

**PHOTOLUMINESCENCE AND PHOTOCONDUCTIVITY OF ZnS:Ti SINGLE CRYSTALS**

The photoconductivity and photoluminescence of ZnS:Ti crystals in the visible spectra region are studied. The scheme of optical transitions within  $Ti^{2+}$  impurity centers is established. It is shown that the high-temperature photoconductivity of ZnS:Ti crystals is controlled by optical transitions of electrons from the  $^3A_2(F)$  ground state to the higher levels of excited states of  $Ti^{2+}$  ions, with subsequent thermal activation of the electrons to the conduction band. Efficient excitation of intracenter luminescence of ZnS:Ti crystals is attained with light corresponding to the region of intrinsic absorption in  $Ti^{2+}$  ions.

**INTRODUCTION**

The zinc sulphide single crystals, doped with transitional metals ions 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 ZnS:Cr crystals, lasers tunable in the wavelength range of 2.35  $\mu\text{m}$  have already been fabricated [1]. In the spectral region were fabricated based on the ZnS:Cr crystals [1]. In [2] it was reported about creation of impulsive laser based on ZnS:Fe crystal with continuous tuning of the laser wavelength within the range of 3.49-4.65  $\mu\text{m}$ . At the same time, essentially nothing is known about possibility of infrared laser radiation realization using ZnS:Ti crystals.

The transition elements, among them titanium, 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 titanium ions on the optical properties of ZnS in the visible region is rather limited. At the same time, the calculation of energy states of titanium impurity centers in ZnS [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 ZnS:Ti crystals in the visible spectral

region presents a topical problem. In previous studies of optical absorption in the range 0.4-3.6 eV [4], we detected absorption bands defined by intracenter transitions in  $Ti^{2+}$  ions.

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

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

**EXPERIMENTAL**

The samples to be studied were fabricated by diffusion doping of initially pure ZnS crystals with the Ti impurity. The undoped crystals were obtained by the technique of free growth on single-crystal ZnS 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 [4]. The titanium 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 indium contacts were fired-in at the temperature 600 K. This was done with the use of a VUP-4 vacuum setup.

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

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.

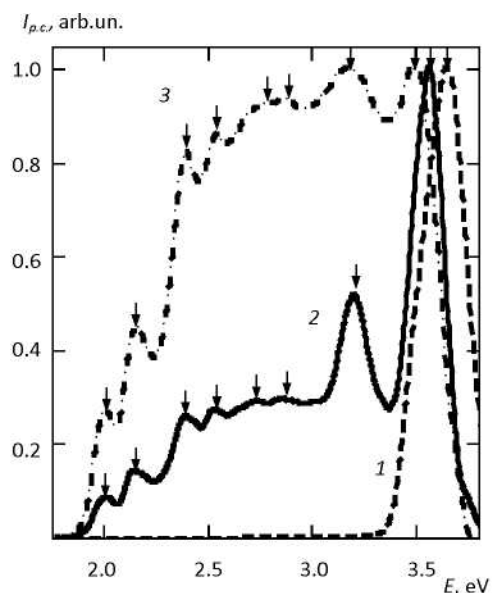
### ANALYSIS OF PHOTOCONDUCTIVITY SPECTRA

Figure 1 shows the photoconductivity spectra of the ZnS:Ti crystals with different Ti 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 3.64 eV at 300 K (Fig. 1, curve 1). This band is due to interband optical transitions. On doping of the crystals with titanium, the band shifts to lower energies. As the Ti concentration is increased, the shift increases and corresponds to the change in the band gap determined from the optical absorption spectra in [4].

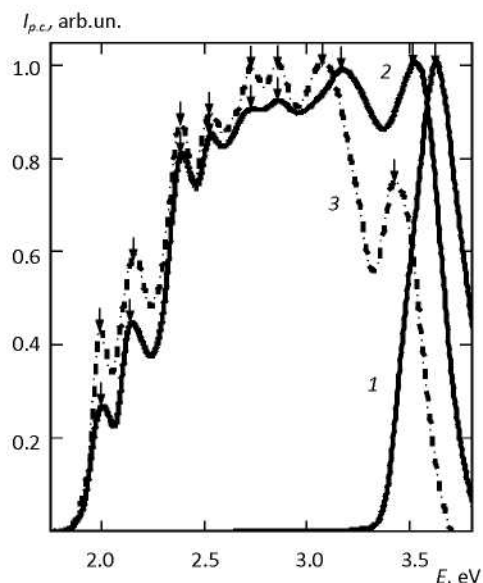
Doping with titanium brings about the appearance of extra photoconductivity bands in the range of photon energies from 1.8 to 3.4 eV (Fig. 1, curves 2, 3). As the Ti concentration is increased, the intensity of these bands increases. We observe well defined bands at 2.0, 2.13, 2.38, 2.52, 2.74, 2.85, and 3.15 eV. The 3.15 eV photoconductivity band changes its position as the Ti concentration is changed. The positions of other bands do not vary with increasing degree of doping.

At the temperature  $T = 77$  K, only one interband 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 and Ni [5,6].



**Fig. 1.** Photoconductivity spectra of (1) ZnS and (2,3) ZnS:Ti crystals. The Ti dopant concentrations are  $[\text{Ti}] = (2) 2 \times 10^{19}$  and  $(3) 5 \times 10^{19} \text{ cm}^{-3}$ .



**Fig. 2.** Photoconductivity spectra of ZnS:Ti crystals at the temperatures (1) 77, (2) 300, and (3) 400 K.  $[\text{Ti}] = 5 \times 10^{19} \text{ cm}^{-3}$ .

Table  
Energies of optical transitions in ZnS:Ti crystals

Line number	Absorption		Photoconductivity	Luminescence	Stokes shift
	$E$ , eV[4]	transition	$E$ , eV	$E$ , eV	$E$ , meV
1	3.15	${}^3A_2(F) + h\nu \rightarrow {}^2E(D) + e^-_{c.b.}$	3.15	---	---
2	2.85	${}^3A_2(F) \rightarrow {}^1T_2(G)$	2.87	---	---
3	2.75	${}^3A_2(F) \rightarrow {}^1E(G)$	2.76	2.72	40
4	2.52	${}^3A_2(F) \rightarrow {}^1T_1(G)$	2.55	2.50	50
5	2.37	${}^3A_2(F) \rightarrow {}^1A_1(G)$	2.39	2.34	50
6	2.13	${}^3A_2(F) \rightarrow {}^3T_1(P)$	2.10	2.07	30
7	2.0	${}^3A_2(F) \rightarrow {}^1T_2(D)$	1.98	1.98	20
8	0.78	${}^3A_2(F) \rightarrow {}^3T_1(F)$	---	0.72	60

As the temperature is elevated from 300 to 400 K (Fig. 2, curves 2, 3), the 3.15 eV photoconductivity band shifts to lower photon energies by 80 meV. Such a shift corresponds to the temperature change in the band gap of ZnS. 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 [4] these absorption bands were attributed to intracenter optical transitions that occur within the  $Ti^{2+}$  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 [4], photoconductivity, and luminescence and in the calculations of energy states of the  $Ti^{2+}$  ions in ZnS [4]. The photoconductivity process in the crystals under study occurs in the manner briefly described below. The 3.15 eV photoconductivity band is associated with optical transitions from the  ${}^3A_2(F)$  ground state of the  $Ti^{2+}$  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 Ti concentration  $[Ti] = 5 \times 10^{19}$

$cm^{-3}$  (3.15 eV) allows us to believe that the level of the ground state of the  $Ti^{2+}$  ion is 360 meV above the top of the valence band.

The other photoconductivity bands are formed in a two-stage process. Initially, the intracenter optical transitions of electrons from the  ${}^3A_2(F)$  ground state to the higher excited states of the  $Ti^{2+}$  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  $Ti^{3+}$  charged state. Later the  $Ti^{3+}$  centers trap electrons and the centers transit to their initial  $Ti^{2+}$  state.

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

#### ANALYSIS OF LUMINESCENCE PROPERTIES OF ZnS:Ti CRYSTALS

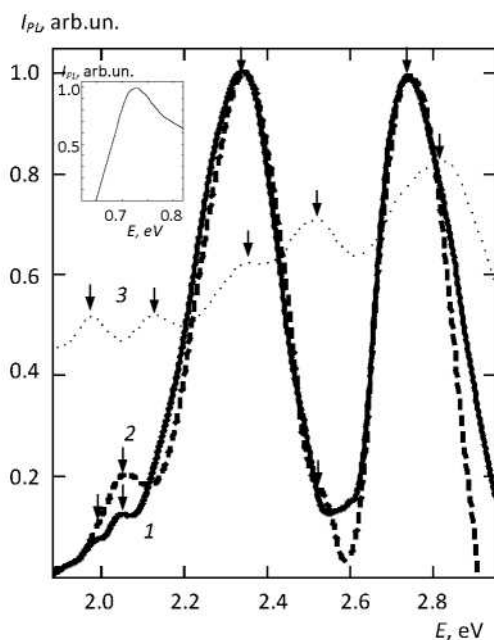
The PL spectra were studied in the temperature range from 77 to 300 K. The PL spectra of undoped crystals do not exhibit emission bands in the visible and IR spectral region.

Doping of the crystals with titanium brings about a series of visible emission lines with peaks at 1.98, 2.06, 2.34, 2.50 and 2.72 eV (Fig. 3, curve 1). As the Ti concentration is increased, the intensity of these emission lines increases, whereas their position remains unchanged.

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 (Fig. 3, curve 2). 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 titanium ions.

Figure 3 (curve 3) shows the absorption spectrum of the ZnS:Ti 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 20-60 meV. The inset in Fig. 3 shows the 0.72 eV IR-emission band.



**Fig. 3. (1, 2) Photoluminescence and (3) absorption spectra of ZnS:Ti crystals. Inset: IR-emission band.**

It is established that the relative luminescence intensity of the ZnS:Ti crystals heavily depends on the photon energy of excitation light.

Emission with the lowest intensity is excited with a nitrogen laser with the photon energy 3.68 eV. The highest emission intensity is attained on excitation with LEDs with the photon energy in the emission peak 3.1 and 2.69 eV. This suggests that the band-to-band excitation of long-wavelength luminescence of the ZnS:Ti 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.

## CONCLUSIONS

The study allows a number of conclusions. These are as follows:

1. It is shown that the high-temperature long-wavelength photoconductivity of the ZnS:Ti crystals is controlled by intracenter optical transitions within the  $Ti^{2+}$  ions and by subsequent thermally induced transitions of electrons from the levels of the excited  $Ti^{2+}$  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 ZnS:Ti crystals are attributed to intracenter transitions in the  $Ti^{2+}$  ions.

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

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

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### Abstract

The photoconductivity and photoluminescence of ZnS:Ti crystals in the visible spectra region are studied. The scheme of optical transitions within  $Ti^{2+}$  impurity centers is established. It is shown that the high-temperature photoconductivity of ZnS:Ti crystals is controlled by optical transitions of electrons from the  $^3A_2(F)$  ground state to the higher levels of excited states of  $Ti^{2+}$  ions, with subsequent thermal activation of the electrons to the conduction band. Efficient excitation of intracenter luminescence of ZnS:Ti crystals is attained with light corresponding to the region of intrinsic absorption in  $Ti^{2+}$  ions.

**Key words:** zinc sulfide, titanium impurity, photoconductivity, photoluminescence

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*Ю. Ф. Ваксман, Ю. А. Ницук*

## ФОТОЛЮМИНЕСЦЕНЦИЯ И ФОТОПРОВОДИМОСТЬ МОНОКРИСТАЛЛОВ ZnS:Ti

### Резюме

Исследована фотопроводимость и фотолюминесценция кристаллов ZnS:Ti в видимой области спектра. Установлена схема оптических переходов, происходящих в пределах примесных центров  $Ti^{2+}$ . Показано, что высокотемпературная фотопроводимость кристаллов ZnS:Fe обусловлена оптическими переходами электронов из основного состояния  $^3A_2(F)$  на более высокие возбужденные энергетические уровни иона  $Ti^{2+}$  с их последующей термической активацией в зону проводимости. Эффективное возбуждение внутрицентральной люминесценции кристаллов ZnS:Ti осуществляется светом из области собственного поглощения ионов  $Ti^{2+}$ .

**Ключевые слова:** сульфид цинка, примесь титана, фотолюминесценция, фотопроводимость.

**ФОТОЛЮМІНЕСЦЕНЦІЯ І ФОТОПРОВІДНІСТЬ МОНОКРИСТАЛІВ ZnS:Ti****Резюме**

Досліджено фотопровідність і фотолюмінесценцію кристалів ZnS:Ti в видимій області спектру. Встановлено схему оптичних переходів, що протікають в межах домішкових центрів  $Ti^{2+}$ . Показано, що високотемпературна фотопровідність кристалів ZnS:Ti обумовлена оптичними переходами електронів з основного стану  $^3A_2(F)$  на більш високі збуджені енергетичні рівні іону  $Ti^{2+}$  з їх подальшою термічною активацією в зону провідності. Ефективне збудження внутрішньоцентрової люмінесценції кристалів ZnS:Ti здійснюється світлом з області власного поглинання іонів  $Ti^{2+}$ .

**Ключові слова:** сульфід цинку, домішка титану, фотолюмінесценція, фотопровідність.