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ELECTRONIC TRANSITIONS AND RECOMBINATION MECHANISMS Cu-DOPED $CdIn_2S_4$ SINGLE CRYSTALS

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The study investigates the spectral distribution of photoconductivity, optical quenching, transient characteristics, thermally stimulated currents, and the temperature dependence of both dark and photocurrent in Cu-doped $CdIn_2S_4$ single crystals. Detailed analysis of the experimental data reveals the presence of deep donor levels with ionization energies located at E_c - 0.17 eV, E_c - 0.66 eV, E_c - 1.2 eV, and E_c - 1.55 eV. At 110 K, optical quenching of the photoconductivity was observed within the photon energy range of 0.86 to 1.63 eV. The energy positions of the photosensitivity centers relative to the valence band maximum were identified, yielding optical ionization energy of E^o_{vr} = 0.86 eV and a thermal ionization energy for the r-type levels of E^t_{vr} = 0.62 eV. The capture cross-sections ratio for holes and electrons at these r-centers was found to be $S_{pr}/S_{nr} = 5\times10^4$. Both optical and thermal quenching phenomena are attributed to charge-state transitions and carrier-exchange dynamics between slow (r) and fast (s) recombination centers. The well-defined electronic structure and high photosensitivity of Cu-doped $CdIn_2S_4$ single crystals suggest they are promising candidates for advanced photodetector applications in the visible and near-infrared spectral regions.
Keywords: *$CdIn_2S_4$; Photoconductivity; Optical quenching; Recombination centers; Deep donor level; Near-infrared photodetectors*
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1. INTRODUCTION

$CdIn_2S_4$ belongs to the family of ternary $A^{II}B_2^{III}C_4^{VI}$ semiconductors, where A represents divalent cations (Zn, Cd), B represents trivalent cations (Ga, In), and C represents chalcogens (S, Se). These compounds are characterized by a wide band gap, intense luminescence, and high photosensitivity in the visible region of the electromagnetic spectrum [1-- 13]. Among these materials, cadmium thioindate ($CdIn_2S_4$) is of significant interest for optoelectronics. However, the intrinsic properties of undoped $CdIn_2S_4$ are often limited by complex intrinsic defect structures. The activation of $CdIn_2S_4$ with copper (Cu) has been shown to significantly enhance its photosensitivity by creating a high density of deep-level sensitizing centers, known as r-centers [14]. These Cu-related centers introduce a high asymmetry in the capture cross-sections for charge carriers, thereby effectively suppressing recombination and increasing the lifetime of photo-excited electrons. Consequently, Cu-doping transforms $CdIn_2S_4$ into a high-performance material suitable for precision photodetectors. The $CdIn_2S_4$ compound crystallizes in a cubic structure with a lattice constant of a = 10.797 Å (space group O_h^7 - Fd3m). At room temperature, the energy of indirect transitions is E_g^{ind} = 2.28 eV [15]. The results of studies on the various photoelectric properties of $CdIn_2S_4$ are presented in [16-21]. Due to its high quantum efficiency and broad absorption in the visible range, $CdIn_2S_4$ is a promising photocatalyst [22-24].

Despite extensive studies, the carrier recombination mechanisms in Cu- doped $CdIn_2S_4$ crystals remain a subject of debate. One of the most informative methods for investigating the energy spectrum of local states and carrier trapping processes is the analysis of the optical and thermal quenching of photoconductivity. These effects allow for the determination of recombination center parameters and provide insight into the interaction dynamics between different types of centers under varying temperature and illumination conditions.

This work is devoted to a comprehensive study of the spectral distribution, kinetics of optical quenching, thermally stimulated currents, temperature dependence of the dark current, and thermal quenching of the photocurrent in Cu-doped $CdIn_2S_4$ single crystals. The primary focus is on determining the energy parameters of photosensitivity centers and clarifying the roles of slow (r) and fast (s) recombination centers in photosensitivity processes.

2. EXPERIMENTAL DETAILS

The copper-doped $CdIn_2S_4$ compound was synthesized from high-purity constituent elements (at least 99,99 wt.%). The copper (Cu) impurity concentration was fixed at 0.002 mol. Single crystals were subsequently grown from the synthesized material using the melt crystallization.

The resulting crystals were characterized using X-ray diffraction and Raman scattering spectroscopy. X-ray diffraction studies, performed with a Bruker D2 Phaser diffractometer, confirmed that $CdIn_2S_4$ crystallizes in a space group O_h^7 - Fd3m. The unit cell parameters were determined to be a = 10.797Å.

Raman spectra of $CdIn_2S_4$ were recorded using a “Nanofinder 30” (Tokyo Instruments, Japan) confocal Raman microspectrometer. A Nd:YAG laser (532 nm second-harmonic output, 10 mW maximum power) served as the excitation source. Using a diffraction grating with 1800 lines/mm, the spectral resolution was better than 0.5 cm^{-1}. All spectra were

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measured in a back scattering geometry. The Raman spectra are in good agreement with previously reported literature, together with X-ray diffraction findings, confirm the high structural quality of the synthesized crystals. The resulting crystals exhibited n-type conductivity. Notably, it was established that neither the introduction of Cu impurities nor a stoichiometric excess of sulfur (or deficiency of cadmium and indium) triggered a carrier type conversion from n-type to p-type. For this study, high-resistivity, photosensitive samples were selected with the following parameters: dark specific resistivity (ρ): $10^6 \div 10^8$ Ω·см. and photosensitivity ratio (R_{dark} / R_{light}) = $10^2 \div 10^5$ (measured at 300 K under 200 lx illumination). Samples were prepared as plane-parallel plates with dimensions of 3 x 2 x 1 мм^3. Metallic indium was used to create ohmic contacts. The applied electric field strength was maintained below 20 V/cm to ensure linear current-voltage (I-V) characteristics and to exclude effects related to space-charge-limited current.

To measure the thermally stimulated current, the sample was kept in the dark at room temperature for 15 hours before being cooled to 100 K. After remaining at this temperature for 30-40 minutes, the sample was illuminated within the intrinsic absorption region.

The experimental setup used to study the optical quenching of photoconductivity is described in Ref. [25]. Intrinsic photoconductivity (background or primary illumination) was excited using an SI-6-300 incandescent lamp. A combination of selective, neutral, and water filters was employed to ensure uniform light absorption throughout the crystal volume. Quenching of the photocurrent was induced using monochromatic radiation in the 0.4-2.0 μm wavelength range, generated by an incandescent lamp coupled with an SF-4A monochromator. The resulting current was recorded using a DC chart recorder. Spectral plots were constructed point-by-point under steady-state conditions using a sequential excitation mode. In order to obtain the true spectral dependence of the photoconductivity, the raw data were normalized by the incident light intensity. Finally, the temperature dependence of the photocurrent was measured as the sample was heated at a constant rate of 0.08 K/s.

3. RESULTS AND DISCUSSION

3.1. Spectral Distribution of Photoconductivity

Experiments show that Cu doped $CdIn_2S_4$ single crystals exhibit photoconductivity within the energy range of 0.62 to 3.0 eV (Figures 1 and 2). Figure 1 illustrates the photocurrent spectrum of these crystals at T = 110 K. Given that the photocurrent values are relatively low (ranging from 10^{-9} to 10^{-6} A), a logarithmic scale is employed to clearly resolve subtle "shoulders" and slopes in the data. Based on the long-wavelength limit of the impurity photocurrent, we identified energy levels at E_c - 0.7 eV, E_c - 1.2 eV, and E_c - 1.55 eV. These levels are associated with the transitions of electrons from deep levels to the conduction band. Figure 2 represents the intrinsic and near-intrinsic regions (1.5 to 3.0 eV). A sharp peak near 1.75 eV corresponds to transitions from impurity levels to the conduction band, while a second, broader peak near 2.48 eV represents the interband transitions. The distinct separation of these two peaks indicates a well-defined electronic structure, suggesting that this crystal is a promising candidate for photodetector applications in the visible to near-infrared ranges.

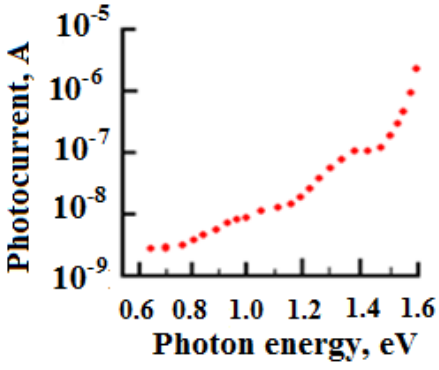

Figure 1. Spectral distribution of photoconductivity in Cu-doped $CdIn_2S_4$ single crystals at T = 110 K within the photon energy 0.6÷1.6 eV

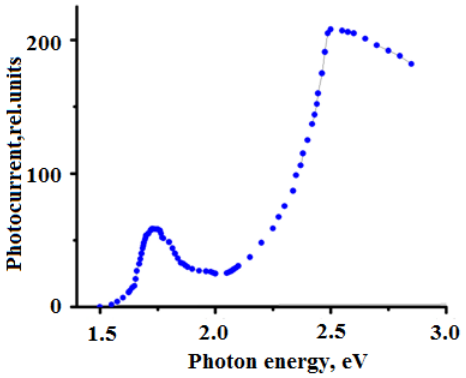

Figure 2. Spectral distribution of photoconductivity in Cu-doped $CdIn_2S_4$ single crystals at T = 110 K within the photon energy 1.5÷3.0 eV

3.2. Optical Quenching of Photoconductivity

Optical quenching of photoconductivity refers to the reduction of the steady-state intrinsic photocurrent when a sample is simultaneously exposed to additional light at impurity wavelengths. The study of optical quenching is an effective method for probing the band structure and the electronic-state system in semiconductors [25-30]. Specifically, this method provides valuable information regarding the parameters of photosensitivity centers (r-centers). The optical ionization energy (depth) of these centers relative to the valence band maximum (E^o_{vr}) is determined from the long - wavelength edge of the quenched spectrum.

The optical photocurrent quenching method was used to study slow r-recombination centers (Rose Class II centers [26]), which account for the high photosensitivity of $CdIn_2S_4$ single crystals. The optical quenching spectrum for copper-doped (Cu) samples is shown in Figure 3. The value of the current corresponding to optical quenching, $\Delta i_{ph} = i_{ph} - i_{ir}$, is plotted on the ordinate axis. Here, i_{ph} represents the primary (background) photocurrent, while i_{ir} is the photocurrent

resulting from simultaneous illumination by both the primary and secondary light sources. As illustrated in Figure 3, optical quenching of the photocurrent is observed in the 0.86÷1.63 eV range at T = 110 K.

The quenching maximum is localized within the 1.13 - 1.27 eV interval. Based on the long-wavelength edge of the quenching spectrum, the optical ionization energy (depth) of the photosensitivity center levels relative to the valence band maximum was determined to be E^{o}_{vr} = 0.86 eV. In the secondary illumination energy range of 0.86 эВ < hν <1.2 eV, only photocurrent quenching is observed (Figure 3). When the secondary radiation is turned off, the photocurrent slowly increases, returning to the steady-state value determined by the primary illumination.

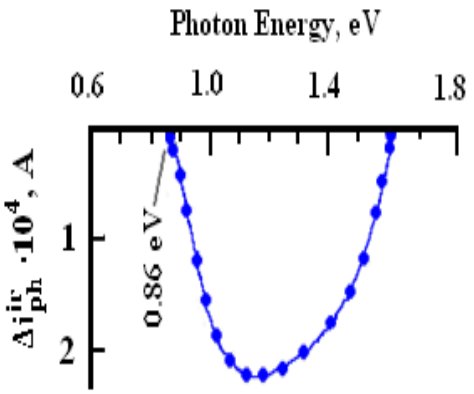

Figure 3. Optical quenching spectrum of intrinsic photoconductivity of $CdIn_2S_4$ single crystals doped with Cu

In $CdIn_2S_4$:Cu, a "flash" behavior of the photocurrent is observed under secondary light illumination. This is clearly illustrated in Figure 3, which displays the transient characteristics of the optical quenching of photoconductivity. Upon exposure to monochromatic light with photon energies hν > 1.2 eV, the photocurrent rises sharply, passes through a maximum and gradually recovers to the steady-state level maintained by the primary illumination at T = 110 K. This kinetic behavior confirms the competition between the rapid optical generation of electrons from donor levels and the subsequent slower recombination processes. This specific type of optical quenching-characterized by transient excitation-is determined by the ratio between the excitation and quenching rates at a given wavelength. As the energy of the secondary radiation increases, the amplitude of the "flash" also increases. At a fixed wavelength, two processes occur simultaneously: 1. Stimulation: An increase in photocurrent due to carrier generation from impurity levels into the conduction band. 2. A decrease in photocurrent resulting from the generation of holes from photosensitivity centers into the valence band. The unique nature of this kinetics allows for the separation of quenching and stimulation effects, as their respective amplitudes are proportional to the spectral dependencies of the photon capture cross - sections. This enables the determination of the long-wavelength excitation threshold. The long-wavelength edge of the photocurrent "flash" occurs at an energy of 1.2 eV. The emergence of this effect at hν > 1.2 eV suggests the presence of donor levels within the band gap, the shallowest of which is located 1.2 eV below the conduction band (E_c). The aforementioned facts indicate that the E_c -1.2 eV level plays an active role in the generation and recombination processes in $CdIn_2S_4$. Given that the optical quenching of the photoconductivity spectra extends up to 1.63 eV, the possibility of double optical transitions involving photosensitivity centers cannot be excluded.

3.3. The Temperature Dependence of Dark Current

The temperature dependence of the dark current, I_{dark} (T), in $CdIn_2S_4$ single crystals was investigated in the temperature range of 110 - 410 K (Figure 4). For undoped $CdIn_2S_4$ single crystals, the activation energy values determined from of lg (I_{dark}) versus 10^3/T plot were E_c - 0.22 eV; E_c - 0.5 eV, and E_c - 1.0 eV (curve 1). In contrast, for Cu-doped crystals, no dark current activation was observed in the temperature dependence up to 230 K (Figure 4, curve 2).

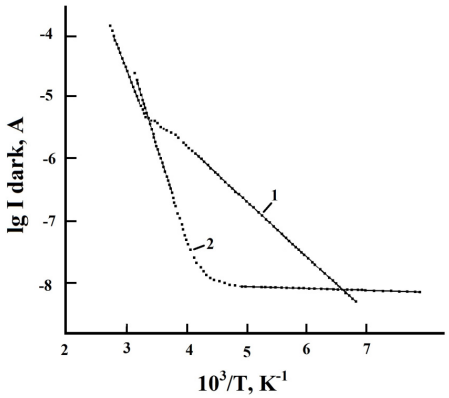

Figure 4. Temperature dependence of dark current in $CdIn_2S_4$ single crystals: 1-undoped; 2-Cu- doped

This fact can be explained by an increase in the concentration of acceptor centers due to Cu doping. In thermodynamic equilibrium, these acceptors are compensated by the existing donors in the crystal, leading to a shift of the Fermi level toward the middle of the bandgap. Consequently, the activation of the dark current occurs at higher temperatures. For Cu-doped $CdIn_2S_4$ crystals, the dark current increases exponentially starting from 230 K. The activation energy for these crystals, determined from the slope of the temperature- dependent dark current, was found to be E_c - 0.66 eV. This result is in close agreement with the E_c - 0.7 eV value derived from the spectral distribution of photoconductivity.

3.4. The Temperature Dependenc of Photoconductivity

The temperature dependence of the intrinsic stationary photocurrent, $I_{ph}(10^3/T)$, in Cu-doped $CdIn_2S_4$ single crystals was investigated at various light intensities (L) within the range of 110-300 K (Figure 5). Experiments demonstrated that at constant light intensity (L), the photocurrent gradually increases with rising temperature. At approximately 230 K, a

transition occurs from high to low photosensitivity, marking the onset of thermal quenching of the photocurrent. As the illumination intensity L increases, the rate of photocurrent grown decreases, and the onset of thermal quenching of the photoconductivity shifts toward higher temperatures. The activation of the photocurrent is likely due to electron trapping centers located below the conduction band. Effective recombination centers to acting trapping centers for holes.

At temperatures T< 230 K, electrons in these traps are thermally excited into the conduction band, thereby increasing the photocurrent. It is well-established that thermal quenching of the photoconductivity occurs due to the recharging of recombination centers. Since the r-photosensitive centers are located in the lower half of the band gap, the ratio of their capture cross-section is highly asymmetric (S_{pr}/S_{nr} >>1). In the thermal quenching of the photoconductivity region, an intensive exchange of charge carriers occurs between the valence band and r-centers. Consequently, the r-centers transition from acting as effective recombination centers to acting trapping centers for holes.

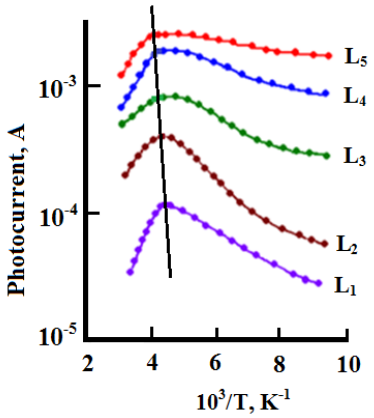

Figure 5. Temperature dependence of photocurrent in Cu-doped single crystals at different intensities of excitation light ($L_1 < L_2 < L_3 < L_4 < L_5$)

The transition from high to low photosensitivity at a fixed light intensity is determined by the following relation:

$$n = (C_{pr}/C_{nr})\, N_v \exp(-E^t_{vr}/kT).$$

Where n is the concentration of free electrons at the onset temperature of thermal quenching of the photoconductivity onset; N_v is the effective density of states in the valence band; E^t_{vr} is the "thermal" ionization energy of the r-centers relative to the top of the valence band. C_{pr} and C_{nr} are the capture probabilities of holes and electrons by the r-centers, respectively. Using the values $N_v = 7.10^{18}$ cm^{-3} and $\mu_p = 10$ $cm^2/V.sec$ (derived from thermoelectric power, conductivity, and photo-hole measurements), the following parameters were determined by analyzing the intersection of the straight line drawn through the thermal quenching onset points on the log I_{ph} vs. $10^3/T$ plot: the "thermal' ionization energy of the r-photosensitivity levels $E^t_{vr} = 0.62$ eV, as well as the ratio of capture cross-sections for holes and electrons by the r-centers $S_{pr} / S_{nr} = 5\times10^4$ indicates a very effective sensitizing center.

3.5. THERMALLY STIMULATED CURRENT

Thermally stimulated conductivity (TSC) was investigated within the temperature range of 110 - 300 K. Experimental results demonstrated that the temperature of the TSC maximum (T_m) is independent of both the duration and intensity of the initial illumination (Figure 6). The peak intensity increases with longer illumination duration due to a higher concentration of filled traps; the position of the maximum temperature remains constant. This invariance of T_m with respect to the initial trap filling level is a characteristic feature of first-order (monomolecular) kinetics, confirming the case of slow retrapping in Cu-doped $CdIn_2S_4$ crystals. This behavior suggests that the retrapping of carriers is negligible compared to the recombination rate. As the heating rate (β) increases from 0.08 K/s to 0.65 K/s, T_m shifts systematically toward higher temperatures (Figure 7).

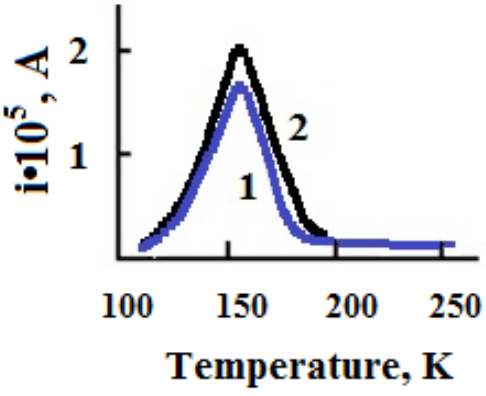

Figure 6. Temperature dependence of thermally stimulated current in Cu-doped $CdIn_2S_4$ single crystals at different illumination duration: (1) 5 min and (2) 60 min (at a constant heating rate β = 0.08 K/s).

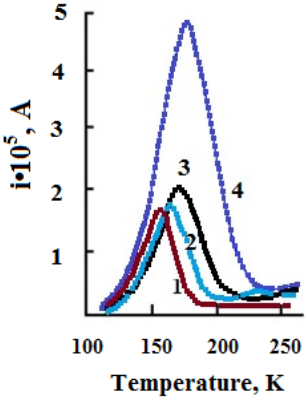

Figure 7. Temperature dependence of thermally stimulated current in Cu-doped $CdIn_2S_4$ single crystals at various heating rates: (1) $\beta_1 = 0.08$ K/s, (2) $\beta_2 = 0.24$ K/s, (3) $\beta_3 = 0.43$ K/s, (4) $\beta_4 = 0.65$ K/s

Following the theory for slow re-trapping, the activation energy (E_t) was determined using the following relation [31]:

$$\frac{E_t}{kT_m} = \ln\left(\frac{T_m^2}{\beta}\right) + \ln\left(\frac{\upsilon\, k\, S\, N_c}{E_t}\right),$$

where E_t is the trap depth, k is the Boltzmann constant, N_c is the effective density of states in the conduction band, S is the capture cross-section, and υ is the thermal velocity. The second term on the right-hand side is independent of temperature. From the slope of the Arrhenius plot ($\ln(T^2_m/\beta)$ vs. $1000/T_m$), the trap depth was calculated to be approximately $E_t \approx 0.14$ eV.

The activation energy (depth) of these levels can also be determined by the following formula [31,32]:

$$E_t = \frac{1.51\, k\, \mathrm{Tmax\, T1}}{\mathrm{Tmax} - \mathrm{T1}}.$$

Where T_1 – is the temperature at which the thermally stimulated current reaches half of its maximum value on the rising side of the peak. A value of 0.17 eV was obtained for the activation energy of the trapping levels. This value is in satisfactory agreement with the previously calculated value of $E_t \approx 0.14$ eV.

4. DISCUSSION

Studies on optical and thermal quenching indicate that the recombination of non-equilibrium carriers in Cu-doped $CdIn_2S_4$ crystals is governed by a three-center model. This framework consists of:

1. Slow r-centers: Deep compensated acceptors responsible for high photosensitivity;
2. Fast s-centers: Centers for rapid recombination with significantly larger electron-capture cross-sections ($S_{nr} \ll S_{ns}$);
3. t-levels: Trapping levels located near the bottom of the conduction band (E_c - 0.17 eV) that regulate the population of the recombination centers via the charge neutrality condition.

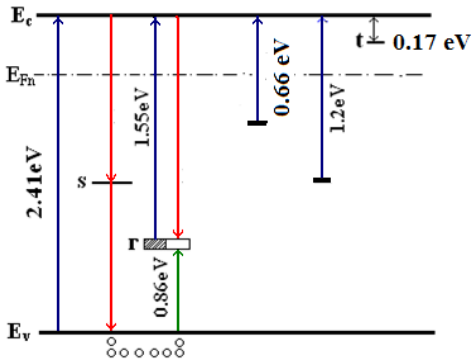

Figure 8. Energy level scheme and electronic transitions in Cu-doped $CdIn_2S_4$ singe crystals at 110 K. Transitions from r-center (1.55 eV) and the valence band (2.41eV) to the conduction band are indicated, alongside trapping levels (t) and fast recombination centers (s)

In stoichiometric $CdIn_2S_4$, cationic vacancies (V_{Cd}) typically act as r-centers. However, in copper-doped samples, Cu atoms occupying tetrahedral lattice sites likely serve this role. The similar ionic radii of Cu^+ (0.96 Å) and Cd^{2+} (0.97 Å) facilitate the substitution of cadmium by copper. In thermodynamic equilibrium, the photosensitivity centers are located below the hole quasi-Fermi level (E_{fp}), acting primarily as hole traps. Upon illumination with intrinsic light, electrons are excited from the valence band to the conduction band, generating a primary photocurrent. As the intensity of intrinsic excitation increases, E_{fp} shifts toward the valence band, transforming the r-centers into active recombination centers.

This increases the electron lifetime and elevates the steady-state photocurrent.

Under secondary illumination (0.86 - 1.63 eV), electronic transitions occur from the valence band to the photosensitivity centers, which is physically equivalent to the release of holes from r-centers into the valence band. These holes are subsequently captured by the fast s-centers, leading to a redistribution of recombination fluxes: recombination through the slow r-centers decreases, while recombination through the fast s-centers increases sharply. The suppression of the r-center channel and the subsequent relocalization of holes to s-centers results in a significant reduction of free electrons in the conduction band, leading to the observed quenching of the photocurrent.

We attributed the 1.55 eV value obtained from the photoconductivity spectrum to electronic transitions from r-photosensitivity centers to the conduction band. This interpretation is supported by the energy balance: the sum of energy levels (1.55 + 0.86 = 2.41 eV) corresponds exactly to the band gap width (E_g) of the $CdIn_2S_4$ at T = 110 K. These results enable a comprehensive explanation of electronic transitions using a three-level energy scheme. By synthesizing our findings with existing literature, we propose this model for the excitation and recombination processes in Cu-doped $CdIn_2S_4$ single crystals (Figure 8).

CONCLUSIONS

In this study, the energy range for the optical quenching of photoconductivity in Cu-doped $CdIn_2S_4$ single crystals at 110 K was determined to be 0.86-1.63 eV. The ionization energies of deep donor levels were identified as E_c - 0.17 eV, E_c - 0.66 eV (refined based on spectral analysis), E_c - 1.2 eV, and E_c - 1.55 eV. Based on the spectral characteristics, the optical energy of the photosensitivity (r) centers relative to the valence band maximum was determined as $E^o_{vr} = 0.86$ eV. Additionally, the thermal energy of these r-centers was found to be $E^t_{vr} = 0.62$ eV, with a hole-to-electron capture cross-section ratio (Spr/Snr) of 5×10^4.

The results demonstrate that the quenching mechanisms are governed by the redistribution of charge carriers between slow (r) and fast (s) recombination centers. In summary, our investigation into the photoconductivity of $CdIn_2S_4$: Cu confirms the existence of several deep donor levels and highly efficient sensitizing r-centers. The high capture cross-

section ratio suggests that these crystals possess superior photosensitivity. These findings indicate that Cu-doped $CdIn_2S_4$ crystals exhibit a well-defined electronic structure, making them excellent candidates for next-generation visible and near-infrared photodetectors.

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ЕЛЕКТРОННІ ПЕРЕХОДИ ТА МЕХАНІЗМИ РЕКОМБІНАЦІЇ МОНОКРИСТАЛІВ $CdIn_2S_4$, ЛЕГОВАНИХ МІДДЮ

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У дослідженні вивчаються спектральний розподіл фотопровідності, оптичне гасіння, перехідні характеристики, термостимульовані струми та температурна залежність як темнового, так і фотоструму в монокристалах CdIn2S4, легованих міддю. Детальний аналіз експериментальних даних показує наявність глибоких донорних рівнів з енергіями іонізації, розташованими при E_c - 0,17 еВ, E_c - 0,66 еВ, E_c - 1,2 еВ та E_c - 1,55 еВ. При 110 K оптичне гасіння фотопровідності спостерігалося в діапазоні енергій фотонів від 0,86 до 1,63 еВ. Було визначено енергетичні положення центрів фоточутливості відносно максимуму валентної зони, що дало енергію оптичної іонізації E^o_{vr} = 0,86 еВ та енергію теплової іонізації для рівнів r-типу E^t_{vr} = 0,62 еВ. Співвідношення перерізів захоплення для дірок та електронів у цих r-центрах було визначено як $S_{pr}/S_{nr} = 5\times10^4$. Як оптичне, так і теплове гасіння пояснюються переходами зарядових станів та динамікою обміну носіями між повільними (r) і швидкими (s) рекомбінаційними центрами. Чітко визначена електронна структура та висока фоточутливість монокристалів CdIn2S4, легованих міддю, свідчать про те, що вони є перспективними кандидатами для передових застосувань у фотодетекторах у видимому та ближньому інфрачервоному спектральних діапазонах.

Ключові слова: *$CdIn_2S_4$; фотопровідність; оптичне гасіння; рекомбінаційні центри; глибокий донорний рівень; фотодетектори ближнього інфрачервоного діапазону*