

## IR luminescence of ZnSe-based scintillators

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The work is aimed at the nature elucidation of IR photoluminescence (PL) bands with peaks at 1.3 and 1.6 eV (970 and 790 nm, respectively) in ZnSe and ZnSe(Te) crystals. Experimental studies of the PL of additionally purified crystals as well as calculations based on the charge carrier statistics in semiconductors with multicharge centers have shown that the IR PL is due to multicharge intrinsic point defects. The 1.3 eV IR band is attributed to intracenter transitions between excited and ground states of singly ionized selenium vacancies, which are double donors, whereas the 1.6 eV one, to radiative transitions of electrons from singly ionized Se vacancies to the acceptor level of the  $[V_{Zn}Te_{Se}]$  complex.

Статья посвящена раскрытию природы полос ИК фотолюминесценции (ФЛ) 1.3 и 1.6 эВ (970 и 790 нм) кристаллов ZnSe и ZnSe(Te). На основе экспериментального исследования ФЛ дополнительно очищенных кристаллов, а также расчетов с использованием статистики носителей заряда в полупроводниках с многозарядными центрами установлено, что ИК ФЛ обусловлена многозарядными собственными точечными дефектами. ИК-полоса 1,3 эВ обусловлена внутрицентровыми переходами между возбужденным и основным состояниями однократно ионизированных вакансий Se, которые являются двузарядными донорами, а ИК-полоса 1,6 эВ — излучательными переходами электронов с однократно ионизированных вакансий селена на акцепторный уровень комплекса  $[V_{Zn}Te_{Se}]$ .

Zinc selenide ( $E_g = 2.67$  eV at 300 K) is a promising scintillation material for X- and  $\gamma$ -radiation detection. Improving the growth process together with studying the luminescent properties of the grown ZnSe crystals would allow to obtain scintillators with unique operating parameters (high quantum efficiency, thermal stability of luminescence and radiation resistance, low afterglow level). The red luminescence band peaked at 640 nm (1.9 eV) is used most widely in ZnSe-based scintillators and has been studied well enough. The existence of luminescence bands in the IR spectral region sets a limit on the quantum efficiency of the red band. That is why the nature elucidation of the IR bands is of both scientific and practical interest.

Recently, researchers have come to the conclusion that a crucial role in the formation of the luminescent properties of undoped crystals of II–VI semiconductor compounds is played by the lattice intrinsic

point defects (IPDs) rather than by unintentional impurities, the role of the latter being reduced to the defect charge compensation and the formation of impurity-defect complexes. In particular, the 1.9 eV red luminescence band in ZnSe is attributed to zinc vacancies  $V_{Zn}$  or to complexes involving those [1–4]. At the same time, there is no agreement among scientists as to the nature of the IR luminescence bands in ZnSe and ZnSe(Te) crystals with peaks at 1.3 and 1.6 eV (approximately 970 and 790 nm, respectively) [2–7].

It is therefore of interest to relate the IR bands to the presence of IPDs, which are two-charge (or double) centers [8] and form alternative energy levels in the semiconductor band gap: depending on temperature, presence of compensating impurities and excitation conditions, each center can reveal one or another level, the level position being defined by ionization energy of the center that exists in a certain charge state.

Doping ZnSe crystals with isovalent (isoelectronic) Te impurity in the growth process results in generation of zinc vacancies, which are the red luminescence centers, and to formation of thermostable  $[V_{Zn}Te_{Se}]$  complexes in ZnSe(Te) crystals, thus providing stability of the red luminescence band within a wide temperature range.

To elucidate the IR luminescence mechanism and to establish the role of IPDs in the luminescent properties formation of ZnSe and ZnSe(Te) crystals, it was necessary to investigate both the crystals grown with conventional techniques and those purified additionally of possible unintentional impurities. That is why the following groups of crystals were chosen for the investigation. As ZnSe crystals, single crystals were used obtained from a raw material of special purity grade (99,99999 mol.%) using the close-spaced vapor transport (CSV) method with  $I_2$  gas as transporter (samples A1) at the laboratory of the Experimental Physics Division, Physics Department of T.Shevchenko Kyiv National University. With the aim to additionally purify of possible impurities, some of A1 crystals were re-sublimated in vacuum (samples A2). Samples A1 were single crystals with the area of the natural faces of approximately  $2 \times 3 \text{ mm}^2$ . PL was excited and measured from natural faces. Samples A2 were an aggregation of tiny crystals with dimensions of approximately  $0.15 \times 0.15 \times 0.15 \text{ mm}^3$ , which covered the inner surface of the quartz ampoule in the cold zone. As tellurium-doped ZnSe(Te) crystals scintillation ZnSe(Te) polycrystals were used (samples B1) grown from the melt using the Bridgman-Stockbarger technique under argon gas pressure at the Scientific-Technological Concern "Institute for Single Crystals", National Academy of Sciences of Ukraine (Kharkiv). The content of unintentional impurities in the ZnSe(Te) crystals did not exceed  $10^{-5} \%$  (mol.) The content of Te isovalent dopant was from 0.4 to 0.75 % (mol.). Samples B1 were slabs with dimensions of  $(5-10) \times 4 \times 2 \text{ mm}^3$  cut from polycrystal cylinders (23 mm in diameter, 4 mm thick). To obtain more pure and more perfect structure crystals, some of samples B1 were recrystallized by the CSV method (samples B2). The dimensions of samples B2 were the same as those of samples A1.

We studied photoluminescence (PL) of the above-mentioned crystals excited by a

pulsed  $N_2$  laser (337 nm, 3.68 eV), and continuous-wave He-Cd (442 nm, 2.81 eV),  $Ar^+$  (488 nm, 2.54 eV) and He-Ne (633 nm, 1.96 eV) lasers, which provided the regimes of strong surface, weak surface (band-to-band excitation:  $h\nu_{exc} > E_g$ ) and weak bulk excitation (excitation in the region of impurity absorption:  $h\nu_{exc} < E_g$ ), respectively. The use of a pulsed  $N_2$  laser allowed us to study also the luminescence decay kinetics under band-to-band excitation. PL was studied within the spectral region of 440 to 1020 nm (1.2 to 2.8 eV) in the temperature range from 80 to 490 K. In the mentioned temperature range, temperature dependences of the peak intensities (TDIs) for all PL bands were also measured on some samples of each group to reveal the temperature influence on the structure and concentration of the emission centers.

PL spectra of A1 samples at room temperature under  $Ar^+$ -laser excitation consist of the red band with a peak at  $h\nu \approx 1.9 \text{ eV}$  and IR band at  $h\nu \approx 1.3 \text{ eV}$  (band IR-I), the IR-I band width being 1.7 times lower than that of the red one. The intensity ratio between the bands depends on the excitation intensity: the red band becomes relatively more intense as the excitation intensity rises. At the temperature lowered to 80 K, the red band predominates (the IR-I band intensity is several orders of magnitude lower than that of the red one). The red band intensity decreases with increasing temperature, whereas the IR-I band intensity first rises, attains a maximum at 220–230 K and then decreases to zero, i.e. shows "anomalous" behavior. The IR-I band is excited by  $Ar^+$ -laser only.

The A2 samples were obtained by re-sublimation of A1 single crystals in vacuum and presented an aggregation of tiny crystals of approximately  $0.15 \times 0.15 \times 0.15 \text{ mm}^3$  size deposited on inner surface of the quartz ampoule in the cold zone. On the ampoule side walls, a red-colored deposit (unreacted selenium) is seen. Here we should note that the crystals of II–VI compounds grown from gas phase (e.g. by CSV or by sublimation in vacuum), are characterized by metal excess (chalcogen deficiency) due to a higher volatility of chalcogen, and exhibit *n*-type conductivity [9]. Thus, there is a rather high probability that selenium vacancies  $V_{Se}$  were generated in A1 and A2 crystals during the growth, which is evidenced by the above-mentioned deposit. Re-sublimation of A1 crystals,

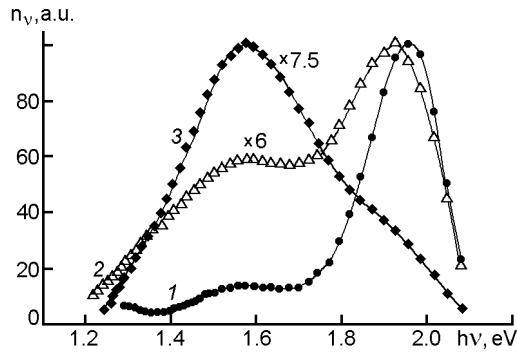


Fig. 1. PL spectra ZnSe(Te) of B1 sample under  $\text{Ar}^+$ -laser excitation at different temperatures: 1 – 80 K; 2 – 290 K; 3 – 347 K.

which already contained Se vacancies, resulted in further increasing concentration of the latter in A2 samples and formation of the red deposit which could be seen even by naked eye.

As a whole, the PL spectra of A2 samples are similar to those of the initial A1 crystals [10], although the 1.3 eV IR-I band observed under the same conditions as for A1 crystals is considerably more intense both in absolute value and as compared to the red band at room temperature. The TDI (temperature dependence of intensity) of the IR-I band for samples A2 is similar to that for samples A1 and is presented in [10]. Thus, the PL spectra of ZnSe crystals obtained by different methods indicate that the 1.3 eV IR band may be due to Se vacancies and its intensity is proportional to the concentration of the latter. The excitation selectivity of this band may indicate that the luminescence is of intracenter nature.

In the spectra of ZnSe(Te) crystals (B1 samples), in addition to the mentioned bands (the 1.9 eV red and 1.3 eV IR ones), we detected one more IR PL band with a peak at 1.5–1.6 eV (denoted as IR-II). Under  $\text{Ar}^+$  laser excitation, all three bands are observed both at room and low temperatures. At elevated temperatures, the IR-II band predominates (Fig. 1). TDIs of the red and the two IR bands are complex. In the spectra of ZnSe(Te) crystals re-crystallized by CSVT (B2 samples), only the 1.6 eV IR-II band is observed at room temperature at any excitation wavelength. This band is excited by radiation of  $\text{N}_2^-$ , He–Cd- (band-to-band excitation) as well as  $\text{Ar}^+$ - and He–Ne-lasers (impurity excitation). The red band shows up at reduced temperatures. It should be noted that at a low temperature, the spectral widths of the red band and the IR-II one are equal to one another. The PL

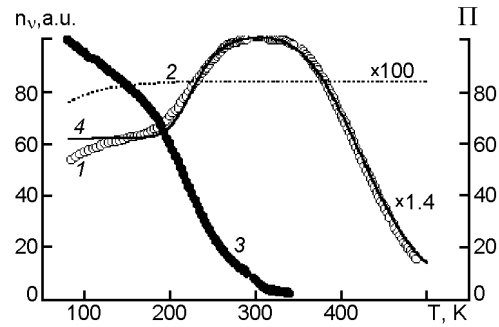


Fig. 2. TDIs of the 1.6 (1) and 1.9 eV (3) PL bands of B2 sample. Plotted are also the sample absorptivity  $\Pi$  at  $\lambda_{las} = 488$  nm (2) and the TDI of the 1.6 eV (4) band calculated according to [10].

spectrum shape is almost independent of the  $\text{Ar}^+$ -laser excitation intensity (in the range between 25 and 155 mW).

It is known [11] that under high-power excitation (e.g. by pulsed  $\text{N}_2$  laser or high-power  $\text{Ar}^+$  laser), when the random potential of impurities is screened by that of the field of nonequilibrium charge carriers, the PL band width is defined mainly by the magnitude of electron-phonon interaction, which is characteristic of a particular type of the lattice defects. This means that the luminescence centers of the two PL bands may contain a common defect. Such a defect, in our opinion, may be a Zn vacancy, to which the great majority of researchers attribute the red PL band. At the same time, different widths of 1.9 and 1.3 eV bands indicate that the respective luminescence centers are of different physical nature.

It was also noted that the absolute intensity of the IR-II band in the samples with 0.4 mol.% of Te is less than in the samples with 0.75 mol.% of Te, which suggests a certain role of Te atoms in the formation of band IR-II. The TDI of the IR-II band for sample B2 is presented in Fig. 2. It is seen to exhibit an anomalous behavior as well. The characteristic feature of this TDI is that the 1.6 eV band intensity is constant in the temperature region 280–340 K (a "trapezium-like" TDI).

The studies of the luminescence intensity decay kinetics of ZnSe(Te) crystals under pulsed band-to-band excitation ( $\text{N}_2$ -laser) have shown that the decay time of the 1.6 eV IR band (150  $\mu\text{s}$ ) is much longer than that of the 1.9 eV red band (about 4  $\mu\text{s}$ ). It should be noted that the relative intensities of the 1.3 eV and the 1.6 eV

bands compared to that of the 1.9 eV red band in crystals of A and B groups decrease with time. Thus, the sets of experiments carried out in the time interval of 2 years have shown that the 1.6 eV band relative intensity is decreased by a factor of three (sample B2, Ar<sup>+</sup>-laser, 80 K). This indicates that the centers of the two IR PL bands are less stable than the red luminescence ones.

It is known that IPDs in the crystals of II-VI semiconductor compounds, in particular, ZnSe, are two-charge (or double) centers. The donor defects (interstitial metal atoms  $M_i$  and chalcogen vacancies  $V_C$ ) may appear in the "0", "+" and "2+" charge states, while the acceptor defects (metal vacancies  $V_M$ ), in the "0", "-" and "2-" states [8]. The theory of multicharge centers in semiconductors was elaborated as long ago as in 1950 s [12], although in the literature there is no mention of its application to explain the luminescent properties of the latter. In this work, we will try to use this theory to describe the TDIs of the 1.3 and 1.6 eV PL bands of the ZnSe and ZnSe(Te) crystals.

The TDIs of the IR bands presented above can be due in principle to three factors: temperature dependence of the luminescence centers concentration, temperature variation of the sample absorptivity  $\Pi$  at the laser radiation wavelength (the quantity  $\Pi$  determines the fraction of absorbed exciting quanta) or non-radiative recombination processes. The analysis made by us has shown that the latter two factors are insignificant. Specifically, Fig. 2 shows the absorptivity  $\Pi$  of samples B2 calculated from experimental transmission spectra measured at different temperatures at 488 nm wavelength as a function of temperature:

$$\Pi = [(1 - R) \cdot (1 - e^{-\alpha d})] / [1 - R \cdot e^{-\alpha d}],$$

where  $R$  and  $\alpha$  are the coefficients of reflection (from the sample surface) and absorption, respectively;  $d$ , the sample thickness. At first glance, the increase in the IR bands intensities with increasing temperature can be attributed to the red band quenching. However, such an assumption can be valid only in the case of a high quantum efficiency of the red luminescence band. In this case, "cutting off" an intense red PL channel could result in a considerable increase in each IR band intensity. Thus, the situation in Fig. 2 could occur under condition that the combined quantum efficiency of the red

and IR bands at 80 K would exceed 60 %, which is unrealistic.

So, to account for the TDIs of the IR bands, we used the formulas that describe the equilibrium electron statistics in an  $n$ -type semiconductor with double donors (owing to the growth process features, such donors in our ZnSe crystals are  $V_{Se}$ ) with total concentration is equal to  $N_d$ , which are compensated in part by simple acceptors (acceptor-like defects, e.g. Zn vacancies) with the concentration  $N_a < N_d$ . Suppose that the 1.3 eV IR luminescence centers are singly ionized double native donors with the concentration  $N_d^+$  and emission occurs according to the scheme:  $N_d^+ + hv_{exc} \rightarrow N_d^{2+} + e \rightarrow N_d^{++} + hv_{lum}$ .

We will assume that the IR-band intensity is proportional to  $N_d^+$ . Increasing  $N_d^+$  concentration (due to ionization of neutral donors with increasing temperature) would result, according to our assumption, in increasing IR luminescence intensity. Further heating would result in further donor ionization ("+"  $\rightarrow$  "2+") and, consequently, in decreasing  $N_d^+$  concentration and the luminescence intensity. The corresponding calculations are presented in detail in [10]. The model of multicharge donor describes well both the TDI of the 1.3 eV band and the "trapezium-like" TDI of the 1.6 eV band (Fig. 2). This suggests a possible connection between these IR bands and double donors (Se vacancies).

In conclusion, the 1.3 eV IR band is observed in both ZnSe and ZnSe(Te) crystals. It is excited only by transitions in the region of impurity absorption and is most intense in purified crystals with a high content of Se vacancies. Computer simulation has shown that the temperature dependence of the 1.3 eV band intensity is described well by temperature variation of the concentration of singly ionized double donors in an  $n$ -type semiconductor, whose role is played by Se vacancies. The fact that re-sublimation of crystals A1 decreases the intensity of the 1.9 eV red band which is attributed to Zn vacancies as well as different widths of the 1.9 and 1.3 eV bands indicate that Zn vacancies are not the centers of IR luminescence peaked at 1.3 eV.

In our opinion, the 1.3 eV IR-band is due to intracenter transitions between excited and ground states of singly ionized selenium vacancies. The 1.6 eV IR band is observed in ZnSe(Te) crystals only. It is excited by both band-to-band and inter-subband transitions and is most intense in the crystals with a maximum Te content and a

high content of Se vacancies. This indicates that the 1.6 eV luminescence centers include Te atoms and Se vacancies. Equal spectral widths of the 1.6 eV IR and the 1.9 eV red bands in ZnSe(Te) crystals at liquid nitrogen temperature suggest that the PL centers which are responsible for these bands include a common defect, that is, Zn vacancy. The studies of the luminescence intensity decay kinetics in ZnSe(Te) crystals indicate that the red luminescence band is due to electron transitions immediately from the conduction band to the luminescence center (short decay time), while the 1.6 eV IR band to mediate transitions via defect levels to the luminescence center (long decay time).

TDI of the 1.6 eV band, like that of the 1.3 eV band, is also well described by temperature variation of the concentration of singly ionized double donors (Se vacancies). We suppose that the 1.6 eV IR band is due to radiative transitions of electrons from singly ionized Se vacancies (donors) to the acceptor level of a  $[V_{Zn}Te_{Se}]$  complex, i.e. is of donor-acceptor nature (Fig. 3). Isovalent Te dopant stabilizes Zn vacancies. It is now easy to explain why annealing ZnSe and ZnSe(Te) crystals in metal atmosphere (Zn or Cd) results in a decreased intensity of the IR bands, thus increasing the intensity of the red band. Quenching of the IR bands is due to the fact that Zn and Cd atoms are introduced into the crystals being annealed. These metal atoms are shallow donors and compensate the charge of ionized Se vacancies which, in turn, results in disappearance of the corresponding deep levels of Se vacancies and to quenching of the 1.3 and 1.6 eV bands.

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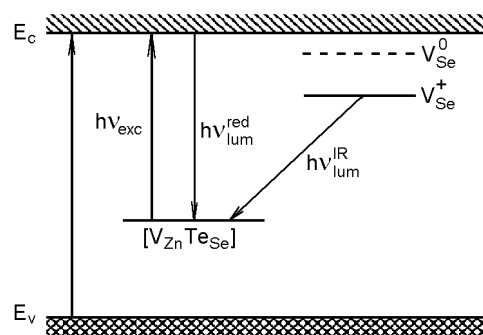


Fig. 3. Energy diagram of the optical transitions which accounts for the origin of the 1.6 eV PL band in ZnSe(Te). Excitation is by both band-to-band and inter-sub-band transitions.

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## **ІЧ люмінесценція сцинтиляторів на основі ZnSe**

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Статтю присвячено виявленню природи смуг ІЧ фотолюмінесценції (ФЛ) 1,3 та 1,6 еВ (970 та 790 нм) кристалів ZnSe і ZnSe(Te). На основі експериментального дослідження ФЛ додатково очищених кристалів, а також розрахунків із застосуванням статистики носіїв заряду у напівпровідниках з багатозарядними центрами встановлено, що ІЧ ФЛ зумовлена багатозарядними власними точковими дефектами. ІЧ-смуга 1,3 еВ зумовлена внутрицентровими переходами між збудженим та основним станами однократно йонізованих вакансій селену, які є двозарядними донорами, а ІЧ-смуга 1,6 еВ — випромінювальними переходами електронів з однократно йонізованих вакансій селену на акцепторний рівень комплексу  $[V_{Zn}Te_{Se}]$ .