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Luminescence of crystals ZnSe ⟨Al⟩:Gd

V.P. Makhniy[1], N.D. Vakhnyak[2], O.V. Kinzerska[1,*], I.M. Senko[1]

[1] *Yu. Fedkovych Chernivtsi National University, 2, Kotsyubinskogo str., 58012 Chernivtsi, Ukraine*

[2] *V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 41, prosp. Nauky, 03680 Kyiv, Ukraine*

[*] *E-mail*: *oksanakinzerska@gmail.com*

Abstract. It has been experimentally shown that the luminescence spectra of ZnSe ⟨Al⟩ crystals doped with Gd from the vapor phase contain two mutually compatible luminescence bands. It is established that the low-energy G-band is due to recombination with association of complexes $\left(V''_{Zn}Al^{\bullet}_{Zn}\right)$ and $\left(V''_{Zn}V^{\bullet}_{Se}\right)$, and the boundary B-band is the result of annihilation of excitons and interband transitions.

Keywords: zinc selenide, luminescence, point defects, associates.

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1. Introduction

One of the interesting and important consequences of doping the semiconductors with rare-earth elements (REE) is the so-called cleaning effect, which causes a significant decrease in the background concentration of impurity defects in many materials. These include, first of all, Ge, Si and III-V compounds, the behavior of REE in them is currently studied in details, and the results are successfully used in technologies of creating the materials themselves and devices on their basis [1]. Proceeding from this, it seems quite attractive to realize the cleaning effect in wide-band II-VI compounds, bulk crystals of which contain a significant number of eigen-type and uncontrolled impurity point defects of different kinds. It is believed [2] that it is precisely in combination with self-compensation processes, which are the main obstacles to obtain these perspective optoelectronic devices based on semiconductors with the necessary properties. Significant weakening of these factors can be achieved by choosing the right kind of method for doping REE of a particular material and conducting appropriate research, the number of which for wide-area II-VI is rather limited. However, the authors have experimentally shown that doping the ZnSe crystals by the Yb admixture in the growth process [3] or annealing in the Bi+Yb or Zn+Yb [4, 5] melting processes not only results in a decrease in the concentration of background impurities, but also in a substantial increase in the intensity of exciton radiation. Later, a similar effect was observed in immobilized (ZnSe) and doped Al (ZnSe ⟨Al⟩) zinc selenide substrates with introduction of Yb impurities by diffusion from the vapor phase [4, 5]. In this work, the effect of the gadolinium REE on the luminescence properties of ZnSe ⟨Al⟩ crystals was investigated for the first time.

2. Results and discussion

The base pads were plates cut from a bulk molten crystal of zinc selenide doped with Al during growth. Technology of processing the basic ZnSe ⟨Al⟩ and the method of their doping with Gd (ZnSe ⟨Al⟩:Gd) as well as the research methodology are similar to those described in [7].

First of all, we note that doping Gd causes appearance of a boundary B-band of luminescence, which is not observed in the basic samples ZnSe ⟨Al⟩ at any level of excitation L. Instead, in contrast to the admixture of Yb [6, 7], gadolinium does not lead to complete "extinction" of the low-energy G-band (Fig. 1), which, according to [8], is caused by associatives. They include negative two-charge vacancies of zinc (acceptors $E_a \approx 1.2$ eV) and positive single-charge donor centers $Al^{\bullet}_{Zn}$ as well as vacancies of selenium $V^{\bullet}_{Se}$ with $E_d \approx 0.03$ eV.

The contribution of each of the associates $\left(V''_{Zn}Al^{\bullet}_{Zn}\right)$ and $\left(V''_{Zn}V^{\bullet}_{Se}\right)$ to formation of the G-band is defined by many factors, namely: the concentration of Al in the melt, conditions of annealing of ZnSe ⟨Al⟩ crystals in zinc, mode of cooling, temperature during measurements, level of excitation, *etc*. Instead, in the used substrates ZnSe ⟨Al⟩ the low-energy band remains dominant over the entire range of L variation. Doping the

base crystals with Gd leads to a significant transformation of the photoluminescence (PL) spectrum, which is the consequence of the rearrangement of the ensemble of proper and admixture point defects. It consists mainly of redundant Gd atoms in vacancies of zinc, since the annealing components and regimes are chosen in such a way as to ensure that the impurity atoms enter the cation sublattice [7].

The mentioned process causes a decrease in the concentration of associates $\left(V''_{Zn}Al^{\bullet}_{Zn}\right)$ and $\left(V''_{Zn}V^{\bullet}_{Se}\right)$, although small donor centers Al_{Zn} and V_{Se} are free of them, they cannot only increase the electron conductivity of the samples but also participate in formation of edge radiation.

Confirmation of this lies in appearance of the edge B-band in the spectrum of PL, the nature of which we consider in more detail.

First of all, pay attention to the large half-width of this band ($\Delta\hbar\omega_{½} \sim kT$), which indicates its complex structure and manifests itself in the differential spectra of radiation N'_{ω}, Fig. 1.

Intersection of the curve *2* with the energy axis corresponds to the position of the maximum $\hbar\omega_m^B$ of the edge band, and the perimeter is consistent with the width of the band gap E_g = 2.7 eV in zinc selenide at 300 K [2, 3]. We note that the difference $E_g - \hbar\omega_m^B$ in the given conditions of excitation is ~0.02 eV and is close to the ionization energy of shallow donor centers $Al^{\bullet}_{Zn}$ and $V^{\bullet}_{Se}$.

Instead, the maximum $\hbar\omega_m^B$ with increasing L decreases toward lower energies (almost to E_g at $L = 10^{16}$ photon/s), which cannot occur at recombination related with shallow levels due to weak electron-phonon interaction [9]. In addition, the intensity of the edge band depends on the degree of excitation by the power law $I_B \sim L^{1.5}$. These features are characteristic of annihilation of excitons under their inelastic scattering by free charge carriers (electrons) [10], since the studied samples have electron conductivity. Offsets $\hbar\omega_m^B$ towards smaller energies are adequately explained by an increase in the concentration of non-equilibrium electrons in the conduction band with increasing L, which enhances the probability of exciton scattering.

Emission in the range ($\Delta\hbar\omega \approx$ 2.7…2.8 eV) is caused by interband transitions, and its presence in crystals ZnSe ⟨Al⟩:Gd is due to two factors. The first of these is an increase in the concentration of equilibrium electrons in the conduction band due to the increase in the number of shallow donor centers $Al^{\bullet}_{Zn}$ and $V^{\bullet}_{Se}$, exempt from the associates $\left(V''_{Zn}Al^{\bullet}_{Zn}\right)$ and $\left(V''_{Zn}V^{\bullet}_{Se}\right)$. The second factor is the result of the cleaning effect caused by REE doping, which, however, is less effective than that for Yb. In our opinion, the most probable cause is much higher solubility of Yb atoms as compared to that of Gd, since the respective doping conditions were identical.

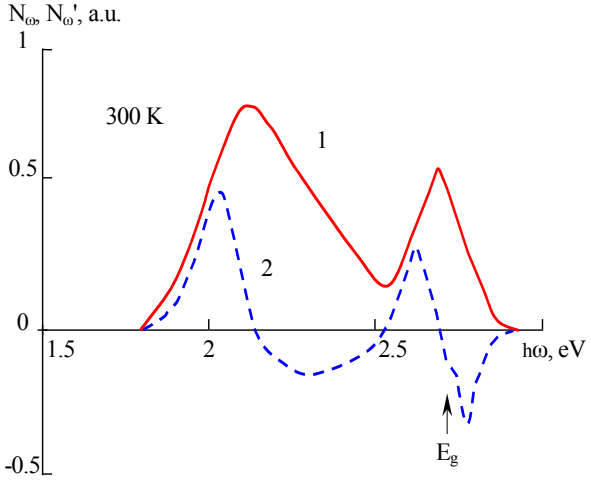

Fig. 1. Normal (1) and differential (2) luminescence spectra of ZnSe ⟨Al⟩: Gd crystals.

The described model of rearrangement of the point defect ensemble is further confirmed by a number of experimental facts. First of all, it concerns the practical equality of the values $\hbar\omega_m^G$ for the samples ZnSe ⟨Al⟩ and ZnSe ⟨Al⟩:Gd at the same values of temperature and excitation intensity L (see Fig. 2).

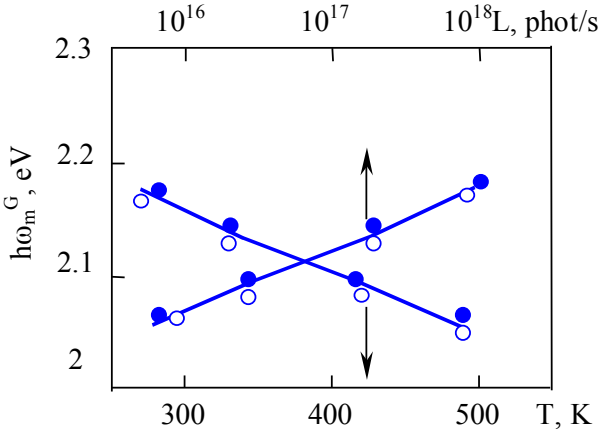

Fig. 2. Dependences of the G-band maximum position on the temperature and excitation intensity at 300 K.

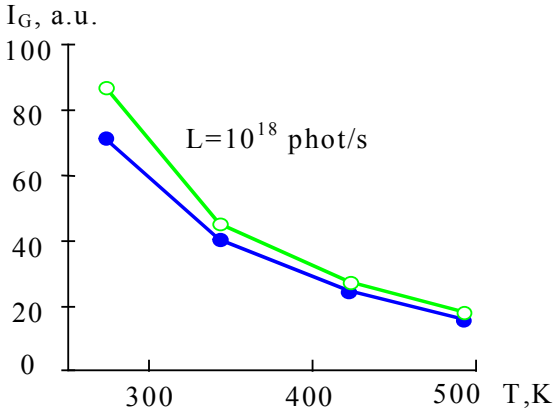

Fig. 3. Temperature dependences of the intensity of the G-band ZnSe ⟨Al⟩ (open circles) and ZnSe ⟨Al⟩: Gd (full circles).

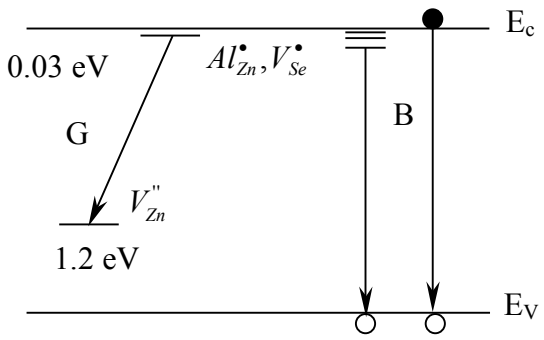

Fig. 4. Energy diagram and scheme of radiative transitions.

On the other hand, the intensity of the G-band doped with gadolinium substrates decreases in comparison with the base, although the dependences remain practically identical, Fig. 3.

The above facts suggest that identical associative centers participate in formation of the G-band in both types of samples, the concentration of which depends on the degree of filling the vacancies of zinc with Gd atoms. Analysis of the obtained results allows us to construct an energy diagram and a scheme of radiative transitions in the objects of research, Fig. 4.

At the same time, in the base substrates, recombination is dominated by the complexes $\left(V''_{Zn}Al^{\bullet}_{Zn}\right)$ and $\left(V''_{Zn}V^{\bullet}_{Se}\right)$, and in the samples with an admixture of Gd, recombination channels appear due to annihilation of excitons and interband transitions. Instead, the efficiency of the edge B-band in the crystals ZnSe ⟨Al⟩:Gd at 300 K does not exceed 5% due to competing action of the G-band.

4. Conclusions

Thus, doping the ZnSe ⟨Al⟩ crystals with the Gd admixture results in appearance of a luminescence edge band, which is comparable to that of the low-energy G-band. The presence of the latter in the samples ZnSe ⟨Al⟩:Gd is caused by incomplete filling the Zn vacancies with Gd atoms, which are part of the complexes responsible for formation of the G-band.

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Authors and CV

***Author1* A.S.:** Deinde Romae dies XXX fere Quinctius commoratur; cum ceteris quae habebat vadimonia differt ut expeditus in Galliam proficisci posset; proficiscitur. Roma egreditur ante diem II kalend.
Organization1
E-mail: hello@email.com

Author2: Deinde Romae dies XXX fere Quinctius commoratur; cum ceteris quae habebat vadimonia differt ut expeditus in Galliam proficisci posset; proficiscitur. Roma egreditur ante diem II kalend.
Organization2E-mail: hello2@email.com