Photoluminescence, stimulated and laser emission in CuInSe$_2$ crystals

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Photoluminescence, stimulated and laser emission in CuInSe2 crystals

Excitonic quality CuInSe2 crystals were studied using low-temperature (10 K) photoluminescence (PL) excited by continuous wave and nanosecond pulsed lasers at power densities from 0.01 to 76 kW/cm². Increasing the excitation power density level to 26 kW/cm² resulted in the appearance of a stimulated emission SE-band in the PL spectra at 1.035 eV. Further increase in the excitation level to 39 kW/cm² generated on the top of the SE band, a structure of equidistant sharp lines attributed to laser emission.

A direct bandgap of 1.05 eV and a high absorption coefficient in excess of 10⁵ cm⁻¹ make the semiconductor CuInSe2 very attractive for applications in the absorber layer of thin films solar cells. Solar cell with Cu(In,Ga)Se2 (a compound derived from CuInSe2 by admixing gallium) as the absorber layer is currently the leading thin film photovoltaic technology with respect to the conversion efficiency of laboratory size single junction devices and stability. The conversion efficiency of such cells has already exceeded 23%. This achievement makes CuInSe2 a technologically important material. On the other hand, these properties along with excellent photostability suggest prospects for applications of CuInSe2 as a laser material. Recent studies in this direction have demonstrated the possibility to achieve stimulated emission and lasing in Cu(In,Ga)Se2 films at rather high doping levels (required for efficient solar cells). However, the main physical processes involved in radiative recombination under high excitation intensity have not been clarified as yet. Understanding of such processes can provide an opportunity to develop a CuInSe2-based near infrared diode laser.

In this paper, we study the effect of high intensity nanosecond pulsed laser excitation on the near-band edge PL spectra of excitonic quality CuInSe2 crystals measured at 10 K.

Crystals of CuInSe2 were freshly cleaved from the middle part of an ingot grown from a near stoichiometric charge of the high purity elements Cu, In, and Se by the vertical Bridgman technique. The elemental composition of the crystals, measured by energy dispersive x-ray analysis (EDX), was close to the ideal stoichiometry Cu: 25.0 at. %, In: 24.9 at. %, and Se: 50.1 at. %.

Continuous laser excitation PL measurements were carried out at 5 K using the 514 nm line of an Ar+ laser with an excitation power
density of about 0.05 kW/cm². PL was collected by a concave mirror and focused on the slits of a 1 m single grating (600 grooves/mm) monochromator with a cooled InGaAs photomultiplier tube sensitive from 0.9 to 1.7 nm. Pulsed excitation PL measurements were carried out at 10 K. To expand the range of excitation intensities of the sample, two lasers were used: a semiconductor laser (λ = 435 nm, τp = 12 ns, f = 137 kHz, providing excitation power densities from 0.01 to 3.2 kW/cm²) and a nitrogen laser (λ = 337.1 nm, τp = 8 ns, f = 525 Hz, with power density from 3.3 to 76 kW/cm²). The laser beam, directed to the surface within 5° from the normal, was focused on the surface of the samples into an area of 1 mm². The cleaved surface contained several micro-size steps (with one plane-parallel whereas the other perpendicular to the surface) and cracks perpendicular to the surface. The power of the lasers was calculated as the ratio of the energy of one pulse to its full width at half maximum (FWHM). PL emission, collected by a lens in the direction close to the surface normal, was registered using a 0.3 m single grating (600 grooves/mm) monochromator and a linear array detector sensitive from 0.9 to 1.7 µm. For both continuous and pulsed excitation regimes, the samples were cooled in a closed-cycle helium refrigerator. To improve cooling of the sample, the crystal was immersed in an indium slab, which was then mounted on the cold finger.

Figure 1(a) shows a PL spectrum, measured at 5 K, excited by the continuous laser with the power density of 0.05 kW/cm². This spectrum reveals two well resolved peaks at 1.042 and 1.045 eV, each with full width at half maximum of 1.5 meV. These peaks are the free A and B excitons, respectively. The spectrum also exhibits several sharp peaks M1, M2, M3, M5, and M6 with FWHMs of 0.5 meV, which are assigned to excitons bound to defects. The figure compares this spectrum with one excited by the 435 nm line of the pulsed semiconductor laser with a power density of 0.06 kW/cm² and measured at 10 K. The two spectra demonstrate that the spectral position of the free and bound exciton lines coincides well.

The higher relative intensity of the M2 and M5 bound exciton peaks in the spectrum excited by the continuous laser can be explained by the lower temperature used during the acquisition of this spectrum, whereas the near absence of the M1 and M3 peaks can be attributed to small differences in the elemental compositions of the areas excited by the continuous and pulsed lasers as well as by differences in the type of the excitation. Figure 2 shows the evolution of PL spectra (measured at 10 K) with excitation power density increasing from 0.01 to 3.2 kW/cm².

When the excitation power density increases above 0.17 kW/cm², a band, denoted as P-band, is generated at 1.037 eV. This band, with a FWHM of 5 meV, is much broader and grows faster than the excitonic lines resulting in a gradual disappearance of these lines from the spectra as shown in Fig. 2. To quantify changes in the spectral position of this band with excitation power rise, we fitted Lorentzian shapes into the M5, M6 narrow bound exciton lines, and a broader Lorentzian to the P-band at the low energy side of the M1 peak as shown in Fig. 1(b). Under increasing excitation power, the P-band gradually red shifts from 1.037 to 1.035 eV. Therefore, we make a preliminary assignment of this band as inelastic exciton-exciton scattering. Some excitons are scattered to an excited state, whereas others decay with energy losses leading to the redshifted P-band (right band

**FIG. 1.** PL spectra of CuInSe₂ (a) excited by the continuous wave Ar⁺ laser with a power density of 0.05 kW/cm² measured at 5 K (1, red line) and pulsed semiconductor laser with a power density of 0.06 kW/cm² measured at 10 K (2-black circles); (b) PL spectrum of CuInSe₂ excited by the pulsed semiconductor laser with a power density of 0.17 kW/cm² measured at 10 K (black squares) and fitted by three Lorentzian shapes: P-band, M5 and M6 bound excitons.

**FIG. 2.** Evolution of the PL spectra of CuInSe₂ (measured at 10 K) excited by the pulsed semiconductor laser with power densities from 0.01 to 3.2 kW/cm².
at 0.52 kW/cm² in Fig. 2). Such bands were observed in the PL spectra of AlN and ZnO at intermediate excitation levels at which excitonic lines are still present in the spectra but the exciton–exciton interaction takes place.¹⁹

Further growth of the excitation power increases the FWHM of the P-band, which becomes 10 meV at an excitation of 2 kW/cm² suggesting the appearance of another band at 1.035 eV. This band, denoted as EHP, can be seen in Fig. 2 merged with the P-band from the low energy side at an excitation power density above 0.52 kW/cm². We preliminarily assign the EHP-band to radiative recombination of free charge carriers in an electron–hole plasma. Once the average distance between excitons becomes comparable to their Bohr radii, the electrons and holes, excited to the conduction and valence bands, screen binding Coulomb forces between electrons and holes. Such screening weakens free excitons, reducing their binding energy, and releases bound excitons.¹⁹ These processes are responsible for the gradual disappearance of excitonic lines from the spectra in Fig. 2. The emission of an electron–hole plasma manifests itself in the spectra after the disappearance of exciton lines with an increase in the excitation level. Such an EHP-band also appeared in high excitation level PL spectra of AlN and ZnO at spectral energies just below that of the P-band.

The further evolution of the PL spectra of CuInSe₂, excited by the pulsed nitrogen laser emission with power densities increasing from 3.3 to 76 kW/cm², is shown in Fig. 3. At excitation power densities in excess of 20 kW/cm², another band at 1.032 eV, denoted as SE, becomes apparent on the low energy side of the EHP-band. We assign this band to stimulated emission. This band becomes dominant at power densities over 26 kW/cm². Figure 4(a) shows two Lorentzians fitted to the PL spectrum, measured at 26 kW/cm², to estimate the FWHM and spectral position of the SE band. Figure 4(b) presents the dependence of the integrated emission intensity from CuInSe₂ on the excitation power density on a logarithmic scale. The gradient of the straight line, fitted to the linear part of the data from 10 to 33 kW/cm², is close to k = 2, which supports the assignment of the recombination mechanism of the EHP band to electron–hole plasma. Figure 4(b) shows the FWHM of the SE band decreasing from 12 to 8 meV at the excitation power density growing from 20 to 40 kW/cm². This narrowing can be taken as a confirmation of the assignment of the recombination mechanism of the SE band to stimulated emission.¹⁹

At excitation power densities from 39 kW/cm², a structure of several sharp equidistant peaks appeared at the top of the SE-band, indicating the onset of the laser emission regime. Together with the spectral narrowing of the SE band, the appearance of the mode structure is characteristic of achieving the stimulated and laser emission regimes. The laser threshold pumping value, determined by the linear extrapolation of the slope of the dependence, in the region of lasing is about 40 kW/cm². Changes in the shape of the PL spectra with the increase in excitation power are also shown in Fig. 5, where several spectra, selected from Figs. 2 and 3, and multiplied by individual constants chosen to fit these spectra to one figure to compare their shapes on a linear scale. Further increase in the excitation power demonstrates the growth of the SE-band intensity, narrowing of its peak and then the appearance of sharp lines at the peak maximum. Their sharpness and an explicit threshold character suggest the achievement of a lasing regime.

At high excitation levels, amplification is provided by recombination processes during interband transitions in a high-density electron–hole plasma. The spectral position of the gain spectrum is determined by the processes of renormalization of the bandgap and band filling.¹⁹

The sharp line oscillation structure at the maximum of the SE-band and the equidistance of their spectral positions suggest that...
they can be formed in a simple two-mirror Fabry–Pérot optical cavity. An additional confirmation of this origin of lasing is the stability of the spectral position of the mode structure with changes in the excitation intensity from 43 to 76 kW/cm² as shown in Figs. 3 and 5(b). This implies the presence in the excited region of the crystal of parallel facets, unintentionally formed by cracks in CdSe/ZnSe layers, and scattered into the vertical direction has previously been reported.20

The thresholds of the stimulated and laser emission regimes were 2.6 and 39 kW/cm², respectively. The regular mode structure (with equidistant longitudinal modes) could possibly be formed due to the presence in CuInSe₂ of parallel facets of microcracks or grain boundaries about 240 μm apart, which act as laser mirrors of the Fabry–Pérot cavity.

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**AUTHOR DECLARATIONS**

Conflict of Interest

The authors have no conflicts to disclose.

**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**REFERENCES**


