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PHOTOELECTRONIC PROPERTIES OF $CdGa_2S_4$ SINGLE CRYSTALS

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Experimental investigations of the photoelectric properties of $CdGa_2S_4$ single crystals were carried out. The study examined the temperature dependence of the photocurrent (within the 110–420 K range), as well as the spectral dependence and transient characteristics of optical quenching at T = 300 K. Optical quenching of the photocurrent was observed within a secondary light beam energy range of 0.6 - 2.49 eV. Measurements revealed energy levels at E_c - 0.21 eV, E_c - 0.42 eV, and E_c - 1.06 eV, as well as sensitizing levels at E_v + 0.89 eV. The decrease in photocurrent at temperatures above 300 K is attributed to thermal quenching. Both optical and thermal quenching of photoconductivity in $CdGa_2S_4$ crystals are ascribed to changes in the charge state and exchange dynamics of sensitizing and recombination centers.
Keywords: *Cadmium thiogallate; Photoconductivity; Defects; Deep levels; Sensitizing centers; Recombination centers; Optical quenching; Thermal quenching*
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INTRODUCTION

$CdGa_2S_4$ belongs to the class of $A^{II}B^{III}_2C^{VI}_4$ ternary semiconductors, where A represents divalent cations (e.g. Zn or Cd), B represents trivalent cations (e.g. Ga or In), and C represents chalcogens (such as S or Se). These compounds are characterized by birefringence, optical activity, high nonlinear susceptibility coefficients, a wide band gap, bright luminescence, and high photosensitivity in the visible range [1-7]. The aforementioned properties make these compounds promising materials for optoelectronic applications.

The band gap of $CdGa_2S_4$ varies from 2.96 eV at T = 300 K [8] to 3.77 eV at T = 10 K [9]. Its complex chemical composition and the presence of two atoms in the cation sublattice result in multiple levels within the band gap. The study of photoconductivity and luminescence in $CdGa_2S_4$ crystals has been widely used to detect localized levels and analyze their nature and properties [10-16]. However, the recombination processes and the specific roles of various centers - including the sensitizing centers involved in these processes-have not yet been sufficiently studied.

This paper presents photocurrent measurements of $CdGa_2S_4$ single crystals to obtain additional information regarding localized states and photoconductivity sensitizing centers within the band gap. We have carried out experiments on excited samples using two beams of radiation. Using UV background illumination in conjunction with secondary below-band-gap illumination at variable wavelengths, the optical quenching of photoconductivity was investigated. Furthermore, we report the temperature dependence of the photocurrent in $CdGa_2S_4$ over the range 110-400 K. This work contributes to refining the localized-state and electronic-transition models for $CdGa_2S_4$, providing valuable insights into its photoelectric properties.

EXPERIMENTAL DETAILS

$CdGa_2S_4$ polycrystals were synthesized from the high-purity elements (99.999%) in stoichiometric proportions within evacuated quartz ampoules. 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 $CdGa_2S_4$ crystallizes in a cation–ordered defect chalcopyrite tetragonal structure (space group $I\bar{4}$, S_4^2). The unit cell parameters were determined to be a = b = 5.5450 Å and c = 10.1470 Å.

Raman spectra of $CdGa_2S_4$ 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. With a diffraction grating with 1800 lines/mm, the spectral resolution was better than 0.5 cm^{-1}. All spectra were measured in a backscattering geometry. The Raman spectra of the $CdGa_2S_4$ crystals are in good agreement with previously reported results [17]. Together, the X-ray diffraction and Raman scattering characterizations confirm the high structural quality of the synthesized $CdGa_2S_4$ crystals.

The synthesized material served as a precursor for the growth of a $CdGa_2S_4$ single crystal via chemical vapor transport, using iodine as the transport agent in a closed tube. This method yielded $CdGa_2S_4$ single crystals with natural faceting, appearing as transparent, light-yellow trihedral prisms with mirror-like surfaces. For experimental measurements, the samples were prepared as plane-parallel plates with dimensions of 3×2×1 mm^3. One face of each corresponded to a natural mirror edge and was used without further processing. For reliable electrical measurements, the electrical contacts were formed using indium solder on the lateral faces of the samples. The crystals exhibited n-type

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conductivity, with a dark resistivity (ρ_d) ranging from 10^9 to $10^{10}\,\Omega \cdot$ cm at 300 K. Estimates of the electron concentration and Hall mobility, derived from Hall coefficient measurements, yielded values of $n \approx 10^8 - 10^9$ cm^{-3} and $\mu_n \approx 1 - 10$ cm^2 / (V · s) at 300 K, respectively.

The experimental setup used to study the optical quenching of photoconductivity is described in Ref. [18]. For excitation within the intrinsic absorption region (background excitation), an incandescent lamp was used in combination with a set of spectral, neutral, and water filters. Secondary (quenching) illumination ($h\nu < E_g$) was provided by a tungsten lamp passed through an SF-4A monochromator. Measurements were performed under direct current using a steady-state method. The electric field strength applied to the samples was kept within the linear region of the current-voltage (I-V) characteristics. The current was recorded using a DC chart recorder and a microvoltmeter F-136. The spectral dependence of the optical quenching was investigated over a secondary illumination wavelength range of 0.4 to 2.0 μm. Special care was taken to ensure that the background photocurrent reached an equilibrium value before each measurement. The optical quenching of the photoconductivity as a function of the secondary light wavelength was plotted point-by-point under sequential excitation.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Optical quenching of photoconductivity is a phenomenon where sub-bandgap illumination reduces the photoconductivity induced by above-bandgap background light. This effect provides a valuable method for investigating the photoelectronic properties of semiconductor defects, such as deep energy levels and trapping mechanisms. Furthermore, it demonstrates potential for infrared photodetection at energies significantly below the semiconductor bandgap.

We observed the quenching of the photocurrent in $CdGa_2S_4$ single crystals over a secondary light beam energy range of 0.62 - 2.49 eV. Figure 1 illustrates the optical quenching of the photoconductivity as a function of the secondary light wavelength at room temperature, measured at a constant secondary light intensity. In the Figure, $I_{int.}$ represents the constant background photocurrent - the steady-state current flowing through the crystal when illuminated solely by fixed-intensity, above – bandgap light.

Measurements of the spectral distribution of the quenching effect indicate the presence of energy levels above the valence band, which are attributed to the optical quenching mechanism. The phenomenon is strongly dependent on the energy of the quenching light. As shown in Figure 1, the optical quenching spectrum of $CdGa_2S_4$ is complex, consisting of three distinct quenching bands extending from 0.62 - 0.89 eV, 0.89 - 1.25 eV, and 1.57 - 2.49 eV. A prominent quenching maximum is observed at approximately 2.05 eV. The three observed regions in the optical quenching spectrum suggest that two distinct sensitizing centers participate in recombination processes in $CdGa_2S_4$ single crystals. Based on the long-wavelength edge shown in Figure 1, the energy level of one sensitizing center was determined to be E^o_{vr} = 0.89 eV above the valence band maximum. While optical quenching was also observed in the 0.6 - 0.89 eV range, limitations in the experimental setup–specifically the spectral range of the monochromator - prevented the determination of the exact long-wavelength edge for this specific region.

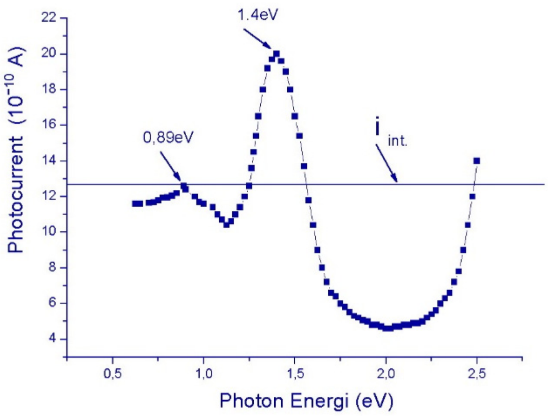

Figure 1. Quenching of the photocurrent (I_{ph}) as a function of the photon energy of the secondary light. The horizontal line ($I_{int.}$) represents the steady-state photocurrent excited solely by above-bandgap illumination in the absence of quenching light (T = 300 K)

As with other semiconductor materials, the photoelectronic and luminescent properties of $CdGa_2S_4$ are significantly influenced by deep centers, which are classified as either trapping or recombination centers. The optical quenching of photoconductivity in $CdGa_2S_4$ single crystals can be explained by the presence of "fast" recombination centers (Class I centers according to the Rose model [19]) and "slow" photosensitizing recombination centers (Class II centers), as well as t-level traps located within the bandgap. Optical quenching of photoconductivity in n-type $CdGa_2S_4$ crystals indicates the presence of hole traps, as only hole-capturing centers in n-type materials can trigger a reduction in photocurrent. When the crystals are illuminated solely with above-bandgap light, free electrons and holes are generated, resulting in steady-state (stationary) photoconductivity. As a result of the redistribution of electrons and holes between the levels of fast and slow recombination centers, the photosensitivity of the crystal increases.

Upon secondary illumination with energy corresponding to deep acceptor levels, electrons are excited from the valence band to these acceptor (hole trap) levels. This process effectively releases holes into the valence band, which then recombine with electrons, either directly from the conduction band or via other fast recombination centers. This redistribution reduces the electron lifetime in the conduction band of $CdGa_2S_4$.Ultimately, both processes reduce the free electron density, resulting in the observed quenching of photoconductivity.

It should be noted that, in addition to the optical quenching spectrum of photoconductivity clearly pronounced impurity photoconductivity band with a maximum of 1.4 eV was observed 1.06 - 1.57 eV energy range. This indicates that interpreting the spectral distribution of the optical quenching requires accounting for the simultaneous ionization of several types of local centers. A study of the transient characteristics of this quenching reveal that the rate of extinction depends on the wavelength and intensity of the secondary light. Figure 2 illustrates the transient characteristics of the photocurrent optical quenching in $CdGa_2S_4$ at 300 K.

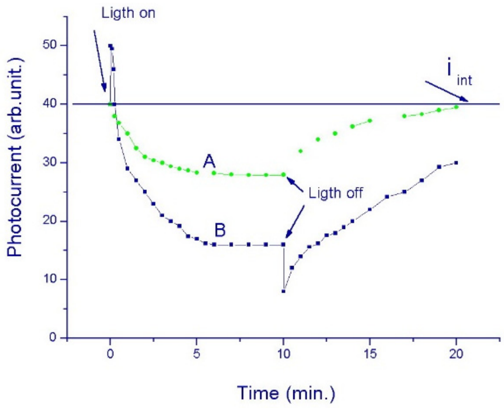

Figure 2. Transient characteristics of the optical quenching of $CdGa_2S_4$ crystals (A) hν < 1.06 eV and (B) hν > 1.06 eV

It can be observed that when the sample is excited by light in the hν < 1.06 eV region, only photocurrent quenching occurs (Curve A). This implies that, at these energies, electrons transition from the valence band to the photoconductivity-sensitizing centers. When the light is switched off, photocurrent recovery processes begin, and the photoconductivity gradually returns to its pre-quenching level. In $CdGa_2S_4$ crystals, “flare-up” transitions in the photocurrent are detected under the influence of secondary light exceeding 1.06 eV. When illuminated with monochromatic light in the hν > 1.06 eV region, the photocurrent initially increases sharply passing through the maximum before decreasing to an equilibrium value (Figure 2, Curve B). The initial increase in photocurrent is attributed to the generation of carriers from local levels into the conduction band, whereas the subsequent decrease results from the transfer of holes from the photoconductivity-sensitizing centers to the valence band. In a certain spectral range, excitation dominates over the quenching caused by the same photons. Consequently, a maximum appears at 1.4 eV in the optical quenching spectrum. In this case, the unique nature of the photocurrent transient characteristics can be utilized to separate the simultaneous effects of quenching and stimulation. At photon energies hν > 1.06 eV, the magnitude of the “flare-up” increases with the energy of the secondary radiation. This suggests the presence of a donor level with an activation energy of 1.06 eV located below the conduction band. Consequently, the band gap of $CdGa_2S_4$ single crystals contains sensitizing centers at $E_v + 0.89$ eV and donor levels at $E_c - 1.06$ eV, both of which are highly active in carrier generation and recombination.

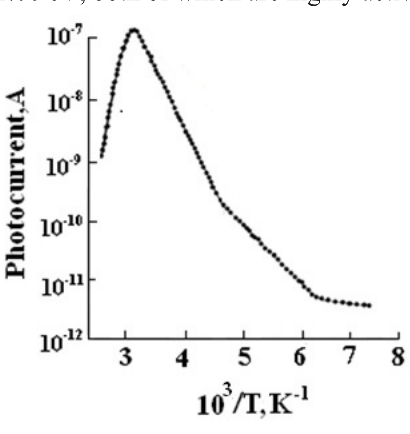

Figure 3. Temperature dependence of the photocurrent in $CdGa_2S_4$ single crystals

Valuable information regarding localized states can be obtained by studying the temperature dependence of the above-bandgap photocurrent, $I_{ph}(T)$. We present the results of our investigation into the temperature dependence of the photocurrent in $CdGa_2S_4$ within the range of 110 - 400 K (Figure 3). As shown, the photocurrent increases exponentially with temperature until reaching a maximum at T_m = 300 K, beyond which the photocurrent begins to decrease.

The decrease in photocurrent at temperatures above 300 K can be attributed to thermal quenching, which stems from a shift in the behavior of sensitizing centers. Specifically, thermal quenching occurs when these centers transition from acting as recombination centers to acting as traps. As the temperature rises at a fixed intensity, a threshold is reached where minority carriers (holes) are thermally released from trapping levels into the valence band. This increases the density of free holes, which are then rapidly captured by deep recombination centers. This process facilitates the recombination of free electrons and holes, effectively reducing the overall photocurrent. This process shortens the lifetime of the majority carriers (electrons), leading to the decrease in photocurrent observed in Figure 3. The plot of log (I_{ph}) vs. 10^3/T shows two distinct regions. In the low–temperature region (150 K < T < 240 K), the photocurrent increases more slowly than in the high-temperature region (240 K < T < 300 K). This increase in photocurrent in $CdGa_2S_4$ is characterized by two exponential sections with thermal activation energies of 0.21 eV and 0.42 eV (electron mobility rises slightly with rising temperature).

Investigation of the spectral distribution of photoconductivity in $CdGa_2S_4$ revealed four maxima at energies of 1.65, 2.25, 2.55, and 2.95 eV [13]. Kerimova et al. determined that the luminescence spectrum of $CdGa_2S_4$ consists of four bands: 1) blue, with a maximum at 2.8 eV, observed at low temperatures; 2) yellow-green, consisting of three elementary bands with maxima at 2.5 eV, 2.37, and 2.2 eV; 3) red, two closely spaced bands with maxima at 2.03 and 1.94 eV; and 4) infrared, a maximum at 1.42 eV, which appears at low temperatures [14].The presence of these diverse energy levels within the band gap of $CdGa_2S_4$ may be ascribed to native structural defects, such as cadmium (Cd), gallium (Ga) and sulfur (S) interstitials or vacancies. $CdGa_2S_4$ single crystals contain a high concentration of native defects (approximately 10^{21} sm^{-3}). Additionally, antisite defects may arise from the interchange of atoms Cd_{Ga}, and Ga_{Cd} within the cationic sublattice. In our opinion, the possibility of cation interchange is due to the similar electronegativity values of cadmium (1.7 eV) and gallium (1.6 eV). Because stoichiometric voids are periodically arranged within the lattice, they do not create localized levels. However, the samples were grown using iodine as a transport agent, and its concentration can be quite high (reaching ~10^{19} cm^{-3} in $ZnIn_2S_4$, for example). By considering the influence of deviations from stoichiometric composition on sample properties, the intrinsic defect nature of deep centers in $CdGa_2S_4$ crystals has been established [13]. The intensity of the blue band increases when the crystals are enriched with cadmium atoms, a phenomenon attributed to the presence of interstitial cadmium (Cd_{int}). In $CdGa_2S_4$, these interstitial atoms form donor levels with an activation energy of approximately 0.2 eV [14]. According to [14], the blue luminescence band originates from an electronic transition from these donor levels to the valence band.

The authors of Ref. [13] suggest that the local level located 1.65 eV below the bottom of the conduction band is associated with Ga_{Cd} antisite defects. In our opinion, these centers act as fast recombination centers within the $CdGa_2S_4$ crystal lattice.

CONCLUSIONS

The optical quenching and temperature dependence of the photocurrent in $CdGa_2S_4$ single crystals were investigated. Local energy levels were identified at E_c - 0.21eV, E_c - 0.42 eV, E_c - 1.06 eV, and E_v + 0.89 eV, which are attributed to the presence of intrinsic (native) defects within the $CdGa_2S_4$ lattice. The temperature dependence of the photocurrent exhibits a maximum at 300 K. The subsequent decrease in photocurrent at temperatures above 300 K is explained by the thermal quenching of photoconductivity. Both optical and thermal quenching are attributed to the redistribution of carriers between photosensitizing and recombination centers.

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ФОТОЕЛЕКТРОННІ ВЛАСТИВОСТІ МОНОКРИСТАЛІВ $CdGa_2S_4$

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Було проведено експериментальні дослідження фотоелектричних властивостей монокристалів $CdGa_2S_4$. У дослідженні вивчали температурну залежність фотоструму (в діапазоні 110 – 420K), а також спектральну залежність та перехідні характеристики оптичного гасіння при T = 300 K. Оптичне гасіння фотоструму спостерігалося в діапазоні енергій вторинного світлового пучка 0,6 – 2,49 еВ. Вимірювання виявили енергетичні рівні при Ec – 0,21 еВ, Ec – 0,42 еВ та Ec – 1,06 еВ, а також сенсибілізуючі рівні при Ev + 0,89 еВ. Зменшення фотоструму при температурах вище 300 K пояснюється термічним гасінням. Як оптичне, так і термічне гасіння фотопровідності в кристалах $CdGa_2S_4$ пояснюється змінами зарядового стану та динаміки обміну сенсибілізуючих та рекомбінаційних центрів.

Ключові слова: *тіогалат кадмію; фотопровідність; дефекти; глибокі рівні; сенсибілізуючі центри; рекомбінаційні центри; оптичне гасіння; термічне гасіння*