

PHOTOLUMINESCENCE IN CdGa₂S₄ SINGLE CRYSTALS

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Abstract

Long wavelength photoluminescence in CdGa₂S₄ single crystals was studied at 10 K. Novel bands were found out associated with donor-acceptor recombination. Interpretation was performed taking into account the data obtained earlier.

Introduction

A growing interest in CdGa₂S₄ compound is determined by its unique properties. It is a wide-band semiconductor ($E_{g\text{ opt}} = 3.71$ eV at 10 K) with high photosensitivity and bright photoluminescence (PL), cathodoluminescence (CL), and X-ray luminescence (RgL) [1-3], which also exhibited birefringence, optical isotropic point, and stimulated radiation with its maximum at 2.1 eV ($T = 80$ K) [1, 4-6]. These properties give evidence that the material is promising for the development of narrow-band tuned optical filters, electrooptical modulators, and lasers on its basis. However, CdGa₂S₄ radiation properties in some peculiar ranges were not virtually investigated.

In the present paper results are presented related to the investigation of photoluminescence (PL) at the temperature of 10 K in the wave range of 400 – 900 nm.

Experimental

CdGa₂S₄ single crystals were grown using a standard Czochralski method without special doping. For PL measurements, the samples were chosen and mechanically treated to form platelets. Photoluminescence spectra were registered using a conventional method with resolution of ± 2 nm at laser excitation ($\lambda = 354$ nm).

Results and discussion

Photoluminescence spectra measured using the crystal face $[1\bar{1}2]$ are shown in Fig. 1. The spectrum contains an intensive red band centered at $\lambda = 710$ nm with its halfwidth $\Delta h\nu = 0.36$ eV ($T=10$ K). Moreover, weak bands at 450 and 510 nm were observed. Taking into account all mentioned above, we can classify the observed features as long wavelength peculiarities, i.e., those generated by transitions in the limits of the forbidden gap. According to the data related to cathodoluminescence (CL) [6], a blue-green band (450 nm) appears owing to the excess of cadmium atoms and their associates in the samples. This is confirmed by the fact that its intensity becomes weaker after the annealing of crystals. According to

data [7], an intensive red band (710 nm) is linked with sulfur vacancies. Analysis of the results on photoconductivity, photoluminescence, cathodoluminescence, X-ray luminescence, and thermostimulated conductivity presented in [1-7] gives evidence that the donor-acceptor mechanism of radiative recombination plays a decisive role in CdGa_2S_4 and related compounds. To this end, the observed photoluminescence bands are evidently generated owing to the donor-acceptor recombination of pairs.

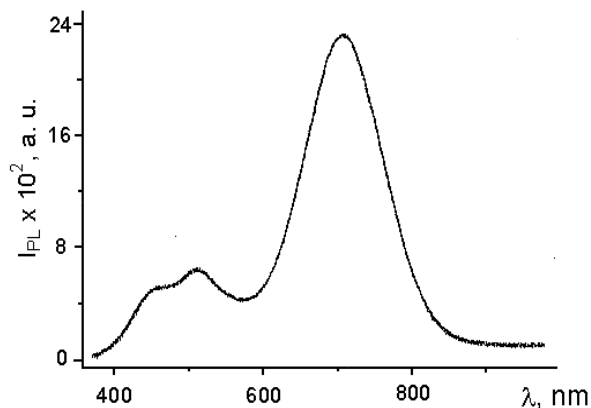


Fig. 1. Photoluminescence spectrum of CdGa_2S_4 single crystals at $T = 10$ K.

A quasi-continuous distribution of electron traps in the range of 0.25 – 0.38 eV below the conduction band bottom, three donor levels at various depth, and two acceptor levels were found. The blue-green band of photoluminescence can be associated with the electron transition from E_c to the acceptor level r_2 . The nature and quantity of levels are more variable in these compounds than in elementary and binary compounds. The main peculiarities are summarized in Table 1.

Generation of main bands (except that shown in the first line, which refers to the inter-band recombination $E_c - E_v$) was elucidated using the model of localized states involving a quasi-continuous distribution of traps in the range from $E_c - 0.24$ eV to $E_c - 0.37$ eV, a donor level $E_c - 0.65$ eV, and acceptor recombination levels $E_v + 0.65$ eV and $E_v + 1.15$ eV. This model allows us to explain in a general way the changes in the photoluminescence spectra dependent on the experimental conditions.

Table 1. Parameters of photoluminescence bands in CdGa_2S_4 .

Method of preparation	Type of luminescence	Luminescence peak, eV	$\Delta h\nu$, eV	T, K	Reference
Melting solution	CL	3.80	0.45	80	[11]
- " -	- " -	3.19	-	80	[11]
Chemical transport reaction	RgL	2.14	0.2	290	[3]
Grown from melt	PL	2.12	0.33	290	[7]
Chemical transport reaction	PL	2.30	0.45	290	[7]
- " -	CL	2.05	-	- " -	[1]
- " -	- " -	2.34	-	- " -	[1]
Grown from melt	PL	1.75	0.36	10	Present paper
- " -	- " -	2.76	-	10	- " -
- " -	- " -	2.43	-	10	- " -

The role of ions in CdGa₂S₄ determined as a result of the EPR studies was described in [8, 9]. The spectra showed the tetragonal symmetry. It was found that Mn²⁺ ions substitute Cd²⁺ in the cation sublattice where they are situated in an axially distorted tetrahedral neighboring of S²⁻ anions. The Cr²⁺ ions occupy one of tetrahedrally coordinated cation positions. In/CdGa₂S₄ barriers and H₂O/CdGa₂S₄ photoelectrochemical cells were described in [10]. On the basis of this research a conclusion was made that it is possible to use these structures as radiation converters.

Conclusion

A long wavelength photoluminescence in CdGa₂S₄ single crystals was studied at the temperature of 10 K. A set of peaks was revealed, which were associated with a donor-acceptor recombination. The interpretation was proposed taking into account the data obtained earlier, as well.

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