

Optical and Luminescence Properties of CdWO₄ and CdWO₄:Mo Single Crystals

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Abstract—Luminescence properties of a pure CdWO₄ crystal and a CdWO₄:Mo crystal doped with molybdenum in different concentrations have been investigated. The effect of molybdenum impurity on the intrinsic luminescence of CdWO₄ has been found, and the role of the impurity in the formation of new luminescence centers has been investigated. The features of the formation of the intrinsic and impurity luminescence excitation spectra of CdWO₄ and CdWO₄:Mo crystals in the fundamental-absorption region have been considered. The reflection spectra of the CdWO₄ crystal have been investigated taking into account the crystal structure anisotropy.

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INTRODUCTION

Cadmium tungstate (CdWO₄) is a promising scintillation material for X-ray tomography, detection of slow neutrons, and dosimetry [1–3]. The large effective atomic number ($z_{\text{eff}} = 61.2$) and, correspondingly, high density (7.99 g/cm³) provide effective scintillation detection even when a crystal is physically small [2]. The luminescence spectrum of this compound is a wide band in the visible spectral range ($\lambda_{\text{max}} \sim 500$ nm) and its luminescence decay time is sufficiently short (about 10 μ s) for operation in intense X-ray fluxes [1]. In addition, CdWO₄ has advantages over other scintillators with respect to the content of radionuclides and is characterized by a high specific light yield ($\sim 38\%$ of the corresponding value for NaI–Tl) [2]. With all this, the optical properties of cadmium tungstate in the fundamental-absorption region have been studied insufficiently. Only recently first theoretical calculations of the density of electron states of the valence and conduction bands of CdWO₄ have been performed [4, 5]. In this paper, the reflection spectra of a high-quality pure CdWO₄ crystal were investigated taking into account the anisotropy of its structure.

The problem of optimization of the luminescence properties of this crystal remains urgent. It is known that doping of another representative of tungstates, PbWO₄, with molybdenum leads to a significant increase in the specific light yield at room temperature

[6]. However, for cadmium tungstate doped with molybdenum, an insignificant decrease in the intensity of low-temperature intrinsic luminescence was previously found [7]. In this study, we performed comparative investigations of the luminescence properties of a high-quality pure CdWO₄ crystal and a CdWO₄:Mo crystal doped with molybdenum in different concentrations at temperatures of 10 and 300 K. The effect of the molybdenum impurity on the intrinsic luminescence of CdWO₄ was found, and the role of the impurity in the formation of new luminescence centers was investigated. The features of the formation of the intrinsic and impurity luminescence excitation spectra of CdWO₄ and CdWO₄:Mo in the fundamental-absorption region in the temperature range of 10–300 K are considered.

EXPERIMENTAL

Measurements of the luminescence excitation spectra and reflection spectra of CdWO₄ in the energy range 3.7–30 eV, as well as the luminescence spectra upon vacuum UV (VUV) excitation, were performed in the temperature range of 10–300 K, using synchrotron radiation, at the SUPERLUMI system, located in the channel of the DORIS III positron storage ring (DESY, Hamburg) [8]. Synchrotron radiation is most effective and convenient for VUV investigations, since it has an intense continuous emission spectrum in the VUV region, high degree of linear polarization, and a tempo-

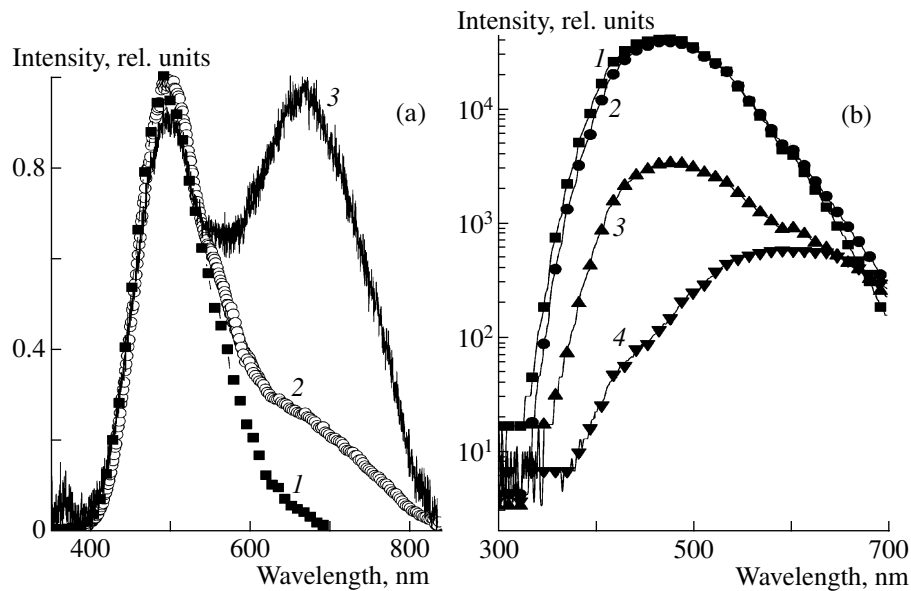


Fig. 1. (a) Luminescence spectra of the (1) pure CdWO_4 and (2, 3) $\text{CdWO}_4:\text{Mo}$ 0.1% crystals at $T = 10$ K, measured at excitation energies of (1) 11.27, (2) 4.43, and (3) 15.5 eV. The spectra are normalized to the maximum intensity. (b) The X-ray luminescence spectra measured under the same experimental conditions at $T = 300$ K for the (1) pure CdWO_4 crystal and (2–4) CdWO_4 crystals doped with molybdenum in concentrations of (2) 0.04, (3) 0.1, and (4) 0.4%.

ral structure in the nanosecond range [9]. The luminescence spectra upon excitation by a white synchrotron X-ray beam were recorded at $T = 300$ K on the experimental setup in the channel 5.6 of the Sibir'-2 storage ring at the Kurchatov Synchrotron Radiation Centre (Moscow). The excitation spectra in the energy range of 3–4.5 eV were recorded on a laboratory setup; a DKSL-1000 lamp was used as a luminescence excitation source. The luminescence spectra upon VUV excitation were normalized to the function of spectral sensitivity of the detecting system; this normalization made it possible to correctly decompose them into Gaussian components. The X-ray luminescence spectra were not normalized to the function of spectral sensitivity of the detecting system; however, they were measured under identical experimental conditions. Hence, their relative intensity can be compared for different samples.

The pure CdWO_4 crystal was grown at the Institute of Single Crystals (Kharkov, Ukraine) by the Czochralski method. The working surface of the samples studied was a fresh cleavage in the (010) plane. $\text{CdWO}_4:\text{Mo}$ single crystals were grown by spontaneous crystallization from high-temperature melts, using the slow cooling technique. The initial charge was 55% Na_2WO_4 –16% CdO –(29–22)% WO_3 –(0–7)% MoO_3 . The crystallization temperature range was 1000–720°C and the cooling rate was 2–3°C/h. The crystals obtained were 4–10 mm in size. Analysis of three $\text{CdWO}_4:\text{Mo}$ samples showed that the molybdenum content in them was 0.04, 0.1, and 0.4 wt %. The crystals were grown by B.I. Zadneprovsky.

Cadmium tungstate is an anisotropic biaxial crystal (monoclinic system, space group C_{2h}^4); therefore, during measurements of the reflection spectra of high-polarized synchrotron radiation, we took into account the orientation of the crystallographic axes of a sample with respect to the direction of the electric field vector \mathbf{E} of the radiation incident on the sample. Such measurements make it possible to obtain additional information about the structure of the energy bands along different axes of the anisotropic crystal. In this study, we performed measurements for two pure CdWO_4 samples with crystallographic axes \mathbf{a} or \mathbf{c} oriented parallel to the projection of the vector \mathbf{E} on the sample plane.

RESULTS AND DISCUSSION

Luminescence Spectra at Room and Liquid-Helium Temperatures

The luminescence spectra of CdWO_4 and $\text{CdWO}_4:\text{Mo}$ crystals are shown in Fig. 1. The luminescence spectrum of pure CdWO_4 can be decomposed into two Gaussian components: a dominant component peaking at 2.46 eV (≈ 505 nm) and a low-intensity one, peaking at 2.07 eV (≈ 600 nm) at $T = 10$ K (Table 1). With an increase in temperature to 300 K, the peaks of both bands shift to high energies, while their relative intensity changes only slightly. The nature of these luminescence bands was previously discussed in [10, 11]. It was established that the band at 2.46 eV corresponds to the radiative decay of an exciton that is self-

Table 1. Results of the decomposition of the luminescence spectra of the CdWO₄ pure crystal and the CdWO₄:Mo (0.1%) crystal, recorded at different temperatures and excitation energies, into Gaussian curves

Crystal	T, K	E_{exc} , eV	E_{max1} , eV ^a	E_{max2} , eV	E_{max3} , eV
CdWO ₄	300	11.27	2.52 (1)	2.09 (0.09)	–
	10	11.27	2.46 (1)	2.07 (0.06)	–
CdWO ₄ :Mo	300	4.43	2.48 (1)	2.10 (0.10)	1.84 (0.48)
	10	4.43	2.46 (1)	2.07 (0.23)	1.76 (0.27)
	10	15.5	2.44 (1)	2.05 (0.19)	1.78 (1.16)

^a The energy position of the luminescence peaks; the areas under the Gaussian curves are given in parentheses (in arb. units).

trapped at a WO₆⁶⁻ oxyanion complex (intrinsic luminescence), while the band at 2.07 eV corresponds to the luminescence from a defect oxyanion complex, which lacks one oxygen atom (defect luminescence). The intrinsic luminescence intensity exceeds that of the defect luminescence upon interband excitation (11.27 eV) by more than an order of magnitude. Doping with molybdenum ions leads to the formation of the third luminescence band (impurity luminescence), peaking in the range 1.76–1.78 eV (\approx 705 nm) at $T = 10$ K (Fig. 1a). The occurrence of an additional band in the red region was previously observed for CdWO₄:Mo at 1.82 eV [7, 12] and for isostructural ZnWO₄:Mo at 1.77 eV [13]. This band was assigned to radiative transitions in the MoO₆ complex [12, 13].

The relative intensity of the impurity luminescence band depends on the excitation energy (Table 2). Upon excitation near the fundamental absorption edge (4.43 eV), the relative weight (area under the Gaussian curve) of this luminescence is 27% of the weight of the intrinsic luminescence band, whereas, upon interband excitation (15.5 eV), its weight increases to 116%, i.e., it becomes dominant in the luminescence spectrum. Such behavior suggests that, during energy transfer to luminescence centers, there is competition between WO₆ and MoO₆ centers. Note also that the relative weight of the defect luminescence band peaking at 2.07 eV increases in the doped crystal.

The X-ray luminescence spectra (Fig. 1b) were recorded under the same experimental conditions; hence, their intensities can be compared. At a low molybdenum concentration (0.04%), the luminescence spectrum of the doped sample almost coincides with that of the pure sample. An increase in the molybdenum concentration in the crystal leads to an increase in the relative intensity of the impurity luminescence band at 1.76 eV. Indeed, this band is not observed in the spectrum of CdWO₄:Mo (0.04%), whereas it dominates in the luminescence spectrum of CdWO₄:Mo (0.4%). In this case, the intrinsic luminescence intensity at 2.46 eV decreases by more than two orders of magnitude. Thus, the presence of molybdenum impurity leads

not only to the formation of an additional low-energy luminescence band but also to quenching of the intrinsic luminescence of cadmium tungstate. Note that an insignificant decrease in the intrinsic luminescence intensity (to 30%) with an increase in the molybdenum concentration to 0.25 wt % in CdWO₄ was previously observed in [7] at the temperature $T = 80$ K. A possible reason for the more pronounced decrease in the intrinsic luminescence intensity with increasing molybdenum concentration, observed at 300 K, is the temperature quenching of intrinsic luminescence, which begins at 270 K.

Luminescence Excitation Spectra

The intrinsic luminescence excitation spectra of pure CdWO₄ at 10, 200, and 300 K are shown in Fig. 2. The first luminescence excitation peak at 4.2 eV for CdWO₄ corresponds to a sharp increase in absorption near the fundamental absorption edge, corresponding to the onset of total absorption of the excitation radiation in the crystal. As was shown in [14], the absorption edge shifts to low energies with an increase in temperature, and the temperature dependence of the slope of the fundamental absorption edge in cadmium tungstate is described by the empirical Urbach rule. The low-energy threshold in the intrinsic luminescence excitation spectrum also shifts to low energies with an increase in temperature. The temperature rise from 10 to 300 K results in a shift of about 0.2 eV.

Further increase in the absorption coefficient leads to a decrease in the light penetration depth in the crystal and an increase in the fraction of nonradiative decay of electronic excitations near the surface. Thus, the maxima in the absorption (reflection) spectrum of CdWO₄ manifest themselves as minima in the luminescence excitation spectra [15, 16]. In the energy range above 10 eV, an increase in the luminescence yield is observed in CdWO₄, which can be attributed to the photon multiplication effect. We should note the unusually sharp increase in the luminescence yield in the photon multiplication region. This increase can be related to the features of the band structure of cadmium tungstate. The

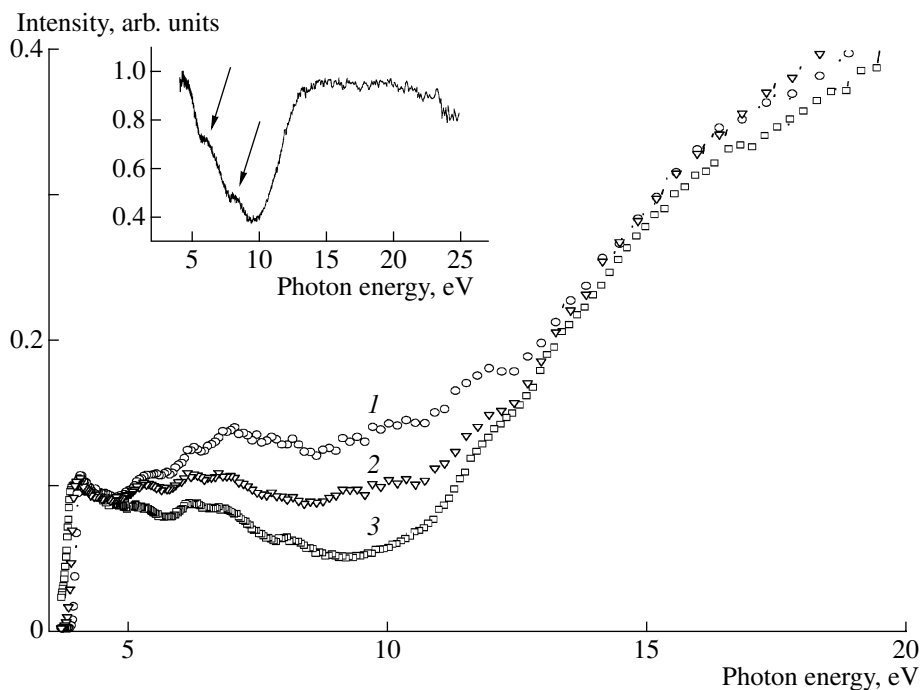


Fig. 2. Intrinsic luminescence excitation spectra ($\lambda_{\text{lum}} = 480$ nm) of CdWO_4 at (1) 10, (2) 200, and (3) 300 K. The inset shows the ratio of the intrinsic luminescence excitation spectra recorded at 300 and 10 K. The peaks at 6.2 and 8.2 eV are indicated by arrows.

bottom of the valence band, according to the calculations [4], is formed by the cadmium $4d$ states, which are characterized by an unusually high electron density of states. The width of the valence band, according to the experimental data of [15, 16] and the calculations [4], is about 6 eV; i.e., it is wider than the band gap of the crystal (4.55 eV [15]). Thus, even at an excitation energy of 11 eV, not only the electrons in the conduction band, excited from the top of the valence band, but also the holes at the bottom of the valence band are involved in photon multiplication. High density of elec-

tron states at the bottom of the valence band provides a large number of holes (potential participations of this process).

The excitation spectra of intrinsic luminescence, which arises as a result of preliminary coupling of an electron and hole into an exciton, are characterized by a decrease in the intensity in the energy range from the fundamental absorption edge to the onset of multiplication of electronic excitations [9]. At conventional excitation densities (up to 10^{10} photons/(s mm^2)), luminescence is a result of the recombination of spatially cor-

Table 2. Energy positions of the reflection peaks (eV) and their relative intensities (in parentheses) for different orientations of the crystallographic axes of CdWO_4 with respect to the vector \mathbf{E} of the incident synchrotron radiation at $T = 10$ K

Peak	$\mathbf{c} \parallel \mathbf{E}$	$\mathbf{a} \parallel \mathbf{E}$	Peak	$\mathbf{c} \parallel \mathbf{E}$	$\mathbf{a} \parallel \mathbf{E}$
1	3.91 (1.0)	3.88 (0.71)	10	9.45 (0.70)	9.25 (0.52)
2	4.07 (0.79)	4.08 (0.60)	11	10.20 (0.63)	10.2 (0.62)
3	4.23 (0.73)	4.20 (0.61)	12	10.65 (0.63)	
4		4.37 (0.64)	13	12.25 (0.64)	12.25 (0.71)
5	4.95 (0.73)	5.35 (0.86)	14	14.20 (0.49)	14.10 (0.59)
6	5.90 (0.65)	6.10 (1.00)	15	16.20 (0.63)	16.20 (0.71)
7	6.25 (0.61)		16	17.40 (0.70)	17.10 (0.76)
8		7.45 (0.68)	17	18.70 (0.65)	18.70 (0.67)
9	8.38 (0.67)	8.37 (0.53)			

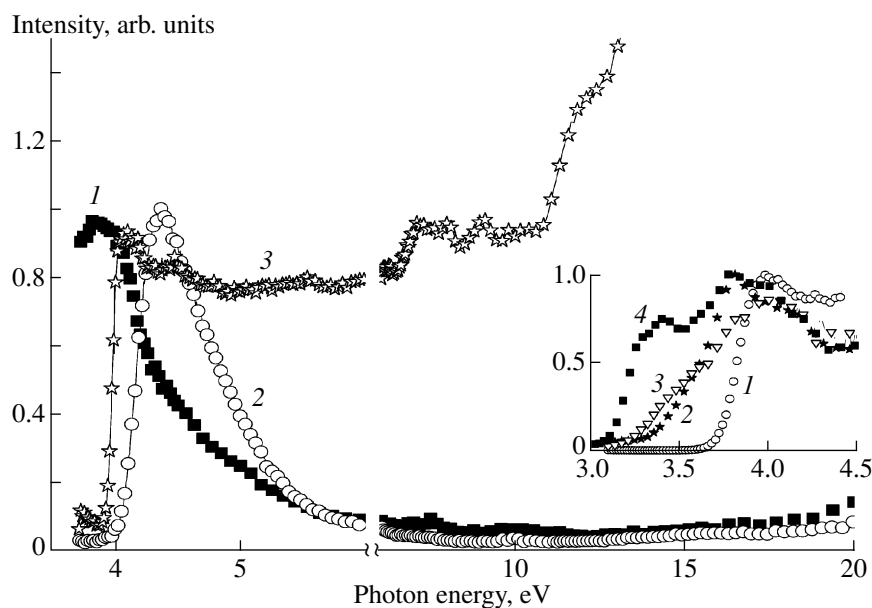


Fig. 3. Excitation spectra of $\text{CdWO}_4:\text{Mo}$ (0.1%) at $\lambda_{\text{lum}} = (1)$ 625 nm (1.98 eV) and (2) 505 nm (2.45 eV) and the intrinsic luminescence excitation spectra ($\lambda_{\text{lum}} = 480$ nm) of (3) CdWO_4 at $T = 10$ K. The inset shows the low-energy region of the excitation spectra of (1) pure CdWO_4 ($\lambda_{\text{lum}} = 480$ nm), (2) $\text{CdWO}_4:\text{Mo}$ (0.04%), (3) $\text{CdWO}_4:\text{Mo}$ (0.1%), and (4) $\text{CdWO}_4:\text{Mo}$ (0.4%); for all samples, $\lambda_{\text{lum}} = 750$ nm at $T = 300$ K.

related electrons and holes. Such pairs in CdWO_4 form excitons that are self-trapped at WO_6^{6-} complexes with subsequent emission of an intrinsic luminescence photon. In the fundamental absorption region, the yield of such luminescence is determined by the competition with the alternative, radiative and nonradiative, energy relaxation channels. The probability for separated electrons and holes to couple into excitons decreases with an increase in their kinetic energy, since the average distance between the components of a thermalized pair increases. This circumstance explains the pronounced decrease in the intensity of the excitation spectrum of CdWO_4 in the photon energy range 4–10 eV at $T = 300$ K.

With a decrease in temperature from 300 to 10 K, the intensity of the intrinsic luminescence excitation spectrum of CdWO_4 gradually increases in the energy range of 5–13 eV. Thus, the probability for separated electron and hole to be coupled into an exciton depends not only on the excitation photon energy but also on temperature. Indeed, the charge-carrier mobility is generally temperature-dependent; hence, with a decrease in temperature, the free path length in a crystal decreases. In addition, a decrease in temperature leads to an increase in the effective radius of the recombination (Onsager) sphere [17]. Due to these two factors, cooling increases the probability of radiative recombination of an electron–hole pair excited at a given energy.

The ratio of the excitation spectra recorded at different temperatures contains information about the temperature dependence of the probability of coupling of spatially correlated electron–hole pairs into excitons as a function of the energy of primary electrons and holes (Fig. 2, inset). The decrease in this ratio in the energy range of 5–10 eV is related to the rise in the kinetic energy of the components of electron–hole pairs. In the photon energy range above 10 eV, an increase in the ratio is observed, which is related to the onset of multiplication of electronic excitations and, as a result, generation of low-energy electrons and holes. The plateau in the energy range 13–20 eV indicates that the energy distribution of excited electrons and holes only slightly depends on the excitation energy.

Note that the structure arising in the excitation spectra as a result of surface losses disappears as a result of spectrum-by-spectrum division. However, such division reveals some new features that are not observed in the initial spectra. For example, there are pronounced peaks at 6.2 and 8.2 eV (arrows in Fig. 2, inset). The nature of these peaks will be discussed below.

The intrinsic and impurity luminescence excitation spectra of the $\text{CdWO}_4:\text{Mo}$ and CdWO_4 crystals are shown in Fig. 3. To obtain the entire impurity luminescence excitation spectrum of the $\text{CdWO}_4:\text{Mo}$ compound, additional investigations were performed on a laboratory setup, since the long-wavelength scanning limit of the primary monochromator of the SUPERLUMI system is 336 nm. The measurements were performed in the long-wavelength region (750 nm) with

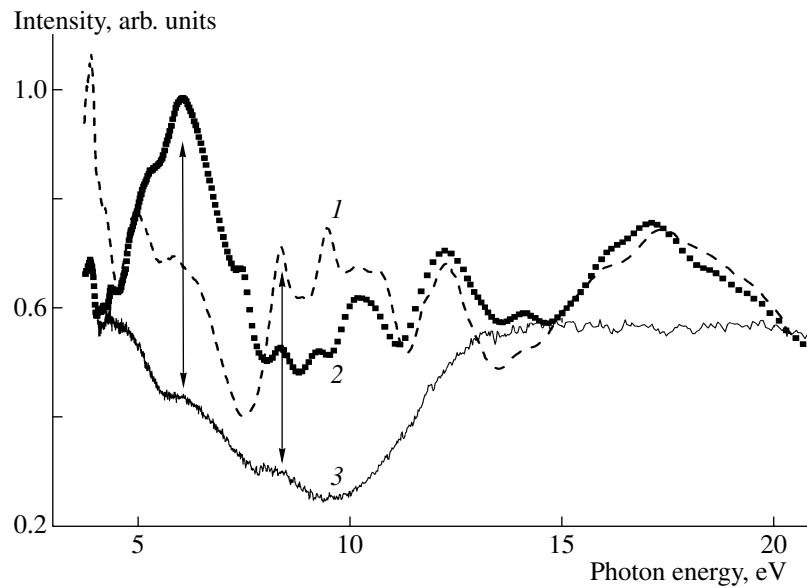


Fig. 4. Reflection spectra of CdWO_4 with the orientations (1) $\mathbf{c} \parallel \mathbf{E}$ and (2) $\mathbf{a} \parallel \mathbf{E}$ at $T = 10$ K and (3) the ratio of the intrinsic luminescence excitation spectra recorded at 300 and 10 K.

respect to the maximum of the impurity luminescence band of $\text{CdWO}_4:\text{Mo}$ to decrease the possible contribution of the intrinsic and defect luminescence excitation spectra of the crystal to the impurity luminescence excitation spectrum. The spectra contain two peaks at 3.8 and 3.35 eV; i.e., in the energy region before the fundamental absorption edge. The intensity of the excitation bands at 3.8 and 3.35 eV directly depends on the molybdenum concentration in cadmium tungstate. We believe that these bands are due to the occurrence of additional $4d$ energy levels of molybdenum at the bottom of the conduction band. The bottom of the conduction band is mainly formed by the $5d$ levels of tungsten [4]; therefore, molybdenum, substituting for tungsten in an oxyanion complex, affects the formation of the bottom of the conduction band rather than the top of the valence band, which is mainly formed by the $2p$ states of oxygen.

Excitation of intrinsic luminescence in the fundamental absorption region for a doped crystal is efficient only near the fundamental absorption edge. The excitation onset threshold for $\text{CdWO}_4:\text{Mo}$ shifts to higher energies by 0.2 eV in comparison with pure CdWO_4 . This fact is related to the competition of the channels of energy transfer to impurity and intrinsic luminescence centers near the Urbach edge of the fundamental absorption region. With an increase in the photon energy, the intrinsic luminescence excitation efficiency rapidly decreases almost to zero. The intrinsic luminescence excitation efficiency for the CdWO_4 pure crystal in the energy range before the threshold of electronic excitation multiplication (10 eV) weakly depends on the excitation energy at $T = 10$ K. Such a difference can be explained by the occurrence of additional (radiative

or nonradiative) competing energy relaxation channel in the $\text{CdWO}_4:\text{Mo}$ crystal. Apparently, this channel specifically provides intrinsic luminescence quenching with an increase in the molybdenum concentration. The excitation spectra indicate that the intrinsic luminescence quenching in $\text{CdWO}_4:\text{Mo}$ is caused specifically by nonradiative relaxation of electronic excitations rather than their trapping by impurity luminescence centers. This mechanism is evidenced by the fact that the excitation efficiency for the impurity luminescence band (Fig. 3, curve 1) does not increase when the excitation efficiency for the intrinsic band decreases with an increase in the excitation energy.

REFLECTION SPECTRA

Figure 4 shows the reflection spectra of two CdWO_4 samples with the crystallographic axes \mathbf{a} (curve 1) and \mathbf{c} (curve 2) oriented parallel to the vector \mathbf{E} of the incident synchrotron radiation. Cadmium tungstate is a biaxial anisotropic crystal; therefore, the reflection spectra of the samples differently orientated with respect to the vector \mathbf{E} differ from each other. The energy positions and relative intensities of the reflection peaks for the samples with different orientations are listed in Table 2. The obtained positions of the reflection peaks in the fundamental absorption region are in good agreement with the values obtained previously for an unoriented CdWO_4 sample [15, 16]. The first reflection peak with a maximum at 3.88 (3.91) eV for the orientation $\mathbf{a} \parallel \mathbf{E}$ ($\mathbf{c} \parallel \mathbf{E}$) is located before the onset of the increase in the intensity of the intrinsic luminescence excitation spectrum in the vicinity of the fundamental absorption edge (3.95 eV). Thus, the max-

imum of the first peak in the reflection spectrum is in the crystal transparency window and is caused by reflection from the substrate.

In the energy range of 4.0–4.5 eV, a group of reflection peaks is observed whose energy position and intensity depend on temperature. It is known that this energy range corresponds to the formation of a Frenkel exciton at a WO_6^{6-} complex [15]. In [14], it was concluded that the nonelementary structure of the exciton peak is related to the distortion of the octahedral coordination in a WO_6^{6-} complex by the crystal field. As a result of the distortion, the oxygen atoms forming an octahedron around a central W atom, are located at distances of 1.78, 1.91, and 2.15 Å [4]. An exciton is formed at the $2p\text{O}-5d\text{W}$ electronic transition; therefore, localization of the hole of an exciton at different oxygen atoms may give rise up to three exciton peaks. In the region under consideration, we observed three reflection peaks for the orientation $\mathbf{a} \parallel \mathbf{E}$ and two reflection peaks for $\mathbf{c} \parallel \mathbf{E}$, which correspond to the formation of excitons. The band gap, determined from the onset of the increase in the reflectance after the exciton structure, is 4.55 eV; it is independent of the crystal orientation.

Previously, we interpreted the reflection peaks in the range of 5–30 eV within the MO–LCAO model, which takes into account only the electronic states of the WO_6^{6-} complex [15]. The role of the $4d$ -shell electronic states of cadmium cations, which are involved in the formation of the middle of the valence band of the crystal, remains unclear.

Figure 4 shows also the ratio of the intrinsic luminescence excitation spectra of CdWO_4 , measured at 300 and 10 K (curve 3). In the vicinity of the peaks at 6.2 and 8.2 eV, the fraction of low-energy electrons increases in the ratio of the excitation spectra; thus, an excited electron and hole cannot migrate at a large distance from each other. The reflection spectra of CdWO_4 also contain peaks in the vicinity of 6.2 and 8.2 eV (Table 2; reflection peaks 6, 7, and 9). Thus, the structure in the ratio spectrum is related to the structural features of the valence and conduction bands. More detailed investigations are necessary to clarify the structural features of the energy bands in CdWO_4 .

CONCLUSIONS

(i) The luminescence properties of pure and Mo-doped CdWO_4 crystals have been investigated. It is shown that the molybdenum impurity leads to the formation of an additional luminescence band, which is due to the transitions at MoO_6^{6-} complexes, and causes significant (by more than two orders of magnitude at a Mo concentration of 0.4 wt %) intrinsic luminescence quenching at room temperature.

(ii) The factors affecting the formation of the intrinsic and impurity luminescence excitation spectra are considered. Dependence of the probability for separated electron and hole to be coupled into an exciton for emission of an intrinsic luminescence photon on the energy of excitation photons and temperature is demonstrated. It is shown that the intrinsic luminescence quenching in $\text{CdWO}_4:\text{Mo}$ is caused by nonradiative relaxation of electronic excitations rather than their trapping by impurity luminescence centers. Since the width of the valence band exceeds that of the conduction band, both electrons and holes are involved in photon multiplication; this fact explains the unusually sharp increase in the intensity in the excitation spectrum at $E > 10$ eV.

(iii) On the basis of the ratio of the excitation spectra obtained at different temperatures, it is shown that the number of low-energy electrons and holes increases upon excitation of a crystal with 6.2- and 8.2-eV photons. It is suggested that this increase is related to the structural features of the energy bands in CdWO_4 .

(iv) The band gap E_g of the crystal is determined to be 4.55 eV. The obtained value of the band gap is independent of the orientation of the crystallographic axes in anisotropic CdWO_4 with respect to the vector \mathbf{E} of the synchrotron radiation incident on the sample.

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