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Full Length Article

Comparative study of low-temperature photoluminescence and thermally stimulated current in quinary $Tl_4Ga_3InSe_6S_2$ layered crystals

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ABSTRACT

Photoluminescence (PL) and thermally stimulated current (TSC) spectra of $Tl_4Ga_3InSe_6S_2$ layered crystals grown by Bridgman method have been studied in the wavelength region of 560–690 nm and the temperature range of 15–45 K (PL) and in the temperature region of 10–90 K (TSC). A broad PL band centered at 620 nm (2.00 eV) was observed at $T=15$ K. Variations of emission band has been studied as a function of excitation laser intensity in the 0.7–36.5 mW cm^{-2} range. Radiative transitions from donor level located at 150 meV below the bottom of conduction band to shallow acceptor level located at 10 meV above the top of the valence band were suggested to be responsible for the observed PL band. TSC curve of $Tl_4Ga_3InSe_6S_2$ crystal exhibited one broad peak at about 41 K. The activation energy of trap level was found to be 11 meV. An energy level diagram showing transitions in the band gap of the crystal was plotted taking into account the results of PL and TSC measurements carried out below room temperature.

1. Introduction

The quinary $Tl_4Ga_3InSe_6S_2$ (TGISS) crystal belongs to the group of layered semiconductors. This compound is a structural analog of $TlGaSe_2$ and $TlInS_2$, in which a quarter (three quarter) of gallium (indium) and selenium (sulfur) ions are replaced by indium (gallium) and sulfur (selenium) ions, respectively [1,2]. The lattice of TGISS consists of strictly periodic twodimensional layers arranged parallel to the (0 0 1) plane (Fig. 1). Each successive layer is rotated by a 90° 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 $Ga_4(In_4)Se_6(S_6)$ adamantane-like units linked together by bridging Se(S) atoms. The Tl atoms are in trigonal prismatic voids resulting from the combination of the $Ga_4(In_4)Se_6(S_6)$ polyhedra into a layer. The Tl atoms form nearly planar chains along the [1 1 0] and [1 1⁻ 0] directions.

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 $TlGaSe_2$ and $TlInS_2$ crystals [3–10]. It was revealed that the fundamental absorption edge is formed by the indirect transitions with band gap energies $E_{gi}=1.98$ and 2.06 eV ($TlGaSe_2$) and $E_{gi}=2.27$ and 2.44 eV ($TlInS_2$) 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 μm make these crystals useful for optoelectronic applications [11].

Earlier we studied the low-temperature photoluminescence (PL) spectra of $TlGaSe_2$ and $TlInS_2$ crystals and observed one and two broad emission bands, respectively, which were assigned to donor–acceptor pair recombination [12,13]. Moreover, recently we have studied the low-temperature PL spectra of $Tl_2InGaSe_4$, Tl_2InGaS_4 and $Tl_4GaIn_3Se_2S_6$ crystals and observed one, three and one broad emission bands, respectively, which were attributed to the transitions from moderately deep donor to shallow acceptor levels [14–16].

One of the determining factors in the eventual device performance of semiconductors is the presence of impurity and/or defect centers in the crystal. 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 variation of the PL emission band with temperature (15–45 K) and excitation laser intensity (0.7–36.5 mW cm^{-2}) in $Tl_4Ga_3InSe_6S_2$ crystals. The analysis of the data suggests that the radiative transitions originate from recombination of charge carriers from donor to acceptor states. Moreover, we established in thermally stimulated current (TSC) curve of $Tl_4Ga_3InSe_6S_2$ crystal one broad peak. The activation energy of trap level was found to be 11 meV.

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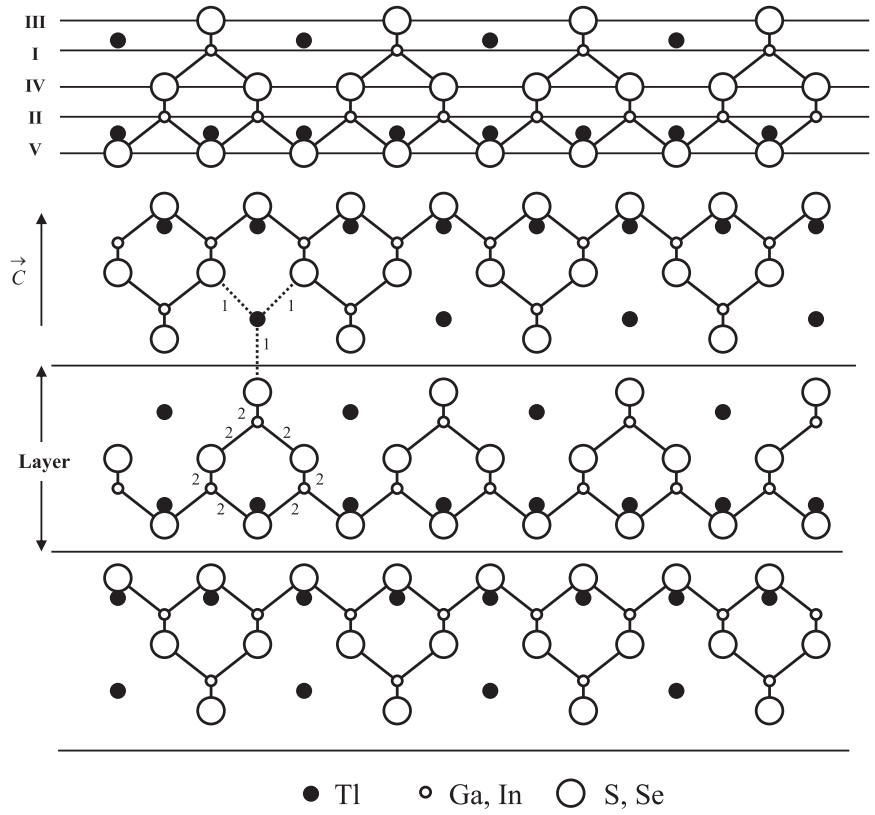

Fig. 1. Projection of the structure in Tl4Ga3InSe6S2 crystal as seen from the *ac*-plane. The ones (1) show the interlayer bonding between Tl and Se atoms; the twos (2) show the intralayer bonding between Ga(In) and Se(S) atoms. From I to V indicate different planes of atoms.

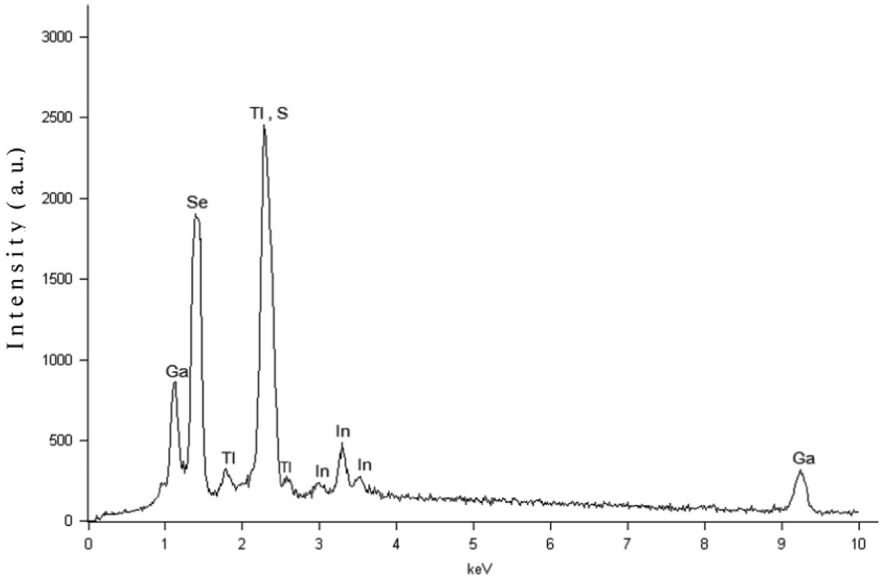

Fig. 2. Energy-dispersive spectroscopic analysis of $Tl_4Ga_3InSe_6S_2$ crystal.

2. Experimental

$Tl_4Ga_3InSe_6S_2$ semiconductor polycrystals were synthesized using high-purity elements taken in stoichiometric proportions. The single crystals were grown by the Bridgman method in evacuated (10^{-5} Torr) silica tubes (10 mm in diameter and about 25 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 °C cm^{-1} at a rate of 1.0 mm h^{-1}. The resulting ingot appeared red in color and the freshly cleaved surfaces were mirror-like. The chemical composition of $Tl_4Ga_3InSe_6S_2$ 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 25.5: 19.0: 6.3: 37.0: 12.2, respectively.

The electrical conductivity of the studied sample was p-type as determined by the hot probe method. Crystals suitable for PL measurements had typical sample dimensions of $10 \times 4 \times 1$ mm^3.

The green line (λ=532 nm) of a continuous frequency-doubled YAG:Nd^{3+} 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 15 K, and the temperature was controlled within an accuracy of $\pm$0.5 K. The PL spectra of the sample in the region 560–690 nm were analyzed using a "Oriel 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 0.7 to 36.5 mW cm^{-2}. All of the PL spectra have been corrected for the spectral response of the optical apparatus.

For TSC experiments, two electrodes were made on the sample using silver paste according to sandwich geometry: one was on the front as a small droplet to allow illumination and the other one was at the back covering the whole surface of the sample to maintain electrical and thermal conductivity. Thin copper wires were used to attach to the electrodes for circuit connection. The copper holder was mounted on the cold finger of the cryostat and the back side was grounded through the sample holder. The TSC measurements were carried out in the temperature range of 10–90 K using a closed cycle helium cryostat. A Lake-Shore 331 temperature controller was utilized to provide constant heating rate of 0.2 K s^{-1}. A Keithley 228 A voltage/current source and a Keithley 6435 picoammeter were employed for TSC measurements. At low temperatures, carriers were excited by a light emitting diode, generating light at a maximum peak of 2.6 eV.

3. Results and discussion

The dependence of the PL spectra on temperature provides important understanding of the nature and analysis of luminescence spectra. Fig. 3 presents the PL spectra of $Tl_4Ga_3InSe_6S_2$ crystals in 15–45 K temperatures range at constant laser excitation intensity L=36.5 mW cm^{-2}. We observed that, at T=15 K the emission band was centered at 620 nm (2.00 eV) and has asymmetrical Gaussian line shape with short- and long-wavelength side half-widths of 0.056 and 0.066 eV, respectively. As seen from the Fig. 3, emission band changes its intensity and peak position as a function of the sample temperature: the peak intensity decreases as the temperature is elevated and the peak position shows several degrees of red shift (about 5 nm) with increasing temperature. Inset 2 of Fig. 3 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 [17].

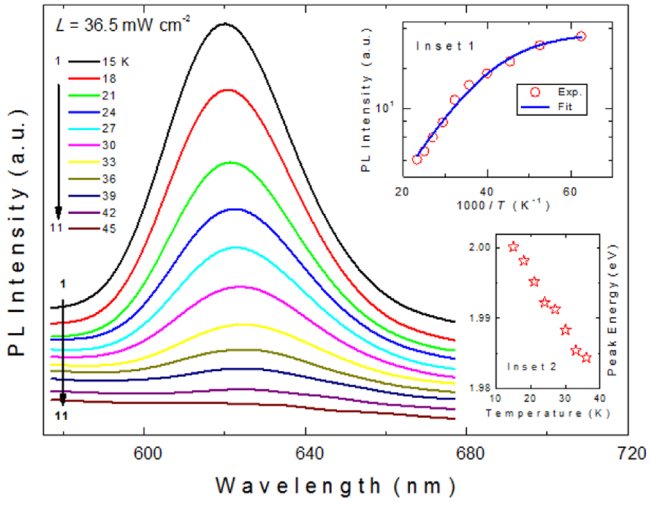

Fig. 3. Temperature dependence of PL spectra from $Tl_4Ga_3InSe_6S_2$ crystals at excitation laser intensity L=36.5 mW cm^{-2}. Inset 1: Temperature dependency of PL band intensity for $Tl_4Ga_3InSe_6S_2$ crystal. Circles are the experimental data. Solid curve shows the theoretical fit using Eq. (1). Inset 2: Temperature dependence of emission band peak energy.

The experimental data for the temperature dependence of PL band intensity can be fitted by the following expression [18]

$$I(T)=\frac{I_0}{1+\sigma_1 T^{3/2}+\sigma_2 T^{3/2}\exp(-E_t/kT)} \quad (1)$$

where I_0 is a proportionality constant, E_t the thermal activation energy, k the Boltzmann's constant, σ_1 and σ_2 are the fitting parameters associated with the temperature dependence of the capture cross sections of the donor and acceptor levels. Inset 1 of Fig. 3 shows the temperature dependence of the emission band maximum intensity as a function of the reciprocal temperature in the 15–45 K range. The best fit using Eq. (1), demonstrated by the solid curve in inset 1 of Fig. 3, has been achieved with parameters I_0=1040, E_t=0.01 eV, σ_1=4.1 $K^{-1.5}$ and σ_2=10.4 $K^{-1.5}$. Since $Tl_4Ga_3InSe_6S_2$ crystal is a p-type semiconductor, we believe that this level is shallow acceptor level located at 10 meV above the top of the valence band.

The laser excitation intensity dependence of PL spectra also provides valuable information about the recombination mechanism responsible for the observed luminescence. Fig. 4 presents the PL spectra for 15 different laser intensities at T=15 K. From analysis of the spectra, we obtained the information about the peak energy position and intensity for emission band at various laser excitation intensities. Our observation reveals that the peak energy position does not show a significant change with laser excitation intensity. In contrast with inhomogenously distributed donor–acceptor pairs where increasing laser intensity excites more pairs that are closely spaced leading to blue shift of the peak energy of the observed bands [17], this result suggests that the donor–

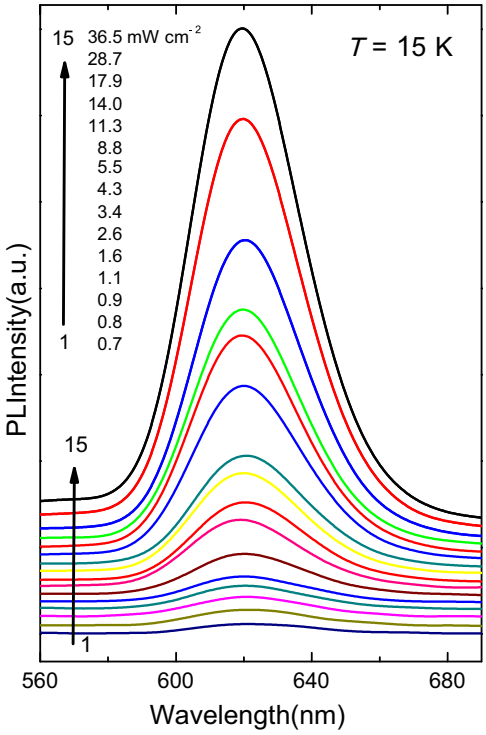

Fig. 4. PL spectra of $Tl_4Ga_3InSe_6S_2$ crystal as a function of excitation laser intensity at T=15 K.

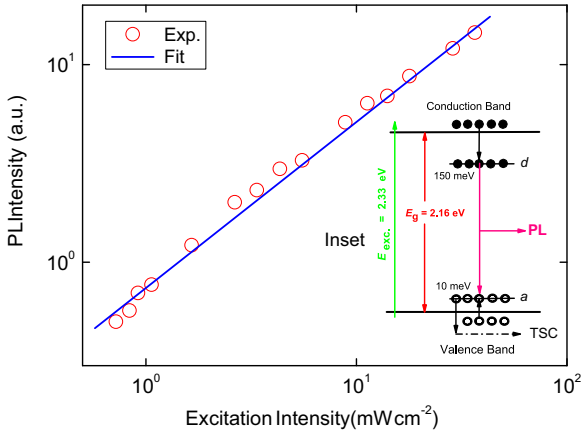

Fig. 5. Dependence of PL intensity at the emission band maximums versus excitation laser intensity at $T=15$ K. The solid line shows the theoretical fit using Eq. (3). Inset: Energy level diagram of $Tl_4Ga_3InSe_6S_2$ crystal at $T=15$ K.

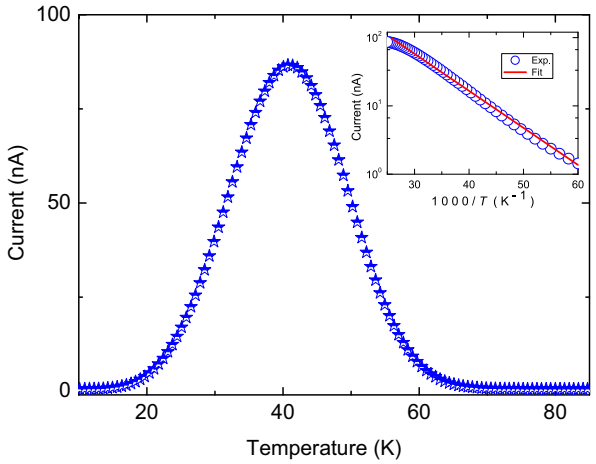

Fig. 6. Experimental TSC curve of $Tl_4Ga_3InSe_6S_2$ crystal with heating rate of 0.2 K/s. Inset: Thermally stimulated current versus $1000/T$ in the temperature range 15–40 K. Circles are experimental data. Solid line is the theoretical fit using initial rise method.

acceptor pairs are located at only closely spaced sites and are distributed homogenously.

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 $Tl_4Ga_3InSe_6S_2$ crystal $T=15$ K (inset of Fig. 5). In the proposed scheme, shallow acceptor level ***a*** is located at $E_a=10$ meV above the top of the valence band. Here, it is necessary to recall the general expression for emission energy of donor–acceptor pair as [19]

$$E_p = E_g - E_d - E_a, \quad (2)$$

where E_g is the band gap energy of $Tl_4Ga_3InSe_6S_2$ crystal, E_d and E_a are the donor and acceptor level energies, respectively. A simple calculation with Eq. (2) for emission band by using the values of $E_g=2.16$ eV, $E_p=2.00$ eV and $E_a=10$ meV gives us the energy of the moderately deep donor level as $E_d=150$ meV (inset of Fig. 5). 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 $Tl_4Ga_3InSe_6S_2$ due to the weakness of the van der Waals forces between the layers [20].

In PL spectra of $Tl_4Ga_3InSe_6S_2$ crystal, the rise in the peak intensities of emission band with increase in the laser excitation intensity was observed. The logarithmic plot of PL intensity versus laser excitation intensity is given in Fig. 5. Experimental data can be fitted by a simple power law of the 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 intensity at the emission band maximum increases sublinearly with increase of excitation laser intensity with the value of $\gamma=0.80$. 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 for free-to-bound and donor–acceptor pair recombination [21,22]. 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.

Fig. 6 presents the TSC curve of $Tl_4Ga_3InSe_6S_2$ crystal registered with the heating rate of 0.2 K s^{-1}. When the front surface of the sample is illuminated, both types of carriers are created in this region. Only one type of carriers will be driven along the whole field zone, while the other type is collected very quickly depending on the bias voltage. Therefore, only the former can be trapped. It was revealed, that if the polarity of the illuminated surface is positive, the intensity of the TSC peak was highest. It means that the holes are distributed in the crystal and then trapped. Therefore, the peak appearing in the TSC spectra of $Tl_4Ga_3InSe_6S_2$ crystal can be assigned to hole traps.

There are several methods to evaluate the trapping parameters from the experimental TSC spectra [23]. We have used the initial rise method for the analysis of the present data. This method is independent of the order of kinetics and therefore can be applied to the TSC curve without considering the retrapping process. As the trapped charge carriers are excited to the non-localized states from trap levels through heating, the initial tail of the TSC curve must arise as proportional to $\exp(-E_t/kT)$ [23]. Then, the logarithmic plot of the TSC intensity as a function of the reciprocal of temperature yields a straight line with slope of $(-E_t/k)$. Inset of Fig. 6 presents this plot giving the activation energy of the revealed trap level as 11 meV.

At this point, it is worthwhile to give an insight into the transitions in the forbidden band gap of $Tl_4Ga_3InSe_6S_2$ crystal by combining the results of PL and TSC studies (inset of Fig. 5). The present result of PL experiment in the 15–45 K temperature range showed the existence of one hole trap with activation energy 10 meV. Taking into account the possible errors (about 5%), the obtained energies of 10 and 11 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 $Tl_4Ga_3InSe_6S_2$ crystals as a function of temperature and excitation laser intensity were studied. A broad emission band centered at 620 nm (2.00 eV) was observed in the PL spectra at $T=15$ K. The variation of the spectra with laser excitation intensity and temperature suggested that the transitions between the donor ($E_d=150$ meV) and acceptor ($E_a=10$ meV) 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 confirms our assignment that the observed emission band in $Tl_4Ga_3InSe_6S_2$ is due to donor–acceptor pair recombination. The analysis of the thermally stimulated current data in $Tl_4Ga_3InSe_6S_2$ established the hole trap

level with activation energy $E_a = 11$ meV. The revealed hole level is thought to be partially compensated allowing for both PL emission and thermally stimulated current. 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.

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