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The Luminescence of $CdWO_4$:Tb,Li Crystals under Synchrotron Excitation at 10 K

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The luminescent properties of $CdWO_4$:Tb,Li crystals have been investigated at 10 K in the region 4–25 eV using synchrotron excitation. It is shown that besides the intrinsic matrix luminescence the number emission lines due to electron f–f-transitions in Tb^{3+} ions are efficiently excited at near-edge region of the fundamental absorption ($E_{\mathrm{exc}} = 4.1$ eV). The weak recombination luminescence of terbium impurity on the background of intensive matrix luminescence is observed under excitation in the region of fundamental absorption ($E_{\mathrm{exc}} = 5.4$ and 13.8 eV). It is shown that the luminescence spectrum of the matrix is a superposition of three elementary bands 2.07, 2.47, and 2.73 eV. The nature of emission bands is discussed.

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1. Introduction

Cadmium tungstate crystals have attracted the interest due to its application as a promising material for creation of radiation and chemically persistent scintillation detectors with high efficiency for registration of high-energy ionizing radiation [1–6]. At room temperature $CdWO_4$ scintillators are characterized by a low afterglow, a high yield of luminescence with maximum in 2.48–2.50 eV region and a decay time ≈ 10 μs [2–4, 7, 8]. The fast component of luminescence with time 50 ns is detected in the scintillations of cadmium tungstate [2]. Authors [7] also registered the weak emission with a decay time ≈ 2 ns. Besides the main band of intrinsic radiation the several weak bands associated with the defects [7] appeared in $CdWO_4$ luminescence spectrum. It was shown in [9] that the doping of material by Li^+ ions leads to the increase of the transparency and the light yield of scintillator. The spectral characteristics of $CdWO_4$ luminescence at the excitation by synchrotron radiation are considered in [7, 8, 10]. It was shown in [8] that the luminescence spectrum of $CdWO_4$ at 10 K can be decomposed into two Gaussian components with maxima near 2.07 and 2.46 eV.

Optical-luminescent properties of $CdWO_4$:Tb under the optical and X-ray excitations are described in [11]. We first briefly reported the results of low-temperature luminescence studies on $CdWO_4$:Tb,Li crystals under synchrotron excitation in Ref. [12]. In this paper the spectral-luminescence characteristics of crystals co-doped with Tb^{3+} and Li^+ under synchrotron excitation in the region 4–25 eV at 10 K are in more detail considered. The main attention is focused on the analysis of luminescence excitation spectra peculiarities in the region of fundamental absorption and on the discussion of emission bands nature.

2. Experiments

The $CdWO_4$:Tb,Li crystals used in this study were grown by the Czochralski method [11]. The terbium (Tb_4O_7) and lithium (Li_2O) impurities entered into the blend in an amount of 1 mass.% and 10 mass.%, respectively. The samples with thickness 1–2 mm and a diameter 15–17 mm were obtained by cleaving of the crystal in the plane (010). Spectral-luminescent characteristics were performed using synchrotron radiation on station SUPERLUMI in the HASYLAB laboratory (Hamburg, Germany) [13]. The registration of the crystal's luminescence, which was mounted on a holder of helium cryostat, was carried out with HAMAMATSU R6358P photomultiplier through the secondary monochromator-spectrograph ARC "Spectra Pro 308". The luminescence spectra in the region 1.38–6.20 eV were measured in the time-integral regime and time-resolved regime in

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the time gates 0–50 ns and 150–200 ns. Excitation spectra were measured in the region 4–25 eV with a primary monochromator with a focal length 2 m both in time-integral and time-resolved registration regimes. Excitation spectra of luminescence were corrected to the intensity of the incident photons flux.

3. Results

Preliminary studies carried out in the temperature range 85–295 K have revealed that the non-elementary band with a maximum near 2.5 eV is registered in $CdWO_4$ under steady-state X-ray excitation. The doping of $CdWO_4$ by terbium impurity leads to the decrease of matrix luminescence and to the appearance of Tb^{3+} ions luminescence. The weak luminescence of terbium impurity is observed on the background of the matrix emission. The yield of X-ray luminescence slightly increases after the lithium impurity entering into the $CdWO_4$:Tb. At the same time the Li^+ practically has no effect on the luminescence spectral composition of matrix. These results are in accordance with the luminescence spectral characteristics of $CdWO_4$ crystals with Tb and Li dopants [11] at the optical and X-ray excitations.

The emission spectrum of $CdWO_4$:Tb,Li crystal obtained under synchrotron excitation with energy 4.1 eV from the long-wavelength edge of the fundamental absorption in the case of the time-integral registration regime is shown in Fig. 1. In this spectrum the several narrow lines due to electronic transitions within the $4f^8$-configuration of Tb^{3+} ion are detected on the background of a broad asymmetric matrix emission band, which is shown in Fig. 1 by dashed line. We carried out the decomposition of the matrix luminescence spectrum of $CdWO_4$:Tb,Li crystal similarly as in [8] on the Gaussian components, which are shown in Fig. 1 by dotted lines. Herewith the dominant band peaking near 2.47 eV, the less intensive band about 2.07 eV and the weak band at 2.73 eV have been obtained.

It is found that the emission spectra of $CdWO_4$:Tb,Li excited by synchrotron radiation with the energies at 5.4 and 13.8 eV are characterized by almost the same shapes. The luminescence spectrum obtained under excitation by photons from low-energy region is shown in Fig. 2. In this figure it is shown that the luminescence spectrum is represented by superposition of the matrix emission band around 2.50 eV (Fig. 2, dashed line) and number narrow lines due to f–f-transitions in Tb^{3+} ions at the recording of emission in the time-integral regime [11, 12]. It should be noted that the matrix emission spectrum of the investigated crystal is almost identical with the luminescence spectrum of undoped $CdWO_4$ at 10 K in the case of excitation by synchrotron radiation with photon's energy 11.27 eV [8]. The decomposition of the matrix luminescence spectrum of $CdWO_4$:Tb,Li crystal into Gaussian components, which are shown in Fig. 2 by dotted lines, the less intensive band about 2.73 eV and the weak band at 2.07 eV are additionally revealed except for the dominant band with maximum at 2.47 eV. It was found that the spectrum of slow luminescence component obtained at registration in the time gate 150–200 ns is characterized by similar features. The weaker emission with maxima at the regions 2.21–2.32 eV and 2.48–2.52 eV is observed in the case of time-resolved registration regime in the time gate 0–50 ns.

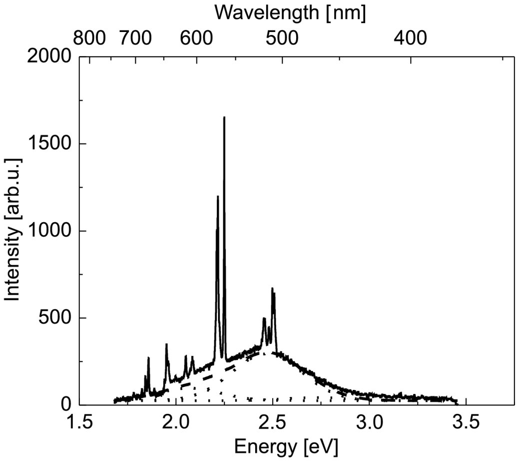

Fig. 1. The luminescence spectrum of $CdWO_4$:Tb,Li crystal at excitation by photon's energy 4.1 eV under integrated registration regime at 10 K. Dashed line shows the matrix luminescence spectrum of $CdWO_4$:Tb,Li crystal, dotted lines — the decomposition of this spectrum into elementary components.

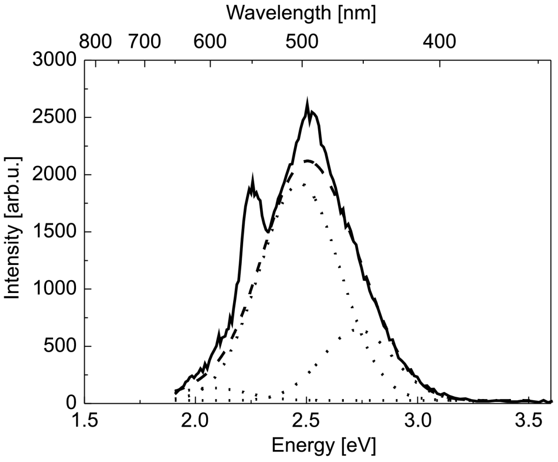

Fig. 2. As in Fig. 1, but for photon's energy 5.4 eV.

The luminescence excitation spectrum with maximum near 2.5 eV of $CdWO_4$:Tb,Li crystal in the case of time-integrated emission registration is shown in Fig. 3. This spectrum is characterized with complex structure. It contains a main peak at 4.12 eV in the region of long-wavelength fundamental absorption edge. The increase of the exciting photons energy up to 8–9 eV leads to a significant weakening of the excitation efficiency of luminescence. With a further rising of the exciting photon's energy up to 25 eV the increase of intrinsic luminescence

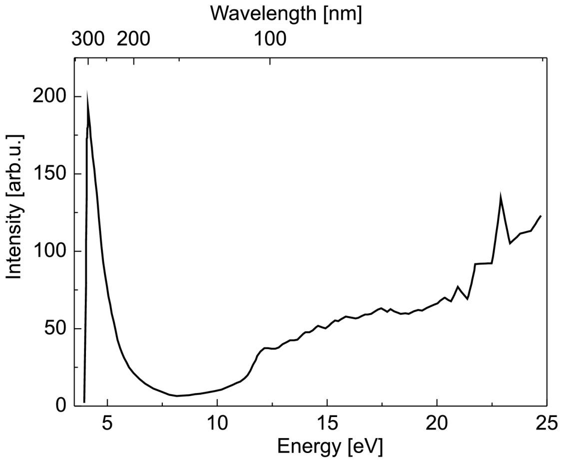

Fig. 3. The excitation spectrum of 2.5 eV emission under integrated registration regime of CdWO$_4$:Tb,Li crystal at 10 K.

yield is observed. Herewith in high-energy region the main peak at 22.9 eV is registered besides a number of weak peaks. The similar excitation spectra are observed for the fast and slow components of luminescence.

4. Discussion of results

From the carried out research it follows that the intrinsic luminescence in CdWO$_4$:Tb,Li at 10 K is effectively excited by the synchrotron radiation mainly in the long-wavelength fundamental absorption edge and in the region of photon multiplication [8, 10]. The luminescence spectra of CdWO$_4$:Tb,Li crystals are the superposition of elementary intrinsic bands and the narrow bands connected with the terbium impurity.

The obtained results of CdWO$_4$:Tb,Li low-temperature spectral-luminescent characteristics under synchrotron excitation are in accordance with the similar studies carried out on the CdWO$_4$ crystals [7, 8, 10]. The similarity of the matrix radiation spectra for the CdWO$_4$:Tb,Li and the emission spectra of undoped CdWO$_4$ [8] at 10 K may indicate that the single charged lithium ion with lesser ionic radius than ones of cadmium impurity (0.68 and 0.99 Å, respectively) does not enter in the coordinated octahedra of CdWO$_4$ and is located in the voids between them — in the interstices [9] during synthesis of co-doped with Tb^{3+} and Li^{+} crystals. At the same time Li$_i^+$ interstitial ions and V$_{\mathrm{Cd}}$ cadmium vacancies form associates.

In case Tb^{3+} ions enter in CdWO$_4$:Tb crystals into Cd^{2+} places without the introduction of single charged ion-compensator, the excess charge of impurity compensates mostly by cadmium vacancies due to the formation of electrically neutral complexes, such as Tb^{3+}–V$_{\mathrm{Cd}}$–Tb^{3+}, which are effective trapping centers of generated nonequilibrium holes. The creation of such centers of charge localization, as well as Tb–Tb interaction in CdWO$_4$:Tb^{3+} [11], causes the decrease of X-ray luminescence at the doping of CdWO$_4$ crystals by terbium impurity.

It was shown [9] that the doping of cadmium tungstate by lithium impurity (0.02 mass%) does not significantly change the defect structure of the crystal, but a slight increase of lattice parameter *b* and unit cell volume of the crystal take place. Thus there is a reduction of defects responsible for color and capture centers. The growing of the integrated luminescence intensity of CdWO$_4$:Tb,Li crystals, probably due to the fact that the Li$^+$, as the ion-compensator of Tb^{3+} excess charge, causes the increase of the terbium impurity transparency in cadmium tungstate due to the formation of Tb^{3+}–Li$^+$ associates [11].

The main band of intrinsic luminescence at 2.47 eV can be attributed to the radiative decay of self-trapped excitons on the oxyanion complexes WO$_6^{6-}$ [8, 14]. The high intensity of self-trapped excitons luminescence at 10 K indicates the absence of self-trapping barrier or its small value. The band at 2.07 eV is associated with emission of the defect oxyanion complexes, in which one oxygen atom is absent. Taking into account the results of the literature data [9–11] we can assume that the identification of additional weak luminescence band with maximum near 2.73 eV is due to the emission of excitons localized near cadmium vacancies. The weak emission with a slow decay time is probably associated with the metastable state of oxyanion excitons [8].

The structure of the excitation spectrum in the region of photon multiplication can be connected with the peculiarities of the band structure of cadmium tungstate crystals [8, 15]. Under excitation in this region the luminescence with maximum at 2.47 eV in the doped crystals arises at preliminary binding of the electron and hole in exciton. The excitation band at 4.12 eV in CdWO$_4$:Tb,Li has been mainly attributed to the self-trapped excitons on the WO$_6^{6-}$ complexes [7, 8].

The significant weakening of luminescence excitation efficiency in CdWO$_4$:Tb,Li crystals with the increase of exciting photon's energy from the fundamental absorption edge up to the energy region 8–9 eV may be due to an increase of nonradiative decay of electron excitations near the surface [8] and the recapture of electronic excitations by the Tb^{3+} centers. With increase of excitation energy from 5.4 to 13.8 eV the absence of relative growth of activator luminescence efficiency in CdWO$_4$:Tb,Li crystals allowed us to suggest that the decrease of luminescence intensity is mainly due to nonradiative relaxation of electronic excitations.

It was shown [11] that the emission spectrum of cadmium tungstate crystals doped with terbium impurity at 290, 77, and 20.4 K consists of only four groups of narrow lines in the spectral region 487–499, 545–554 nm and the bands 590 and 630 nm under the optical excitation. The observed groups of the lines and the bands are assigned to transitions from the excited $^5D_4$-state to the $^7F_{3,4,5,6}$ split levels. In the case of synchrotron excitation of CdWO$_4$:Tb,Li crystals with photon's energy 4.1 eV, besides the lines, which were connected with these transitions, at 10 K the group of narrow lines in the spectral region 1.82–1.87 eV associated with the transition $^5D_4 \to {}^7F_2$ is additionally recorded. The lines due to electronic transitions $^5D_4 \to {}^7F_5$ have a maximum brightness.

5. Summary

The luminescence in $CdWO_4$:Tb,Li crystals at 10 K is efficiently excited by synchrotron radiation in the region of long-wavelength edge of the fundamental absorption and in the region of photon multiplication. The luminescence spectra are the superposition of three elementary matrix bands at 2.07, 2.47, and 2.73 eV and lines associated with $f-f$-transitions in Tb^{3+} ions. The main band of luminescence with maximum near 2.47 eV is due to the radiative decay of self-trapped excitons on oxyanion complexes WO_6^{6-}. The band at 2.07 eV is associated with the defect oxyanion complexes, in which one oxygen atom is absent. The detected luminescence band with maximum near 2.73 eV can be due to the emission of excitons localized on the cadmium vacancies.

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