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Rapid Research Note

Deep and edge photoluminescence emission of $CuInTe_2$

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Photoluminescence studies of chalcopyrite $CuInTe_2$ were conducted. Three edge (1.041 eV, 1.030 eV, and 1.019 eV) and two deep level (0.999 eV and 0.957 eV) emission bands were observed at 11 K. The excitation intensity dependence of PL spectra was recorded. As possible band sources one excitonic and four band-to-defect recombination mechanisms are proposed in this paper.

$CuInTe_2$ (CIT) and other chalcopyrite ternary crystals have recently attracted worldwide interest because of their optimal bandgap (about 1 eV) for photovoltaic conversion devices. Also, they provide high conversion efficiencies at relatively low expense.

Photoluminescence (PL) is an easy-to-use and sensitive probe of defect levels inside forbidden band. However, the most interesting and challenging part is the interpretation of the experimental spectra.

In the present paper we discuss the photoluminescence spectrum of chalcopyrite $CuInTe_2$. Previously, Rincón et al. have studied the photoluminescence of CIT crystals in Refs. [1, 2]. In these papers edge and excitonic PL radiation was presented. In addition, we report also the radiative emission of deep recombination centres.

The $CuInTe_2$ powder samples were synthesised from the elements at 810 °C in fused quartz ampoules. The treatment continued with homogenising annealing at 665 °C, which is slightly lower than the peritectic temperature in $CuInTe_2$ [3]. The starting Cu/In concentration ratio was 1.03. The final polycrystalline $CuInTe_2$ ingot showed a well-defined chalcopyrite pattern in the XRD scan.

The sample was cooled inside a closed-cycle He cryostat (T = 8–300 K) and excited with a 441 nm He–Cd laser with maximum output power 40 mW. The PL signal was recorded by using standard lock-in technique, computer-controlled SPM-2 grating monochromator (f = 40 cm) and InGaAs detector. The detected signal was corrected in conformity with grating efficiency and detector sensitivity spectra.

The experimental PL spectrum of a CIT sample at 11 K is presented in Fig. 1. We distinguished five different PL bands – three near the band-edge bands (E_1, E_2, and E_3) and two deep bands (D_1 and D_2) with their phonon replicas. We found that the replicas appear according to the LO-phonon energy $\hbar\omega_{LO}$ = 23.2 meV. The corresponding peak positions and the possible band origins are presented in Table 1. The results were compared with theoretical calculations of defect levels in CIT [4], where the model of effective mass theory was applied.

We identified that three types of recombination mechanisms governed our bands: excitonic, donor to valence band, and conduction band to acceptor emission. It is known that shallow levels, because of the

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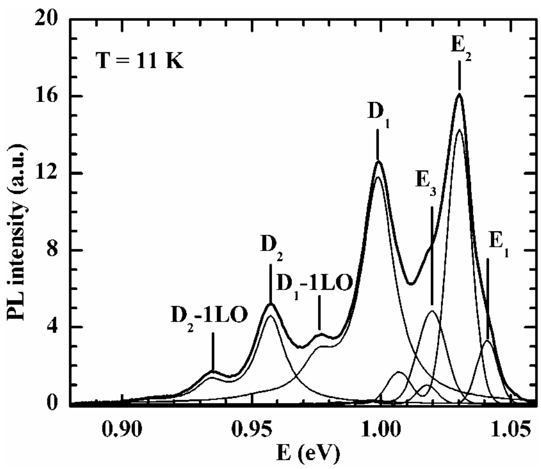

Fig. 1 PL spectra of $CuInTe_2$ single crystal at 11 K. Measured PL spectra were fitted using five different peaks and their phonon replicas.

broad amplitude of their wavefunction, tend to form donor–acceptor pairs (DAP). Nevertheless, we cannot attribute DAP emission to near the band-edge emission in CIT. Because of the overlapping of edge emission bands it was difficult to identify their behaviour regarding to excitation power and temperature changes.

The activation energies of relevant defect levels in Table 1 are calculated by using the expression

$$E_a = E_g - h\nu_{max} , \qquad (1)$$

where $h\nu_{max}$ is the band's peak position and E_g is the band gap energy. In CIT, E_g is between 1.02 and 1.06 eV [5]. In our calculations we used the value $E_g = 1.06$ eV, which is reasonable, because we observe a luminescence intensity up to 1.06 eV.

Edge emission can also be analysed using the relation $I \sim L^k$ [6, 7], where I is PL band's intensity, L is excitation power, and as a rule k is a factor that is >1 for excitons and ≤1 for non-excitons. Our fitting proved that $k > 1$ for E_1. Accordingly, it is highly probable that band E_1 at $h\nu_{max} = 1.041$ eV has an excitonic origin. Presumably, it is not a consequence of emission by one exciton but rather a sum of several excitonic radiations. Moreover, Refs. [1, 2] report excitonic emission in the same region.

Band E_2 at $h\nu_{max} = 1.030$ eV is not excitonic, because $k < 1$ for this band. Its activation energy according to Eq. (1) is 30 meV, which is in good coherence with the theoretical activation energy of a donor level at 26 meV [4]. Its possible physical origin is a telluride vacancy $V_{Te}^{\bullet}$ or an antisite defect $In_{Cu}^{\bullet}$ [4].

The exact position of band E_3 was not easy to determine, because it is located between the two more intensive bands E_2 and D_1. However, the fitting for E_3 showed that $h\nu_{max} = 1.019$ eV, which corresponds to $E_a = 41$ meV. The closest defect level for this is a donor level at 37 meV that is caused by an interstitial defect $In_i^{\bullet}$.

The deep bands D_1 and D_2 are most probably radiative emissions between conduction band and an acceptor level. They cannot be DAPs because altering the laser power did not generate any j-shift of these bands (see Fig. 2). The peak D_1 is located at 0.999 meV and is close to the theoretical acceptor

Table 1 Experimental values of PL band positions compared with theoretical calculations. Activation energies were calculated with $E_g = 1.06$ eV.

PL band	$h\nu_{max}$ (eV)	E_a (meV)		possible origins [4]
		experimental	theoretical [4]	
E1	1.041			excitons
E2	1.030	30	26	$V_{Te}^{\bullet}$, $In_{Cu}^{\bullet}$
E3	1.019	41	37	$In_i^{\bullet}$
D1	0.999	61	70	V'_{Cu}, Te'_{In}, Cu'_{Te}
D2	0.957	103	120	Te'_i, Cu'_{In}

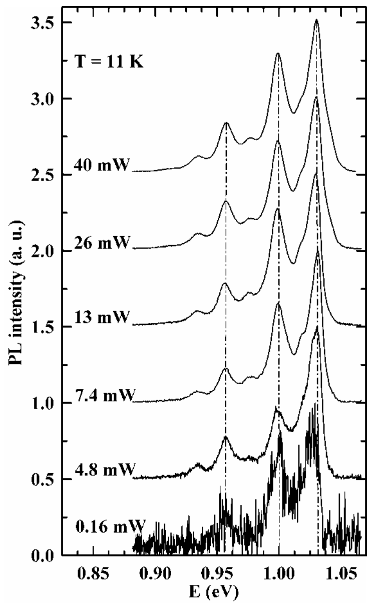

Fig. 2 Normalised $CuInTe_2$ PL spectrum dependence on laser excitation power. It is evident that peaks D_1 and D_2 do not shift with altering excitation power, thus, they do not originate from donor–acceptor pairs.

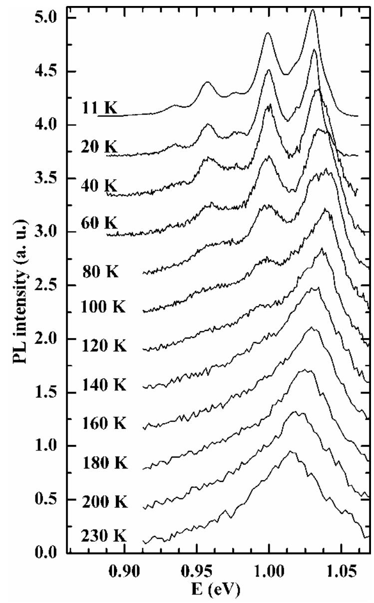

Fig. 3 Normalised $CuInTe_2$ PL spectrum dependence on sample temperature.

state at 70 meV. We observed the same PL band in heavily doped CIT crystal [8]. According to Ref. [4], this band can be caused by copper vacancy V'_{Cu} or antisite point defects Te'_{In} or Cu'_{Te}. The position of peak D_2 (E_a = 103 meV) is close to the theoretical deep acceptor level that is situated at 120 meV [4]. Most likely, interstitial Te'_i or antisite defect Cu'_{In} causes this level. Previously, we observed a deep band with similar properties in the PL spectrum of $CuGaTe_2$ [9]. To wit, the Huang-Rhys factor of band D_2 is $S \approx 0.22$ whilst for the deep band in $CuGaTe_2$ it was 0.29.

The temperature dependence of the PL spectrum of CIT is presented in Fig. 3. In the edge region, the excitonic peak starts to dominate if temperature rises, i.e. bands E_2 and E_3 fade much faster than excitonic E_1. The red shift of the edge region can be attributed to a decrease of the bandgap with increasing temperature. Deep bands D_1 and D_2 can be observed up to 160 K.

We measured photoluminescence properties of polycrystalline $CuInTe_2$. Our spectra prove that edge and deep PL bands can be observed in CIT. More work should be done to investigate the origins and possible fine structure of the PL bands.

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