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Influence of chromium interaction with native and impurity defects on optical and luminescence properties of ZnSe:Cr crystals

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Luminescent properties of the chromium doped zinc selenide crystals with various concentrations of the doping impurity in 0.03–0.30 at. % range within the temperature interval from 6 K to 300 K were studied. Chromium doping was performed in various technological processes: during the growth by chemical vapor transport method; during the growth from melt; by thermal diffusion from the Bi + Cr melt or by thermal diffusion from gas. Possibility of chromium-bound excitons formation was shown, as well as chromium impurity participation in formation of emission bands in IR spectral region. A mechanism of chromium doping impurity interaction with uncontrolled background impurities and zinc selenide structural defects was proposed based on experimental data. An assumption about resonant energy transfer between double charged chromium ions and complexes based on crystals vacancy defects was made. © 2013 AIP Publishing LLC.

I. INTRODUCTION

Infra-red (IR) lasers tunable in wide spectral range have found their applications in many fields: acousto-optical gas detection and determination of gas concentrations, environment monitoring, electronic communications, as well as numerous medical or military applications.1–3 Obtaining of tunable emission in IR spectral range is possible using, for example, optical parametric oscillators (OPO), which may generate electro-magnetic waves in a range from ultraviolet (UV) to middle-IR spectral region.4 OPO’s main disadvantages are large dimensions and high price. Usage of quantum cascade lasers may be a good alternative to OPO, but they may function only at low temperatures, their production is extremely expensive and tunability range is narrow.5 These factors attracted attention to development of diode-pumped solid state lasers (DPSSL) on the base of Zn and Cd chalcogenides doped with transient metals (TM), for example, Cr2+ and Fe2+. Despite a smaller tunability range, comparing to OPO, these lasers have many advantages, like low production cost, room-temperature functioning, flexible pulse format modes,4,6 also their electrical pumping may be developed.2,7

One of the most studied TM doped zinc chalcogenide is ZnSe:Cr. Spectroscopic properties of this material: close to one quantum efficiency at room temperature, wide absorption band near 1.8 μm, which allows optical pumping of intra-shell transitions with various methods and absence of significant absorption on excited state in middle-IR spectral range,5,8 make it a valuable source of coherent emission in middle-IR spectral range. Intensive study of ZnSe:Cr crystals allowed not only to determine the structure of the doping impurity energy levels,10 its optical11,12 and luminescent12,13 properties but also to elaborate few prototypes of the laser system working in pulsed14,15 and continuous modes.16,17

One of the main obstacles on the way of mass production of the lasers based on chromium doped zinc selenide is difficulty in growth of large amounts of ZnSe:Cr crystals with repeatable properties controllable within a narrow range of values, caused by well known troubles in equilibrium doping of large band-gap II-VI compounds.18 Various technological processes lead to inevitable formation of different native defects, which along with deviations from stoichiometry and uncontrolled doping with background impurities, may result in significant change of crystals emission properties.19 Probably, particularly these differences in crystal growth and doping processes lead to contradictory data, for example, about maximum position of Cr2+ ions intra-shell emission band: 1.8 μm (0.67 eV),20 2.1 μm (0.59 eV),21,22 2.2 μm (0.56 eV),23 2.4 μm (0.51 eV).24

There are many publications describing photoluminescent (PL) properties of chromium doped zinc selenide crystals. However, in most cases possible interaction of the doping impurity with native defects and background impurities is not taken in account. In this work, we have studied few concentration series of ZnSe:Cr crystals, grown and doped by various technological methods with the aim to reveal influence of the growth and doping techniques on optical and emission properties of the crystals in visible and middle-IR spectral ranges, as well as to establish possible mechanisms of chromium interaction with native or impurity defects.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

Four series of ZnSe:Cr samples, grown and doped by various methods have been studied. Doping impurity concentration in each series was varied within 0.00–0.10 at. %
Cr range. In the series of samples doped during the growth process by chemical vapor transport (CVT) method, a sample with chromium concentration of 0.30 at. % was additionally obtained. Selection of the concentration range is determined by the fact that IR emission efficiency of the double charged chromium ions decreases sharply at increase of impurity concentration. Earlier it was established, that for practical applications concentration of the chromium impurity in zinc selenide should be smaller than $1.4 \times 10^{19}$ cm$^{-3}$ ($\sim 0.0063$ at. %).

First series contained 5 ZnSe:Cr [I] samples with Cr concentrations varied within 0.00–0.30 at. % range, doped during the growth process by CVT method using iodine as transport agent. Synthesis from the elements and crystal growth was performed in high vacuum pumped (<0.1 Pa) silica ampoules. Iodine amount introduced in ampoules was taken as 5 mg/cm$^3$. Chromium concentration considered in the samples corresponds to chromium amount in the source material. During synthesis ampoule with substances was placed for 2–3 days in zone of reverse gradient, i.e., temperature in the source zone was smaller than in the growth zone, such position prevents substance transport and allows to synthesize zinc selenide. Synthesis was performed at temperatures of $\sim 1020$ K. After the synthesis, the ampoule was placed in the growth position with direct gradient (temperature in the source zone is 10–15 K higher than in the growth zone), in which it was maintained during the whole crystal growth time (8–14 days depending on the crystal dimensions). After the growth, ampoule was rapidly cooled to the room temperature, at the same time the sample-free end of the ampoule was cooled quicker to guarantee solidification of the transport agent in it. Grown crystals were washed in boiling ethanol for removing iodine from their surfaces. For study of optical and luminescent properties, single-crystal blocks were cut out from bulk samples by wire-saw, and the surface damaged by cutting was mechanically polished. The growth face, used for PL study, was not polished neither mechanically nor chemically.

Second series contained three ZnSe:Cr [Bi] samples doped during high-temperature annealing in Bi + Cr melt with concentration varied in 0.00–0.10 at. % Cr range. Bismuth usage as of annealing media allows avoiding deviations from crystals stoichiometry, as, for example, in case of annealing in zinc melt. Also annealing in Bi media may probably lead to extraction of shallow donor impurities from the samples in the melt. Before annealing, all the samples were cut out from the intrinsic high resistivity n-ZnSe crystal grown from melt (by the Bridgman method) and mechanically polished for giving them a necessary shape. Prior to annealing crystals surface was cleaned by etching in solution of bromide in methanol (Br$_2$ + CH$_2$OH) and after that boiled in sodium hydroxide and deionized water. Annealing was performed during 120 h at 1160 K temperature. The ratio between the sample volume and melt volume was maintained 1:7, respectively, in every annealing process. The doping level was controlled by chromium concentration in melt ((100-X) at. % Bi + X at. % Cr). Thermal annealing was performed in evacuated and sealed silica ampoules. After annealing, the ampoules were turned in a way, which provides transfer of the melt to the sample-free end of ampoule, and the samples were rapidly cooled to room temperature. Crystal surfaces were treated in a concentrated solution of iron chloride (III) to eliminate the rest of the melt after solidification, next the samples were boiled in sodium hydroxide and deionized water. It should be mentioned that high-temperature annealing of zinc selenide crystals in bismuth melt leads to their partial dissolution. Because of this, prior to study of optical and PL properties, all the crystals were newly mechanically polished and chemically etched in bromide in methanol solution. Selenium residuals, formed as a result of chemical etching, were eliminated from the samples surfaces by the last boiling in concentrated solution of sodium hydroxide.

The third series contained 3 high resistance n-ZnSe crystals, grown from melt. Chromium impurity concentrations used further (0.00, 0.01, and 0.10 at. %) correspond to the impurity concentration in the source material used for the crystal growth. For study of optical and PL properties, samples were chipped from the ingot, chip surfaces were not polished mechanically or chemically. Further, we will name the samples from this series as ZnSe:Cr (melt).

The fourth series contained crystals grown by the physical vapor transport (PVT) method and doped with chromium by diffusion from the vapor phase. Before the crystal growth the zinc selenide powder was synthesized from highly pure elements additionally purified by sublimation in vacuum. Synthesis was performed in silica ampoules of special construction, which was necessary to maintain stoichiometry of the compound. Crystal growth was performed in vertical furnaces during 14 days. After the growth, plates of 1 mm thickness were cut from samples in direction perpendicular to the growth axis (111). After mechanical and chemical treatment, similar to that used prior to annealing of zinc selenide crystals in bismuth melt, samples were doped by diffusion during 80 h at 1320 K temperature. The crystal doping was performed in sealed silica ampoules in vapors of preliminary synthesized inferior chromium selenide (CrSe) and low pressure (≈100 Torr) zinc atmosphere, which was necessary to prevent sublimation of the samples. After the doping, the sample surfaces were mechanically and chemically polished (bromide in methanol solution). Further, we will name the samples from this series as ZnSe:Cr (PVT).

Luminescence in 420–800 nm range was excited by radiation of pulsed nitrogen SRS NL100 laser with 337.1 nm wavelength, pulse energy of $\sim 170 \mu$J, and registered by Hamamatsu R943-02 photomultiplier tube. In middle-IR spectral range (800–3000 nm) a solid state YAG:Nd$^{3+}$ laser (532 nm, $\sim 300$ mW) and photoresistance Hamamatsu P394A on PbS basis were used. A halogen incandescence lamp with current stabilized power source was used for transmittance measurements. Spectra were analyzed with MS257 diffractometer monochromator, with resolution better than 1.3 nm. The input slit was covered with correspondent spectral filter to prevent registration of higher orders of the diffraction grids. Studied samples were mounted on the cold finger of the open cycle helium cryostat Janis Research ST-100.

Absorption coefficient was calculated using Beer–Lambert–Bouguer law. Taking into account that imaginary
part of the refraction coefficient may be neglected in the studied spectral range, reflection $R$ was calculated using

$$R = \frac{(n - 1)^2}{(n + 1)^2}. \tag{1}$$

Dependence of the refraction coefficient $n(\lambda)$ on wavelength $\lambda$ is given by

$$n^2(\lambda) = 9.01536 + \frac{0.24482}{\lambda^2 - 0.29934^2} + \frac{3.0889}{(\lambda^2/48.38^2) - 1}. \tag{2}$$

In the results section if a scale coefficient is given near the PL spectrum, then presented PL curve was obtained by multiplying of real emission intensity by this coefficient. Transmittance and emission spectra measurements were made for the same samples for all the series. Sample thickness was determined by the sample optical transparency and was the same within the whole series ($\text{ZnSe:Cr [I]}$ (0.70 ± 0.05 mm), $\text{ZnSe:Cr [Bi]}$ (1.00 ± 0.05 mm), $\text{ZnSe:Cr (melt)}$ (0.70 ± 0.05 mm), $\text{ZnSe:Cr (PVT)}$ (1.00 ± 0.05 mm)). Laser emission used for the excitation of the PL bands in the IR spectral range is absorbed in the crystal volume, and not only in the near-surface layer. In such a case, larger sample thickness will result in a greater number of the chromium ions capable to emit a photon in the mid-IR spectral range. This means that different sample thicknesses will result in incomparable PL band intensities, because the intensity depends not only on the chromium concentration but also on the size of the sample.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

### A. Luminescent properties of ZnSe:Cr crystals in visible spectral range

PL spectra of ZnSe:Cr [I] crystals in exciton region for all doping impurity concentrations are presented in Fig. 1(a). Emission spectrum of undoped crystal shows a relatively broad band of edge emission (full width at half maximum (FWHM) is 46.4 meV) with maximum localized at 444.4 nm at liquid helium temperature. Considering the large FWHM of the band, it may be assumed that it is not elementary but the temperature dependence of its maximum position repeats with high accuracy the shape of free exciton maximum position temperature dependence, calculated by Varshni equation.\textsuperscript{27,28} This reveals its excitonic nature and allows to conclude that the band consists of free exciton emission overlapped with few bound-exciton emission lines. The conclusion is also confirmed by the band temperature evolution (Fig. 2).

In the general case, sharp intensity decrease of the PL bands with the temperature increase may be explained by means of emission transition probability dependence on temperature. Temperature evolution of the PL bands intensity $I(T)$ may be described by the following relation:\textsuperscript{29}

$$I(T) = \frac{I_0}{1 + A \exp \left( \frac{-E_A}{k_B T} \right)}.$$ \tag{3}

where $I_0$ is emission intensity in a temperature region without thermal quenching, $E_A$ is a thermal quenching activation energy, $A$ is a constant resulted from ratio of the transition probabilities at different temperatures, and $k_B$ is the Boltzmann constant. Activation energy calculated from Eq. (3) is equal to ~26 meV, which with high accuracy corresponds to energy position of halogen impurities within zinc selenide band gap.\textsuperscript{30,31} This indicates that there are excitons bound to iodine and chlorine impurities. The presence of halogens in the samples grown by CVT method may be explained by iodine usage as of transport agent, however, maximum position of the edge band (444.4 nm) is very close

![FIG. 1. PL spectra of ZnSe:Cr [I] (a) and ZnSe:Cr [Bi] (b) crystals in exciton spectral range at $T = 6.5$ K. Inset: the dependence of the ZnSe:Cr [Bi] edge band maximum position on Cr concentration.](image)

![FIG. 2. Temperature evolution of the PL bands in exciton spectral range of ZnSe [I] (a), ZnSe:Cr [I] 0.10 at. % (b), ZnSe:Cr [Bi] 0.10 at. % (c) and ZnSe:Cr (melt) 0.01 at. % (d) crystals spectra. Insets: determination of activation energy of the temperature quenching.](image)
to position of excitons bound to zinc vacancies, this shows participation of zinc vacancy bound excitons in formation of the edge emission.

Temperature quenching activation energy of the exciton lines should comply with exciton-impurity complexes collapse energy, which for the iodine-bound excitons is $\sim 24$ meV. The presence of few exciton lines in a complex band should change the bands temperature quenching activation energy, because of different contribution of elementary lines to the complex emission. Despite the stated above, activation energy of the edge band in spectrum of the zinc selenide crystal grown by CVT method practically does not differ from the activation energy of iodine-bound excitons. This situation may occur in case when iodine-bound excitons’ contribution to the complex emission is much bigger than the contribution of other components. In this case, maximum position of such a band may be calculated according to the Hynes rule $2.8015 \, eV - 0.0260 \, eV/5 = 2.7963 \, eV$ (443.1 nm). However, the calculated value does not correspond to the experimental data (Fig. 1(a)). The obtained results may be explained, if we assume, that excitons bound to zinc vacancies collapse not because of zinc vacancies ionization but because of interaction of the zinc vacancies with another impurity with smaller activation energy. For example, temperature increase leads to ionization of shallow donor impurity, which tends to form complexes with acceptor-like zinc vacancies on account of coulombian forces. In this case, activation energy of the excitons’ temperature quenching will correspond not to zinc vacancies ionization energy but to the energy of the shallow excitons’ bound energy to the donor impurity, which forms complexes with the zinc vacancies.

Taking into account that exciton bound energy to the acceptor-like zinc vacancies is higher than excitons’ bound energy to shallow donor impurity $E_B(V_{Zn}) > E_B(D)$, at moment when ionization of the zinc vacancies will begin most of the zinc vacancy bound excitons will collapse due to formation of $[D, V_{Zn}]$ complexes, where $D$ is a shallow donor impurity. This explains absence of a slope caused by ionization of zinc vacancies on $ln(I/I_0) \sim 1/T$ dependence, and corresponds to the experimental data. Stated above and presence of only one slope, corresponding to iodine activation energy, on dependence of the edge band PL intensity logarithm vs. inverse temperature allow to assume, that CVT grown crystals contain $[I_{se}, V_{Zn}]$ complexes, studied in zinc selenide earlier.

Introduction of 0.03 at. % Cr in reactor during crystal growth by CVT method does not lead to intensity decrease of the edge emission, however, its FWHM increases up to 68.8 meV (Fig. 1(a)). Larger FWHM of the band combined with practically unchanged intensity may be caused by appearance of a new additional component in the band composition. Taking into account that maximum position of the band does not change, nor its shape, it may be assumed that contribution of the new component is smaller than contribution of emission lines from excitons bound to iodine and zinc vacancies. Increase of the chromium concentration in samples up to 0.05 at. % leads to the shift of the bands’ maximum position to longer wavelengths (453.0 nm) and decrease of its intensity, at the same time, shorter wavelength components, caused by radiative recombination of excitons bound to native defects and iodine, practically disappear. It should be mentioned that decrease of the emission intensity in the visible spectral range with increase of the doping impurity concentration in the zinc selenide crystals is characteristic for the all doping elements from the iron group, including chromium. Further increase of the chromium concentration up to 0.10 at. % or higher in reactor during the growth process leads to more significant decrease of the edge band intensity and increase of its FWHM, which includes spectral range from $\sim 436$ nm to $\sim 455$ nm.

The influence of excitation power on PL spectrum of ZnSe:Cr [I] 0.30 at. % sample was studied with the aim to resolve individual components in the complex edge band emission (Fig. 3). Decrease of excitation irradiation power leads to detection of 453 nm component, previously observed in PL spectrum of ZnSe:Cr [I] 0.05 at. % crystal. Also it may be observed that decrease of excitation power leads to more noticeable quenching of the edge band emission short wavelength components than longer ones, which indicates that impurities responsible for formation of the last have energy levels placed deeper in the band gap of the zinc selenide. It is known that PL intensity $(I)$ depends on the excitation power $(P)$ as $I \sim P^k$. Also it is accepted that if excitation energy is greater than the materials’ band gap, which is the situation here, then the power factor $k$ falls into one of the following ranges: $1 < k < 2$ for the free-to-bound exciton emission or $0 < k < 1$ for the free-to-bound radiative recombination, such as free hole and neutral donor recombination (h, D), free electron and neutral acceptor recombination (e, A), or donor-acceptor pair recombination (DAP). It may be observed from the Fig. 3 (inset) that power factors of the both components show on their exciton nature. Taking into account that excitons bound to acceptors are placed in longer wavelength region of the PL spectra, we may use the Hynes rule $E_A = 10E_B$ to determine position of the energy level, responsible for formation of the long wavelength component of the edge band: $E_A = 10 \times (2.8015 \, eV - (1239 \, eV \times nm)/(453.0 \, nm)) = 0.66 \, eV$. This value corresponds to position of

![FIG. 3. Dependence of the ZnSe:Cr [I] 0.30 at. % crystal PL intensity on excitation power at $T = 6.5 \, K$. Inset: power function approximation of the emission maximums intensities on excitation power.](image-url)
the unexcited state of $Cr^{2+}$ ion above the valence band of zinc selenide, if band gap is considered to be 2.820 eV at $T = 4.2 \, K$. Also it should be mentioned that presence of excitons bound to chromium acceptor levels is in the good agreement with known excitation mechanisms of chromium intra-shell emission in zinc selenide. Double charged chromium ions are considered to be acceptors in non-equilibrium state.

Concentration dependence of the ZnSe:Cr [I] crystals PL spectra intensity shows both general intensity decrease in the excitation spectral region and concentration emission quenching of the excitons bound to double charged chromium ions. Temperature quenching activation energy of the complex edge band increases with increase of the doping impurity concentration in the crystals (Figs. 2(a) and 2(b)), this is caused by more significant contribution to the edge band of the chromium bound excitons emission, which has greater temperature quenching activation energy.

Influence of the doping impurity concentration on emission bands intensity in the PL spectra excitonic region of the ZnSe:Cr (PVT), ZnSe:Cr [Bi] or ZnSe:Cr (melt) in general is similar to concentration dependence observed for ZnSe:Cr [I] crystals. Increase of the chromium ion concentration in the crystals results in decrease of the PL intensity in the excitonic spectral range until complete quenching, as it was observed, for example, in case of ZnSe:Cr (melt) 0.10 at. % and ZnSe:Cr (PVT) crystal, doped by annealing in chromium selenide vapors during 80 h. Particularity of the edge band, caused by presence of excitons bound to $Cr^{2+}$ ions remains (Fig. 2(d)) but shifts to shorter wavelengths, which is probably caused by different contribution of the individual components to the complex edge band emission. Also it is worth to mention that presence of excitons bound to chromium ions may not be observed in the PL spectra in form of individual bands or some particularities of the spectra. For example, chromium doping from the Bi melt (Fig. 1(b)) does not lead to appearance of the features in $\sim 450 \, nm$ region of the PL spectra even in case of significant chromium concentrations in the doping melt. However, increase of the chromium bound exciton contribution to the edge band emission may be observed from shift of the band to the long wavelength region of the spectra with chromium concentration increasing in the melt (Fig. 1(b) inset). Another detail characteristic for increase of chromium impurity concentration in ZnSe:Cr [Bi] crystals is the increase of the PL band intensity with maximum close to 459.0 nm with its phonon replicas distanced 32 meV from the main maximum, which corresponds to LO-phonon energy in zinc selenide. Position of this band maximum close to 459.0 nm with its phonon replicas displaced 32 meV from the main maximum, which corresponds to LO-phonons in zinc selenide. Double charged chromium ions are considered to be acceptors in non-equilibrium state.

Dependence of the edge PL band temperature quenching activation energy on the chromium doping technique (Fig. 2) shows significant variation in the temperature quenching activation energies, even in the case of considerable concentration of chromium impurity in the crystals. In some cases (Fig. 2(b)), the complex structure of the band and the change of the elementary components contribution to the edge band emission may result in light increase of the edge band intensity with increasing temperature. This means that despite a number of above mentioned characteristics of the chromium doping, as, for example, decrease the PL bands intensity in the visible spectral range and formation of $Cr^{2+}$ bound excitons, emission in the visible spectral range is determined not only by the doping impurity. However, it strongly depends on structural defects of the doped crystals, their concentrations, and sets of background impurities.

Luminescent emission in long wavelength part of the visible spectra is observed only for the ZnSe:Cr [I] crystal series (Fig. 4). Broad and structured bands of self-activated (SA) luminescence in this part of the spectra are usually associated with complex defects based on aluminum impurity or $[Cl_{Se}, V_{Zn}]$. Taking into account the similarity of chemical properties of chlorine and iodine, as well as usage of iodine as transport agent during the growth process, it is rational to assume that in the case of these samples $V_{Zn}$-$I_{Se}$ complexes, but not $V_{Zn}$-$Cl_{Se}$, are responsible for the SA-band. The presence of iodine based complexes in crystals grown by CVT method was also presupposed above in the discussion of the edge band PL. Increase of the chromium doping impurity concentration in the samples leads to change in intensity ratio of the SA-band maximums. In the undoped DAP emission, resulting in $R_0$ band, and chromium bound exciton recombination energy, determined from PL spectra of ZnSe:Cr [I]. Presence of small Stokes shift does not contradict the assumption. In this case, the increase of the $R_0$ band intensity should be considered a result of the chromium doping. Also the obtained result allows us to assume that the absence of the emission caused by radiative recombination of excitons bound to $Cr^{2+}$ ions in ZnSe:Cr PL spectra may be caused by presence of a number of structural or impurity defects in the crystals.

![FIG. 4. Normalised PL spectra of ZnSe:Cr [I] crystals in the visible spectral range at $T = 6.5 \, K$. Inset: dependence of the emission maximums ratio on chromium concentration.](image-url)
crystal PL spectrum intensity of the main maximum close to 538 nm decreases with increasing of doping impurity concentration and at concentration of 0.10 at. % Cr becomes equal with intensity of the secondary maximum located close to 604 nm in PL spectra. In the samples with highest chromium impurity concentration (0.30 at. %), the ratio of the 538 nm maximum intensity to the 604 nm maximum intensity becomes less than 1 (Fig. 4, inset). It should be mentioned that in the case of zinc selenide crystals grown by iodine transport, but doped with another TM impurity, only integral quenching of the SA-band intensity was observed, and the ratio of the maximums intensities remained unchanged. This allows us to conclude that the change in SA-band maximum intensities ratio is caused by doping with chromium.

Taking into account the acceptor nature of Cr$^{2+}$ ions and their possibility to release a hole in the valence band under optical excitation with photon energy greater than $\sim 1.9$ eV, it may be assumed that observed change in SA-band maximum intensities ratio is caused by resonant energy transfer from DAP-emission to absorption on chromium ions in this spectral region. In this case, the mechanism of the concentration quenching of the 538 nm maximum corresponds to the mechanism of sub-band excitation of Cr$^{2+}$ ions emission as a result of resonant energy transfer from center responsible for SA-band to Cr$^{2+}$ ions, the last is ionized releasing a hole in the valence band. This free hole subsequently may be captured by a single charged chromium ion, which will result in appearance of Cr$^{2+}$ ion in excited state, capable to emit a photon in middle-IR spectral region; or it may be captured by a background acceptor, which has energy level localized near the valence band edge. In the last case, the probability of radiative recombination of the hole bound to acceptor level, with a free electron from the conductance band or an electron bound to shallow donor level, is higher. This is observed as increase of the 604 nm maximum intensity in PL spectrum of chromium doped zinc selenide samples.

Mechanism of the concentration change of the SA-band maximum intensities described above may be applied only in case when the band is complex and the components with maximums close to 538 nm and 604 nm are caused by competing recombination channels. It should be mentioned that in case when mechanism responsible for emission with 538 nm and 604 nm do not compete, chromium doping should result only in integral decrease of the SA-band intensity without any change in its maximum intensities ratio. The fact that SA-band is not elementary is confirmed by its temperature evolution (Fig. 5). The position of the 604 nm maximum is practically unchanged with the temperature increase. This indicates on the change of the elementary components’ contribution to the bands shape at different temperatures. Temperature evolution also confirms that 538 nm and 604 nm components are competitive: at low temperatures quenching of the short wavelength component takes place but the long wavelength component maintains its intensity, which in the simplest case is caused by energy transfer between the bands. Even more, when 538 nm maximum is completely quenched, the intensity of the 604 nm maximum increases sharply (Fig. 5, inset), which unambiguously shows that mechanisms responsible for emission in this spectral range are competitive.

### B. Absorption of ZnSe:Cr crystals in middle-IR spectral range

Concentration dependencies of absorption spectra of ZnSe:Cr crystals, doped by various techniques, are presented in Fig. 6. Absorption maximum in 1.77 $\mu$m range, characteristic for ZnSe:Cr crystals, was observed in ZnSe:Cr (melt) (Fig. 6(a)) and ZnSe:Cr (PVT) (Fig. 6(b)) crystals. Absorption in this range is usually associated with $5T_2 \rightarrow 5E$ intrashell transitions of Cr$^{2+}$ ions between ground ($5T_2$) and first excited ($5E$) states. The concentration of the doping impurity in the samples may be evaluated from\(^4\)

$$a = 11.34 \times 10^{19} n_{Cr}[cm^{-3}],$$  \(\text{(4)}\)

where $a$ is absorption coefficient in 0.72 eV region and $n_{Cr}$ is chromium impurity concentration. However, as it is seen

![FIG. 6. Absorption spectra at T = 300 K of the ZnSe:Cr (melt) (a), ZnSe:Cr (PVT) (b), ZnSe:Cr [I] (c), and ZnSe:Cr [Bi] (d) crystals.](image)
from Fig. 6, chromium doping results in both appearance of intra-shell absorption band and general absorption increase in the IR spectral region. Because of this, absolute value of the absorption coefficient used for determination of the chromium impurity in the samples was taken as referring to the medium impurity in the IR spectral range out of the chromium intra-shell absorption band. Comparison of the chromium concentration determined from the absorption spectra according to Eq. (4) with technological conditions of the samples doping is presented in Table I.

<table>
<thead>
<tr>
<th>Chromium concentration in the source material</th>
<th>Chromium concentration determined from optical absorption</th>
<th>Diffusion duration</th>
<th>Chromium concentration determined from optical absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 × 10^{18} cm^{-3} (0.01 at. %)</td>
<td>2.6 × 10^{18} cm^{-3} (0.01 at. %)</td>
<td>0 h</td>
<td>0 cm^{-3} (0.00 at. %)</td>
</tr>
<tr>
<td>2.1 × 10^{19} cm^{-3} (0.10 at. %)</td>
<td>2.3 × 10^{19} cm^{-3} (0.10 at. %)</td>
<td>80 h</td>
<td>2.6 × 10^{18} cm^{-3} (0.01 at. %)</td>
</tr>
</tbody>
</table>

Chromium doping in case of ZnSe:Cr [I] and ZnSe:Cr [Bi] crystals results only in general increase of optical absorption in the middle-IR spectral range. The same was observed in spectra of samples doped during the growth from melt or by diffusion from the vapors. Decrease of the transparency of the samples may be caused by increase of native defect concentration during the growth process. However, considering that absorption level increases with the increase of the doping impurity concentration, when all other technological parameters are unchanged, it is more probable that the transparency decrease is caused by distortions of the crystal lattice periodicity, caused by chromium doping. In such a case, decrease of the samples optical transparency is caused not by increase of the absorption coefficient but by internal dispersion of light in the samples due to random distribution of the chromium doping impurity. This assumption is confirmed by the similar value of the background absorption for the similar doping levels (Table I, Figs. 6(a) and 6(b)). It also shows that optical transparency decrease is caused by both chromium impurity concentration and concentration of the background native and impurity defects. Thus, to avoid unwanted losses in the 2.0–2.4 μm range, it should be used the method, which gives the smallest lose in this range for the undoped crystal. For the studied series, these methods are CVT and growth from the melt.

C. Luminescent properties of ZnSe:Cr crystals in IR spectral range

A single band with maximum close to 0.95 μm is presented in near-IR spectra of ZnSe:Cr crystals (Fig. 7). FWHM of the band is ~120 meV at T = 6 K and depends weakly on concentration of the doping impurity. Intensity of the band increases with increasing chromium concentration in the samples (Fig. 7, inset). In crystals doped from the Bi melt, the discussed band is shifted to the long wavelength region of the spectra and its maximum is located near 1.1 μm (Fig. 8(a)). This shift is probably caused by the partial overlapping of the band in near-IR spectral range with the PL band located close to 1.5 μm, observed only in PL spectra of ZnSe:Cr [Bi] crystals. Taking into account the ability of Bi impurity to form point defects such as Bi_{5/2} and Bi_{3/2}, as well as Bi_{22/2} V_{Zn} complexes with native impurities, it can be assumed that band with 1.5 μm maximum is caused by incorporation of the bismuth atoms from melt. Temperature quenching activation energy of the 1.5 μm band (Fig. 9) calculated from Eq. (3) is equal to ~30 meV. This value is in a good agreement with the bismuth center activation energy, which confirms the made assumption. However, a strong dependence of the bands...
intensity on the chromium concentration, which repeats the dependence of the 1.1 µm band intensity (Fig. 8(a), inset), allows us to suppose that both bismuth and chromium impurities participate in formation of the band. It is interesting to mention that 1.5 µm maximum band is partially overlapped with the band of intra-shell absorption of the double charged chromium ions, observed in spectra of other crystals (Figs. 6(a) and 6(b)). This leads to the conclusion that modification of the chromium doping technology from the bismuth melt in a way which will allow to obtain both types of emission centers responsible for 1.5 µm band and double charged chromium ions responsible for absorption in 1.77 µm, may significantly improve the pumping of the chromium intrashell emission in the middle-IR spectral range.

Energy position of the 0.95 µm emission band is in the good agreement with energy difference between ground (5T2) and second excited (5T1) states of Cr2+ ion, however, there is also an assumption that this band may be caused by 5T1(G) → 6A1(S) radiative transitions within Cr+ ion. Taking into account that mechanism of the IR luminescence excitation by 2.32 eV energy quanta assumes appearance of both Cr2+ and Cr+ non-equilibrium states, unequivocal determination of the bands nature is difficult. However, 3T1 → 5T2 transitions are competitive with 5E → 5T2, responsible for emission in ~2.0 µm range, which should result in quenching of middle-IR band when intensity of the near-IR band increases and, opposites, increase of the middle-IR intensity when near-IR band quenches. Temperature dependence of the ZnSe:Cr PL bands intensity in near and middle-IR spectral range is complicated and non-uniform (Fig. 10). In 6–100 K temperature range, intensity of 0.95 µm band increases but the intensity of the band in middle-IR spectral range decreases in the same temperature interval. Further temperature increase from 100 K to 295 K results in quenching of 0.95 µm band and significant increase of 2.07 µm band intensity in middle-IR range. It should be mentioned that maximum position of the 0.95 µm
and 2.07 μm bands is unchanged at temperature increase, which reveals the intrashell nature of the emission. The obtained result may be considered as evidence of the competitive character of the bands in near and middle-IR range. It is most probably that both discussed bands observed in IR spectra of ZnSe:Cr crystals are caused by intrashell transitions within Cr$^{2+}$. The conclusion above also founds its confirmation in literature.53

In middle-IR spectral range, a wide structural PL band with a few maxima may be observed (Fig. 11). The bands FWHM as well as its maximums’ ratio strongly depend on the crystals doping method and temperature. At liquid helium temperatures and low concentrations of the chromium impurity, the main maximum is localized at 2.2 μm (Fig. 12(a)). Increase of the chromium concentration leads to increase of 2.07 μm maximum even at low temperatures (Fig. 12(a), inset). At room temperature, the peak close to 2.07 μm is main in spectra of all studied ZnSe:Cr crystals (Fig. 12(b)), which is in good agreement with data of more efficient emission of chromium ions in middle-IR spectral range when the temperature is increased.24 The large FWHM of the discussed band, presence of few maximums in its shape, as well as change in the maxima ratio depending on the chromium concentration or doping method at low temperatures (Fig. 12(a), inset), allows us to conclude that 2.07 μm band is complex, consisting of a number of elementary bands. This assumption does not contradict with literature about intrashell emission of the chromium ions in IR spectral range but may explain differences in experimental data presented in literature and enumerated in the introduction of this article. Even more, secondary maxima mentioned above (Figs. 11 and 12) repeat with sufficient accuracy position of the middle-IR band given in other papers.6,21–24

In case if band with the main maximum at room temperature located at ~2.07 μm is complex, we may try to associate its components with radiative transitions. The component

![FIG. 11. Normalised PL spectra of ZnSe:Cr crystals in IR spectral range at T = 6.5 K. Inset: (a) influence of the annealing in zinc vapors on PL spectra of the ZnSe:Cr (PVT) crystal doped by diffusion from the gas phase during 80 h at T = 85 K; (b) dependence of the mid-IR band intensity in maximum (2.07 μm) on the chromium doping impurity concentration at T = 295 K.](image)

![FIG. 12. PL spectra of ZnSe:Cr [I] crystals in IR spectral range at T = 6.5 K (a) and T = 300 K (b). Inset: dependence of the emission intensity in the bands maximum on doping impurity concentration.](image)
The PL emission intensity in the middle-IR spectral region decreases with increasing chromium doping impurity concentration in ZnSe crystals, which is usually explained by one of the three causes: \(^\text{23}\) interaction between chromium ions by means of “turn-by-turn” energy transfer via non-radiative transitions from one ion to another and after a number of transfer steps, finally to a quenching site (for example, a defect state); recombination of Cr with Se; or because of incorporation of chromium atoms in interstitial sites or segregation of the chromium metallic phase. Taking into account complex character of the band in the middle-IR spectral region, as well as energetic closeness of the bands components, a resonant energy transfer between the band components may be assumed, in this case chromium impurity should be considered as sensitizer of the emission in spectral range of \(\sim 2.0 \mu \text{m}\). This is in good agreement with the fact that 2.07 \(\mu \text{m}\) is located in the short wavelength part of the complex IR band. Increase of chromium concentration, which occupies zinc nodes of the zinc selenide crystal lattice, will lead to destruction of zinc vacancy complexes, participating in formation of middle-IR spectral band. It will also result in increasing concentration of point defects, by means of background impurities which were included in complexes with zinc vacancies. These both facts indicate that concentration quenching, which may be explained in the frame of the first mechanism, depends not only on Cr ions concentration in ZnSe but also on defect-impurity concentration of the crystals, mainly determined by the doping method.

The experimental data (Fig. 11, inset (b)) confirm the conclusion made. The crystal growth by the CVT method leads to generation of a larger amount of zinc vacancies comparing to the melt growth, because some of the zinc atoms, after the interaction with the transport agent, may sediment in other parts of the ampoule than the crystal growth zone. Increase of the zinc vacancy nodes stimulates incorporation of the chromium ions but also results in increase of complex defects concentration, which participate in formation of the mid-IR emission. These two facts allow to explain a considerably larger intensity of the mid-IR band in ZnSe:Cr [1] crystals PL spectra. Large concentration of the defects based on the zinc vacancies in the crystals grown by the chemical vapor transport method results in larger probability of resonant energy transfer from a Cr\(^{2+}\) ion to a defect, which participates in formation of the mid-IR band, rather than to a singular non-radiative defect. Concentration quenching of the mid-IR PL band, most probably, will depend on concentrations ratio between non-radiative defects, which amount will increase with increase of chromium concentration in the crystals, and zinc vacancy-based complex defects. The concentration of the zinc vacancy-based defects participating in formation of the mid-IR band is larger in the case of the CVT grown samples, thus, concentration quenching should appear at larger chromium concentrations that may be observed from the experimental data.

**IV. CONCLUSIONS**

Optical and photoluminescent properties of ZnSe:Cr crystals with impurity concentration within 0–0.30 at. % Cr...
range and doped by various technological methods were studied. By means of excitonic spectroscopy energy position of Cr$^{2+}$ levels was established to be 0.66 eV above the zinc selenide valence band, and acceptor nature of non-equilibrium double charged chromium ions was revealed. Active participation of chromium impurities in resonant energy transfer with DAP-centers was shown, which results in significant change of impurity PL bands intensities with increasing of chromium concentration in crystals. An assumption about complex composition of emission band in the middle-IR spectral range was made and it was argued that this band consists of both intrashell emission of Cr$^{2+}$ ions, which are activators for middle-IR emission band, and emission caused by complexes based on zinc vacancies and background impurities. Obtained results show that emission of ZnSe:Cr crystals is determined not exclusively by the doping impurity but strongly depends on structural defects of the doping crystals, their concentrations, and sets of background impurities.

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