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OPTICAL PROPERTIES OF COMPOUNDS WITH SUBMICRON POINTS OBTAINED THROUGH Ga_2S_3 INTERCALATION WITH Cd

Racoveţ O.[1], Evtodiev I.[1*], Caraman Iu.[2], Rotaru I.[1], Lazăr G.[2]
Moldova State University, 60, Alexei Mateevici str., Chisinau, MD-2009, Republic of Moldova
"Vasile Alecsandri" University of Bacau, 157, Calea Marasesti, Bacau, 600115, Romania
*e-mail: ievtodiev@yahoo.com

Luminescence and optical absorption spectra of Ga_2S_3 single crystals were investigated at temperatures of 78 K and 293 K. Optical band gap is equal to 3.27 eV and 3.457 eV at 293 K and 78 K respectively. Luminescence spectrum of single crystal lamellas at temperature of 78K consists of three bands with peaks at 2.04 eV, 1.84 eV and 1.66 eV. Native structural defects form deep recombination and electronic capture levels localized within the Ga_2S_3 band gap.

Keywords: Ga_2S_3, single crystals, intercalation, photoluminescence, absorption.

Au fost obţinute spectrele de luminiscenţă şi absorbţie ale monocristalelor Ga_2S_3 la temperaturi de 78 K şi 293 K. Banda optică interzisă are mărimea de 3,27 eV la 293K şi 3,457 eV la 78 K. Spectrul de luminescenţă al peliculelor monocristalaluluipentru temperatura de 78 K este format din trei benzi cu valorile maxime de 2.04 eV, 1.84 eV şi 1.66 eV. Defectele structurale proprii iniţiază formarea nivelelor de recombinare şi captare de electroni, localizate în interiorul benzii interzise.

Cuvinte-cheie: Ga_2S_3, monocristale, intercalare, fotoluminescenţă, absorbţie.

INTRODUCTION

Interest towards $A_2^{III}B_3^{VI}$ semiconductors, which are still little studied, has increased with appearance of papers demonstrating that compounds of this group may have technical applications in various fields of optoelectronics, photonics and interferential optics [1 - 6].

Ga_2S_3 belongs to the class of materials with native structural defects Ga_2S_3, which are less investigated. High concentration of native structural defects determines the physical properties of this material, and primarily, the low electrical conductivity. Being a semiconductor with wide band gap, Ga_2S_3 is characterized by strong photoconductivity in the blue-violet region of the spectrum [7, 8]. $\beta - Ga_2S_3$ has wurtzite-type structure with cell parameters: α = 3,678Å, c = 16,018 Å [9, 10]. Due to specific structural bonds, single crystals of $\beta - Ga_2S_3$ can be easily split in the perpendicular direction to the *C* axis. Ga_2S_3 is considered a prospective material for various technological applications: neutral layer heterojunctions [4, 5, 11], optical and optoelectronic applications [12, 13], photovoltaic structures [14, 15] and luminescent screens [16, 17]. In recent years, the attention of researchers is focused on radiative properties of gallium sulphide doped with Mn^-, Ag^-, Cu^-, *Ge* şi *Sm* [19-21]. These dopants form deep recombination levels and luminescence centers related to vacancy of metal sublattice.

Fundamental band edge absorption (*AO*) spectra and photoluminescence (*PL*) spectra of Ga_2S_3 compound intercalated with *Cd* in vapor phase are analyzed in the paper.

EXPERIMENTAL METHODS

PL and *AO* spectra were measured for plan-parallel plates of Ga_2S_3 and Ga_2S_3 intercalated with *Cd* in vapor phase. Optically homogeneous Ga_2S_3 single crystal layers with 2…8 mm^2 area and thickness varied from ~50 µm to 1…2 mm, were obtained using I_2 vapor transport at normal atmospheric pressure. As transport material, single crystals grown by Bridgman method from primary elements of *Ga* (4N) and S in stoichiometric proportions were used. Optically transparent plates of $\beta - Ga_2S_3$ with perfect surfaces were grown at temperature gradient of ~20^o cm^{-1}. Single crystal plates of $\beta - Ga_2S_3$ were intercalated with *Cd* from vapor phase by means of heat treatment at T = 500 K for 6 h.

Photoluminescence at 78 K and 293 K was registered for single crystal layers of Ga_2S_3 with the optical axis (C_6) perpendicular to the sample surface. *Cd* excess was evaporated from the Ga_2S_3 plate surface by heat treatment in vacuum at temperatures of 400…420 ^oC for 30 min.

The spectral characteristics of *AO* and *PL* spectra were registered using a spectrophotometer assembled on MDR-2 monochromator with diffraction grating (1200 mm^{-1} and 600 mm^{-1}). As a light source for optical measurements (transmission and reflection) at temperature of 293 K, a lamp with W filament was used. Photoluminescence was excited with He - N_2 laser radiation (λ= 337,4 nm). Excitation radiation density was varied using neutral density filters (thin layers of *Pt* on amorphous quartz supports).

EXPERIMENTAL RESULTS

Absorption spectra of $\beta-Ga_2S_3$ single crystals with hexagonal crystalline structure are shown in Figure 1 at 78 K (curve 1) and 293 K (curve 2). Two pronounced sectors with slopes of 3,15…3,20 eV and 3,33…3,35 eV are manifested on the line of $\alpha(h\nu)$ dependence at *T*=293 K. The second sector probably corresponds to the direct optical transitions between the valence band (VB) top and conduction band (CB) bottom. Fundamental band edge absorption in Ga_2S_3 crystals at 293 K is located in the energy range of 3,32…3,36 eV. Extrapolating linear segment of the $f(h\nu)$ dependence at $\alpha \to 0$, it was appreciated the width of band gap of $\beta-Ga_2S_3$ crystals equal to 3,27 eV. Relatively high values of absorption coefficient in the region of 3,20…3,33 eV are caused by the interaction of photon-electron-phonon type.

At low temperatures (Figure 1, curve 1), two narrow absorption lines are manifested at 3,48 eV and 3,42 eV. Rapid decrease of these bands intensity with increasing temperature indicates the excitonic nature of these lines. Considering the excitons in $\beta-Ga_2S_3$ crystals with structural defects as having large radii (Vanier Mott excitons), the binding energy of the electron-hole pair is estimated to be equal to 72 meV, width of band gap is equal to 3,475 eV at *T*=78 K.

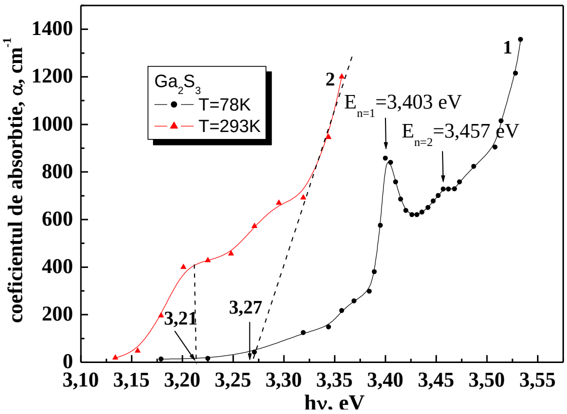

Fig. 1. $\beta-Ga_2S_3$ single crystals absorption spectra at 78 K (curve 1) and 293 K (curve 2).

Photoluminescence spectrum of $\beta-Ga_2S_3$ crystals at *T*=78 K (Fig. 2) consists of a dominant intensity band at 1,873 eV and a low intensity one with maximum at 2,84 eV. Since Ga_2S_3 crystals are of *n*-type, energy of levels corresponding to these *PL* bands can be equal to 0,43 eV and 1,40 eV above the valence band maximum.

Relatively large width of the dominant *PL* band and the lack of vibrational structure indicates a strong phonon emission. *PL* band half-width in the temperature range of $80 \div 293K$ weakly depends on temperature (increases by about 30 meV), which is in good correlation with the Debay temperature ($\theta \approx 280K$).

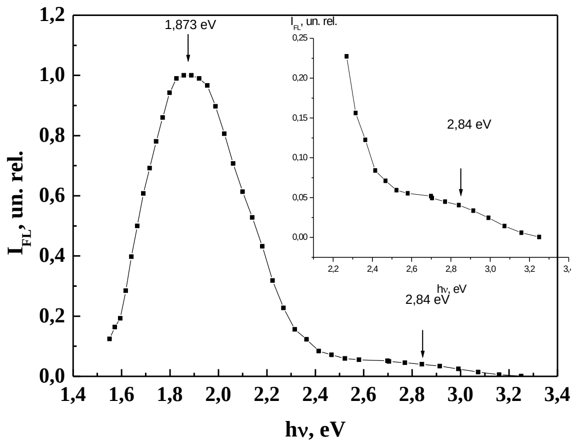

Fig. 2. Photoluminescence spectra of Ga_2S_3 single crystal at 78K.

If we admit that the luminescence is caused by radiative transitions of electrons from the conduction band to deep acceptor levels, then the energies of these two levels of recombination (electron-hole) are found at 0,72 eV, and, respectively, at 1,62 eV above the valence band maximum.

Currently, there is no well-argued theory regarding the energy states of intrinsic and dopant electros. But analyzing the obtained results for two limiting cases, the strongly doped semiconductors [4, 5] and amorphous semiconductors [6], we can admit that the electronic bands on the edge of Brillouin band are easily curved, entering the band gap. Thus, optical transitions can occur between the *VB* and *CB* tails. Relatively high absorption coefficient in the middle slope can be explained by the presence of these absorption mechanisms.

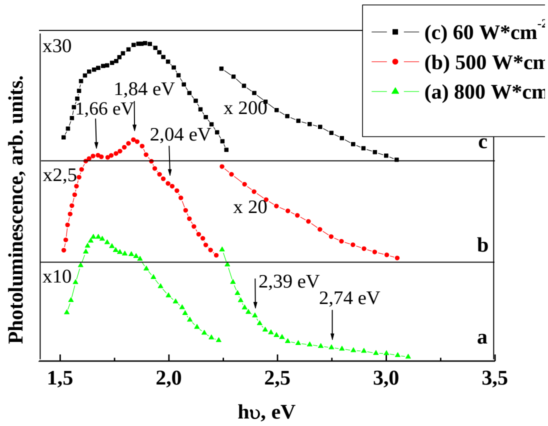

Fig. 3. Photoluminescence spectra of Ga_2S_3 single crystal layers (*d*=58 μm) at temperature 78 K for various excitation densities.

Further, we analyze the the photoluminescent properties of Ga_2S_3 single crystal plates with thickness of 58 µm. *PL* spectra at three excitation densities (800 W/cm^2, 500 W/cm^2 and şi 60 W/cm^2) of Ga_2S_3 single crystal plates at 78K are shown in Fig, 3. As we can see, PL spectra cover the wide range of energies from 1,5 eV up to 3,1 eV. *PL* intensity slowly increases in the range of absorption band edge, which, as noted above, may be determined by electronic transitions between the energy bands tails. The low intensity of photoluminescence is probably caused by high probability of non-radiative transitions between these states.

The intensive luminescence begins at energies less than 2,5 eV. Starting with the energy of 2,5 eV, *PL* increases rapidly irrespective of excited beam density and reaches the maximum value at 1,84…1,95 eV. The *PL* band in this spectral region is due to overlapping of three *PL* bands with maxima at 2.04 eV, 1.84 and 1,67…1,65 eV. As we can see, comparing the curves a, b and c (Fig. 3), the intensity of this band depends ambiguously on the excitation beam intensity. Peculiarities at 2,39 eV and 2,74 eV (Fig. 3) are determined by the presence of two acceptor levels localized at 0,92 eV, and, 0,47 eV respectively above the valence band edge [7].

PL spectra of Ga_2S_3 single crystals subjected to the heat treatment at 480 °C for 6 h in *Cd* vapors are shown in Fig. 4, a. Energy of PL bands, as well as probable interpretation of the PL spectrum structure are presented in the Table.

Particles energy in absorption and luminescent spectra of Ga_2S_3 and Ga_2S_3:*Cd* single crystals.

Compound	Optical band gap E_g, eV		Luminescence, arb. unit.					
	293 K	78 K						
Ga_2S_3	3.27	3.457	B_1	B_2	B_3	B_4	B_5	
			2.74	2.39	2.04	1.84	1.66	
Ga_2S_3 tratat în vapori de *Cd*			A_1	A_2	A_3	A_4	A_5	A_6
			2.92	2.75	1.90	1.76	1.64	1.38

The *PL* integral intensity of the dominant band ($h\nu \approx 1{,}83 eV$) decreases by more than 5 times in the temperature range from 78 K up to 293 K (room temperature). The temperature quenching of the dominant *PL* band with a maximum in the region of 1,64…1,76 eV is shown in Fig. 4, b. As one can see, the *PL* intensity (L) of Ga_2S_3 crystals intercalated with *Cd* is well described by the formula:

$$L = L(0)\left(1 + \exp\frac{\Delta E}{kT}\right) \qquad (1)$$

where *ΔE* is the energy of temperature quenching of photoluminescence, L(0) is *PL* intensity at *T*=0K, K is the Stefan-Boltzmann constant.

The *PL* intensity decreases by exponential law with the factor of 60 meV in the temperature range of 79…293 K, and this quenching is stronger at higher temperatures, the exponent factor being 100 meV. Thus, in Ga_2S_3 crystals intercalated with *Cd*, the thermal activation energy for orange band is 60 meV and 100 meV.

The *PL* spectra of Ga_2S_3 crystals at excitation densities from 60 W/cm^2 to 800 W/cm^2 are presented in Fig. 5. As one can see, the *L(W)* dependence may be described by a power law of type:

$$L \propto W^p \qquad (2)$$

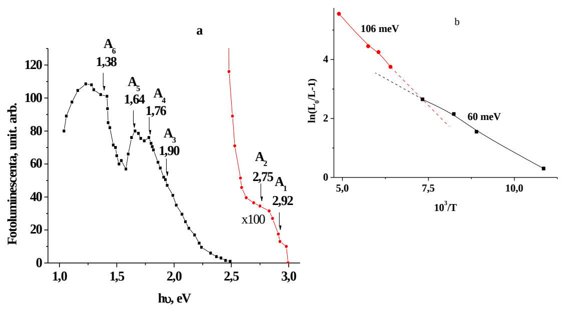

Fig. 4. Photoluminescence spectra of Ga_2S_3 single crystals intercalated with *Cd* (a) and temperature quenching of the dominant *PL* band with a maximum in the region of 1,64…176 eV (b).

The *p* index is a photoluminescence kinetics characteristic, which can be found from Fig. 5. This parameter is equal to 0.9 and 1,0 for 2,04 eV and 1.84 eV bands respectively, that indicates that these bands are due to monomolecular kinetic processes. The *p* parameter is equal to 1,4 for 1,65 eV band and this band is of recombination nature.

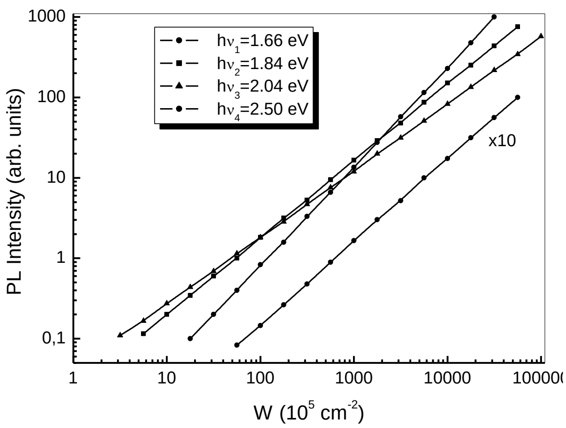

Fig. 5. The dependence of *PL* intensity, *L*, on excitation density power, *W*, for single crystal layers of Ga_2S_3.

From the analysis of the absorption and photoluminescence spectra at temperature 78 K and 293 K, as well as temperature quenching, the diagrams of possible radiative energy transition in Ga_2S_3 and Ga_2S_3 crystals intercalated with *Cd* were elaborated (Fig. 6).

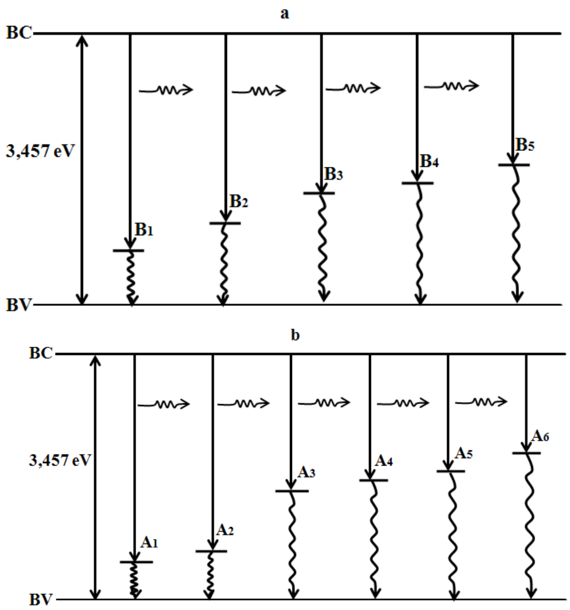

Fig. 6. Diagram of recombination levels in Ga_2S_3 (a) and Ga_2S_3 crystals intercalated with *Cd* (b) at temperature of 78K.

CONCLUSIONS

Heat treatment of single crystals in *Cd* vapors at temperature of 480 °C changes the diagram of levels of recombination luminescence. *Cd* atoms intercalated in Ga_2S_3 form recombination deep levels with energy of 0,72 eV and 1,62 eV.

The diagram of radiative levels within the band gap of Ga_2S_3 compound, formed as a result of heat treatment in *Cd* vapors at temperature 480 °C, was elaborated.

It was established that direct optical transitions in single crystal layers of $\beta - Ga_2S_3$ take place both at the temperature of 78 K and 293 K. The band gap energy is equal to 3,27 eV at temperature of 293 K, and 3,457 eV at 78 K.

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