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Low-temperature visible photoluminescence spectra of $TlGaSe_2$ layered crystal

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Abstract

The photoluminescence (PL) spectra of $TlGaSe_2$ layered single crystals were investigated in the 8.5–35 K temperature, 0.2–15.2 W cm^{-2} excitation laser intensity, and in the 600–700 nm wavelength range. The PL spectrum has a slightly asymmetric Gaussian lineshape with a peak position located at 1.937 eV (640 nm) at 8.5 K. The PL is quenched with increasing temperature. The blue shift of the PL peak and the sublinear increase of the PL intensity with increasing laser intensity is explained using the inhomogenously spaced donor–acceptor pair recombination model. Analysis of the data indicates that the PL band is due to donor–acceptor recombination. A shallow acceptor level and a moderately deep donor level are, respectively, introduced at 0.012 eV above the top of the valence band and at 0.317 eV below the bottom of the conduction band. An energy-level diagram for radiative donor–acceptor pair recombination in $TlGaSe_2$ layered single crystals is proposed

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1. Introduction

Recently, ternary thallium chalcogenides received a great deal of attention due to their optical and electrical properties in view of possible optoelectronic device applications [1–4]. These III–III–VI_2 family of crystals have both layered (e.g., $TlGaS_2$, $TlGaSe_2$, $TlInS_2$) and chain (e.g., $TlInSe_2$, $TlInTe_2$, $TlGaTe_2$) structures. At room temperature, layer-structured thallium chalcogenide crystals belong to the monoclinic system, and their space group is C2/c. The crystal lattice consists of alternating two-dimensional layers arranged parallel to the (0 0 1) plane. Each successive layer is rotated by a 90° angle with respect to the previous layer. Long-wave optical phonons in these crystals were investigated by infrared reflection and Raman scattering experiments [5]. Recently, we have studied the photoluminescence (PL) of $TlGaS_2$ and $TlInS_2$ single crystals [6,7], and observed broad emission bands, which we have attributed to donor–acceptor pair recombination.

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In the present paper, we report the results of the PL investigation of single crystals of $TlGaSe_2$, which has a band gap of $E_g = 2.187$ eV at $T = 8.5$ K and $dE_g/dT = -2 \times 10^{-4}$ eV/K [8,9]. The PL investigation is conducted within the 600–700 nm wavelength, 0.2–15.2 W cm^{-2} excitation laser intensity, and in the 8.5–35 K temperature range. The PL spectra and their temperature and excitation intensity dependencies were studied in detail in order to propose a model for the recombination process of photoexcited carriers and a scheme for the impurity levels.

2. Experimental

$TlGaSe_2$ polycrystals were synthesized from high purity elements(at least 99.999% pure) prepared in stoichiometric proportions. Single crystals of $TlGaSe_2$ were grown by the modified Bridgman method. No intentional doping of the crystals were performed. The analysis of X-ray diffraction data showed that, $TlGaSe_2$ crystallizes in a monoclinic unit cell with lattice parameters: $\boldsymbol{a} = 10.756$ Å, $\boldsymbol{b} = 10.730$ Å and $\boldsymbol{c} = 15.596$ Å and $\beta = 99.92^\circ$. The samples were prepared by cleaving an ingot parallel to the crystal layer, which was perpendicular to the c-axis. The typical sample dimensions are $4 \times 2 \times 1$ mm^3. The electrical conductivity of the studied samples was p-type as determined by the hot probe method. A "Spectra-Physics" argon ion laser operating at a wavelength 514.5 nm (2.410 eV) 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 (0 0 1) plane. A "CTI-Cryogenics M-22" closed-cycle helium cryostat was used to cool the samples from room temperature down to 8.5 K. The temperature was controlled within an accuracy of 0.5 K. The PL spectra in the 600–700 nm wavelength range were analyzed using a "U-1000 Jobin-Yvon" double grating spectrometer and a cooled GaAs photomultiplier tube equipped with the necessary photon counting electronics. A set of neutral-density filters was used to adjust the excitation laser intensity from 0.20 to 15.2 W cm^{-2}. This excitation laser intensity is the mean value of the laser intensity over the Gaussian spatial profile of the laser beam. The PL spectra have been corrected for the spectral response of the optical apparatus.

3. Results and discussion

Fig. 1 shows the PL spectra of the $TlGaSe_2$ crystal measured in the 600–700 nm wavelength and in the 8.5–35 K temperature range at a constant excitation laser intensity of 15.2 W cm^{-2}. We observed a broad PL band centered at 640 nm ($E_p = 1.937$ eV) at 8.5 K. The PL spectra have a Gaussian lineshape with a slight asymmetry. The PL intensity decreases, and the PL peak energy position slightly shifts towards lower energies with increasing temperature, and disappears at 35 K. These features are typical of PL, which is due to donor–acceptor pair transitions observed in ternary semiconductors [7,10–12]. The red shift of the donor–acceptor emission in ternary chalcogenides was explained [11] by the transition involving donor and acceptor levels bound strongly to the band edge.

The variation of the PL peak with respect to temperature is plotted in Fig. 2. In the 8.5–18 K

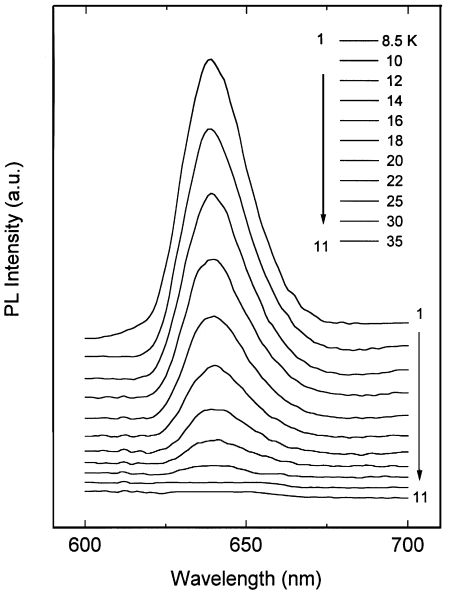

Fig. 1. PL spectra of $TlGaSe_2$ in the 8.5–35 K temperature range at $L = 15.2$ W cm^{-2}.

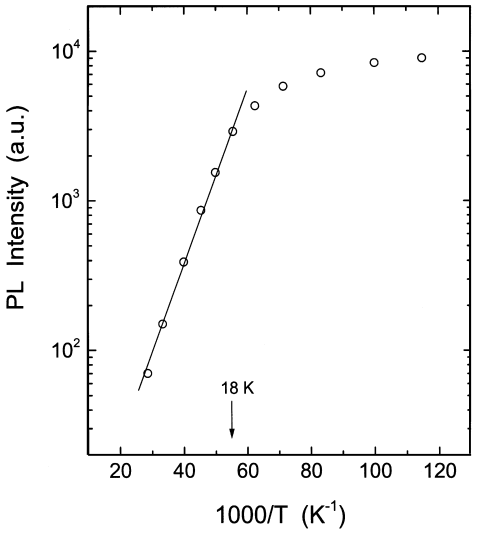

Fig. 2. Temperature dependence of $TlGaSe_2$ PL intensity at the emission band maximum. The arrow at 18 K shows the starting point of the intensive quenching.

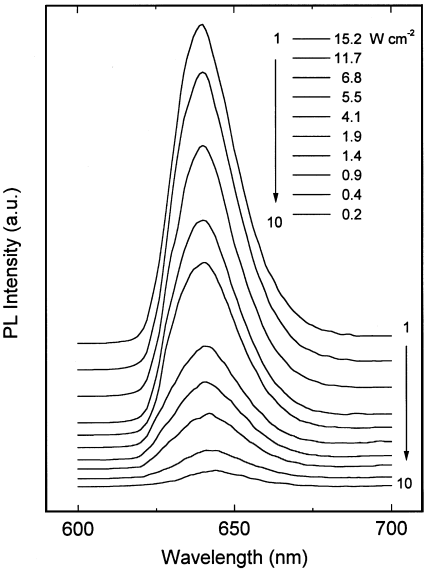

Fig. 3. PL spectra of $TlGaSe_2$ in the 0.2–15.2 W cm^{-2} laser intensity range at 8.5 K.

range, the PL intensity decreases slowly. Above 18 K, however, the PL intensity decreases at a larger rate due to a thermal quenching process. The activation energy ΔE for this thermal quenching process can be derived in the 18–35 K temperature range using a nonlinear least-squares fit to the following equation:

$$I = I_0 \exp(\Delta E/k_B T), \quad (1)$$

where I is the PL intensity, I_0 a proportionality constant, and k_B the Boltzmann's constant. The semilog plot of the emission band intensity as a function of the reciprocal temperature gives a straight line in the 18–35 K region. An activation energy of $E_a = 0.012$ eV for the emission band is derived from the slope of the straight line fit. Since the $TlGaSe_2$ crystal is a p-type semiconductor, we consider that the impurity level is an acceptor level ***a*** located at 0.012 eV above the top of the valence band. This shallow acceptor level ***a*** in undoped $TlGaSe_2$ layered crystal may be associated with the presence of defects and unintentional impurities [13].

Fig. 3 presents the PL spectra for 10 different laser intensities at 8.5 K. The observed PL band slightly shifts towards higher energies ($\Delta E_p = 11$ meV) with increasing excitation intensity from 0.2 to 15.2 W cm^{-2} (i.e., 6 meV per decade of excitation laser intensity). This behaviour is a characteristic of the donor–acceptor pair recombination [14,15]. In donor–acceptor pair recombination, photoexcited carriers trapped at ionized donors and acceptors recombine radiatively. 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 large enough excitation laser intensities more impurity levels trap carriers which lead 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 decrease [15]. Furthermore, radiative transition probabilities for different pair separations are different and decrease exponentially as a function of the pair distance [16]. We, therefore, observe a shift of the emission band peak energy to higher energy as the intensity of the excitation laser increases.

The semilog plot in Fig. 4 shows the excitation laser intensity (L) as a function of the emission band

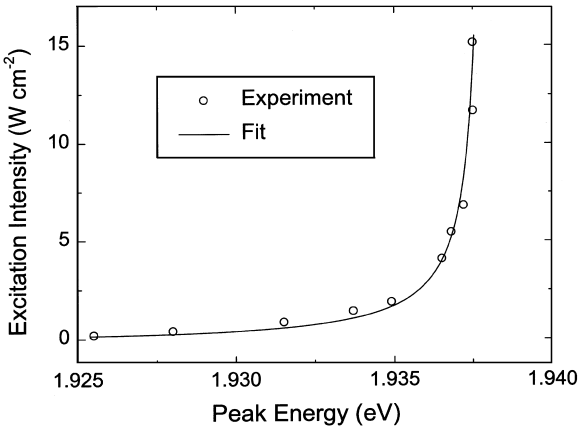

Fig. 4. Excitation laser intensity versus $TlGaSe_2$ emission band peak energy at 8.5 K. The solid curve gives the theoretical fit using Eq. (2).

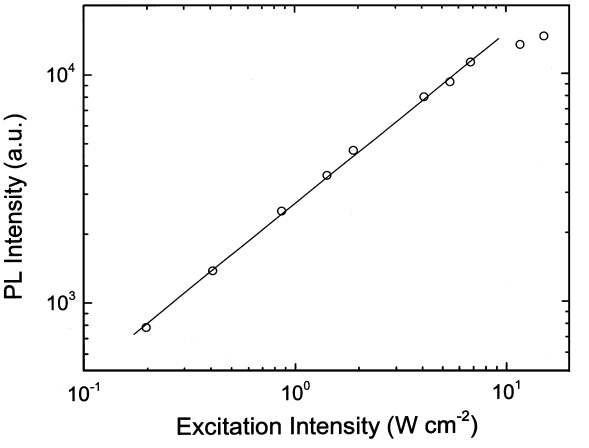

Fig. 5. Dependence of $TlGaSe_2$ PL intensity at the emission band maximum versus excitation laser intensity at 8.5 K. The solid curve gives the theoretical fit using Eq. (3).

peak energy (E_p) at 8.5 K. The experimental data in Fig. 4 is then fitted by the following equation [17]:

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

where L_0 is a proportionality constant, E_B the emitted photon energy of a close donor–acceptor pair separated by a shallow impurity Bohr radius (R_B), and E_∞ the emitted photon energy of an infinitely distant donor–acceptor pair. From a non-linear least-squares fit of Eq. (2) 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 $E_\infty = 1.858$ eV and $E_B = 2.018$ eV, respectively. These limiting photon energy values are in good agreement with the band-gap energy ($E_g = 2.187$ eV) and the observed values of the peak energy position (i.e., $E_\infty < 1.926\,\text{eV} < E_p < 1.937\,\text{eV} < E_B < E_g$) at 8.5 K.

We have also investigated the intensity variation of the maximum of the emission band versus the excitation laser intensity at $T = 8.5$ K (Fig. 5). The experimental data can be fitted by a simple power law:

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

where I is the PL intensity, L the excitation laser intensity, and γ a dimensionless exponent. It was found that, the PL intensity increases sublinearly (i.e., $\gamma = 0.75$) with respect to the excitation laser intensity (Fig. 5). Saturation of the PL starts at $L > 6.8\ \text{W cm}^{-2}$. For an 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 [18]. Thus, the obtained value of $\gamma = 0.75$ confirms our assignment of the observed emission band in $TlGaSe_2$ 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 donor–acceptor levels located in the forbidden energy gap of the $TlGaSe_2$ crystal. These donor–acceptor levels are involved in the radiative recombination of the photoexcited carriers observed in this work. In our proposed scheme (Fig. 6), a shallow acceptor level ***a*** located at 0.012 eV above the top of the valence band, is introduced into the forbidden energy gap of $TlGaSe_2$.

On the basis of general expression for the emission energy of donor–acceptor pair [15] and taking into account E_g and E_∞, the sum of the activation energies of the donor (E_d) and acceptor (E_a) levels,

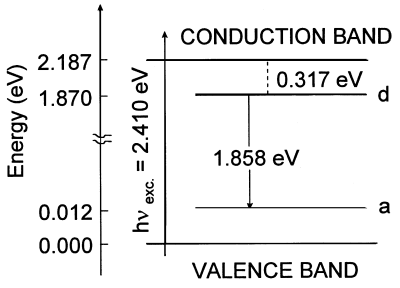

Fig. 6. Proposed energy-level diagram of $TlGaSe_2$ at 8.5 K.

involved in the emission band, has been estimated as being

$$E_d + E_a = E_g - E_\infty = 2.187\ \text{eV} - 1.858\ \text{eV} = 0.329\ \text{eV}. \quad (4)$$

Consequently, a donor level ***d***, located at 0.317 eV below the bottom of the conduction band, is introduced into the forbidden energy gap of $TlGaSe_2$. We propose that the moderately deep donor level in p-type $TlGaSe_2$ layered crystal can be associated with stacking faults or dislocations, which are quite producible in these materials, due to the weakness of the forces (van der Waals) between adjacent layers. Similarly, moderately deep donor levels were also revealed in p-type GaSe layered crystal [13,19]. Taking into account the above assignments, we attribute the observed PL band to the radiative recombination of an electron occupying a donor level ***d*** ($E_d = 0.317$ eV) and a hole occupying an acceptor level ***a*** ($E_a = 0.012$ eV).

4. Conclusions

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 $TlGaSe_2$ crystal. Rapid thermal quenching of the PL band is observed above $T = 18$ K indicating the presence of a shallow impurity. This behavior was understood in terms of a shallow acceptor level located at 0.012 eV above the valence band in p-type $TlGaSe_2$.

A moderately deep donor level located at 0.317 eV below the conduction band, is then introduced into the energy-band diagram of $TlGaSe_2$ crystal. The blue shift of the emission band peak energy with increasing excitation laser intensity is explained using the inhomogenously spaced donor–acceptor pair model. Moreover, the PL intensity increases sublinearly with respect to the excitation laser intensity and confirms our assignment that the observed PL in $TlGaSe_2$ is due to donor–acceptor pair recombination.

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