

Yu. F. Vaksman, Yu. A. Nitsuk, A. V. Korenkova

I. I. Mechnikov Odesa National University
e-mail: nitsuk@onu.edu.ua

STUDY OF THE IMPURITY PHOTOCONDUCTIVITY AND LUMINESCENCE IN ZnTe:V CRYSTALS

The photoconductivity and photoluminescence spectra of ZnTe:V crystals in the visible spectral region are studied. It is established that the high-temperature impurity photoconductivity of ZnTe:V crystals is controlled by the optical transitions of electrons from the ground state 4T₁(F) to high-energy excited states, with subsequent thermally activated transitions of electrons to the conduction band. A photoconductivity band associated with the photoionization of V impurities is revealed. The intracenter luminescence of ZnTe:V crystals is efficiently excited with light corresponding to the intrinsic absorption region of V²⁺ ion

Introduction

In the last few years, ZnTe crystals doped with transition metals have been extensively used as materials for various laser- and nonlinear-optical applications. ZnTe:Cr crystals were used to achieve lasing at 2.5 μm [1]. ZnTe:Fe crystals served as a basis for the production of tunable lasers emitting in the wavelength range from 4.35 to 5.45 μm [2]. The use of ZnTe:V crystals for attaining lasing in the IR region is hindered by the problem of the observation of IR luminescence at temperatures higher than 150 K [3].

At the same time, the above-mentioned crystals can be used as photodetectors for visible and microwave radiation [4]. Therefore, studies of the photoconductivity and luminescence of ZnTe:V crystals in the visible spectral region present a topical problem.

In this study, we explore and identify structural features of the photoconductivity and luminescence spectra of ZnTe:V crystals in the visible spectral region. It is shown that, in the spectra, there are photoconductivity and luminescence bands associated with the V impurity.

The goals of this study is to identify structural features of the photoconductivity and lumines-

cence spectra of ZnTe:V crystals in the visible spectral region.

Experimental

The samples to be studied were produced by the diffusion doping of initially pure ZnTe crystals with V. The nominally undoped crystals were produced by the free growth method on a ZnSe single crystal substrate oriented in the (111) plane. The advantage of diffusion doping is the possibility of obtaining specified impurity concentrations and doping profiles. The V content in the crystals was determined from the variation in the band gap of ZnTe crystals under variations in the V impurity concentration. The vanadium concentration varies from $3 \cdot 10^{17}$ to $3 \cdot 10^{19}$ cm⁻³. For reference samples, we used specially produced and studied ZnTe samples subjected to heat treatments at the same temperatures as those of the treatments of V-doped crystals.

The photoconductivity spectra were recorded with an MUM-2 monochromator with a 1200 groove mm⁻¹ diffraction grating. A halogen lamp served as the source of light. The power of the light flux from the lamp was kept constant at different wavelengths.

The photoluminescence (PL) spectra were recorded with an ISP-51 prism spectrograph. The emission was detected with an FEU-100 photoelectric multiplier. The luminescence signal was excited with Edison Opto Corporation light-emitting diodes (LEDs) and an ILGI-503 nitrogen pulse laser. The photon energies corresponding to the emission peak of the LEDs were 3.1, 2.69 and 2.25 eV, and the photon energy of laser emission was 3.74 eV.

Analysis of the photoconductivity spectra

The undoped ZnTe crystals exhibit only one photoconductivity band with a peak at 2.26 eV at 300 K (Fig. 1, curve 1). This band arises from interband optical transitions. On doping of the crystals with vanadium, this band shifts to lower energies. As the V concentration is increased, the shift increases and corresponds to a change in the band gap determined from the optical absorption spectra.

Doping with vanadium brings about the appearance of series photoconductivity bands in the photon energy range from 1.4 to 2.1 eV (Fig.1, curves 2–3). The intensity of these bands increases, as the V concentration is increased. In the spectra, we can distinguish bands at 1.47, 1.55, 1.7, 1.8, 1.87 and 2.09 eV. It is established that the 2.09 eV band changes position under variations in the V concentration. The position of other bands remains unchanged, as the degree of doping is increased.

At the temperature $T = 77$ K, only one interband photoconductivity band is observed in all of the crystals under study. As the temperature is elevated from 77 to 350 K, the impurity photoconductivity makes a weightier contribution to the spectrum. We observed a similar effect previously in studying the photoconductivity of ZnSe crystals doped with Fe, Ni, Cr [5,6].

As the temperature is elevated from 300 to 350 K the 2.09 eV photoconductivity band shifts to lower photon energies by 20 meV. Such shift corresponds to the temperature change in the band gap of ZnTe. 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 [7] visible absorption bands were attributed to intracenter optical transitions that occur within the V^{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, photoconductivity and luminescence.

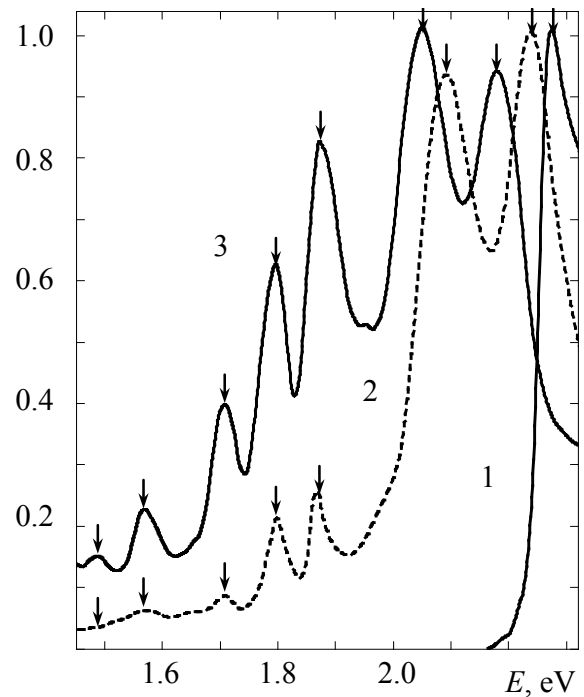


Fig. 1. Photoconductivity spectra of (1) ZnTe and (2, 3) ZnTe:V crystals. The V dopant concentrations are $[V] = (2) 5 \cdot 10^{18}$ and $(3) 3 \cdot 10^{19} \text{ cm}^{-3}$.

The photoconductivity process in the crystals under study occurs in the manner briefly described below. The 2.09 eV photoconductivity band is associated with optical transitions from the ${}^4T_1(F)$ ground state of the V^{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 V concentration $[V] = 5 \cdot 10^{18} \text{ cm}^{-3}$ (2.23 eV) allows us to believe that the level of the ground state of the V^{2+} ion is 140 meV above the top of the valence band.

Energies of optical transitions in ZnTe:V crystals

Line No	Absorption		Photoconductivity, E, eV	Luminescence, E, eV	Stokes shift, E, meV
	E, eV	Transition			
1	---	${}^4T_1(F) \rightarrow {}^3A_2(F) + e^-_{c.b}$	2.09	---	---
2	2.19	${}^4T_1(F) \rightarrow {}^2E(D)$	---	2.13	60
3	2.08	${}^4T_1(F) \rightarrow {}^2E(G)$	---	2.06	20
4	1.87	${}^4T_1(F) \rightarrow {}^2T_2(D)$	1.87	1.85	20
5	1.80	${}^4T_1(F) \rightarrow {}^2T_1(P)$	1.80	1.78	20
6	1.70	${}^4T_1(F) \rightarrow {}^2T_1(H)$	1.7	1.67	30
7	1.54	${}^4T_1(F) \rightarrow {}^2E(H)$	1.55	1.52	20
8	1.46	${}^4T_1(F) \rightarrow {}^2T_1(H)$	1.47	1.42	40
9	1.36	${}^4T_1(F) \rightarrow {}^2T_2(H)$	---	1.33	30
10	1.26	${}^4T_1(F) \rightarrow {}^4T_1(P)$	---	1.24	20
11	1.23	${}^4T_1(F) \rightarrow {}^2T_2(G)$	---	1.20	30

The other photoconductivity bands are formed in a two-stage process. Initially, the intracenter optical transitions of electrons from the ${}^4T_1(F)$ ground state to the higher excited states of the V^{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 V^{3+} charged state. Later the V^{3+} centers trap electrons and the centers transit to their initial V^{2+} state.

It should be noted that the results of studies of the thermoelectric power are indicative of the electron photoconductivity of the ZnTe:V 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 2.31 eV (Fig. 2, curve 1). In previous studies the 2.31 eV emission band was attributed to emission of excitons localized at neutral zinc vacancies [6].

Upon doping of the crystals with vanadium, the excitonic emission bands shift to lower energies (Fig. 2, curve 2). The shift corresponds to the change in the band gap with the vanadium concentration [V] in ZnTe.

Doping of the crystals with vanadium brings about a series of long-wavelength emission lines with peaks at 1.20, 1.24, 1.33, 1.42, 1.52, 1.67, 1.78, 1.85, 2.06, 2.13 eV (Fig. 2, curve 2). As the V 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 ZnTe:V 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.

It is established that the relative luminescence intensity of the ZnTe:V 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 3.67 eV. The highest emission intensity is attained on excitation with LEDs with the photon energy in the emission peak 2.25 eV. This suggests that the band-to-band excitation of long-wavelength luminescence of the ZnTe:V 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.

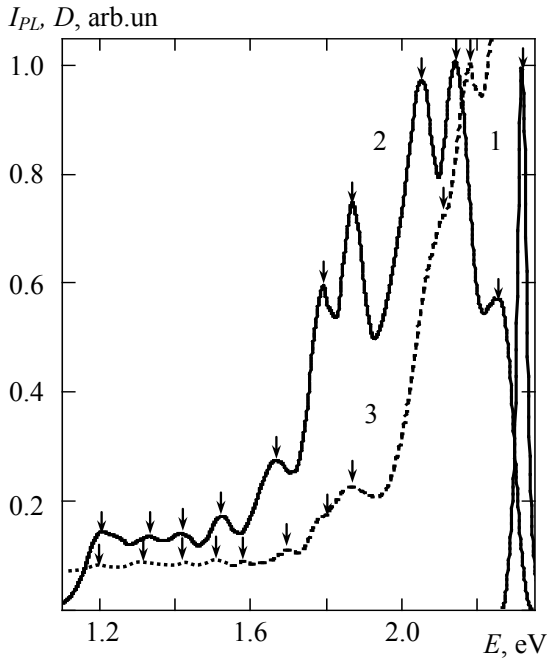


Fig. 2. (1, 2) Photoluminescence and (3) absorption spectra of (1) ZnTe and (2, 3) ZnTe:V crystals.

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

Conclusions

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

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

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

References

1. Kisiel V.E., Tolstik N.A., Scherbitsky V.G. et.al. Growth and spectroscopic characterization of Cr:ZnTe laser crystals //CLEO/Europe. 2005 Conference on Lasers and Electro-Optics Europe. – 12-17 June 2005.

2. Frolov M.P., Korostelin Yu.V., Kozlovskii V.I. et al. Laser radiation tunable within the range 4.35-5.45 μm in a ZnTe crystals doped with Fe^{2+} ions // Journal of Russian Laser Research. – 2011. V.11, N.6. – P.528-532.
3. Peka P, Lehr M.U, Schulz H., Pohl U.W. Vanadium centers in ZnTe crystals. I. Optical properties//Phys. rev. B. – V. 53(4). - P.1907-1916.
4. Arunas Kadys, Kestutis Jarasiunas, Markas Sudzius et. al. Photoelectric properties of highly excited ZnTe:V(Al, Sc) bulk crystals // Phys. Stat. Sol.(c). – 2005. - V. 2, P. 1389–1392.
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. Ницук Ю.А., Ваксман Ю.Ф., Яцун В.В. Исследование примесной фотопроводимости и люминесценции в кристаллах ZnSe:Ni в видимой области спектра// ФТП. – 2012. – Т. 46, В. 10. – С. 1288-1292.
7. Ницук Ю.А. Оптическое поглощение ванадия в кристаллах ZnSe //ФТП. – 2014. – Т.48, №2. – С. 152-157.

This article has been received in April 2016

Yu. F. Vaksman, Yu. A. Nitsuk, A. V. Korenkova

STUDY OF THE IMPURITY PHOTOCONDUCTIVITY AND LUMINESCENCE IN ZnTe:V CRYSTALS

Abstract

The photoconductivity and photoluminescence spectra of ZnTe:V crystals in the visible spectral region are studied. It is established that the high-temperature impurity photoconductivity of ZnTe:V crystals is controlled by the optical transitions of electrons from the ground state $^4T_1(F)$ to high-energy excited states, with subsequent thermally activated transitions of electrons to the conduction band. A photoconductivity band associated with the photoionization of V impurities is revealed. The intra-center luminescence of ZnTe:V crystals is efficiently excited with light corresponding to the intrinsic absorption region of V^{2+} ion

Key words: zinc telluride, diffusion doping, vanadium impurity, photoconductivity, photoluminescence.

Ю. Ф. Ваксман, Ю. А. Ницук, А. В. Коренкова

ИССЛЕДОВАНИЕ ПРИМЕСНОЙ ФОТОПРОВОДИМОСТИ И ЛЮМИНЕСЦЕНЦИИ В КРИСТАЛЛАХ ZnTe:V

Резюме

Исследована фотопроводимость и фотолюминесценция кристаллов ZnTe:V в видимой области спектра. Установлено, что высокотемпературная фотопроводимость кристаллов ZnTe:V обусловлена оптическими переходами электронов из основного состояния $^4T_1(F)$ на более высокие возбужденные энергетические уровни иона V^{2+} с их последующей термической активацией в зону проводимости. Эффективное возбуждение внутрицентральной люминесценции кристаллов ZnTe:V осуществляется светом из области примесного поглощения ионов V^{2+} .

Ключевые слова: теллурид цинка, диффузионное легирование, примесь ванадия, фотопроводимость, фотолюминесценция.

ДОСЛІДЖЕННЯ ДОМІШКОВОЇ ФОТОПРОВІДНОСТІ ТА ЛЮМІНЕСЦЕНЦІЇ В КРИСТАЛАХ ZnTe:V

Резюме

Досліджено фотопровідність і фотолюмінесценцію кристалів ZnTe:V у видимій області спектру. Встановлено, що високотемпературна фотопровідність кристалів ZnTe:V обумовлена оптичними переходами електронів з основного стану $^4T_1(F)$ на більш високі збуджені енергетичні рівні іону V^{2+} з їх подальшою термічною активацією в зону провідності. Ефективне збудження внутрішньоцентрової люмінесценції кристалів ZnTe:V відбувається світлом з області домішкового поглинання іонів V^{2+} .

Ключові слова: телурид цинку, дифузійне легування, домішка ванадію, фотопровідність, фотолюмінесценція.