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Study of the multiband exciton spectrum of ZnSe in the range of 477−490 nm

© N.K. Morozova[1], I.I. Abbasov[2], E.M. Gavrishchuk[3,4], M.A. Musayev[2],
J.I. Huseynov[5], A.J. Mammadova[6]

[1] National Research University „Moscow Power Engineering Institute“,
111250 Moscow, Russia
[2] Azerbaijan State Oil and Industry University,
AZ1010 Baku, Azerbaijan
[3] Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, BOX-75,
603951 Nizhny Novgorod, Russia
[4] Lobachevsky University of Nizhny Novgorod,
603022 Nizhny Novgorod, Russia
[5] Azerbaijan State Pedagogical University,
AZ1000 Baku, Azerbaijan
[6] Institute of Biophysics, National Academy of Sciences of Azerbaijan,
AZ1141 Baku, Azerbaijan

E-mail: MorozovaNK@mail.ru, ibrahimabbasov179@gmail.com

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The photoluminescence spectra of CVD (chemical vapour deposition) ZnSe polycrystalline grown with a large excess of selenium and containing $\{O^*_{Se}-Cu_i^+\}$ complexes at stacking faults are studied. Absorbance was measured to complement these data. The features of the PL spectra in comparison with cathodoluminescence are considered. It is shown that PL bands identical to CL are observed as somewhat shorter wavelengths. For the studied crystals, a band model is presented according to the data obtained in this work. The low-energy shift of the PL spectra with decreasing excitation energy corresponds to a shift on the energy scale of the band model with a corresponding change in the type of radiative transitions. Changes have been introduced that characterize the nature of the group of equidistant bands 477−490 nm, which are characteristic of ZnSe samples with an excess of oxygen and Se. The results can be useful for a more complete study of the structure of multiphonon exciton spectra of photo and cathodoluminescence of $A^{II}B^{VI}$ crystals.

Keywords: band model, narrow-line multi-photon spectra, exciton radiation, stacking faults, isoelectronic oxygen impurity, carrying effective negative charge.

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1. Introduction

Zinc selenide has two-side region of homogeneity. Unlike other zinc chalcogenides, it is characterized with wide area of compositions with excess of selenium ZnSe(Se) [1–5]. The luminescence of ZnSe(Se) has been little studied. In studying the spectral range of the edge spectrum there are some works [4], dedicated to study of self-activated irradiation of ZnSe(Se). For chemical vapour deposition (CVD) of ZnSe, grown with excess of selenium in gaseous phase [2,5], the unusual narrow-line multi-photon cathodoluminescence (CL) spectra were observed in exciton area (Fig. 1). Equidistant series of bands with the main series lines of 460, 477, 508 nm at 80 K were observed at low temperatures [1]. According to the analysis data, the studied crystals, despite the large excess of selenium, contained oxygen $\sim 10^{20}\,\text{cm}^{-3}$. In this case, due to the formation of complexes with the Cu_i^+ interstitial copper impurity present in CVD ZnSe as a background impurity, oxygen entered in the form of stable complexes during growth. Particularly, the authors of works [6–10], based on the band anticrossing (BAC) theory, studied the variation of ZnSe band structure depending on oxygen content.

The aim of the performed study of photoluminescence (PL) of such samples was to obtain more complete information on structures and nature of such equidistant bands. The advantage of photoexcitation is in deep penetration of excitation light into crystal volume. This differentiates the photoluminescence spectra from CL and allows to excite the spatially distributed luminescence centers.

Electromagnetic wave, appearing in volume, while passing through crystal, interacts with phonons, which energy can transfer to exciton and back, and also it is subject to scattering on phonons [11]. Due to these interactions the radiation (PL) comes out of crystal with wavelength changed compared to initial one. PL spectra and their measurements in volume currently almost unexplored.

Therefore, we studied the photoluminescence of CVD ZnSe crystals with multi-phonon spectrum of CL, known in advance (Fig. 1) [1–3].

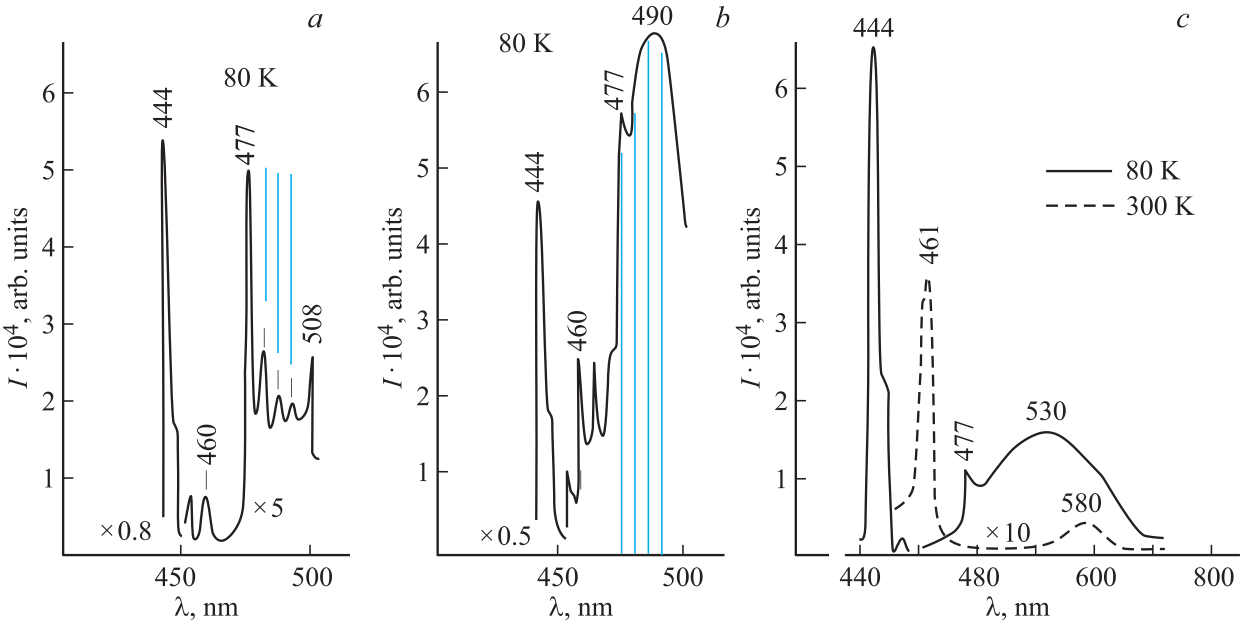

Figure 1. CL spectra of various sections of CVD ZnSe(O), heavily doped during deposition with oxygen and various doping level Se: *a* — with excess of Se, *b* — of stoichiometric composition, *c* — with some excess of Zn [1,2]. $[\mathrm{O_{Se}}] \leq 10^{20}\,\mathrm{cm}^{-3}$ (*a*), $[\mathrm{O_{Se}}] \sim 10^{20}\,\mathrm{cm}^{-3}$ (*b, c*).

2. Experimental procedure

Zinc selenide was produced using chemical vapour deposition (CVD) in the Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences (Nizhny Novgorod) [12]. Stacking faults (SF) are typical for CVD ZnSe. During growth the samples were not doped on purpose. The general impurity content was $< 10^{16}-10^{17}\,\mathrm{cm}^{-3}$. Concentration of copper background impurity was $\sim 10^{16}\,\mathrm{cm}^{-3}$. Under regular growth conditions the oxygen solubility in ZnSe(O) with excess of selenium is low — $\leq 10^{19}\,\mathrm{cm}^{-3}$ [1]. Concentration of oxygen $[\mathrm{O_{Se}}]$ in the examined crystals was $\sim 10^{20}\,\mathrm{cm}^{-3}$. With excess of selenium and oxygen on gaseous phase during growth process the isoelectronic impurity of oxygen $\mathrm{O^*_{Se}}$,carrying the effective negative charge, is included in ZnSe lattice, while capturing copper to complexes $\{\mathrm{O^*_{Se}}-\mathrm{Cu}_i^+\}$.

Using the method of quantitative X-ray microanalysis ZnSe phase composition and chemical elements distribution on the examined sample surface were defined. Analysis of the observed results shows the surface homogeneity and stoichiometry variation within the homogeneity range towards the excess of selenium.

Photoluminescence spectra (Figs. 2–4) were observed using universal fluorescence spectrometer (Fluo Time 300 Easy Tau). 300 W xenon lamp was used as excitation source. Monochromators allow to achieve the spectral resolution of up to 0.1 nm in the wide wavelength range from 200 to 1700 nm. Spectrally filtered excitation radiation from monochromator exit slit was collimated at first using a quartz lens. This structure provides high measurement rate of up to 10 million counts per second and high stable crystal-calibrated time resolution of 4 ps. All measurements were made at 300 K. PL spectra were registered from growth surface on samples with size of 4 × 4 × 3 mm.

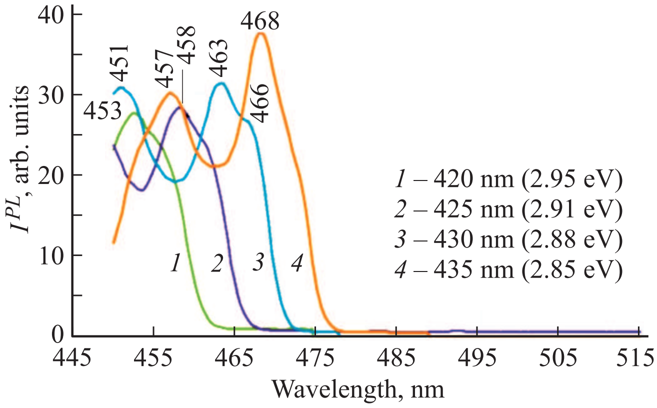

Figure 2. Photoluminescence spectra of polycrystal CVD ZnSe at excitation with various wavelengths of 420–435 nm.

UV-visible absorption spectra of polycrystal CVD ZnSe were registered using „Specord-250“ unit at 300 K (Fig. 5). Spectra (see Fig. 5) were built, including observance of linear sections, using „Excel“software. Extrapolation of linear sections to intersection with abscissa axis also reveals absorption bands. Value of forbidden band width of ZnSe at 300 K was accepted as 2.714 eV [1–3,13]. At large extension of the linear section, the extrapolation provides the better correspondence to maximum of absorption, than extrapolation of the whole absorption range.

3. Experimental results

The examined CVD ZnSe crystals with excess of selenium and concentration of $[O_{Se}] \sim 10^{20}\,\mathrm{cm}^{-3}$ are stable by means of appearing stacking faults, that segregate the oxygen centers. Figures 2–4 shows PL spectra, observed at excitation with powerful xenon lamp at Fluo Time 300 Easy unit. Spectra were made at variation of excitation energy. Time 300 unit allows to make it at variation of excitation wavelength with high accuracy.

Figures 2 and 3 show data for wavelengths of excitation light from 420 nm (2.95 eV) to 455 nm (2.72 eV) with interval, close in LO energy to ZnSe phonon of 30 meV [3,13].

At various pumping wavelengths the different photoluminescence (PL) bands are observed (Figs. 2 and 3). At the same time, the PL spectra appear, starting with excitation with energy of ~ 2.9 eV, corresponding to wavelengths of 420–425 nm. At excitation with shorter wavelengths of 400, 410, 415 nm there was no luminescence.

Initially (Fig. 2, curves *1* and *2*) PL in the region of the free ZnSe exciton — the 457-nm band. With decrease of excitation energy, its LO or 2LO phonon repetitions (463, 468 nm and others, see Figs. 2, 3), i.e. longer-wave phonon bands within multi-phonon spectrum of up to 490 nm, corresponding to CL spectrum, are added to this exciton band (Fig. 1).

With decrease of excitation light energy from initial 2.95 eV to ~ 2.8 eV in Figs. 2 and 3 the intensive band of 468 nm ($\Delta\lambda \leq 20$ meV) is distinguished (curves *4* and *2* in Figs. 2 and 3, respectively). With excitation variation the phonon repetitions of bands are observed: 470–473, 483, 488–486 nm (Figs. 3, 4), similar to multiphonon spectrum, observed earlier in CL [2], but described as SAL(II) irradiation. These bands in crystal with SF is related with pure layers [1].

Let's look into the model of crystal multi-band with stacking faults (Fig. 6), built similar to CVD ZnSe in study [3]. Peculiarities and additional data, observed at our crystals study, are considered.

Let's examine the experimental data (PL spectra) with the band model application according to the method of optical diagnostics of single-crystal systems with defects [1]. Marks on ordinate axis in Fig. 6 correspond to conditions of spectra making, particularly to PL excitation energies.

As per Fig. 6, *b* the appearance of PL at 420(425) nm (see Fig. 2) is related to reaching the level of ~ 2.9 eV — conductivity sub-band E_+^{SF} at stacking faults. This sub-band appears according to the band anticrossing theory [1,13] at increased concentration of isoelectronic oxygen centers O_{Se}^* at SF. Excitation of the whole crystal is possible through a complex system of multi-band levels. At the same time, in PL we observe the exciton radiation band 457 nm. As per multi-band scheme (Fig. 6, *a*) and data [2,3], it corresponds to transitions $E_-^{\mathrm{CC}} \to E_V$ from the bottom of conductivity sub-band (2.7 eV) of ZnSe pure layers.

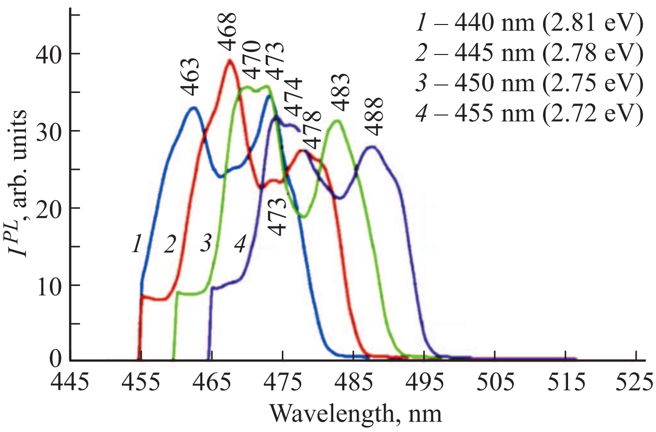

Figure 3. Photoluminescence spectra of polycrystal CVD ZnSe at excitation with various wavelengths of 440–455 nm.

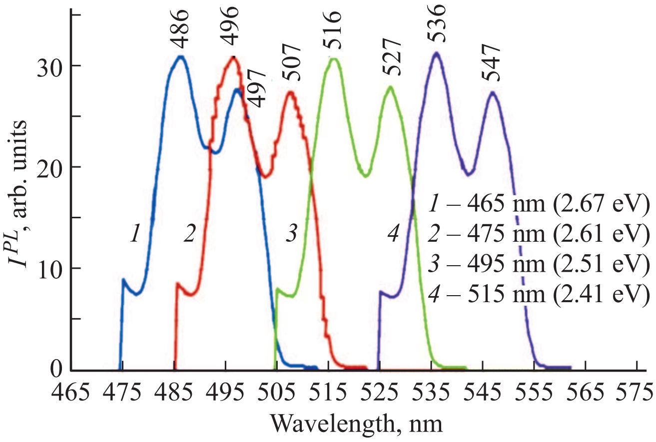

Figure 4. PL spectra of CVD ZnSe at excitation with wavelengths: 465–515 nm.

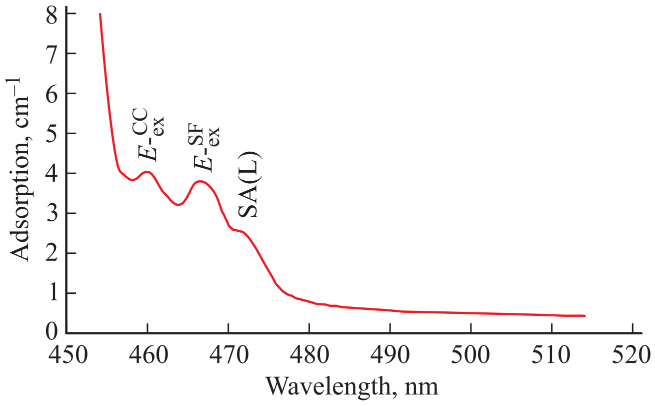

Figure 5. Spectra of absorption of polycrystal CVD ZnSe at 300 K.

Due to location of levels E_-^{CC} in the band, their depopulation with radiation, particularly at excitons annihilation, happens before the rest.

At PL excitation with wavelengths of 435–445 nm (energy ~ 2.8 eV) (Figs. 2 and 3) the second, most effective

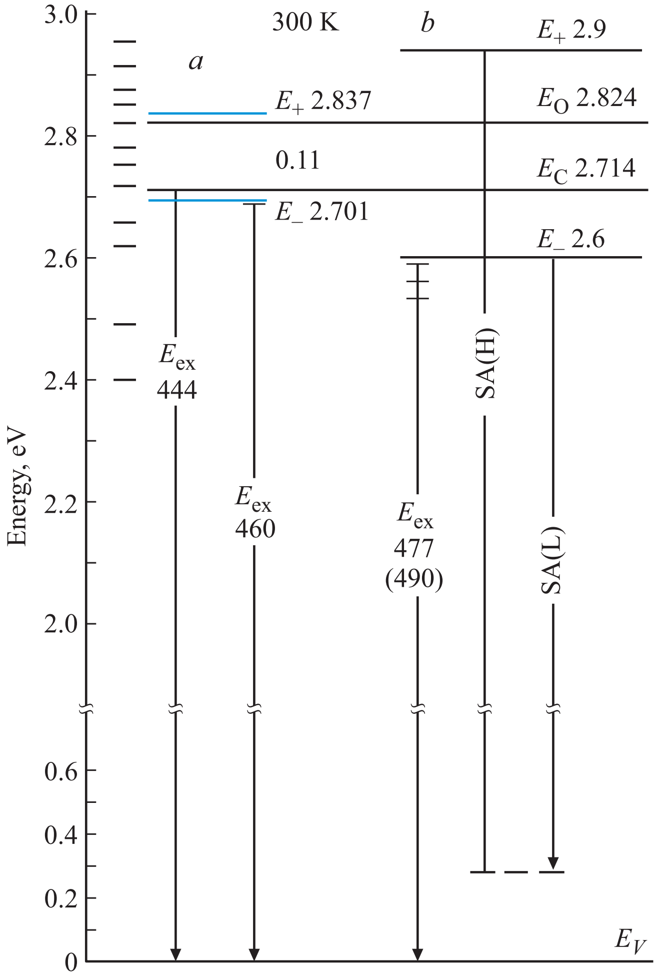

Figure 6. Band model of CVD ZnSe with SF. $E_C = 2.714$ eV at 300 K. The value of sub-band shift by ~ 1 mol% $[O_{Se}]$ in ZnSe is 100 meV. Oxygen concentration $[O_{Se}]$ in „pure“light SEM layers is $10^{19}\,cm^{-3}$ (*a*), in SF layers is $\sim 10^{20}\,cm^{-3}$ (*b*).

channel of recombination $E_-^{SF} \to E_V$ is added— radiation with participation of level of conductivity sub-band bottom E_-^{SF}, stacking faults layers, oxygen concentration in which is $\sim 10^{20}\,cm^{-3}$. In PL spectra (Figs. 2 and 3) this defines the band with high intensity, 468 nm, the same as appearance of its longer-wave phonon repetitions: 476, 488 nm (Fig. 3). These data at elaboration of the band model levels define the exciton band $E_-^{SF} \to E_V$ as 477 nm at 300 K. CL spectra (Fig. 1, *b*) show that this band corresponds to „abnormal edge irradiation“ of 477–490 nm, described in studies [1–3,5] in detail. The nature of similar bands is clarified in CdS spectra [14].

SA(L) irradiation transitions, specified in Fig. 6, *b*, correspond to presence of center of self-activated SA in ZnSe(O) with participation of deep recombination levels [1,2]. Self-activated irradiation band was observed for ZnSe(O)Se crystals, similar to ours, in study [2] as a band on wavelength of 530 nm at 80 K (Fig. 1, *c*) or as summation band of SA(L) and SA(H) with maximum of ~ 580 nm at 300 K. In PL spectra its components appear — maximums in the region of 440 nm at 300 K (Fig. 4, curve *4*).

If excitation energy is less than $E_-^{SF} \sim 2.6$ eV, the radiation bands observance is possible by means of energy absorption with SA center. However, due to composition of the examined samples, the concentration of SA centers is insignificant, and at wavelengths of > 515 nm its PL spectra were not measured.

The presented conclusions correspond to studies of such samples absorption spectra. Three bands were observed in the region, available for our measurements (Fig. 5).

The shortest-wave absorption was at exciton band of E_-^{CC} 2.696 eV (12 meV) of light layers.

The main maximum in absorption spectrum of 2.661 eV (Fig. 5) $E_-^{SF} \to E_V$ corresponds to the exciton radiation band of 477 nm near the bottom of conductivity sub-band E_-^{SF}. The longer-wave band of 2.638 eV in Fig. 5 in the region of 470 nm can be compared with SA(L) center absorption.

4. Conclusion

Thus, the measured PL bands are directly related to the band model of the examined crystal. The bigger depth of light penetration compared to CL electron excitation indicates some peculiarities of PL multi-phonon spectra and structure of luminescence centers in radiation range of 470–490 nm. Unlike CL, where these bands are observed only at 80 K, the multi-phonon exciton bands in the range of 477–490 nm of ZnSe are also observed in photoluminescence spectra at 300 K.

Elaboration of irradiation nature of 477–490 nm of both PL and CL of ZnSe allows to assume, similar to CdS, that this is a radiation of localized excitons in a lattice, maximum saturated with oxygen.

It is shown, that variation of PL spectrum with excitation energy is explained in terms of the band model of crystal with SF in accordance with the band anticrossing theory.

Wavelengths of PL bands, presenting in spectra, were shorter than in CL. This is, for instance, the position of free exciton of ZnSe (457 nm) compared to regular data and spectra of CL (460 nm) at 300 K.

The latter is explained in terms of polaritons formation. Processes of variation of electromagnetic wave, moving inside a crystal, are described by M. Kardona [11] at low temperatures. During our studies it was observed at 300 K. As per study [11], photon field energy absorption in crystal volume is observed.

Conflict of interest

The authors declare that they have no conflict of interest.

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