

**PHOTOCONDUCTIVITY AND PHOTOLUMINESCENCE OF ZnSe:Cr CRYSTALS IN THE VISIBLE SPECTRAL REGION**

The photoconductivity and photoluminescence of ZnSe:Cr crystals in the visible spectra region are studied. The scheme of optical transitions within Cr<sup>2+</sup> impurity centers is established. It is shown that the high-temperature impurity photoconductivity of ZnSe:Cr crystals is controlled by optical transitions of electrons from the 5T<sub>2</sub>(D) ground state to the higher levels of excited states of Cr<sup>2+</sup> ions, with subsequent thermal activation of the electrons to the conduction band. Efficient excitation of intracenter luminescence of ZnSe:Cr crystals is attained with light corresponding to the region of intrinsic absorption in Cr<sup>2+</sup> ions.

**INTRODUCTION**

Zinc selenide single crystals doped with chromium are promising materials for use as laser media. At present lasing in such crystals in the mid-infrared (IR) region is being extensively studied. On the basis of ZnSe:Cr crystals, lasers tunable in the wavelength range from 1.9–3 μm [1].

The transition elements, among them chromium, are thought to form centers that suppress luminescence in the visible spectral region. For this reason, the number of studies concerned with the effect of chromium ions on the optical properties of ZnSe in the visible region is rather limited. At the same time, the calculation of energy states of chromium impurity centers in ZnSe [2,3] suggests that radiative transitions with the photon energy close to the band gap of the semiconductor can really occur. In this context, the study of optical properties of ZnSe:Cr crystals in the visible spectral region presents a topical problem. In previous studies of optical absorption in the range 1.7–2.6 eV [3], we detected absorption bands defined by intracenter transitions in Cr<sup>2+</sup> ions.

In this study, we analyze and identify the structure of the photoconductivity and photoluminescence (PL) spectra of ZnSe:Cr crystals in the visible spectral region. The photoconductivity and PL bands associated with transitions within chromium ions are observed.

The purpose of this study is to identify the photoconductivity and PL spectra in ZnSe:Cr crystals.

**EXPERIMENTAL**

The samples under study were fabricated by diffusion doping of initially pure ZnSe crystals with the Cr impurity. The undoped crystals were obtained by the technique of free growth on single crystal ZnSe substrate oriented in the (111) plane. The advantage of diffusion doping is that it is possible to vary the impurity concentration and profile. The procedure of doping and the studies of optical absorption in the crystals are described in detail elsewhere [3,4]. The chromium content in the crystals was determined from the change in the band gap as a function of the dopant concentration.

The photoconductivity spectra were recorded with the use of an MUM-2 monochromator. For the source of excitation light, we used a halogen lamp. The power of the light flux was kept constant by controlling the filament current of the lamp. For the photoconductivity measurements, ohmic indium contacts were deposited onto the crystals.

The PL spectra were recorded with the use of an ISP-51 prism spectrograph. The emission signal was detected with an FEU-100 photomultiplier.

The PL signal was excited with light-emitting diodes (LEDs), Edison Opto Corp., the emission

peaks of which corresponded to the wavelengths 400, 460, and 500 nm, and with an ILGI-503 nitrogen pulse laser emitting at the wavelength 337 nm.

### ANALYSIS OF PHOTOCONDUCTIVITY SPECTRA

Figure 1 shows the photoconductivity spectra of the ZnSe:Cr crystals with different Cr concentrations.

The photoconductivity spectrum of the undoped crystal is shown in Fig. 1 for comparison. The undoped crystals exhibit a single photoconductivity band with a peak at 2.65 eV at 300 K (Fig. 1, curve 1). This band is due to interband optical transitions. On doping of the crystals with chromium, the band shifts to lower energies. As the Cr concentration is increased, the shift increases and corresponds to the change in the band gap determined from the optical absorption spectra in [3].

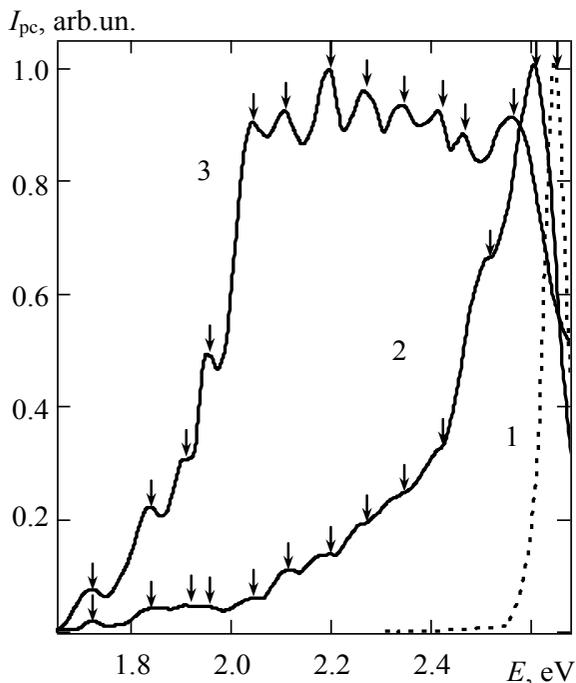


Fig.1. Photoconductivity spectra of (1) ZnSe and (2, 3) ZnSe:Cr crystals. The Cr dopant concentrations are  $[Cr] = (2) 2 \cdot 10^{18}$  and  $(3) 2 \cdot 10^{19} \text{ cm}^{-3}$ .

Doping with chromium brings about the appearance of series photoconductivity bands in the range of photon energies from 1.7 to 2.6 eV

(Fig. 1, curves 2, 3). As the Cr concentration is increased, the intensity of these bands increases. We observe well-defined bands at 1.74, 1.85, 1.92, 1.97, 2.04, 2.07, 2.14, 2.22, 2.31, 2.42 and 2.50 eV. The band at 2.50 eV changes its position as the Cr concentration is changed. The positions of other bands do not vary with increasing degree of doping.

At the temperature  $T = 77 \text{ K}$ , only one inter-band photoconductivity band is observed in all of the crystals under study (Fig. 2, curve 1). As the temperature is elevated from 77 to 350 K, the impurity photoconductivity makes a weightier contribution to the spectrum (Fig. 2). We observed a similar effect previously in studying the photoconductivity of ZnSe crystals doped with Fe [5].

As the temperature is elevated from 300 to 350 K the 2.50 eV photoconductivity band shifts to lower photon energies by 20 meV. Such shift corresponds to the temperature change in the band gap of ZnSe. Other impurity photoconductivity bands do not change their position with temperature, suggesting that the corresponding transitions are of intracenter character. In addition, the position of the above mentioned bands agrees well with the position of optical absorption bands detected for these crystals previously. In [3] these absorption bands were attributed to intracenter optical transitions that occur within the  $\text{Cr}^{2+}$  ions. The above result suggests that these photoconductivity bands are due to the same optical transitions as those involved in optical absorption. The energies and identification of optical transitions are given in the table. The table summarizes the data obtained in studies of optical absorption [3], photoconductivity and luminescence.

The photoconductivity process in the crystals under study occurs in the manner briefly described below. The 2.50 eV photoconductivity band is associated with optical transitions from the  ${}^5T_2(D)$  ground state of the  $\text{Cr}^{2+}$  ion into the conduction band. Comparison of the photon energy corresponding to the peak of this photoconductivity band with the energy position of the intrinsic photoconductivity peak for the crystals with the Cr concentration  $[Cr] = 2 \cdot 10^{18} \text{ cm}^{-3}$  (2.60 eV) allows us to believe that the level of the ground state of the  $\text{Cr}^{2+}$  ion is 100 meV above the top of the valence band.

Energies of optical transitions in ZnSe:Cr crystals

Line No	Absorption		Photoconductivity, E, eV	Luminescence, E, eV	Stokes shift, E, meV
	E, eV[3]	Transition			
1	---	${}^5T_2(D) \rightarrow {}^4T_1(F) + e^-_{c.b}$	2.5	---	---
2	2.6	${}^5T_2(D) \rightarrow {}^1A_2(I)$	---	2.58	20
3	2.49	${}^5T_2(D) \rightarrow {}^3T_2(D)$	---	2.46	30
4	2.41	${}^5T_2(D) \rightarrow {}^1T_2(I)$	2.42	2.38	30
5	2.31	${}^5T_2(D) \rightarrow {}^1A_1(G)$	2.31	2.30	20
6	2.22	${}^5T_2(D) \rightarrow {}^1E(I)$	2.22	2.20	20
7	2.14	${}^5T_2(D) \rightarrow {}^3T_1(F)$	2.14	2.12	20
8	2.07, 2.04	${}^5T_2(D) \rightarrow {}^3E(G)$	2.07, 2.04	2.02	20
9	1.97	${}^5T_2(D) \rightarrow {}^3A_2(F)$	1.97	1.95	20
10	1.92	${}^5T_2(D) \rightarrow {}^1T_2(I)$	1.92	---	---
11	1.85	${}^5T_2(D) \rightarrow {}^3T_2(G)$	1.85	1.81	40
12	1.74	${}^5T_2(D) \rightarrow {}^3E(H)$	1.74	1.72	20
13	1.67	${}^5T_2(D) \rightarrow {}^3T_2(F)$	---	1.62	50
14	1.58	${}^5T_2(D) \rightarrow {}^3T_1(H)$	---	1.54	40
15	1.19	${}^5T_2(D) \rightarrow {}^3T_2(H)$	---	1.16	30

The other photoconductivity bands are formed in a two-stage process. Initially, the intracenter optical transitions of electrons from the  ${}^5T_2(D)$  ground state to the higher excited states of the  $Cr^{2+}$  ions (table) occur; then thermally activated transitions of these electrons to the conduction band are observed. As a result the local centers transit to the  $Cr^{3+}$  charged state. Later the  $Cr^{3+}$  centers trap electrons and the centers transit to their initial  $Cr^{2+}$  state.

It should be noted that the results of studies of the thermoelectric power are indicative of the electron photoconductivity of the ZnSe:Cr crystals.

### ANALYSIS OF LUMINESCENCE PROPERTIES

The PL spectra were studied in the temperature range from 77 to 300 K. The PL spectra of undoped crystals excited with nitrogen laser radiation ( $\lambda = 337$  nm) at  $T = 77$  K exhibit one emission band with peak at 2.77 eV (Fig. 2, curve 1). In our previous studies the 2.77 eV emission band was attributed to emission of excitons localized at neutral zinc vacancies [6].

Upon doping of the crystals with chromium, the excitonic emission bands shift to lower ener-

gies (Fig. 2, curve 2). The shift corresponds to the change in the band gap with the chromium concentration  $[Cr]$  in ZnSe, as determined in [3].

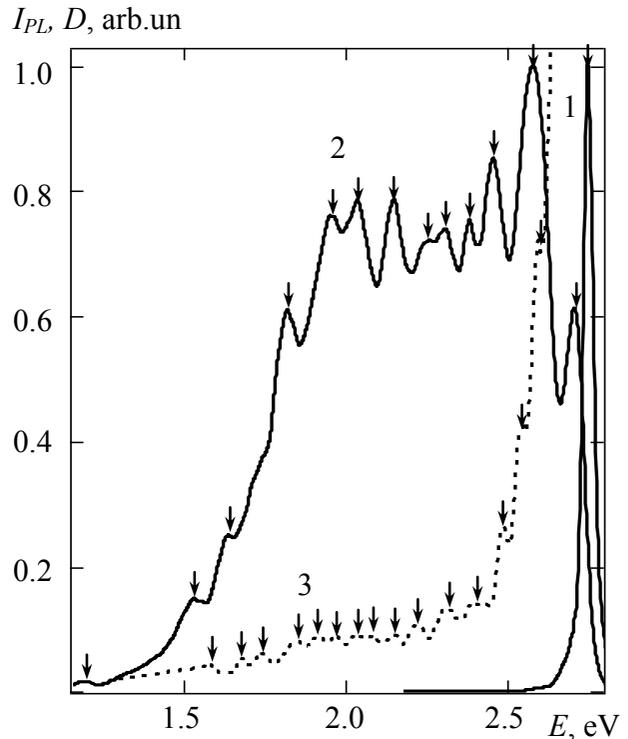


Fig. 2. (1, 2) Photoluminescence and (3) absorption spectra of (1) ZnSe and (2, 3) ZnSe:Cr crystals.

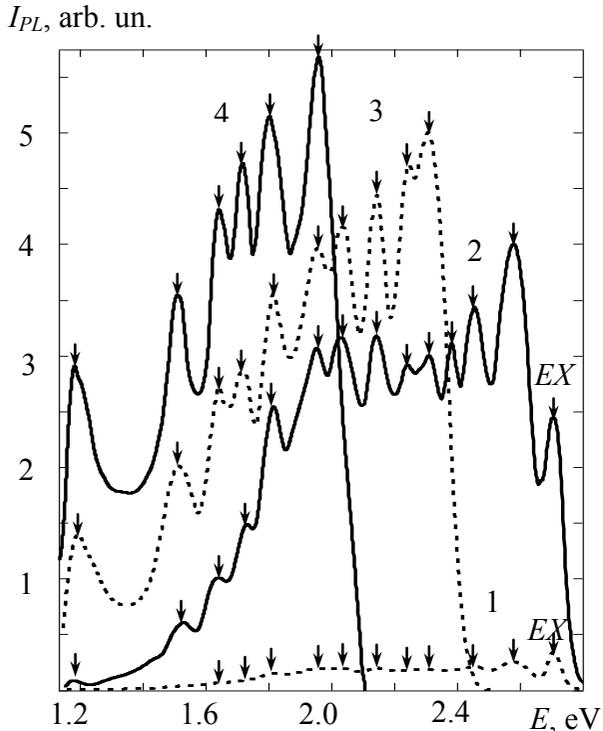


Fig. 3. Photoluminescence spectra of ZnSe:Cr crystals.  $E_{ex} = 3.74$  (1), 3.1 (2), 2.69 (3) and 2.25 eV (4).

Doping of the crystals with chromium brings about a series of long-wavelength emission lines with peaks at 1.16, 1.54, 1.62, 1.72, 1.81, 1.95, 2.02, 2.12, 2.20, 2.30, 2.38, 2.46, 2.58 (Fig. 2, curve 2). As the Cr concentration is increased, the intensity of these emission lines increases, whereas their position remains unchanged.

Figure 2 (curve 3) shows the absorption spectrum of the ZnSe:Cr crystals at  $T = 77$  K. The spectrum involves lines that correlate with the emission lines observed in this study. As can be seen from the table, the Stokes shifts of the PL lines with respect to the corresponding absorption lines are in the range 10–50 meV.

It is established that the relative luminescence intensity of the ZnSe:Cr crystals heavily depends on the photon energy of excitation light (Fig. 3, curves 1–4).

Emission with the lowest intensity is excited with a nitrogen laser with the photon energy 3.67 eV. The highest emission intensity is attained on excitation with LEDs with the photon energy in the emission peak 2.69 and 2.25 eV (Fig. 3, curves 3, 4). This suggests that the band-to-band excitation of long-wavelength luminescence of the ZnSe:Cr crystals is inefficient. At the same

time, under changes in the excitation photon energy, the position of emission peaks remains unchanged. It is also established that, as the excitation photon energy is lowered, the contribution of low-energy bands to the luminescence spectrum increases. This effect is typical of intracenter luminescence.

As the temperature is elevated from 77 to 300 K, the intensity of all emission lines decreases, while the positions of the peaks remain unchanged. Similar temperature behavior was observed for the corresponding absorption

lines. This suggests that the absorption and luminescence lines under study are due to intracenter optical transitions that occur within chromium ions.

## CONCLUSIONS

1. It is shown that the high-temperature long-wavelength photoconductivity of the ZnSe:Cr crystals is controlled by intracenter optical transitions within the  $Cr^{2+}$  ions and by subsequent thermally induced transitions of electrons from the levels of the excited  $Cr^{3+}$  states into the conduction band.

2. It is established that doping with iron gives rise to a series of emission lines in the visible spectral region. The luminescence bands detected for the ZnSe:Cr crystals are attributed to intracenter transitions in the  $Cr^{2+}$  ions.

3. Efficient excitation in impurity-related luminescence of the ZnSe:Cr crystals is attained with light corresponding to the region of intrinsic absorption in the  $Cr^{2+}$  ions.

## REFERENCES

1. Moskalev I.S. Fedorov V.V., Mirov S.B. Tunable, single-frequency, and multi-watt continuous-wave  $Cr^{2+}$ :ZnSe Lasers // Optics express. – 2008. – V. 16, № 6. – P. 4145-4153.
2. Zunger A. Electronic structure of 3d-transition atom impurities in semiconductors // Solid State Physics. – 1986. – V.39. – P. 27674.
3. Ницук Ю.А. Энергетические состояния иона  $Cr^{2+}$  в кристаллах ZnSe// ФТП. – 2013. – Т. 47, В. 6. – С. 728-

- 731.
4. Ваксман Ю.Ф., Павлов В.В., Ницук Ю.А. Оптическое поглощение и диффузия хрома в монокристаллах ZnSe // ФТП. - 2005. - Т. 39, №4. - С. 401-404.
  5. Ваксман Ю.Ф., Ницук Ю.А., Яцун В.В., Влияние примеси железа на люминесценцию и фотопроводимость кристаллов ZnSe в видимой области спектра // ФТП. – 2011. – Т. 45, В. 9. – С. 1171-1174.
  6. Vaksman Yu. F., Nitsuk Yu. A., Purtoov Yu. N., Shapkin P. V. Native and impurity defects in ZnSe:In single crystals prepared by free growth // Semiconductors. – 2001. – V.3. – P. 883-889.

This article has been received within 2015 .

UDC 621.315.592

*Yu. F. Vaksman, Yu. A. Nitsuk*

## **PHOTOCONDUCTIVITY AND PHOTOLUMINESCENCE OF ZnSe:Cr CRYSTALS IN THE VISIBLE SPECTRAL REGION**

### **Abstract**

The photoconductivity and photoluminescence of ZnSe:Cr crystals in the visible spectra region are studied. The scheme of optical transitions within Cr<sup>2+</sup> impurity centers is established. It is shown that the high-temperature impurity photoconductivity of ZnSe:Cr crystals is controlled by optical transitions of electrons from the <sup>5</sup>T<sub>2</sub>(D) ground state to the higher levels of excited states of Cr<sup>2+</sup> ions, with subsequent thermal activation of the electrons to the conduction band. Efficient excitation of intra-center luminescence of ZnSe:Cr crystals is attained with light corresponding to the region of impurity absorption.

**Key words:** zinc selenide, diffusion doping, chromium impurity, photoconductivity, photoluminescence.

УДК 621.315.592

*Ю. Ф. Ваксман, Ю. А. Ницук*

## **ФОТОПРОВОДИМОСТЬ И ФОТОЛЮМИНЕСЦЕНЦИЯ КРИСТАЛЛОВ ZnSe:Cr В ВИДИМОЙ ОБЛАСТИ СПЕКТРА**

### **Резюме**

Исследована фотопроводимость и фотолюминесценция кристаллов ZnSe:Cr в видимой области спектра. Установлена схема оптических переходов, происходящих в пределах примесных центров Cr<sup>2+</sup>.

Показано, что высокотемпературная фотопроводимость кристаллов ZnSe:Cr обусловлена оптическими переходами электронов из основного состояния <sup>5</sup>T<sub>2</sub>(D) на более высокие возбужденные энергетические уровни иона Cr<sup>2+</sup> с их последующей термической активацией в зону проводимости. Эффективное возбуждение внутрицентральной люминесценции кристаллов ZnSe:Cr осуществляется светом из области примесного поглощения.

**Ключевые слова:** селенид цинка, диффузионное легирование, примесь хрома, фотопроводимость, фотолюминесценция.

УДК 621.315.592

*Ю. Ф. Ваксман, Ю. А. Ницук*

## **ФОТОПРОВІДНІСТЬ І ФОТОЛЮМІНЕСЦЕНЦІЯ КРИСТАЛІВ ZnSe:Cr У ВИДИМІЙ ОБЛАСТІ СПЕКТРУ**

### **Резюме**

Досліджено фотопровідність і фотолюмінесценцію кристалів ZnSe:Cr у видимій області спектру. Встановлено схему оптичних переходів в межах домішкових центрів Cr<sup>2+</sup>.

Показано, що високотемпературна фотопровідність кристалів ZnSe:Cr обумовлена оптичними переходами електронів з основного стану  $^5T_2(D)$  на більш високі збуджені енергетичні рівні іону Cr<sup>2+</sup> з їх подальшою термічною активацією в зону провідності. Ефективне збудження внутрішньоцентрової люмінесценції кристалів ZnSe:Cr відбувається світлом з області домішкового поглинання іонів Cr<sup>2+</sup>.

**Ключові слова:** селенид цинку, дифузійне легування, домішка хрому, фотопровідність, фотолюмінесценція.