Excitation and Temperature Tuned Photoluminescence in $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ Layered Crystals

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Photoluminescence spectra of $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ layered single crystals have been studied in the wavelength region of 535–725 nm and in the temperature range of 22–58 K. Two photoluminescence bands centered at 564 (2.20 eV, A-band) and 642 nm (1.93 eV, B-band) were observed at $T = 22$ K. Variations of both bands have been investigated as a function of excitation laser intensity in the range from 16 to 516 mW cm^{-2} . These bands are attributed to recombination of charge carriers through donor–acceptor pairs located in the band gap. Radiative transitions from shallow donor levels located 0.02 and 0.01 eV below the bottom of conduction band to acceptor levels located 0.05 and 0.44 eV above the top of the valence band are suggested to be responsible for the observed A- and B-bands in the photoluminescence spectra, respectively.

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1. Introduction

$\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ compound belongs to the group of layered semiconductors. This crystal is a structural analog of TlInS_2 , in which one quarter of sulfur atoms are replaced by selenium atoms [1, 2]. The crystal lattice consists of alternating two-dimensional layers arranged parallel to the (001) plane. Each successive layer is rotated by a 90° angle with respect to the previous layer. Interlayer bonding is formed between Tl and S(Se) atoms while the bonding between In and S(Se) atoms is of intralayer type. The fundamental structural unit of a layer is the $\text{In}_4\text{S}_{10}(\text{Se}_{10})$ polyhedron representing a combination of four elementary $\text{In}_4\text{S}_6(\text{Se}_6)$ tetrahedra linked together by bridging S(Se) atoms. The Tl atoms are in trigonal prismatic voids resulting from the combination of the $\text{In}_4\text{S}_{10}(\text{Se}_{10})$ polyhedra into a layer. The Tl atoms form nearly planar chains along the [110] and $[\bar{1}\bar{1}0]$ directions.

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These crystals are characterized by clearly defined anisotropy in their mechanical properties.

Optical and photoelectrical properties of TlInS_2 crystal were studied in Refs. [3–7]. The fundamental absorption edge is formed by indirect and direct transitions with $E_{\text{gi}} = 2.28$ eV and $E_{\text{gd}} = 2.33$ eV, respectively [3]. A high photosensitivity in the visible range of spectra and high birefringence in conjunction with a wide transparency range of 0.5–14 μm make this crystal useful for optoelectronic applications [7]. Previously, we studied the photoluminescence (PL) of TlInS_2 crystal and observed two broad emission bands centered at 515 and 816 nm, which we assigned to donor–acceptor pair recombination [8]. The room temperature indirect and direct optical energy gaps, $E_{\text{gi}} = 2.18$ eV and $E_{\text{gd}} = 2.42$ eV, of $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ crystal were determined from transmission and reflection measurements in the wavelength range of 400–1100 nm [9].

In the present paper we report the intensity variations of the PL emission bands with temperature (22–58 K) and excitation laser intensity (16–516 mW cm^{-2}) in $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ 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

Single crystals of $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ were grown by the Bridgman method from stoichiometric melt of starting materials sealed in evacuated (10^{-5} Torr) silica tubes with a tip at the bottom. The resulting ingots (orange in color) showed a good optical quality and the freshly cleaved surfaces were mirror-like. The chemical composition of $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ crystals was determined by energy dispersive spectroscopic analysis (EDSA) using a JSM-6400 electron microscope (Fig. 1). The composition of the studied samples (Tl : In : S : Se) was found to be 25.9 : 26.1 : 35.9 : 12.1, respectively. Moreover, EDSA indicates that carbon, oxygen, and silicon impurities are present in $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ crystals.

The electrical conductivity of the studied sample was *n*-type as determined by the hot probe method. Crystals suitable for PL measurements had typical sample dimensions of $6 \times 3 \times 1$ mm^3 . The green line ($\lambda = 532$ nm) of a continuous frequency-doubled YAG:Nd³⁺ laser was used as the excitation light source. PL experiments were carried out by collecting the light from the laser-illuminated face of the sample in a direction close to the normal of the layer. A “CTI-Cryogenics M-22” closed-cycle helium cryostat was used to cool the sample from room temperature down to 22 K, and the temperature was controlled within an accuracy of ± 0.5 K. The PL spectra of the sample in the region of 535–725 nm was analyzed using an “Oriel MS-257” grating monochromator and “Hamamatsu S7010-1008” FFT-CCD image sensor with a single stage electric cooler. Sets of neutral density filters were used to adjust the exciting laser intensity from 16 to 516 mW cm^{-2} . PL spectra have been corrected for the spectral response of the optical apparatus.

Fig. 1. Energy dispersive spectroscopic analysis of $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ crystal.

All the spectra have been analyzed by using a fitting program “Peak Fit for Win 32 Version 4”.

3. Results and discussion

Figure 2 presents the PL spectra of $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ crystals in 22–58 K temperature range at the constant laser excitation intensity $L = 78 \text{ mW cm}^{-2}$. All spectra have been analyzed using a fitting procedure to decompose the overlapped bands. A typical result of fitting two Gaussian peaks to A- and B-bands is shown in Fig. 3. The procedure yields the peak position, full-width at half-maximum (FWHM) and intensity of the bands. The observed emission bands are centered at 564 nm (2.20 eV, A-band) and 642 nm (1.93 eV, B-band) at $T = 22 \text{ K}$. As seen from Fig. 2, emissions bands change as temperature is increased: the peak positions show several degrees of red shift, the FWHM increases and the peak intensities decrease. With increasing temperature, the FWHM rises from 0.15 to 0.20 eV and from 0.42 to 0.52 eV for A- and B-bands, respectively.

The inset of Fig. 4 illustrates the shifts of the peak energies 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 [10]. The experimental data for the temperature dependence of PL bands intensities can be fitted by the following expression [11]:

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

where I_0 is a proportionality constant, E — the thermal activation energy, k — the Boltzmann constant and α is the recombination process rate parameter. Figure 4 shows the temperature dependence of the emission band maximum intensities as a function of the reciprocal temperature in the 22–58 K range. The best fits us-

Fig. 2. Temperature dependence of PL spectra from $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ crystal at excitation laser intensity $L = 78 \text{ mW cm}^{-2}$. Note that for curves 16–18, intensities have been multiplied by a factor of four.

Fig. 3. Decomposition of the PL spectrum from $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ crystal into two Gaussian lineshapes ($T = 22 \text{ K}$, $L = 516 \text{ mW cm}^{-2}$).

ing Eq. (1), demonstrated by the solid curves in Fig. 4, have been achieved with parameters $I_{0A} = 3.5$, $E_A = 0.02 \text{ eV}$, $\alpha_A = 1128.3$ and $I_{0B} = 26.7$, $E_B = 0.01 \text{ eV}$, $\alpha_B = 141.8$ for A- and B-bands, respectively. Since $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ crystal is an n -type semiconductor, we believe that these levels are shallow donor levels located

Fig. 4. Temperature dependences of PL bands intensities for $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ crystal. Circles are the experimental data. Solid curves show the theoretical fits using Eq. (1). The inset: temperature dependences of emission A- and B-bands peak energies.

at $E_{\text{dA}} = 0.02$ eV and $E_{\text{dB}} = 0.01$ eV below the bottom of the conduction band. These shallow levels can be considered as originating from point defects due to deviations in stoichiometry or from uncontrolled impurities. The latter may be attributed to the presence of Si impurities introduced into $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ during the crystal growth process in ungraphitized ampoules.

The laser excitation intensity dependence of PL spectra also provides valuable information about the recombination mechanism responsible for the observed luminescence. Figure 5 presents the PL spectra for 16 different laser intensities at $T = 22$ K. From the analysis of the spectra, we obtained the information about the peak energy position and intensity for emission bands at different laser excitation intensities. Our analysis reveals that the peak energy position of A-band (E_{pA}) does not change with laser excitation intensity, while that of B-band (E_{pB}) shifts slightly towards higher energies with increasing excitation intensity (blue shift). The behavior of the emission B-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 [10, 11]. A careful inspection of the data shows that the B-band maximum slightly shifts towards higher energies ($\Delta E_{\text{pB}} = 30$ meV) with increasing excita-

Fig. 5. PL spectra of $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ crystal as a function of excitation laser intensity at $T = 22$ K.

tion laser intensities from 16 to 516 mW cm^{-2} (i.e., 20 meV per decade of exciting radiation intensity). The magnitude of the observed blue shift is typical of ternary and quaternary compounds such as CdGeAs_2 [12], HgInGaS_4 [13], $\text{Tl}_2\text{InGaS}_4$ [14], $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ [15], which are 10–15, 20, 20, 15 meV per decade of intensity of exciting radiation, respectively.

At low excitation laser intensities only a small fraction of the donor and acceptor levels trap carriers. This leads to recombination from distant pairs only. At high enough excitation laser intensities all donors and acceptors are excited, which leads to a contribution from closer pairs as well. The energy of the emitted photon during a donor–acceptor pair transition has a positive contribution from a Coulombic interaction between ionized impurities. This contribution increases as the separation between the pairs decreases [10]. Furthermore, radiative transition probabilities for different pair separations are different and decrease exponentially as a function of the pair distance [10]. Distant pair recombination (contributing to the low part energy part of a donor–acceptor pair emission band) saturates at high excitation laser intensities, whereas close pairs have a larger transition probability and can accommodate more carriers. We, therefore, observe a shift of the emission band peak energy to a higher energy as the excitation laser intensity increases.

The dependence of the B-band peak energy (E_{PB}) at $T = 22$ K as a function of excitation laser intensity (L) is given in Fig. 6. The experimental data in Fig. 6

Fig. 6. Excitation laser intensity versus emission peak energy for B-band at $T = 22$ K. The solid curve represents the theoretical fit using Eq. (2). The inset: dependence of PL intensities at the emission maxima versus excitation laser intensity for A- and B-bands at $T = 22$ K. The solid lines show the theoretical fits using Eq. (3).

are then fitted by the following expression:

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

where L_0 is a proportionality constant, E_{BR} is the emitted photon energy of a close donor–acceptor pair separated by a shallow impurity Bohr radius (R_{BR}), and E_∞ is the emitted photon energy of an infinitely distant donor–acceptor pair [16]. 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_{BR} are found to be $E_\infty = 1.82$ eV and $E_{BR} = 2.07$ eV, respectively. These limiting photon energy values are in good agreement with the band gap energy ($E_{gi} = 2.27$ eV) and the observed values of the peak energy position (i.e., $E_\infty < 1.91$ eV $< E_{pB} < 1.94$ eV $< E_{BR} < E_{gi}$) at $T = 22$ K. The indirect band gap energy $E_{gi} = 2.27$ eV at $T = 22$ K was evaluated using the temperature coefficient of E_{gi} reported for TlInS_2 crystal ($dE_{gi}/dT = -3.2 \times 10^{-4}$ eV K^{-1} [6]).

In PL spectra of $\text{Tl}_2\text{In}_2\text{S}_3\text{Se}$ crystal, the increase in the peak intensities of A- and B-bands with increase in the laser excitation intensity was also observed. The logarithmic plot of PL intensities versus laser excitation intensities are given in the inset of Fig. 6. Experimental data can be fitted by a simple power law of the following form:

$$I \propto L^\gamma, \quad (3)$$

where, I corresponds to the PL intensity, L corresponds to excitation laser intensity and γ is a dimensionless constant. We find that PL intensities at the emission bands maxima increase sublinearly with an increase in excitation laser

intensities with the value of $\gamma = 0.87$ and 0.76 for A- and B-bands, respectively. It is well known that for excitation laser photon energy exceeding the band gap energy E_g , the exponent γ is generally $1 < \gamma < 2$ for free- and bound-exciton emission, whereas $0 < \gamma \leq 1$ is typical of free-to-bound and donor-acceptor pair recombination [17, 18].

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 $\text{Ti}_2\text{In}_2\text{S}_3\text{Se}$ crystal $T = 22$ K. In the proposed scheme, shallow donor levels d_A and d_B are located at $E_{dA} = 0.02$ eV and $E_{dB} = 0.01$ eV below the bottom of the conduction band, respectively. On the basis of general expression for the emission energy of donor-acceptor pair [10] and taking into account E_{gi} and E_∞ , the sum of the activation energies of the donor (E_{dB}) and acceptor (E_{aB}) levels, involved in the emission B-band, has been estimated as:

$$E_{dB} + E_{aB} = E_{gi} - E_\infty = 2.27 \text{ eV} - 1.82 \text{ eV} = 0.45 \text{ eV}.$$

Considering that the donor level d_B is located at $E_{dB} = 0.01$ eV below the bottom of the conduction band, the above energy sum suggests that the acceptor level a_B involved in the emission B-band is placed at $E_{aB} = 0.44$ eV above the top of the valence band. For the A-band, the shallow donor level at $E_{dA} = 0.02$ eV and the observed peak energy at $T = 22$ K ($E_{pA} = 2.20$ eV), results in an acceptor level, which is located at $E_{aA} = 0.05$ eV above the top of the valence band. Taking into account the above considerations, the observed emission A- and B-bands in the PL spectra have been attributed to the radiative transitions from the donor level d_A to the acceptor level a_A and from the donor level d_B to the acceptor level a_B , respectively.

4. Conclusions

The PL spectra of $\text{Ti}_2\text{In}_2\text{S}_3\text{Se}$ crystals as a function of temperature and excitation laser intensity were studied. Two broad emission bands centered at 564 (2.20 eV, A-band) and 642 nm (1.93 eV, B-band) were observed at $T = 22$ 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 sub-linearly with respect to the excitation laser intensity and confirms our assignment that the observed emission bands in $\text{Ti}_2\text{In}_2\text{S}_3\text{Se}$ are due to the donor-acceptor pair recombination. As the studied crystals were not intentionally doped, the donor states are thought to originate from uncontrolled impurities or point defects, created during crystal growth.

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