# Temperature behaviour of the photoluminescence spectra of polycrystalline ZnSe films with different surface treatment

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**Abstract.** We present the photoluminescence spectra obtained in the case of normal incidence of exciting radiation at both polished and unpolished surfaces of chemical-vapour deposited ZnSe films in the temperature range 12–300 K. The luminescence has been excited using either a continuous-wave He–Cd laser with the wavelength $\lambda_{ex} = 325$ nm (i.e., under the condition $h\nu_{ex} > E_g$ for the photon energy) or a semiconductor laser with $\lambda_{ex} = 532$ nm (i.e., $h\nu_{ex} < E_g$). We show that the temperature dependences of intensity, spectral position and half-width of a green photoluminescence band detected in the both alternative cases are very different in the region 12–80 K. However, their behaviours become very close to each other when the temperature increases up to 180 K. Finally, the above spectral parameters are almost the same in the region 180–300 K.

## 1. Introduction

Luminescent properties of ZnSe have been studied in a huge number of works, using different methods. Nonetheless, the appropriate results obtained thus far are often different and, sometime, even contradictory. This can be caused by the fact that excitation conditions, temperature, crystal purity and synthesis conditions affect notable the photoluminescence (PL) and, in particular, its intensity and the wavelengths of its peaks [1–5]. Note that the studies of PL spectra in semiconductors in a wide enough temperature range have many fundamental and applied consequences, since the temperature dependences of energy shift and bandgap expansion can provide important information on the electron–phonon interactions, the behaviour of defects and the excitonic effects in semiconductors [6–12].

It is important that the temperature dependences of luminescence in ZnSe crystals have been often examined either near 4 K or in a narrow temperature region around this point [6–12]. The role of surface in the luminescent processes has been studied recently in the works [13–15]. The analysis for the temperature behaviour of luminescent properties in relation to the surface structure of crystalline substances (e.g., thin films or grains of powder phosphors) is also of great interest. This is associated with the fact that the electrical, photoelectric and optical properties of these

structures are strongly influenced by the electronic and molecular processes occurring on their surface.

In the present work, we analyze the PL spectra of ZnSe in a wide temperature range (from 12 to 300 K). The spectra are excited using a He–Cd laser with the wavelength $\lambda_{ex}$=325 nm (so that the energy of exciting photon is larger than the bandgap, $hv_{ex}>E_g$) and a semiconductor laser with $\lambda_{ex}$=532 nm (then an alternative condition $hv_{ex}<E_g$ holds true). We examine both polished and unpolished surfaces of the same sample of polycrystalline chemical-vapour deposited (CVD) ZnSe.

## 2. Methods and experiments

Polycrystalline CVD ZnSe samples with the thicknesses 3 mm were obtained with a standard chemical-vapour deposition technique [16, 17]. It is evident that the crystal growth from the vapour phase occurred at lower temperatures when compared with the melt technologies. This helped us to reduce the concentration of bulk defects and also hindered contamination of a growing crystal with ampoule materials.

The PL signal was recorded using an MS5204i monochromator-spectrograph (SOL Instruments) equipped with a diffraction grating (1800 line/mm). It was detected with an ANDOR IDUS (DU420-OE) CCD detector. The PL spectra were reconstructed after adjusting for the spectral sensitivity of detecting system. They were measured in the temperature range 12–300 K for the two alternative cases of excitation of CVD ZnSe. These were normal incidence of the excitation quanta on either polished or unpolished surface. Initially, the measurements were carried out using the polished surface of the sample, when the luminescence was excited by a continuous-wave He–Cd laser with the wavelength $\lambda_{ex}$=325 nm (i.e., $hv_{ex}>E_g$). Then the same laser was employed to excite the unpolished (side) surface of the sample. In addition, in the latter case the sample was excited by a continuous-wave semiconductor laser with the wavelength $\lambda_{ex}$=532 nm (i.e., under the condition $hv_{ex}<E_g$). The temperature dependences of the PL spectra were studied in a closed system based on a helium cryostat. The system consisted of a cold head (RDK-101D (Sumitomo Heavy Industries, Tokyo), an SRDK-series cryocooler and CAN-11B series compressors (Sumitomo CAN-11 Helium Compressor Unit). The temperature changes were monitored using a cryogenic temperature controller (Model 9700, Scientific Instruments).

## 3. Results and discussion

Let us analyze at first the PL spectra obtained when the sample is excited from its polished surface (see Fig. 1). At the temperature 12 K, one observes the following maxima in the spectrum: $\lambda_{max}$=561 nm (2.21 eV), 477 nm (2.61 eV), 464 nm (2.68 eV) and 458 nm (2.71 eV). The authors of Refs. [9, 18, 19] have associated the peak located at 458 nm with the radiation occurring during recombination of free electrons with holes bound at acceptors. The peak at $\lambda_{max}$=464 nm can be attributed to recombination of electrons bound at shallow donors with holes bound at acceptors [18–20]. According to the spectral position of the main zero-phonon line of edge luminescence, the depth of the acceptor levels participating in such a donor–acceptor pair should be 0.12 eV less than the bandgap. The distance between these bands is equal to the energy of longitudinal optical phonon, which is of the order of 31 meV for zinc selenide. Notice that our data yields the value 30 meV. Moreover, the character of the PL spectrum described above is confirmed by a donor–acceptor mechanism for the edge luminescence. The narrow line observed at the wavelength $\lambda_{max}$=477 nm has been considered [19] as an anomalous edge luminescence, which appears due to selenium excess and strong doping of sample with oxygen. In our case, one can speak of a

background impurity. Besides, there is a wide and intense (if compared to the peaks discussed above) long-wavelength band at $\lambda_{max}$ = 561 nm and 12 K (a so-called yellow-green band – see Fig. 1a). Many authors (see Refs. [8, 10, 19, 21, 24]) consider this band as a result of defect-impurity luminescence. They associate it with the occurrence of uncontrolled oxygen and copper impurities (i.e., background impurities), which are available in the crystalline lattice of CVD ZnSe.
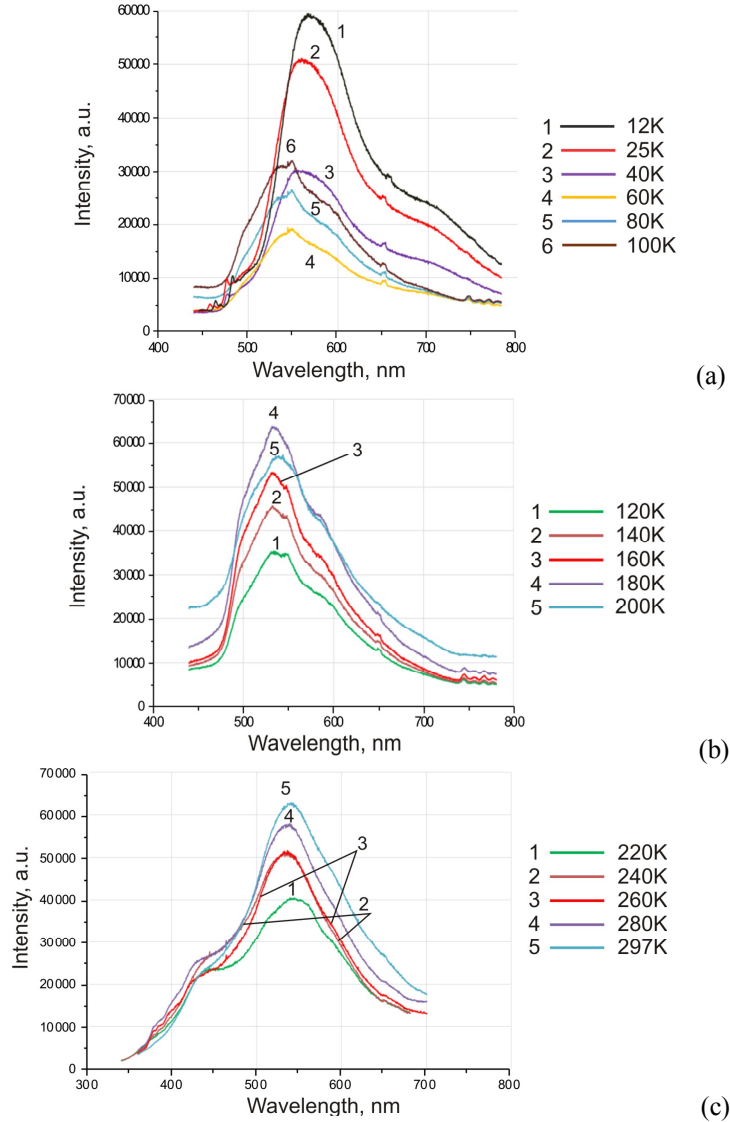


**Fig. 1.** PL spectra of polycrystalline CVD ZnSe excited from polished surface ($\lambda_{ex}$ = 325 nm), as observed at $T$ = 12–100 K (a), 120–200 K (b) and 220–300 K (c).

Now we discuss in a more detail the behaviour of the wide long-wavelength band located at $\lambda_{max}$=561 nm with changing temperature. When the temperature increases from 12 to 25 K, we observe no essential changes in the PL spectrum. However, the peaks located at the wavelengths 464 and 458 nm disappear at 40 K, and the maximum of the wide band, which has been observed initially at $\lambda_{max}$=561 nm, is now detected at 555 nm (see Fig. 2b). In addition, a new peak (a dark-red band) appears at $\lambda$=750 nm. It can be associated with the self-activated centres that appear in ZnSe under condition of maximum selenium excess within a homogeneity region [1, 21, 24].
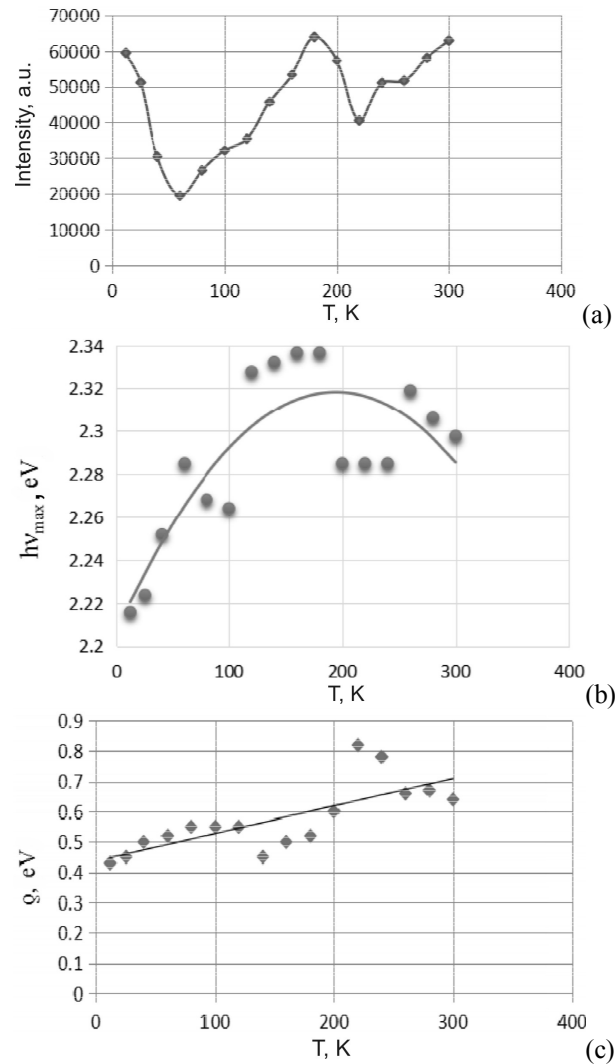
**Fig. 2.** Temperature dependences of intensity (a), spectral position $hv_{max}$ (b) and half-width $\rho$ (c) of the PL band located at $\lambda_{max}$=561 nm, as observed upon laser excitation ($\lambda_{ex}$=325 nm) from polished surface of polycrystalline CVD ZnSe.

When the temperature increases from 40 to 60 K, the peak 477 nm also disappears, the green band located at $\lambda_{max}$=561 nm shifts to 544 nm, and the peak $\lambda$=750 nm shifts to 745 nm. In other words, increasing temperature shifts the maxima towards shorter wavelengths. When the temperature changes from 12 to 60 K, the temperature coefficient of displacement of the spectral maximum corresponding to $\lambda_{max}$=561 nm (2.21 eV) undergoes the following changes: $\sim7.31\times10^{-4}$ eV/K (12–25 K), $9.3\times10^{-4}$ eV/K (25–40 K), and $9.7\times10^{-4}$ eV/K (40–60 K). On average, we have the value $\sim 8.77\times10^{-4}$ eV/K. Under the same temperature increase (from 12 to 60 K), the decrease in the bandgap $E_g$ is given by the average temperature coefficient $\sim 5.1\times10^{-4}$ eV/K [10].

A doublet structure of the PL spectrum is observed at the temperature 80 K, with the maxima located at 541 nm (2.298 eV) and 548 nm (2.268 eV – see Fig. 1a). Here the short-wave component is less intense than the long-wave one. With temperature increase up to 120 K, the intensity of the short-wave component increases (see Fig. 1b). The intensities of the both components become the same at 120 K and a shift towards the short-wave region (up to the

wavelength 532 nm) is observed. When the temperature further increases to 200 K, one observes the opposite situation: the intensity of the short-wave component increases if compared with the long-wave one, and the maximum shifts from $\lambda_{max}$=532 nm to 544 nm. Note also that, at 180 and 200 K, we observe a shift of the long-wavelength component towards the yellow-green band that corresponds to 578 nm (2.15 eV) and 573 nm (2.17 eV). Here the energy difference between the maxima amounts to ~ 0.02 eV.

Now we proceed to discussion of the behaviour of PL spectrum at the highest temperatures ($T$ = 200–300 K – see Fig. 1c). The PL intensity increases monotonously up to the wavelength 451 nm (2.76 eV) at the temperature 220 K. Then this intensity does not change till the wavelength 465 nm (2.67 eV). Subsequently, the intensity increases monotonously again and has a maximum located at $\lambda$=544 nm. However, the effect of 'saturation' of the spectral PL intensity disappears when the temperature increases up to 300 K, though some 'inflection' remains. At 300 K, the PL maximum and the PL inflection are observed at 538 and 447 nm, respectively. In this instance, the band observed at the wavelength 451 nm is due to recombination of free excitons, since the bandgap in ZnSe corresponds to 2.764 eV at 220 K [10]. It is also known that, for most of the samples, free-exciton emission occurring at low temperatures has an asymmetric line shape, which is very different from Lorentzian.

Fig. 2 demonstrates the temperature behaviour of the intensity, the spectral position and the half-width corresponding to the maximum located initially at $\lambda_{max}$=561 nm. The location of the latter varies from 2.21 eV ($\lambda_{max}$=561 nm) to 2.3 eV (539 nm) when the temperature changes in the range 12–300 K.

At this moment, we can state that our studies of the PL spectra obtained upon excitation from the polished surface of CVD ZnSe in the range 12–300 K allow us to distinguish the following characteristic temperature regions: (a) 12–80 K, (b) 80–180 K and (c) 180–300 K. To be more specific in our further analysis, we divide the short-wavelength part of the PL spectrum of our $A^{II}B^{VI}$ compound into the two following main parts: the free-exciton bands X and (I, X) and the luminescence bands with lower energies. The latter correspond to radiative transitions of donor–acceptor pairs, (D, h)-transitions from the donor levels to the valence band, and (e, A)-transitions from the conduction band to the acceptor levels [22, 23]. An increase in temperature to 80 K leads to predominant quenching of the short-wavelength bands (see Fig. 1a). It is conceivable that this behaviour is due to the presence of uncontrolled nonradiative recombination centres in our sample. Consequently, filling of the levels closer to the valence band causes a decrease in the number of transitions of the type X (I, X), which involve donor–acceptor pairs, until they disappear.

As seen from Fig. 1a, increase in the temperature makes quenching of the short-wavelength components located at 458 and 463 nm faster than that associated with the band at 477 nm. The green band located at $\lambda_{max}$=561 nm is, most likely, associated with the PL of impurity-defective complexes. These can be the complexes of intrinsic point defects ($Zn_i$, $V_{Zn}$) with oxygen and copper [8, 10, 19, 21, 24]. Depending on the distance between the elements of these complexes, they can have slightly different modifications, and this changes the energy levels. We believe that, when the temperature increases from 12 to 300 K, the changes in the energy levels are different. This is because the Fermi level gets higher in the bandgap with increasing temperature, thus resulting in complex recharge of the centres [10, 20, 24]. In its turn, this induces changes in the distance between the elements of the complexes mentioned above. In the temperature regions 80–180 K and 220–280 K, where the intensities of the PL bands increase (see Fig. 2a), one deals with the interaction of luminescence centres via free carriers. The temperature dependence of the

spectral position for the band located initially at $\lambda_{max}$=561 nm (see Fig. 2b) has a complex character: at first the $h\nu_{max}$ value increases monotonically with increasing temperature (12–80 K), then the increase slows down (80–180 K) and, finally, it becomes nearly zero (160–180 K). In the region 180–300 K, the spectral position of the band shifts downwards and we have $\lambda_{max}$=538 nm (2.31 eV) at 300 K. This indicates that the band consists of several close subbands with different temperature dependences of their intensity.
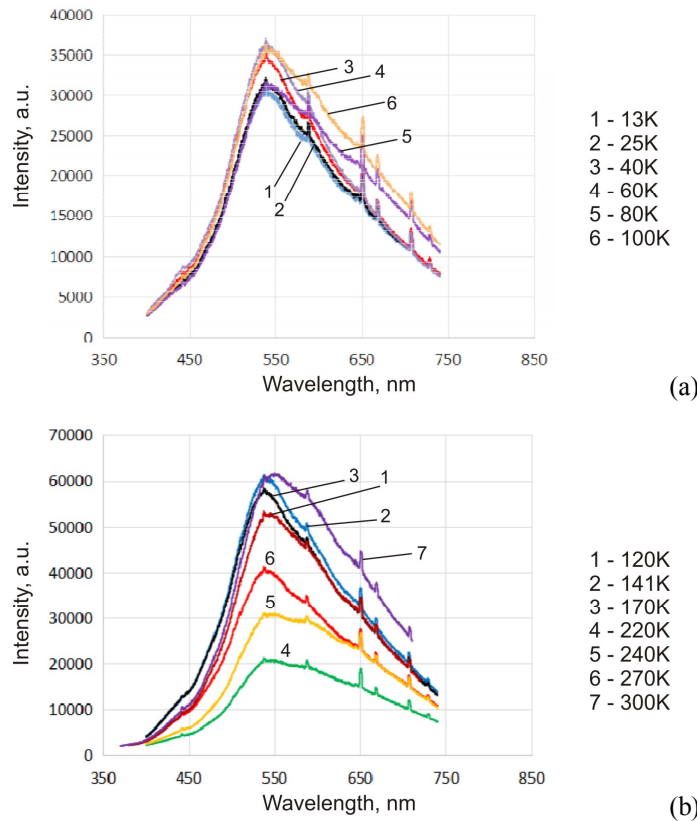


**Fig. 3.** PL spectra of polycrystalline CVD ZnSe (unpolished surface and $\lambda_{ex}$ = 325 nm), as obtained at $T$ = 13–80 K (a) and 100–280 K (b).

The temperature dependence of the half-width for the band located at 561 nm (see Fig. 2c) has also a complex character. In general, one observes a monotonous increase, which remains true in the overall range 12–300 K. This is due to increasing population of vibrational levels of the excited electronic states of PL centres, which occurs with increasing temperature. Moreover, a monotonously increasing temperature dependence of the half-width points to applicability of the model [4] adopted for the configuration of luminescence centres in polycrystalline CVD ZnSe.

Now we analyze the PL spectrum in the temperature region from 13 to 280 K, which is observed upon excitation by the laser with $\lambda_{ex}$=325 nm (see Fig. 3) and the semiconductor laser with $\lambda_{ex}$=532 nm (see Fig. 5) from the side (unpolished) surface of our sample. Fig. 4 demonstrates the temperature dependence of the intensity, the spectral position and the half-width of the band that corresponds to the maximum located initially at $\lambda_{max}$=538 nm upon excitation by the laser with $\lambda_{ex}$=325 nm. Similarly, Fig. 6 shows the temperature dependences of the intensity, the spectral position and the half-width for the band initially located at $\lambda_{max}$=630 nm, which is observed upon excitation of CVD ZnSe by the semiconductor laser.
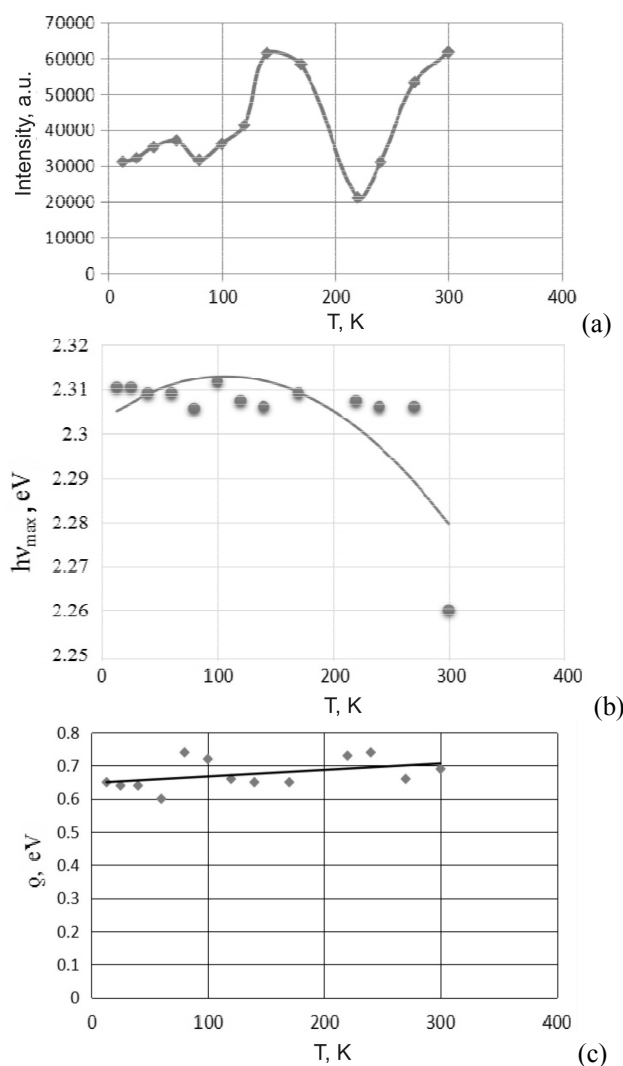
**Fig. 4.** Temperature dependences of intensity (a), spectral position $hv_{max}$ (b) and half-width $\rho$ (c) of the PL band located at $\lambda_{max}$=538 nm, as observed upon laser excitation ($\lambda_{ex}$=325 nm) from unpolished surface of polycrystalline CVD ZnSe.

As shown in Fig. 3, the intensity maxima in the PL spectrum detected at $T$ = 13 K are observed at the wavelengths 443 nm (2.81 eV), 588 nm, 668 nm, 707 nm and 728 nm. These are shallow peaks. In addition to these peaks, a wide green band is observed at $\lambda_{max}$=538 nm. This band differs from the above peaks. Indeed, when the temperature increases up to 280 K, the intensity of the green band changes, contrary to the intensities of the other peaks. The peaks located at 443, 588, 650, 668, 707 and 728 nm have earlier been discussed by us [15]. They can be called as 'spurious'.

A wide PL emission band with the maximum located at 630 nm is clearly seen in Fig. 5a at the temperature equal to 13 K. Our results agree very well with the data reported at 300 K in the work [15], where the half-widths of the band detected at 13 K and 300 K are equal respectively to 0.48 eV and 0.56 eV (with the energy difference 0.08 eV). When the temperature increases from 13 to 280 K, the initial PL spectra displayed in Fig. 5 reveal a decrease in the maximum intensity at the wavelength 630 nm (see Fig. 6a). The temperature shift in the spectral position of the maximum and the temperature dependence of the half-width in this case are shown in Fig. 6b and
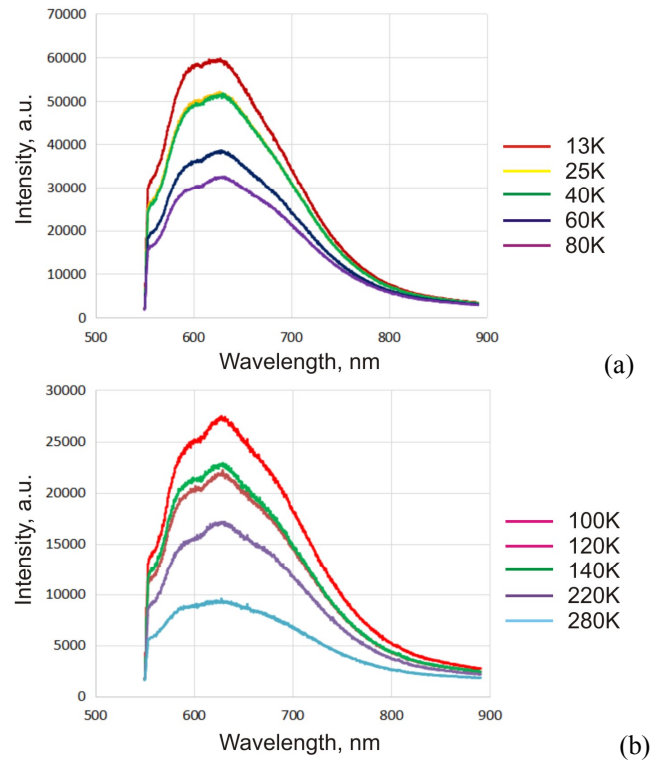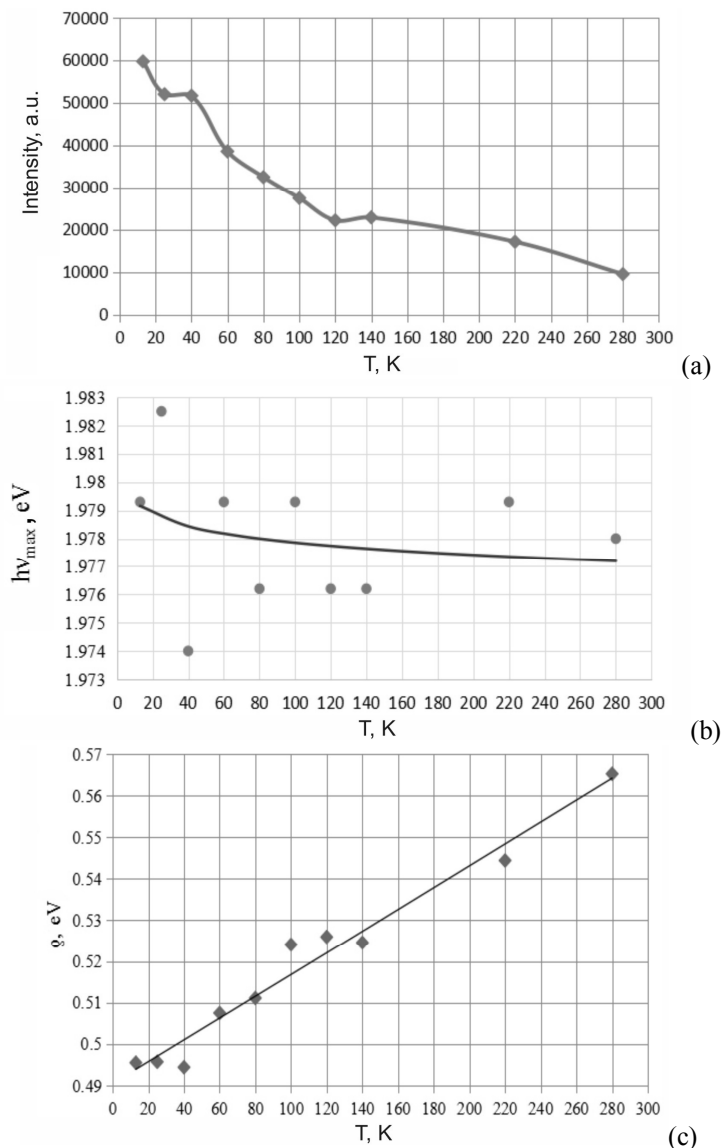
**Fig. 5.** PL spectra of polycrystalline CVD ZnSe (unpolished surface and $\lambda_{ex}$=532 nm), as obtained at $T$ = 13–80 K and $T$ =100–280 K (b).

Fig. 6c, respectively. The band with the maximum located at $\lambda_{max}$=630 nm has been discussed in sufficient detail by the authors [25–27].

In the spectra shown in Fig. 3a and Fig. 3b, we observe slightly different patterns. When the temperature increases from 13 to 280 K, the PL intensity corresponding to the maximum $\lambda_{max}$=538 nm varies in an ambiguous manner (see Fig. 4a). The temperature shift in the spectral position of the maximum (see Fig. 4b) is very small at the temperatures less than 80 K. Then it corresponds to a maximum shift observed for the case of $\lambda_{max}$=561 nm when the temperature increases to 300 K (see Fig. 2b). The temperature dependence of the half-width for the band $\lambda_{max}$=538 nm (see Fig. 4c) also reveals a monotonic increase in the range from 13–300 K. However, it is very slow, if compared to that taking place for the half-width of the maximum $\lambda_{max}$=561 nm (see Fig. 2c).

It is well known that increasing temperature decreases the bandgap in all of the $A_{II}B_{VI}$ semiconductors. In its turn, this affects the positions of energy levels of the local centres in the bandgap, including the luminescence centres. At the same time, there should also occur a decrease in the energy difference between the excited and ground levels of the recombination luminescence centres. Therefore, the increase in the sample temperature has to impose a long-wavelength shift of the PL band maxima. All of these arguments applied to the band with the maximum located at $\lambda_{max}$=561 nm (for the case of polished surface) and the band with the maximum at $\lambda_{max}$=538 nm (for the case of unpolished surface) are readily testified in the region 180–300 K (cf. Fig. 2b and Fig. 4b). The change in the spectral position for the band with the maximum located at 538 nm is insignificant when the temperature increases up to 100 K. Then it becomes abrupt in the region 100–180 K (see Fig. 4b).

**Fig. 6.** Temperature dependences of intensity (a), spectral position $hv_{max}$ (b) and half-width $\rho$ (c) of the PL band located at $\lambda_{max}$= 630 nm, as observed upon semiconductor-laser excitation ($\lambda_{ex}$=532 nm) from unpolished surface of polycrystalline CVD ZnSe.

It is interesting that, for the case of polished surface, the long-wavelength shift for the maximum at $\lambda_{max}$=532 nm also begins at the same temperature, 180 K. When the temperature increases from 12 to 180 K, there is a shift towards the short-wave region for the band located at $\lambda_{max}$=561 nm, up to the wavelength 532 nm. As the temperature increases to 80 K, the displacement of the 561 nm maximum is monotonic. An abrupt shift is observed with further temperature increase up to 180 K (see Fig. 2b). Furthermore, it is noteworthy that one can observe similar patterns for these maxima in the temperature dependences of the intensity (cf. Fig. 3a with Fig. 5a) and the half-width (cf. Fig. 2c with Fig. 4c).

The authors of a number of works [10, 19, 21, 24, 28–30] argue that the 'green' band observed in the region 508–550 nm is related to stoichiometric composition of CVD ZnSe, dissolved oxygen $O_{Se}$ and a presence of copper. If oxygen and copper are present as background

impurities ($\leq 10^{16}$ cm$^{-3}$), the short-wavelength bands located at 508–510 nm (at 80 K) are observed in the test samples. On the other hand, a shift occurs in ZnSe doped with copper and oxygen (with the excess of selenium) and the long-wavelength bands are observed at 525 nm (at 80 K) and 550 nm (at 300 K) [19, 24, 28]. These authors have also revealed that the short-wavelength bands do not change with increasing temperature (i.e., there is no temperature shift), while the long-wavelength bands of copper change, following the change occurring with the bandgap. Note that the appropriate measurements have been performed only at 80 and 300 K and no direct examination of the effect has ever been made in a wide enough temperature range (e.g., from 12 to 300 K, as in our case).

In the ZnSe sample studied by us, oxygen and copper are both present at the level of background impurity. Basing on the models suggested in Refs. [19, 21, 28, 29], we also assume that the green glow is due to the transitions of electrons from shallow donors to associative {Cu$_i$O$_{Se}$} acceptor centres (with Cu$_i$ being interstitial copper ions). The distributions of concentration and dissolution of oxygen (as well as the same distributions for copper) inside the samples depend on the growth conditions and the stoichiometric composition is most often heterogeneous. Therefore, one can assume that the associative acceptor centres {Cu$_i$O$_{Se}$} in the samples with different surface quality behave very differently when the temperature increases to 80 K. Following from what is know of the transformations of these centres, one can decide that their behaviour almost converges when the temperature increases to 180 K. With further temperature increase above 180 K, the effects of ionization of shallow donors and radiative recombination of free electrons with holes to associative acceptor centres take place. In its turn, this leads to identical behaviours of these centres at $T > 180$ K.

## 4. Conclusions

1. Upon excitation of our sample from the polished surface at 12 K under condition $h\nu_{ex} > E_g$, the edge luminescence and the yellow-green band with $\lambda_{max}$=561 nm are observed. When the unpolished surface is excited by the same source and at the same temperature, only a green band located at $\lambda_{max}$=538 nm is observed. In the both cases, the temperature dependences of the intensity, the spectral position and the half-width for the green band in the PL spectra are very different in the region 12–80 K. However, the behaviour of those parameters becomes very close to each other when the temperature increases to 180 K. Finally, they do not differ from each other in the region 180–300 K.

2. The above facts can suggest that, at the temperatures less than 80 K, the defects (the stable complexes {Cu$_i$O$_{Se}$}) associated with the polished surface has a different behaviour if compared to the defects associated with the unpolished surface. When the temperature increases from 80 K to 180 K, transformation of the energy positions of these defects occurs and they become almost identical at the temperatures higher than 180 K. Therefore, one can assume that the centres responsible for the PL, which correspond to the maxima located at $\lambda_{max}$ = 561 and 538 nm, have a single energy position only in the temperature region 180–300 K.

3. One of the results of Ref. [15] and the present work can be of a particular and independent interest. It is the green band observed in the PL spectrum under conditions when the He–Cd laser ($\lambda_{ex}$=325 nm, i.e. $h\nu_{ex} > E_g$) excites polycrystalline CVD ZnSe from the unpolished surface either at the room temperature (as in Ref. [15]) or in the temperature range 12–300 K (as in the present work). In the future, this result can be used when creating green LEDs based on polycrystalline CVD ZnSe.

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***Анотація**. Представлено спектри фотолюмінесценції, одержані в діапазоні температур 12–300 К за умов нормального падіння збуджуючого випромінювання на відполіровану або невідполіровану поверхню плівок ZnSe, хімічно висаджених з парової фази. Люмінесценцію збуджували за допомогою He–Cd лазера безперервної дії з довжиною хвилі $\lambda_{ex} = 325$ нм (тобто, за умови $hv_{ex} > E_g$ для енергії фотона) або напівпровідникового лазера з $\lambda_{ex} = 532$ нм (тобто, $hv_{ex} < E_g$). Показано, що температурні залежності інтенсивності, спектрального положення та напівширини зеленої смуги фотолюмінесценції, знайдені для обох альтернативних випадків, сильно відрізняються в області 12–80 К. Однак їхня поведінка стає дуже близькою, якщо температура зростає до 180 К. Нарешті, вищевказані спектральні параметри майже однакові в області 180–300 К.*