

Infrared photoluminescence from TlGaS₂ layered single crystals

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Photoluminescence (PL) spectra of TlGaS₂ layered crystals were studied in the wavelength region 500-1400 nm and in the temperature range 15-115 K. We observed three broad bands centered at 568 nm (A-band), 718 nm (B-band) and 1102 nm (C-band) in the PL spectrum. The observed bands have half-widths of 0.221, 0.258 and 0.067 eV for A-, B-, and C-bands, respectively. The increase of the emission band half-width, the blue shift of the emission band peak energy and the quenching of the PL with increasing temperature are explained using the configuration coordinate model. We have also studied the variations of emission band intensity versus excitation laser intensity in the range from 0.4 to 19.5 W cm⁻². The proposed energy-level diagram allows us to interpret the recombination processes in TlGaS₂ crystals.

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1 Introduction

In recent years, the III-III-VI₂ family layer-structured thallium chalcogenides such as TlBX₂, where B = Ga or In and X = S or Se, have been studied extensively [1]. At room temperature, these thallium chalcogenides belong to the monoclinic system, and their space group is *C2/c*. The lattice of these crystals 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.

TlGaS₂, a member of this family of crystals, is a semiconductor with indirect band gap of about 2.46 and 2.55 eV at 300 and 10 K, respectively [2]. In view of its possible applications in optoelectronic devices, a great deal of attention has been devoted to study the optical and electrical properties of TlGaS₂ [2-7]. In this regard, detailed information on the impurity levels is very useful for the fabrication of high-quality devices. Song et al. [6] have investigated the impurity levels of TlGaS₂ crystals in the temperature range 90-350 K by thermally stimulated current (TSC) and photo-induced current transient spectroscopy techniques. The activation energies of the observed four peaks were found to be 0.18, 0.23, 0.36 and 0.66 eV. Recently we have studied the shallow levels of TlGaS₂ crystal in the low-temperature range of 10-60 K by TSC method and observed three trap levels with activation energies 0.006, 0.012 and 0.026 eV [8]. Long-wave optical phonons in TlGaS₂ crystals were investigated by infrared reflection and Raman scattering experiments [7, 9].

In the present paper, we report the results of the PL investigation of TlGaS₂ single crystals in the 500-1400 nm wavelength and in the 15-115 K temperature range. The shift of the emission band peak energy as well as the change of the half-width of the emission band with temperature and excitation laser intensity was also studied. The observed results were analyzed using the configurational coordinate (CC) model.

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2 Experimental

TlGaS₂ polycrystals were synthesized from high-purity elements (at least 99.999% pure) prepared in stoichiometric proportions. Single crystals of TlGaS₂ were grown by the modified Bridgman method. The analysis of X-ray diffraction data showed that, TlGaS₂ crystallizes in a monoclinic unit cell with lattice parameters: $a = 1.031$, $b = 1.043$ and $c = 1.507$ nm, and $\beta = 99.60^\circ$. The samples were prepared by cleaving an ingot parallel to the crystal layer, which was perpendicular to the c -axis, with typical sample dimensions of $8 \times 4 \times 2$ mm³. The electrical conductivity of the samples was p -type as determined by the hot probe method. A "Spectra-Physics" argon ion laser operating at a wavelength 476.5 nm was used as the excitation source. The PL was observed from the laser illuminated face of the samples, in a direction close to the normal of the (001) plane. A "CTI-Cryogenics M-22" closed-cycle helium cryostat was used to cool the crystals from room temperature down to 15 K. The temperature was controlled within an accuracy of 0.5 K. The PL spectra in the 500–860 nm wavelength range were analyzed using a "U-1000 Jobin-Yvon" double grating spectrometer and a cooled GaAs photomultiplier equipped with the necessary photon counting electronics. The PL spectra in the 600–1400 nm wavelength range were obtained by means of "CVI Digikrom DK-480" monochromator and Hamamatsu TE cooled InGaAs infrared detector. A set of neutral-density filters was used to adjust the excitation laser intensity from 0.4 to 19.5 W cm⁻².

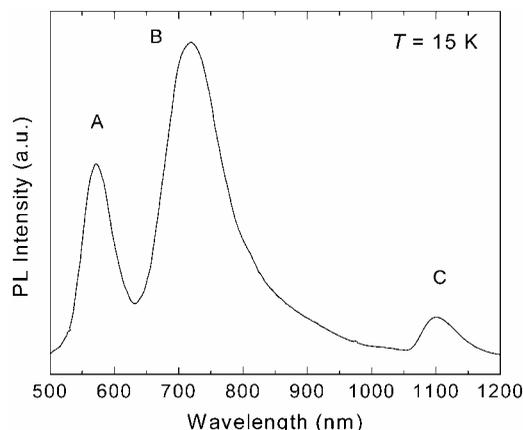


Fig. 1 PL spectrum of TlGaS₂ crystal in the 500–1200 nm wavelength range at $T = 15$ K. Excitation laser intensity $L = 19.5$ W cm⁻².

3 Results and discussion

Figure 1 shows the PL spectrum of the TlGaS₂ crystal measured at $T = 15$ K and excitation laser intensity of 19.5 W cm⁻² in the 500–1200 nm wavelength range. We observed three broad bands with an asymmetric Gaussian line shapes centered at 568 nm (2.183 eV, A-band), 718 nm (1.727 eV, B-band) and 1102 nm (1.125 eV, C-band) in the PL spectrum. The observed bands have half-widths of 0.221, 0.258 and 0.067 eV for A-, B- and C-bands, respectively. The emission bands intensity, half-width and peak position changed with temperature. These features are typical of the emission bands due to donor-acceptor pair transitions observed in ternary semiconductors [10].

In our previous paper [11] we presented the results of detailed analysis of the A- and B-bands behavior in the PL spectra of TlGaS₂ crystals with respect to the temperature and excitation intensity. It was shown that in the temperature range of 10–90 K, the intensity of the A-band decreases, while the intensity of the B-band increases. For $T > 90$ K, when the A-band becomes very weak, the intensity of the B-band decreases drastically as the temperature increases. The activation energies $\Delta E_A = 0.005$ eV and $\Delta E_B = 0.085$ eV for A- and B-bands, respectively, have been obtained from semilog plots of PL intensities as a function of reciprocal temperature. The A- and B-bands were found to be due to the radiative transitions from the deep donor levels at 0.362 eV (d_1) and 0.738 eV (d_2) below the conduction band to the shallow acceptor levels at 0.005 eV (a_1) and 0.085 eV

(a_2) above the valence band, respectively. The presence of two acceptor levels allowed to explain the thermal quenching behavior of A- and B-bands in PL spectra of TlGaS₂ crystal, where the intensity of the B-band increases in the temperature range (10-90 K) for which the quenching of the A-band is observed. Quenching of the A-band may be associated with the thermal release of holes from the acceptor level a_1 to the valence band. The thermally released holes are then captured by the acceptor level a_2 . Finally, this results in the increase of the intensity of the B-band in the same temperature range where quenching of the A-band occurs.

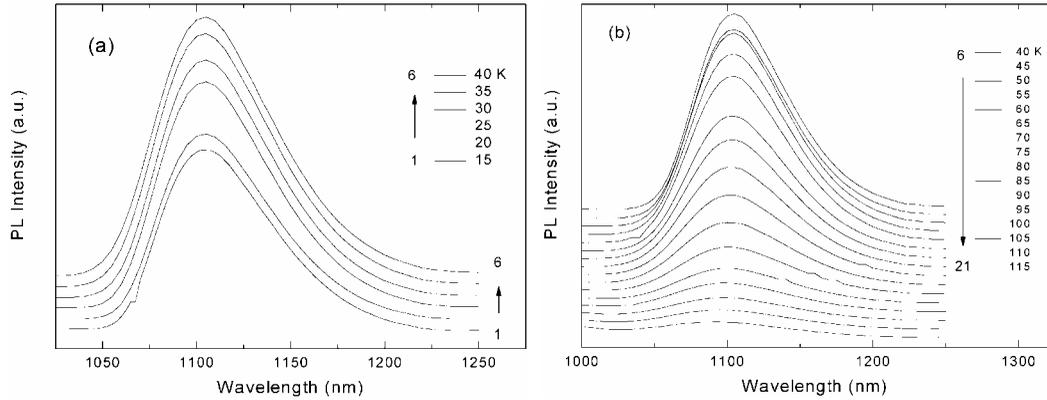


Fig. 2 PL spectra of TlGaS₂ crystal in the 15-115 K temperature range and 1000-1250 nm wavelength region. Excitation laser intensity $L = 19.5 \text{ W cm}^{-2}$.

Figure 2 shows the PL spectra of the TlGaS₂ crystal (C-band) measured in the 1000-1250 nm near-infrared wavelength range and in the 15-115 K temperature region at a constant excitation laser intensity of 19.5 W cm^{-2} . From Figure 2 it can be seen that in the temperature range of 15-40 K the intensity of the C-band increases with increasing temperature, while for $T > 40 \text{ K}$ the intensity of the band decreases. Figure 3 shows the integrated C-band intensity as a function of the reciprocal temperature in the 15-115 K range and temperature dependence of the C-band peak energy. The increase of C-band intensity in the temperature range of 15-40 K may be related to the thermal release of holes from the above-mentioned acceptor level a_1 to the valence band. Probably, such released holes are captured not only by the acceptor level a_2 but also by the acceptor level a_3 , responsible for appearance of C-band in the PL spectra. The decrease of the C-band intensity in the temperature range of 40-115 K is associated with the thermal release of holes from the acceptor level a_3 when the contribution of captured holes released from level a_1 becomes very small. A rapid thermal quenching of the PL band is observed above $T = 60 \text{ K}$. The experimental data for the temperature dependence of the integrated C-band intensity can be fitted by the following expression [12]

$$I(T) = \frac{I_0}{1 + \alpha_1 T^{3/2} + \alpha_2 T^{3/2} \exp(-\Delta E / kT)} \quad (1)$$

where I_0 is a proportionality constant, ΔE the thermal activation energy, k the Boltzmann constant, α_1 and α_2 are the fitting parameters associated with the temperature dependence of the capture cross sections of the donor and acceptor impurity levels. The best fit in the temperature range 40-115 K using Eqn. (1), demonstrated by the solid curve in Fig. 3, has been achieved with parameters $I_0 = 2.6 \times 10^5$, $\Delta E = 0.035 \text{ eV}$, $\alpha_1 = 1.6 \times 10^{-4}$ and $\alpha_2 = 2.9 \times 10^{-1}$.

For understanding the nature of luminescence from semiconductors, excitation laser intensity dependence of the PL spectra is an important consideration. In Figure 4, we present the excitation laser intensity dependence of the PL spectra of TlGaS₂ crystal. The C-band is visible even at the lowest laser excitation intensity and the intensity of this band rises as the excitation intensity increases. Detailed analysis of the peak position of this band as a function of excitation laser intensity did not yield any variation of the peak energy

values. We, therefore, concentrated on the analysis of PL intensity as a function of excitation laser intensity. The experimental data can be fitted by a simpler power law of the form:

$$I \propto L^\gamma \tag{2}$$

where I is the PL intensity, L is the excitation laser intensity and γ is a dimensionless exponent. It was found that the integrated intensity of the emission band increases sublinearly with respect to the excitation laser intensity (Fig. 5). The value of γ was found to be 0.97. It is well known that for excitation laser photon with an energy exceeding the band gap energy, E_g , the coefficient γ is generally $1 < \gamma < 2$ for the free- and bound-exciton emission, and $\gamma \leq 1$ for free-to-bound and donor-acceptor pair recombination [13]. Thus, the obtained value of $\gamma < 1$ further confirms our assertion that C-band in the PL spectra of TlGaS₂ is due to donor-acceptor pair recombination.

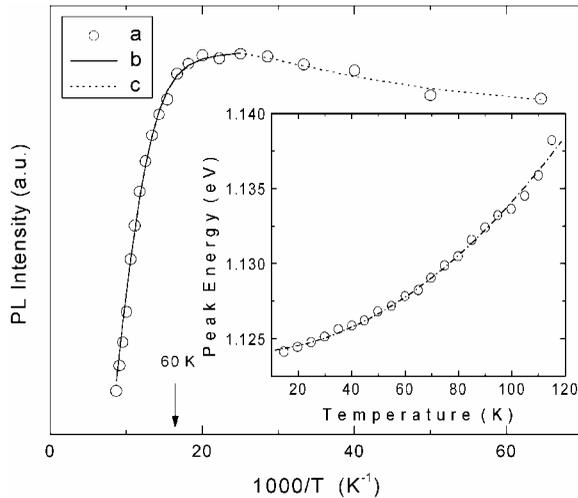


Fig. 3 Temperature dependence of integrated C-band intensity for TlGaS₂ crystal. The arrow at $T = 60$ K shows the starting point of the intensive quenching process. (a) the experimental data, (b) the theoretical fit using equation (1), (c) the guide for eye. Inset: Temperature dependence of C-band peak energy for TlGaS₂ crystal. The dotted line is only guide for the eye.

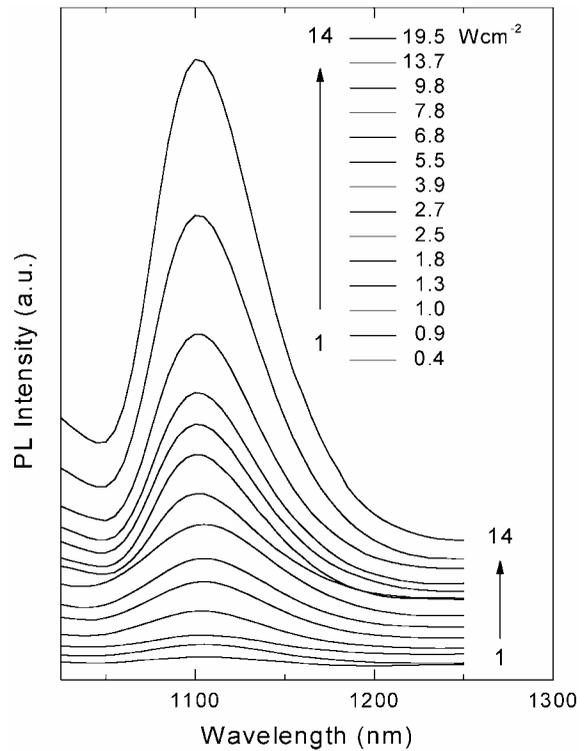


Fig. 4 PL spectra of TlGaS₂ crystal as a function of excitation laser intensity at $T = 15$ K.

Peak energy of C-band does not change with increasing excitation laser intensity (Fig. 4). This result rules out the model of "distant" donor-acceptor pair recombination process where a shift toward higher energies are expected as the excitation laser intensity is increased [14]. It is known that in general, the emission energy from a donor-acceptor pair separated by a distance of r is obtained from [15]

$$E(r) = E_g - (E_A + E_D) + \frac{Z_D Z_A e^2}{\epsilon r} \tag{3}$$

where, E_g is the band gap energy, E_A and E_D are the acceptor and donor ionization energies, ε is the dielectric constant, Z_D and Z_A are the charges of the donor and acceptor states, respectively. From Eq. (3), it is clear that as the excitation laser intensity is increased, the contribution of closer pairs will increase leading to the expected blue shift of the peak energy of the emission. Since this is in contrast with the observed data, we conclude that, only close pairs such as the nearest or next-nearest neighbors are involved in the transitions.

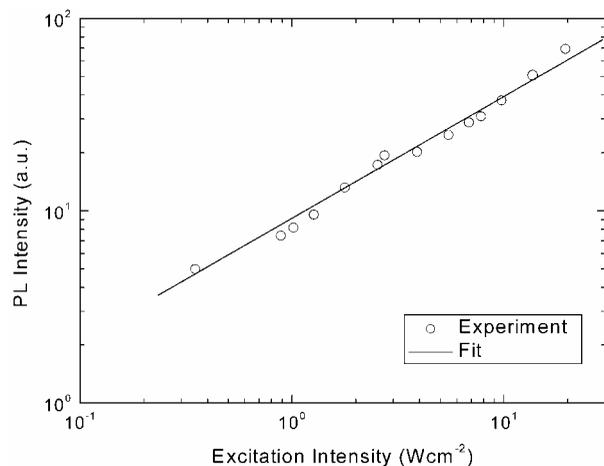


Fig. 5 Dependence of integrated PL band intensity on excitation laser intensity at $T = 15$ K. The solid curve gives the theoretical fit using equation (2).

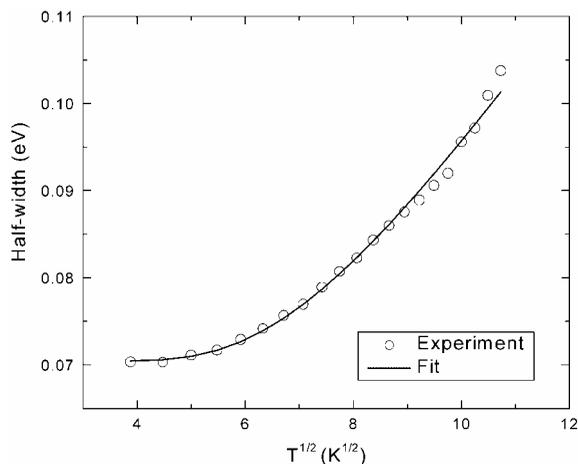


Fig. 6 Variation of the half-width with square root of temperature for the emission band in TlGaS₂ crystal. The solid curve is a plot of equation (4) with $h\nu_c = 0.011$ eV.

Inset of Figure 3 shows the shift of the emission peak energy as a function of temperature. The emission band peak energy increases with increasing temperature. This is opposite to the behavior of the band gap energy shift, which decreases with increasing temperature [2]. The total range of the peak energy shift is 0.014 eV. Similar behavior for the peak energy shift as well as the above-mentioned half-width increase with temperature has been observed for the emission bands of *p*-GaAs [16] and layered *p*-GaSe [17]. The 1.37 eV (GaAs) and 1.20 eV (GaSe) emission bands were associated with a vacancy-acceptor complex center, and the recombination mechanism was interpreted as self-activated luminescence in terms of the CC model [18]. Since the CC model was so successful in explaining the behavior of the luminescence associated with such a localized center in layered *p*-GaSe, it was also applied here for layered TlGaS₂ which belongs to the same III-VI family as GaSe with a layered crystal structure.

Figure 6 presents the temperature dependence of the C-band half-width W , which appears to follow the CC model equation [18]

$$W = W_0 [\coth(h\nu_c/2kT)]^{1/2}, \quad (4)$$

where W_0 is a constant, whose value is equal to W as the temperature approaches 0 K, and $h\nu_c$ is the energy of the vibrational mode of the excited state. The half-width measurements were not performed above 115 K, because of the reduced PL intensity. However, the changes in the half-width between 15 and 115 K are large enough to show the functional dependence of Eq. (4). The solid line in Fig. 6 is a plot of Eq. (4) with parameters $W_0 = 0.071$ eV and $h\nu_c = 0.011$ eV. The fact that the excited state vibrational energy ($h\nu_c$) is lower than the longitudinal optical phonon energy of 0.039 eV (315 cm^{-1}) measured by IR reflection [9], shows the localized nature of the centers and the validity of applying the CC model [16].

Figure 7 shows the CC model for the TlGaS₂ crystal. Following the *p*-GaAs [16] and *p*-GaSe [17] works, let us assume that the ground state of the localized center is derived from an acceptor level a_3 , the excited state originates from a sulphur vacancy donor level d_3 , and the zero point of both states lie within the band gap. Actually, in compound semiconductors a deviation from stoichiometry generates donors for the case of anion

vacancy [19]. The acceptor level a_3 above the top of the valence band may be linked, as in GaSe [20], to the defects and stacking faults, which are due to the weak interlayer interactions in the studied crystals. Electron transitions from the excited state of the donor level to the ground state of the acceptor level gives rise to the PL with emitted photon energy E_{em} . Also, according to the CC model, when the ground-state vibrational energy is larger than the excited-state vibrational energy, the peak shift of the emission band with temperature is opposite to the band gap energy shift [16].

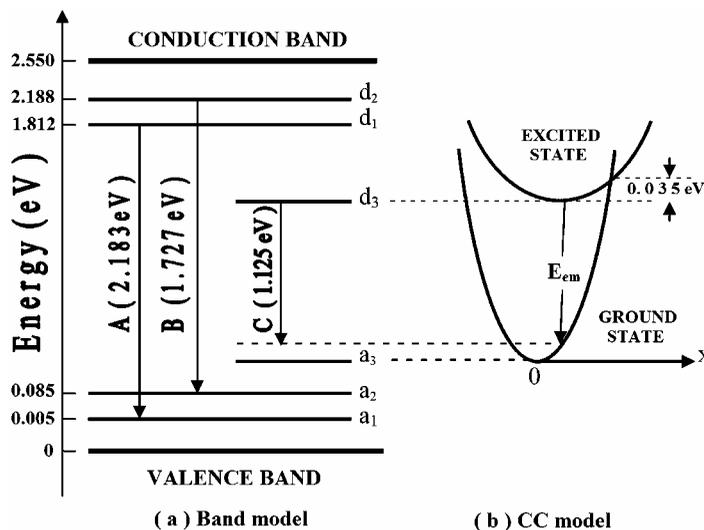


Fig. 7 Band model (a) and configurational coordinate (CC) model (b) of TlGaS₂ crystal at $T = 15$ K.

In terms of the CC model, the observed quenching of the C-band in the PL spectra with increasing temperature (Figs. 2 and 3) is due to an increased electron population of the excited state at higher displacement coordinates. These electrons then return to the ground state through nonradiative recombination. Thus, the activation energy $\Delta E = 0.035$ eV, obtained from the thermal quenching of the PL, is the difference in the energies of the lowest excited state and the intersection point of the excited and the ground state CC curves (Fig. 7).

4 Conclusions

We measured low-temperature PL spectra of layered single crystal TlGaS₂ grown by modified Bridgman method. Three PL bands centered at 568 nm (2.183 eV, A-band), 718 nm (1.727 eV, B-band) and 1102 nm (1.125 eV, C-band) have been observed. The analysis of the PL spectra as a function of temperature and excitation laser intensity allows one to obtain a possible model for the donor-acceptor levels located in the forbidden energy gap of the TlGaS₂ crystal. In our proposed CC model for C-band, the emission band is associated with a vacancy-acceptor complex center, and the recombination mechanism is interpreted as self-activated luminescence. The excited state originates from a sulphur vacancy donor level d_3 . The acceptor level a_3 above the top of the valence band may be linked to stacking faults in the studied layered crystal. The difference in the energies of the lowest excited state and the intersection point of the excited and the ground state CC curves is equal to the activation energy $\Delta E = 0.035$ eV, which was obtained from the thermal quenching of the PL. Sublinearly increase of PL intensity with respect to the excitation laser intensity confirms our assignment that the observed PL in TlGaS₂ crystal is due to donor-acceptor pair recombination.

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