PHOTOLUMINESCENT PROPERTIES OF $CuInS_2$

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$CuInS_2$ crystals were grown by the Bridgman method and characterized by X-ray diffraction and Raman scattering methods. Photoluminescence of $CuInS_2$ was studied by confocal laser microscopy. A nonlinear dependence of the luminescence intensity on the intensity of the exciting light was established.

Keywords: $CuInS_2$, exciton, photoluminescence, Raman scattering, confocal laser microscopy
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1. INTRODUCTION

Ternary semiconductor compounds $A^I B^{III} C_2^{VI}$ crystallizing in tetragonal chalcopyrite structure have attracted considerable attention due to their potential application in photovoltaic solar energy conversion [1-6]. Ternary semiconductor $CuInS_2$ is considered as one of the most promising materials for the fabrication of thin-film solar cells due to its optimal band gap of 1.5 eV. Solar cell technologies using chalcopyrites $A^I B^{III} C_2^{VI}$ have made rapid progress in recent years [7]. The efficiency of thin-film solar cells based on $CuInS_2$ is ~24%. In [8, 9], the optical absorption of $CuInS_2$ and the band gap at 2°K are 1.55 eV for $CuInS_2$ [8], and in [9] at 300 K the band gap is 1.48 eV. According to [10, 11], the band gap in $CuInS_2$ is 1.3 eV. The luminescent properties were studied in [12-19]. In [12] the luminescence was measured as a function of temperature from 8 to 300 K. Ten different peaks were present in the band edge region. Four peaks at 1.5347, 1.5324, 1.5288, and 1.5281 eV, due to acceptor or donor-bound excitons, were observed at 8 K. It was found that luminescence persisted even at room temperature. These peaks were also observed in [13]. In [17], time-resolved PL spectra of free excitons were obtained and analyzed for the first time for $CuInS_2$ single crystals, and the radiative lifetime of free excitons was obtained at low temperatures. The radiative lifetime of a free exciton A was found to be 320 ± 30 ps at 10 K. $CuInS_2$ quantum dots are promising light emitters, demonstrating a high photoluminescence quantum efficiency (PLQE) of 65% at a long emission wavelength of 920 nm [18].

This paper presents the results of the photoluminescence investigation of $CuInS_2$ at 300 K using confocal laser microscopy, with the aim of obtaining additional information on the photoluminescent properties of $CuInS_2$.

2. EXPERIMENTAL PROCEDURE

The $CuInS_2$ compound was synthesized by direct alloying of the initial ultra-pure components Cu, In and S, taken in a stoichiometric ratio, in quartz ampoules evacuated to 10^{-4} Torr. $CuInS_2$ crystals were grown by the Bridgman method by slow cooling of melts of stoichiometric composition. The obtained crystals were characterized by X-ray diffraction (Fig. 1) and Raman scattering (Fig. 2). $CuInS_2$ crystallizes in a tetragonal structure (space group $I\bar{4}2d$). The lattice parameters are a = 5.519 Å, c = 11.133 Å, c/a = 2.017.

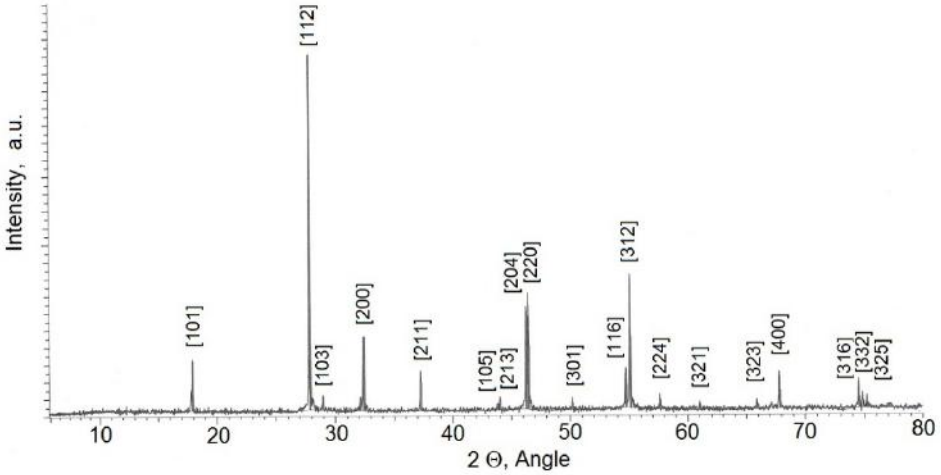

Fig. 1. X-ray diffraction pattern of the compound $CuInS_2$

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The luminescence and Raman scattering spectra of $CuInS_2$ were measured on a Nanofinder 30 confocal Raman microspectrometer (Tokyo Instr., Japan). An Nd:YAG laser with an output wavelength of 532 nm and a maximum power of 10 mW was used as an excitation source. The spectral resolution was no worse than 0.5 cm^{-1}. The radiation detector was a cooled (thermoelectrically to -100^0C) CCD camera (1024 by 128 pixels) operating in the photon counting mode. The Raman scattering spectra of $CuInS_2$ were measured in the backscattering geometry in unpolarized light.

3. RESULTS AND DISCUSSION

Fig. 2 shows the Raman spectrum of $CuInS_2$. The spectrum consists of several lines with maxima at 127 cm^{-1}, 257 cm^{-1}, 296 cm^{-1} and 339 cm^{-1}. There are 8 atoms in the primitive cell of CuInS2 crystals, and the vibrational spectrum consists of 24 normal modes, of which 21 are optical, described by the following irreducible representations: Γ=1A_1 +2A_2 + 3B_1 + 3B_2 + 6E, where A_1, B_1, B_2 and E modes are Raman active, B_2 and E modes are also IR active, and A_2 modes are optically inactive [20]. Figure 2 clearly shows the A_1 mode at 296 cm^{-1}.

Fig. 3 shows the photoluminescence spectra of $CuInS_2$ at 300 K at different intensities (1 mW-10 mW) of the exciting light. The spectrum consists of a narrow band with a maximum position at ~811 nm (1.529 eV) and a half-width of 30 nm (55 meV). The position of the maximum does not change with increasing of excitation intensity and is close to the value of the band gap, so this gives reason to believe that this is edge luminescence. The position of the maximum corresponds to the literature data.

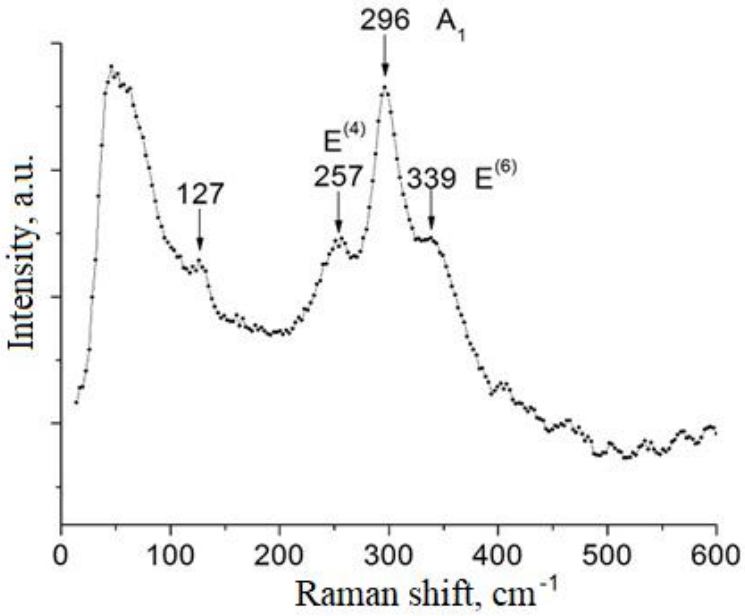

Fig. 2. Raman scattering spectrum of $CuInS_2$ crystals.

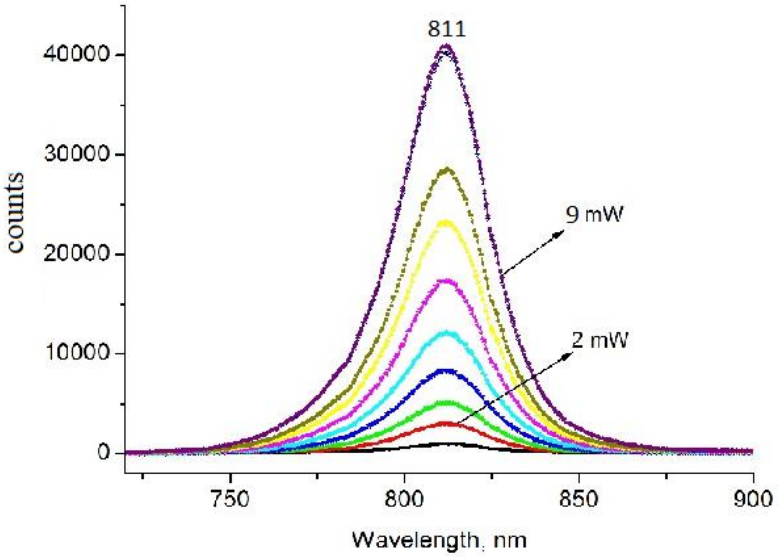

Fig.3. Photoluminescence spectra of $CuInS_2$ at different laser light intensities.

In [8], from studies of the optical absorption edge, the band gap of $CuInS_2$ has a value of 1.55 eV at 2 K, and in [9], at 300 K, the band gap is 1.48 eV. In [14], the PL spectra of pure $CuInS_2$ and doped Yb:$CuInS_2$ were studied. For both crystals, a small PL peak is observed at about 1.50–1.53 eV. The position of the peak almost coincides with the energy of the band gap of $CuInS_2$ ~1.53 eV, and the authors attribute it to exciton recombination. In [21], in high-quality $CuInS_2$ single crystals, sharp exciton peaks were observed in the near-boundary region of the PL spectra at 4.2 K. According to the authors, the lines at 1.536 and 1.554 eV in the spectra are associated with transitions of free excitons. In the PL spectra, the exciton line splits into two peaks at 1.5348 and 1.5361 eV, which the authors attributed to the lower and upper branches of the exciton polariton, respectively.

The exciton nature of photoluminescence is confirmed by the quadratic dependence of the PL intensity on the excitation intensity (Fig. 4).

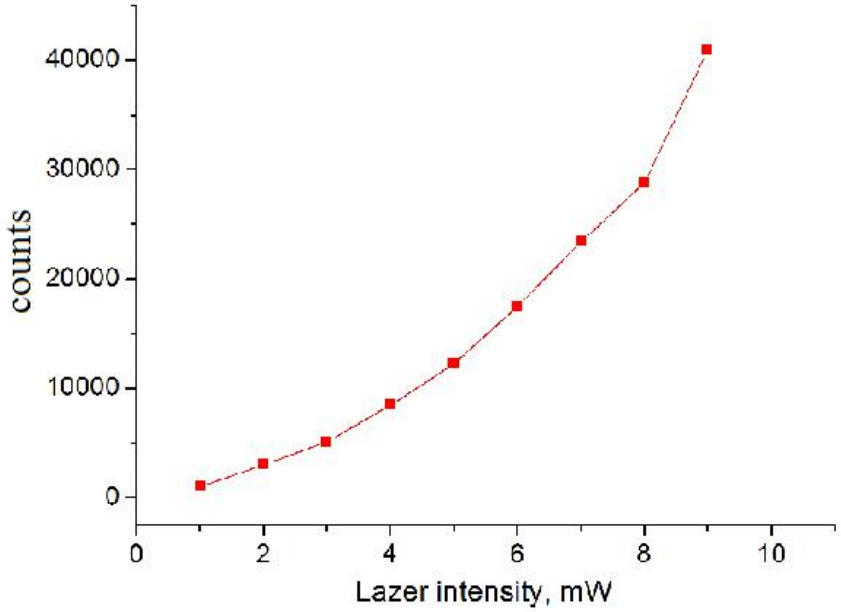

Fig.4. Photoluminescence intensity of $CuInS_2$ as a function of excitation level

Fig.4 shows the dependence of photoluminescence intensity on the intensity of the exciting light. As can be seen, the dependence is nonlinear. Since at the beginning of the dependence, the PL band intensity increases with the excitation level according to the law $I_{PL} \sim I_{ex}^{1,6}$, and then increases according to $I_{PL} \sim I_{ex}^{1,8}$ and at high excitation levels PL increases according to the quadratic law $I_{PL} \sim I_{ex}^{2}$. Such behavior of the PL band intensity at 1.51 eV was observed at 90 K in [22]. With an increase in the excitation rate, the spectrum narrows, indicating the onset of a stimulated emission mode, which is confirmed by the superlinear dependence of the emission intensity on pumping. In [8], the authors associate the observed emission line with an energy of 1.53 eV with the resonant annihilation of free excitons.

4. CONCLUSION

$CuInS_2$ crystals were grown by the Bridgman method with slow cooling of melts of stoichiometric composition. The photoluminescence band with a maximum at ~ 811 nm and a half-width of 30 nm was observed at 300 K. It was found that the dependence of the photoluminescence intensity on the intensity of the exciting light is nonlinear.

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