

# RECOMBINATION PROPERTIES OF $\text{ZnIn}_2\text{S}_4\text{:Cu}$ SINGLE CRYSTALS

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**Abstract**—Recombination characteristics of  $\text{ZnIn}_2\text{S}_4$  single crystals doped with high copper concentration were investigated. The spectra of photoconductivity, spectra of excitation and radiation of luminescence at 20 °C are given. Their peculiarities are described and analyzed. Comparison of the spectra allowed to propose the model for recombination processes and the dominating mechanism of radiation transitions for single crystals of this compound. It was shown that these processes are determined by the system of deep levels and by exponentially distributed states.

## 1. INTRODUCTION

$\text{ZnIn}_2\text{S}_4$  compound is a direct-gap semiconductor ( $E_g^{\text{opt}} = 2.85$  eV, 20 °C) that is intensively investigated, because it is promising for application in various domains of electronic engineering. It was mentioned in [1] that in particular these materials found wide application in all branches of the electric engineering, in energy conversion and are approaching a breakthrough in the illuminating engineering. Effective sensors of ultraviolet radiation were made on the natural faces of  $\text{Zn}_x\text{In}_2\text{S}_{3+x}$  ( $x = 1, 2, 3$ ) single crystalline thin platelets [2]. Electrochemical solar cells were also made on the basis of these compounds [3, 4]. Wide-gap semiconductors are so important and attractive that a special article was devoted to their preparation in space conditions [5]. A special attention was also paid in it to In and Ga compounds.

However, the problem of doping of this material with  $x = 1$  was weakly studied. We investigated the influence of doping with nickel and manganese [6, 7] on its optical properties. It was shown that Ni exerts the greatest influence on the recombination processes at its concentration of  $1.2 \times 10^{19} \text{ cm}^{-3}$ , when the mechanism of the phenomenon changes. In

connection with this, the goal of this paper was to describe how the copper impurity influences the recombination properties.

## 2. EXPERIMENTAL

$\text{ZnIn}_2\text{S}_4$  single crystals doped with Cu were grown using the method of chemical transport reactions with iodine as a transport agent. Especially pure chemical elements were used in the initial load as well as hyperstoichiometric copper in the proportion of 1.6 at.%. The growth method was described earlier [8]. The obtained samples were mirror-like platelets, dark if compared with undoped samples. The composition of the crystals was analyzed using a Lamm-100 mass spectrometer. The copper concentration corresponds the loaded concentration and was uniformly spreaded over the platelet.

Thermal vacuum evaporation was employed to prepare the electrodes for photoconductivity measurements. The measurements were performed at direct current using a precise electrometer [6]. The luminescence excitation spectra were measured according to method [10].

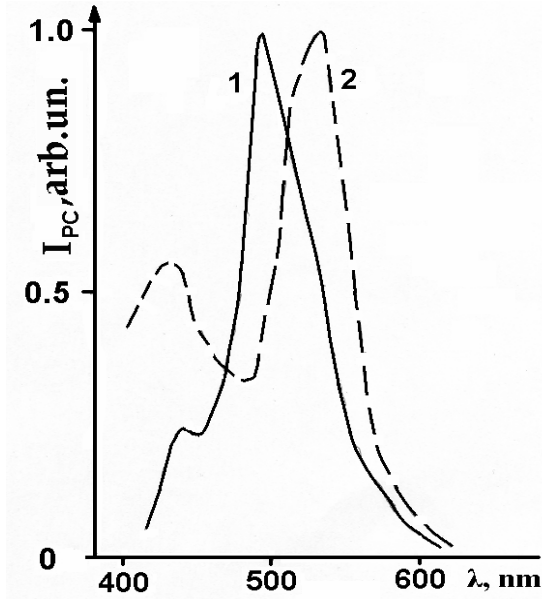
The photoluminescence (PL) spectra were measured using excitation by a monochromatic beam of a nitrogen LGI-21 laser ( $\lambda = 337.1$  nm). A multi-channel OVA-284 analyzer was used to measure the radiation of samples at room temperature. Platelets with various thickness were used for the measurements. The signal was usually registered at the face (0001).

## 3. RESULTS AND DISCUSSION

The doping of single crystalline platelets with Cu of various concentrations changes all characteristics of the samples (Fig. 1 and Table 1).

**Table 1.** Main photoelectrical parameters of ZnIn<sub>2</sub>S<sub>4</sub>:Cu single crystals

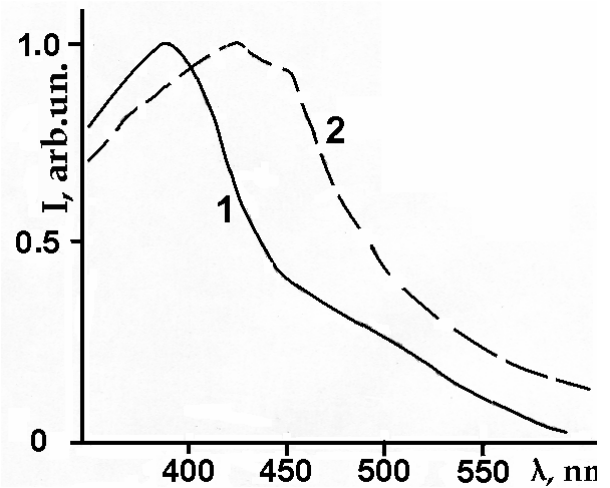
| Impurity concentration, cm <sup>-3</sup> | $\lambda_{\text{intr}}^{\text{max}}$ , nm | $\lambda_{\text{imp}}^{\text{max}}$ , nm | $\lambda_{1/2}$ , nm | Dark resistivity $\rho_D$ , $\Omega \cdot \text{cm}$ | $\rho_{\text{Light}}$ at 100 lx, $\Omega \cdot \text{cm}$ | $\rho_D/\rho_{\text{Light}}$ at 100 lx |
|------------------------------------------|-------------------------------------------|------------------------------------------|----------------------|------------------------------------------------------|-----------------------------------------------------------|----------------------------------------|
| $1.2 \times 10^{19}$                     | 430                                       | 530                                      | 556                  | $1.3 \times 10^{11}$                                 | $10^7$                                                    | $1.3 \times 10^4$                      |
| $1.9 \times 10^{19}$                     | 440                                       | 490                                      | 536                  | $6.3 \times 10^7$                                    | $6.3 \times 10^5$                                         | $10^2$                                 |

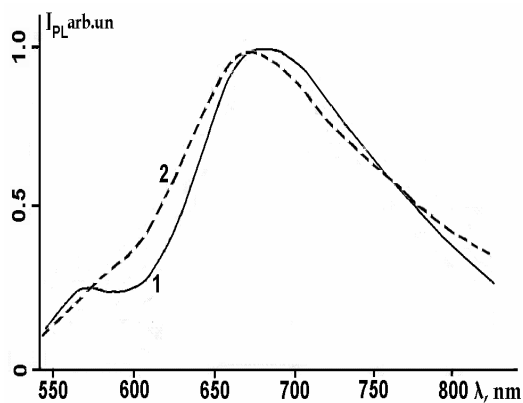
**Fig. 1.** Spectral distribution of photoconductivity of copper doped ZnIn<sub>2</sub>S<sub>4</sub> single crystals for Cu concentrations, cm<sup>-3</sup>: 1 -  $1.2 \times 10^{19}$ , 2 -  $1.9 \times 10^{20}$ .

In particular, a shift in the long wavelength range appears, this can be explained by a photoexcitation of current carriers from the respective impurity levels. Note that the greatest relative photosensitivity was reached at small concentrations ( $1.2 \times 10^{19} \text{ cm}^{-3}$ ). The subsequent increasing in the copper content leads to the decrease in this parameter, i. e. a kind of concentration quenching is observed. The increase in the copper concentration not only shifts the long wavelength peak to the short-wavelength range (see table,  $\lambda_{\text{imp}}^{\text{max}}$ ), but the quenching of the intrinsic photoconductivity occurs, as well. A small shift of the peak of the intrinsic photoconductivity  $\lambda_{\text{intr}}$  is also observed. Evidently, this is linked with the tailing of the zone edge owing to the large impurity

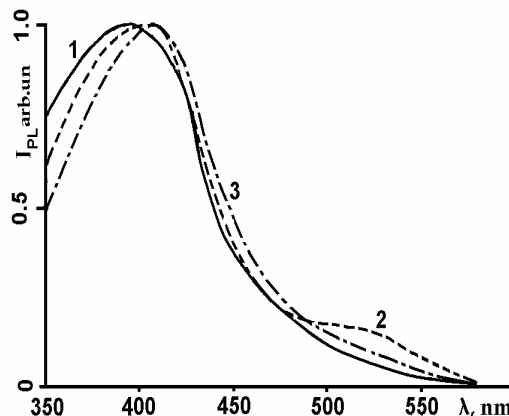
concentration and the presence of intrinsic defects.

The excitation spectra of ZnIn<sub>2</sub>S<sub>4</sub>: Cu single crystals for two copper concentrations are presented in Fig. 2. Their peculiar feature is that the shift of the long-wavelength wing is clearly observed, when the impurity concentration increases. This shift is especially significant for the concentration of  $1.9 \times 10^{20} \text{ cm}^{-3}$ . In the impurity range the maximum at 498 nm (2.5 eV) can be also clearly seen. The small copper concentrations were investigated earlier [9, 10]. We made measurements using the method similar to [10]. Analysis of our data and those given in the papers mentioned above suggests the conclusion that copper forms a level with energy of 2.5 eV in the forbidden zone.

**Fig. 2.** Excitation spectra of photoluminescence in ZnIn<sub>2</sub>S<sub>4</sub>:Cu for Cu concentrations, cm<sup>-3</sup>: 1 -  $1.2 \times 10^{19}$ , 2 -  $1.9 \times 10^{20}$ .



**Fig. 3.** Spectral distribution of photoluminescence in  $\text{ZnIn}_2\text{S}_4\text{:Cu}$  single crystals with Cu concentration  $1.9 \times 10^{20} \text{ cm}^{-3}$

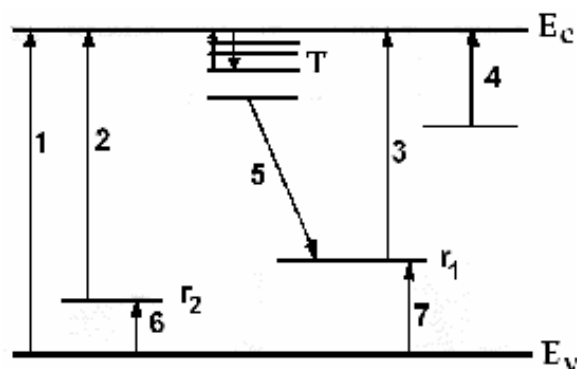


**Fig. 4.** Excitation spectra of photoluminescence in  $\text{ZnIn}_2\text{S}_4\text{:Ag}$  single crystals with Ag concentrations,  $\text{cm}^{-3}$ : 1 - undoped, 2 -  $3.7 \times 10^{19}$ , 3 -  $1.0 \times 10^{20}$

The radiation spectrum of  $\text{ZnIn}_2\text{S}_4\text{:Cu}$  single crystal is shown in Fig. 3. It consists of a wide band  $\approx 0.4 \text{ eV}$  with an intensive maximum at 675 nm (1.8 eV) and of a slightly seen shoulder at 600 nm ( $\approx 2.1 \text{ eV}$ ). The given spectrum closely coincides with the spectrum of undoped samples [11].

The influence of a silver impurity is similar. For example, in the excitation spectra of photoluminescence two ranges can be mentioned. The strong maximum near 400 nm is evidently associated with the excitation of carriers from the valence band to the conduction band. Using the Moss principle (as in the case of photoconductivity) we obtain  $E_g = 2.81 \text{ eV}$ . This well coincides with the meaning obtained using the data on the optical absorption. The second peculiar feature of the spectra is located in the region of 520 nm (Fig. 4). Since this feature is not observed in the spectra of undoped crystals, it can be associated with the energy level, which appears in the forbidden gap owing to silver or to a cluster involving silver. Doping with silver at its concentration of  $3.7 \times 10^{19} \text{ cm}^{-3}$  exerts the most pronounced action on the parameters of the compound.

The model of energy levels and the possible most probable optical transitions for the case of undoped samples are shown in Fig. 5. This was made on the basis of the analysis of publications related to this semiconductor.



**Fig. 5.** Model of energy levels and recombination processes.

T denotes the exponentially distributed electronic traps near the conduction band. The comparison of optical absorption and photoconductivity in the compound allows to suggest that the intrinsic and impurity absorption appear owing to the photoelectrical transitions 1 and 2-4, respectively. Optical transitions 2-4 occur from the levels located at the depth of 2.5, 2.25 and 1.4 eV below the bottom of the conduction band  $E_c$ . A peculiar feature of the radiation is that the electronic transition 5 associated with the donor-acceptor recombination corresponds to the dominating radiation band. The transitions obtained from the kinetics and optical quenching of photocurrent are denoted by 6 and 7.

The validity of the proposed model, which involves two acceptors, is also confirmed by the results of investigations of photocurrent oscillations in a similar compound  $\text{CdIn}_2\text{S}_4$  [12]. The following most probable centers can be ascribed to the levels  $r_1$ ,  $r_2$  and A: zink or cadmium on the In or Ga site and one- or double-charged zink or cadmium vacancy, respectively. This model is also applicable for  $\text{CdGa}_2\text{S}_4$  and other sulphides. Note, that the chosen impurities Ni, Mn [6, 7] and Cu significantly influence all the main parameters of the compound. However, the electronic type of conductivity retains.

#### 4. CONCLUSIONS

In the conclusion note that using the spectra of photoconductivity, excitation and radiation spectra of luminescence, analysing their characteristic parameters in comparison with the available published data we determined those concentrations of nickel, manganese, and copper impurities that significantly influence the parameters of layered  $\text{ZnIn}_2\text{S}_4$  compound. The similar changes in parameters can be performed using doping with silver, but silver is more expensive.

The scheme of levels of radiative recombination and the model of main photoelectrical processes in the layered semiconductor  $\text{ZnIn}_2\text{S}_4$  was presented. The nature of defects is more various in comparison with those in binary and ternary non-defect semiconductors. It was shown that the main electronic processes in this substance doped with different impurities are governed by the system of deep levels and the exponentially distributed states near the conduction band.

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