



Low-temperature photoluminescence in CuIn_5S_8 single crystals

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MS received 1 February 2015; revised 14 April 2015; accepted 7 July 2015

DOI: 10.1007/s12043-015-1181-7; ePublication: 13 February 2016

Abstract. Photoluminescence (PL) spectra of CuIn_5S_8 single crystals grown by Bridgman method have been studied in the wavelength region of 720–1020 nm and in the temperature range of 10–34 K. A broad PL band centred at 861 nm (1.44 eV) was observed at $T = 10$ K. Variations of emission band has been studied as a function of excitation laser intensity in the 0.5–60.2 mW cm^{-2} range. Radiative transitions from shallow donor level located at 17 meV below the bottom of the conduction band to the acceptor level located at 193 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 has been presented.

Keywords. Semiconductors; photoluminescence; donor–acceptor recombination; defects.

PACS Nos 78.55.–m; 78.20.–e

1. Introduction

The ternary semiconducting compound CuIn_5S_8 has the same cubic spinel structure as CdIn_2S_4 [1]. CuIn_5S_8 crystal can be derived from CdIn_2S_4 , if the divalent cadmium cations are replaced by the univalent copper cations and trivalent indium cations, according to the following transformation: $\text{CdIn}_2\text{S}_4 \rightarrow [\text{Cu}_{1/2}\text{In}_{1/2}]_t[\text{In}_2]_o \rightarrow \text{Cu}_{1/2}\text{In}_{5/2}\text{S}_4 \rightarrow \text{CuIn}_5\text{S}_8$. Thus, in the CuIn_5S_8 crystal, 1/5 of the indium cations have tetrahedral (t) and 4/5 of the indium cations have octahedral (o) coordination. The optical and electrical properties of CuIn_5S_8 have been studied in refs [2–7]. CuIn_5S_8 compound has been reported to be favourable choice in the photoelectrochemical and conventional solar cells [8]. The energy band gap of the direct optical transitions was 1.51 eV at 300 K and 1.57 eV at 96 K [9]. Infrared reflection and Raman scattering spectra of CuIn_5S_8 have also been investigated and analysed [10].

In this article, we present the results of a systematic experimental analysis of the photoluminescence (PL) of CuIn_5S_8 crystals in the 720–1020 nm wavelength region and in the

10–34 K temperature range. The PL spectra and their temperature and excitation intensity dependencies were studied in detail so that a model can be proposed for the recombination process of photoexcited carriers and a scheme for the defect levels in the band gap of CuIn₅S₈ crystals.

2. Experimental details

CuIn₅S₈ polycrystals were synthesized from particular high-purity elements (at least 99.9999%) prepared in stoichiometric proportions. Single crystals of CuIn₅S₈ were grown by Bridgman method. The X-ray diffraction patterns of CuIn₅S₈ revealed that it has a single-phase cubic spinel structure. The obtained lattice constant $a = 1.06736$ was in good agreement with that reported by several workers [1,6,11]. In the PL measurements, samples with a typical size of $10 \times 8 \times 4$ mm³ were used. The electrical conductivity of the studied sample was n-type as determined by the hot probe method. PL experiments were carried out by collecting light from the laser-illuminated face of the sample. The green line ($\lambda = 532$ nm) of a continuous frequency-doubled YAG:Nd³⁺ laser was employed as the excitation light source. A ‘CTI-Cryogenics M-22’ closed-cycle helium cryostat was used to cool the sample from room temperature to 10 K, and the temperature was controlled within an accuracy of ± 0.5 K. The PL spectra of the sample in the 720–1020 nm region were analysed 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 0.5 to 60.2 mW cm⁻². All of the PL spectra have been corrected for the spectral response of the optical apparatus.

3. Results and discussion

The dependence of the PL spectra on temperature provides a very good understanding about the nature of luminescence spectra. Figure 1 presents the PL spectra of CuIn₅S₈ crystals in 10–34 K temperature range at a constant laser excitation intensity of $L = 60.2$ mW cm⁻². The observed emission band has asymmetrical Gaussian line shape and centred at (861 ± 2) nm [(1.44 ± 0.003) eV] at $T = 10$ K. As seen from figure 1, emission band changed its peak position, full-width at half-maximum (FWHM) and intensity as a function of the sample temperature: the peak position showed slight shift towards higher wavelengths with increasing temperature; the FWHM increased and the peak intensity decreased as the temperature was increased. The FWHM increased from (0.23 ± 0.01) eV to (0.26 ± 0.01) eV with increasing temperature in the range of 10–34 K. Inset of figure 2 illustrates the shift of the peak energy to lower energies with increasing temperature. It is well known that the donor–acceptor pair transition energy decreased along with the band gap energy when the temperature was increased [12].

The experimental data for the temperature dependence of the PL band intensity can be fitted by the following expression [13]:

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

where I_0 is a proportionality constant, E_t is the thermal activation energy, k is the Boltzmann constant and α is the recombination process rate parameter. Figure 2 shows

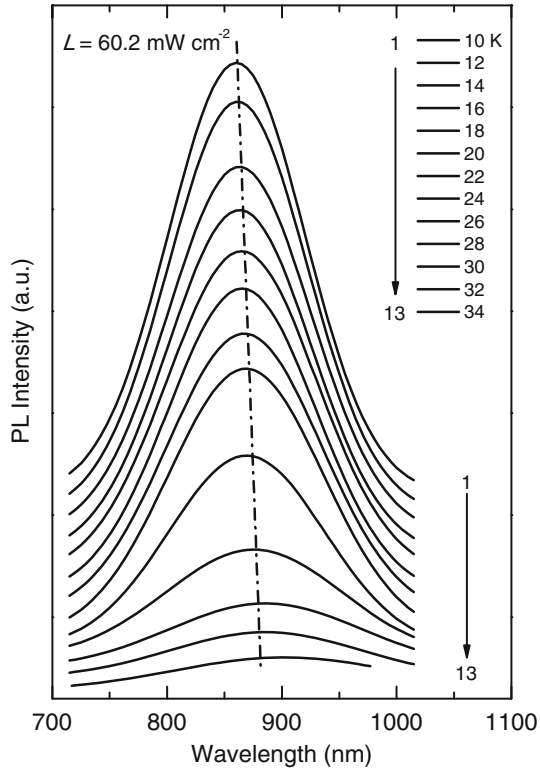


Figure 1. Temperature (10–34 K) dependence of the PL spectra from CuIn_5S_8 crystals at the excitation laser intensity $L = 60.2 \text{ mW cm}^{-2}$. The PL intensity decreased with increasing temperature. The dashed line shows the shift of the peak positions towards higher wavelengths with increasing temperature.

the temperature dependence of the maximum intensity of the emission band as a function of the reciprocal temperature in the 10–34 K range. After a nonlinear least squares fit, the quenching activation energy for emission band was found to be 17 meV. As CuIn_5S_8 crystal was an n-type semiconductor, we believed that this level was a shallow donor level located at $E_d = (17 \pm 1) \text{ meV}$ below the bottom of the conduction band. This shallow level can be considered to be originating from the deviations in the stoichiometry (i.e., sulphur vacancies) [11,14]. From the electrical resistivity and Hall effect measurements of CuIn_5S_8 crystals, the activation energy of a similar donor level was found to be 16 and 17 meV [11,14].

The laser excitation intensity dependence of the PL spectra also provides valuable information about the recombination mechanism responsible for the observed luminescence. Figure 3 presents the PL spectra of the CuIn_5S_8 crystals for 15 different laser intensities at $T = 10 \text{ K}$. By analysing the spectra, we obtained the information about the peak energy position and intensity of the emission band at various laser excitation intensities. This analysis revealed that the peak energy position changed with laser excitation intensity (blue shift). The behaviour of the emission band was in agreement with the idea of inhomogeneously distributed donor–acceptor pairs for which increasing laser excitation

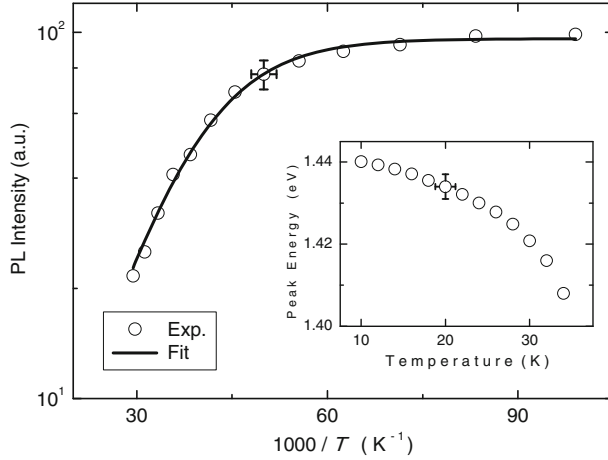


Figure 2. Temperature dependencies of PL band intensity for CuIn₅S₈ crystal. Circles are the experimental data. Solid curve shows the theoretical fit using eq. (1). Inset: temperature dependence of the emission band peak energy presenting the shift towards lower energies with increasing temperature.

intensity leads to blue shift of the band by exciting more pairs that were closely spaced [12]. A careful inspection of the data shows that the emission band maximum slightly shifted towards higher energies ($\Delta E_p = 37$ meV) with increasing excitation laser intensities from 0.5 to 60.2 mW cm⁻² (i.e., 18 meV per decade of exciting intensity). The magnitude of the observed blue shift was typical of ternary and quaternary chalcogenide compounds such as Tl₂InGaS₄ [15], HgInGaS₄ [16], CuIn_{1-x}Ga_xSe₂ [17] and Tl₄Ga₃InSe₈ [18] which are 20, 20, 15 and 14 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, leading 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 [12]. Furthermore, radiative transition probabilities for different pair separations decrease exponentially as a function of the pair distance [12]. Distant pair recombination (contributing to the low energy part of a donor–acceptor pair emission band) saturates at high excitation laser intensities, whereas close pairs have larger transition probability and can accommodate more carriers. We, therefore, observed a shift of the emission band peak energy to higher energy as the excitation laser intensity increased.

The dependence of the emission band peak energy (E_p) at $T = 10$ K as a function of excitation laser intensity (L) is given in figure 4. The experimental data in figure 4 were then fitted by the following expression [19]:

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

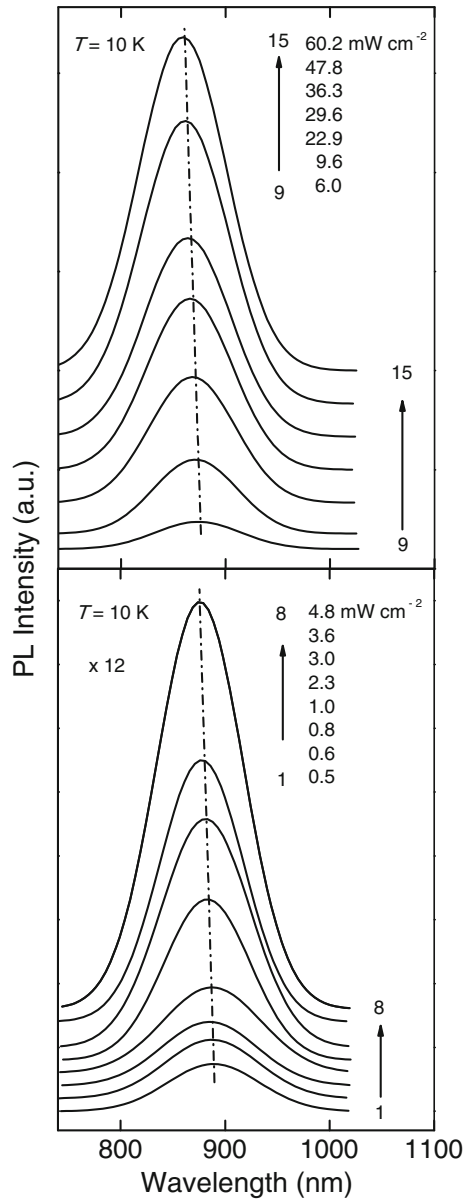


Figure 3. PL spectra of CuIn_5S_8 crystal as a function of excitation laser intensity ($0.5\text{--}60.2\text{ mW cm}^{-2}$) at $T = 10\text{ K}$. The dashed lines show the shifts of the peak positions towards shorter wavelengths with increasing excitation intensity.

where L_0 is a proportionality constant, E_B is the energy of the emitted photon of a close donor–acceptor pair separated by the Bohr radius (R_B) of the shallow impurity and E_∞ is the energy of the emitted photon of an infinitely distant donor–acceptor pair. From a nonlinear least square fit to the experimental data, the photon energy values for an

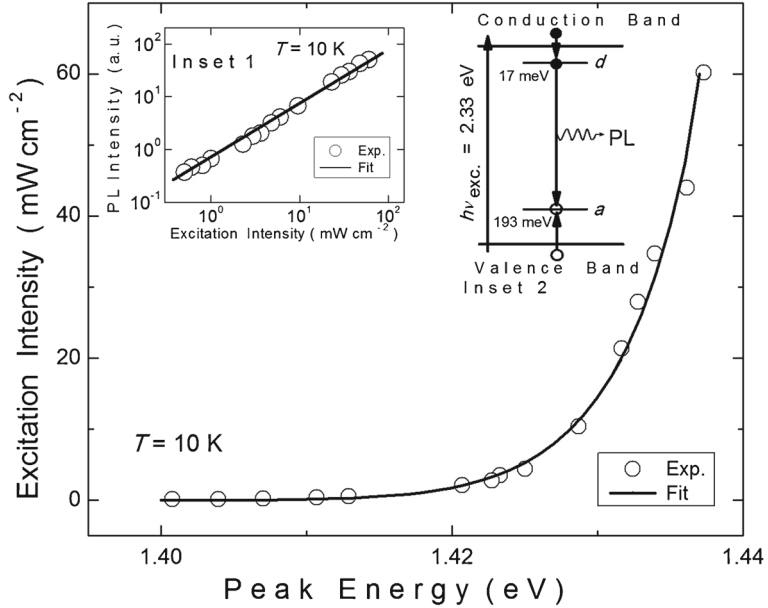


Figure 4. Excitation laser intensity ($0.5\text{--}60.2\text{ mW cm}^{-2}$) vs. emission band peak energy ($1.40\text{--}1.44\text{ eV}$) at $T = 10\text{ K}$. Circles are the experimental data. The solid curve represents the theoretical fit using eq. (2). Inset 1: Dependence of PL intensity at the emission band maxima vs. excitation laser intensity ($0.5\text{--}60.2\text{ mW cm}^{-2}$) at $T = 10\text{ K}$. The solid line shows the theoretical fit using eq. (3). Inset 2: Energy level diagram of CuIn_5S_8 crystal at $T = 10\text{ K}$ presenting the transitions from the donor (d) to the acceptor (a) levels.

infinitely distant donor–acceptor pair and a close donor–acceptor pair separated by R_B were found to be $E_\infty = (1.37 \pm 0.02)\text{ eV}$ and $E_B = (1.53 \pm 0.02)\text{ eV}$, respectively. These limiting photon energy values were in good agreement with the band-gap energy ($E_g = 1.58\text{ eV}$) and the observed values of the peak energy position (i.e., $E_\infty < 1.40\text{ eV} < E_p < 1.44\text{ eV} < E_B < E_g$) at $T = 10\text{ K}$.

In the PL spectra of the CuIn_5S_8 crystal, the increase in peak intensities of the emission band with increase in laser excitation intensity was also observed. The logarithmic plot of PL intensity vs. laser excitation intensity is given in the inset 1 of figure 4. Experimental data can be fitted by a simple power law of the form

$$I \propto L^\gamma, \tag{3}$$

where I is the PL intensity, L is the excitation laser intensity and γ is a dimensionless constant. We found that PL intensity at the emission band maximum increased sublinearly with increase in excitation laser intensity with the value of $\gamma = 0.97 \pm 0.02$. It is well known that if excitation energy of the laser photon exceeds the band-gap energy E_g , the exponent γ is generally $1 < \gamma < 2$ for free- and bound-exciton emissions, whereas $0 < \gamma \leq 1$ is typical for free-to-bound and donor–acceptor pair recombination [20,21]. Thus, the obtained value of $\gamma < 1$, for the band was a further evidence that the observed emission was due to donor–acceptor pair recombination.

The analysis of the PL spectra as a function of temperature and excitation laser intensity allowed one to obtain a possible scheme for the states located in the forbidden energy gap of the CuIn₅S₈ crystal (inset 2 of figure 4). In the proposed scheme, shallow donor level **d** was located at 17 meV below the bottom of the conduction band. On the basis of the general expression for the emission energy of the donor–acceptor pair [12] and taking into account E_g and E_∞ , the sum of the activation energies of the donor (E_d) and acceptor (E_a) levels, involved in the emission band, is estimated as

$$E_d + E_a = E_g - E_\infty = 1.58 \text{ eV} - 1.37 \text{ eV} = 0.21 \text{ eV}.$$

Considering that the donor level **d** was located 17 meV below the bottom of the conduction band, this result suggested that the acceptor level **a**, involved in the emission band, was located at 193 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**. As the studied crystals were not intentionally doped, we proposed the presence of structural vacancies in the cation sublattice as the origin of a deep acceptor level **a** located above the valence band in n-CuIn₅S₈ crystal, by analogy with the isostructural n-CdIn₂S₄ crystal, where a relatively deep acceptor level ($E_a = 200 \text{ meV}$) was assigned to similar vacancies [22].

4. Conclusions

The PL spectra of CuIn₅S₈ crystals as a function of temperature and excitation laser intensity were studied. A broad emission band centred at 861 nm (1.44 eV) was observed in the PL spectra at $T = 10 \text{ K}$. The variation of the spectra with laser excitation intensity and temperature suggested that the transitions between the donor and acceptor levels can be responsible for the observed emission band. Also, the intensity of the emission band increased sublinearly with respect to the excitation laser intensity and confirmed our assignment that the observed emission band in CuIn₅S₈ was due to the donor–acceptor pair recombination. As the studied crystals were not intentionally doped, these centres were thought to originate from anion and cation vacancies caused by nonstoichiometry, formed during crystal growth.

Acknowledgement

The author is grateful to Dr A Seyhan for her assistance.

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