Turan, *Physica B* 395 (2007) 116–120.
- [18] S. Delice, M. Isik, T. Yildirim, *Fizika* 19 (2013) 26–29.
- [19] J.I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall, New Jersey, 1971.
- [20] P.Y. Yu, M. Cardona, *Fundamentals of Semiconductors*, Springer, Berlin, 1995.
- [21] N.M. Gasanly, A. Serpenguzel, O. Gurlu, A. Aydinli, I. Yilmaz, *Solid State Commun.* 108 (1998) 525–530.
- [22] A. Anedda, M.B. Casu, A. Serpi, I.I. Burlakov, I.M. Tiginyanu, V. V. Ursaki, *J. Phys. Chem. Solids* 58 (1997) 325–330.
- [23] B. Bacewicz, A. Dzierzega, R. Trykozko, *Jpn. J. Appl. Phys.* 32 (Suppl. 3) (1993) 194–195.
- [24] K. Goksen, N.M. Gasanly, R. Turan, *Cryst. Res. Technol.* 41 (2006) 822–828.
- [25] E. Zacks, A. Halperin, *Phys. Rev. B* 6 (1972) 3072–3077.
- [26] T. Schmidt, K. Lischka, W. Zulehner, *Phys. Rev. B* 45 (1992) 8989–8994.
- [27] A. Bauknecht, S. Siebentritt, J. Albert, M.C. Lux-Steiner, *J. Appl. Phys.* 89 (2001) 4391–4400.
- [28] V. Capozzi, *Phys. Rev. B* 28 (1983) 4620–4627.