

## Luminescence of CWO single crystals containing various defects

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Influence of dopant-induced defects on luminescence and performance characteristics of CWO crystals has been studied. Mo and Fe have been shown to give rise to a specific "red" emission component with decay time of several hundreds of microseconds or more, while trivalent dopants cause formation of deep charge carrier traps responsible for the millisecond range afterglow. These defects give rise also to the color centers causing absorption in the intrinsic emission band, thus deteriorating the crystal scintillation parameters. The studies performed allowed to develop a technology of large high-quality CWO crystals. The tomographic elements manufactured from those crystals showed an afterglow of less than 100 ppm after 20 ms and the light yield of about 20,000 photons per MeV.

Исследовано влияние примесных дефектов на люминесцентные и функциональные характеристики кристаллов CWO. Показано, что Mo и Fe образуют в кристаллах специфические "красные" компоненты свечения с временами высвечивания несколько сотен и более микросекунд, трехвалентные примеси приводят к образованию глубоких ловушек носителей заряда, ответственных за послесвечение в миллисекундном диапазоне. Эти дефекты также ответственны за образование центров окраски, поглощающих в области собственного свечения, что ухудшает сцинтилляционные характеристики кристаллов. Проведенные нами исследования позволили разработать технологический процесс получения крупногабаритных кристаллов CWO улучшенного качества. Томографические элементы, изготовленные из этих кристаллов, имели послесвечение менее 100 ppm через 20 мс, световой выход ~ 20000 фотонов/МэВ.

Cadmium tungstate (CWO) crystals are under study for a long time. This is associated with good properties of the material providing its application in detecting blocks of various tomographic and spectrometric devices as well as with possible improvement of those properties and regulation of optimum parameter combinations for specific applications. CWO single crystals belong to luminophors with so-called "intrinsic" luminescence [1]. The crystal is characterized by a broad asymmetric X-ray luminescence spectrum being a superposition of several luminescence bands. Studies of the photoluminescence have shown that, besides of the

main "blue-green" emission band with a maximum in the 500 nm region, there are emission bands in the "yellow" region ( $\lambda_{max} = 570$  to 580 nm) [2] and in the "red" one ( $\lambda_{max} = 630$  to 670 nm) [3, 4]. According to [2], the emission around 500 nm is due to transition in the tungstate group  $WO_6^{6-}$ , while the emission at  $\lambda_{max} \sim 570$  to 580 nm is associated with the defect tungstate group containing an oxygen vacancy. The emission in the red range is inherent in the CWO matrix [3] as well as is due to non-intentional uncontrollable impurities [4]. Thus, essentially all authors have stated that it is just the molecular electron orbitals of the tung-

state group modified substantially by various defects that contribute mainly to energy structure formation of an emission center in CWO. In this connection, this work is a continuation of our studies [5] on the influence of extrinsic defects on the luminescence of cadmium tungstate crystals. A particular attention is given to the nature of the luminescence slow component that defines the most important performance parameter, namely, the afterglow.

It has been shown before [5] that the photoluminescence spectrum of a nominally pure CWO sample taken at room temperature comprises an asymmetric band peaked at 500 nm. A plateau (450 to 460 nm) can be distinguished in that band. A strong asymmetry is typical of the spectrum long-wavelength part; as the impurity concentration rises, the asymmetry is converted in an additional band. As the temperature is lowered down to 77 K and further to 4.2 K, the luminescence spectrum takes a more and more complex shape. Under excitation with a light of a wavelength shorter than 315 nm, the main band is peaked at 495–510 nm. At the exciting wavelength of 315 to 345 nm, the main emission band intensity drops sharply and a "red" component (670–700 nm) is formed with a plateau at 575–630 nm; that component is due to extrinsic defects. Under excitation with light of a wavelength longer than 345 nm, the "yellow" emission (575 to 630 nm) starts to be observable while the "red" contribution becomes reduced. A detailed study of the emission spectra in the temperature range of 4.2 to 450 K has shown that the "yellow" band is not elementary and the "blue-green" and "red" ones are interrelated [5].

Moreover, it has been shown that there is a group of samples having the photoluminescence spectra similar to those of the nominally pure crystals. That group includes the samples containing impurities of univalent metal cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Ag}^+$ , etc.) and bivalent ones ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , etc.), see curve 1 in Fig. 1. This fact is explained by that the isovalent substitution of bivalent Cd cations distorts only slightly the CWO crystal lattice, so the luminescence and excitation maxima of those crystals are shifted insignificantly as compared to the pure crystals. The spectra are influenced slightly also by singly charged alkali metal cations, that seem to compensate the charge of uncontrollable impurities. However, trivalent impurities must cause a substantial distortion of both

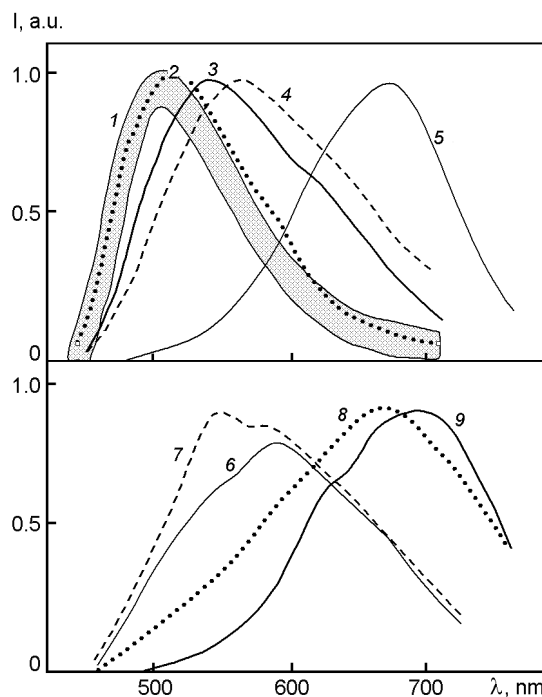


Fig. 1. Luminescence spectra of CWO crystals ( $\lambda_{ex} = 337.1$  nm) at 290 K: 1, doped with 1- and 2-valent cations; 2, Ce (0.05 mass.%); 3, Bi ( $5 \cdot 10^{-3}$  mass.%); 4, Bi ( $2.5 \cdot 10^{-1}$  mass.%); 8, Mo ( $5 \cdot 10^{-1}$  mass.%) and at 77 K: 5, undoped; 6, ( $2.5 \cdot 10^{-1}$ – $5 \cdot 10^{-3}$ ) mass. % Bi,  $\text{Bi/Li} = 1/6$ ; 7,  $2.5 \cdot 10^{-1}$  mass. % Bi,  $\text{Bi/Li} = 1/1.5$ ; 9,  $5 \cdot 10^{-1}$  mass.% Mo.

anionic and cationic sublattices of the CWO crystal resulting in a considerable change in the luminescence spectra under excitation of the tungstate emission centers. The spectrum change extent must depend on the manner in which the charge compensation occurs (Fig. 1, curves 6 and 7). Thus, emission centers absent in CWO crystals containing  $\text{Me}^{1+}$  and  $\text{Me}^{2+}$  must be formed in the crystals with  $\text{Me}^{3+}$  impurities. When the crystals are doped with  $\text{Mo}^{6+}$ , it substitutes the  $\text{W}^{6+}$  ions giving rise to formation of molybdate groups distorted as compared to cadmium molybdate. The luminescence of those groups is observed in the "red" spectral region, thus being in agreement with the results of [6].

In this work, were studied the X-ray luminescence (XRL) in the  $\lambda > 650$  nm, the decay time of individual components of the luminescence, as well as the thermally stimulated luminescence (TSL) in the temperature range of 80 to 320 K. The samples studied were the CWO crystals doped with molybdenum, iron, holmium, and bismuth.

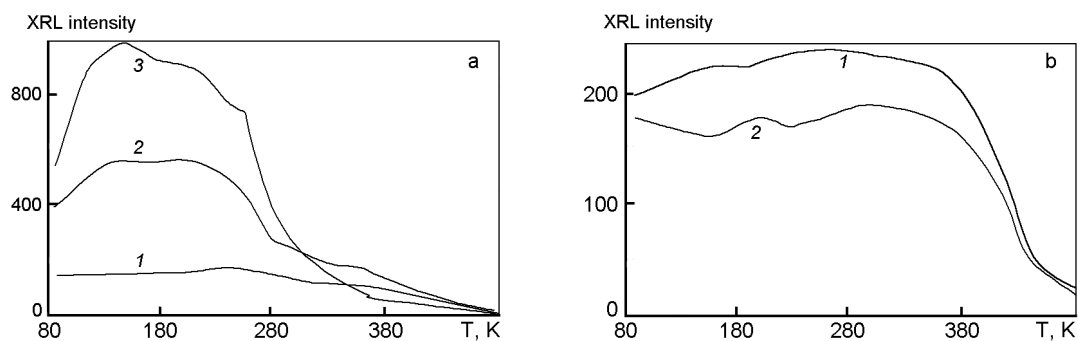


Fig. 2. Temperature dependence of XRL intensity ( $\lambda > 600$  nm) of crystals CWO doped with (a) Mo (1 —  $10^{-4}$  mass. %, 2 —  $10^{-2}$  mass. %, 3 —  $10^{-1}$  mass. %), (b) Fe (1 —  $10^{-4}$  mass. %, 2 —  $10^{-3}$  mass. %).

The study of Mo-doped CWO crystals has shown that a slow luminescence component with the intensity damping time  $T_{1/2} = 400$   $\mu$ s ( $T_{1/2}$  is the intensity halving time at  $T < 150$  K) peaked at 650–700 nm. That component is absent in nominally pure samples. The concentration and temperature dependences of that XRL band intensity (Fig. 2a) differ considerably from the intrinsic emission [7], thus confirming that the emission is related to a center containing a molybdenum ion. It can be assumed that at Mo concentrations lower than 0.1 %, isolated  $\text{MoO}_4$  groups (but not the  $\text{CdMoO}_4$  phase) are formed in CWO. It is just those groups that are the centers of the slow "red" luminescence. The TSL spectrum of the Mo-containing samples comprises two bands peaked at 500 and 600–700 nm, the contribution thereof being different. The positions of TSL maxima ( $T = 90$ – $100$ , 220, 270, 320 K) is typical of the Mo-containing CWO crystals [6].

In Fe-doped CWO samples, the "red" XRL component is present, too, but the quenching begins at higher temperatures as compared to CWO:Mo (Fig. 2). As the Fe impurity content increases, the stationary XRL intensity drops, the XRL spectrum is broadened, its maximum is shifted towards shorter wavelengths due to reducing contribution from the "red" luminescence band. The intensity of TSL in the 600–700 nm region is reduced, respectively (Fig. 3). At Fe concentration exceeding  $10^{-3}$  %, the TSL drops down to the noise level. This phenomenon is not typical of other impurities studied where the peak intensities increase with the concentration. Thus, the response time extension in the CWO:Fe crystals should not be associated with the light sum storage. Iron in crystals is known to form emission centers with a low prob-

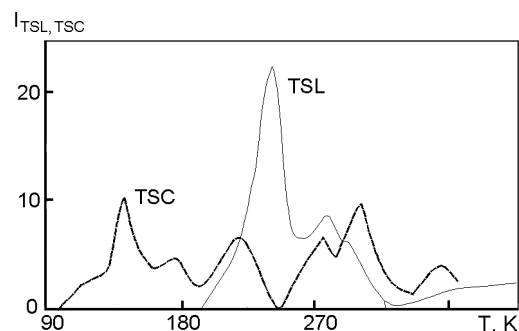


Fig. 3. Curves of TSL and TSC ( $\lambda > 600$  nm) of CWO crystals doped with Fe ( $5 \cdot 10^{-4}$  mass. %).

ability of emissive transitions, the energy captured by those centers being converted into emission only to a small extent [8]. Such centers may have several excited electron states characterized by intersecting potential curves. In this case, a cascade type non-radiative transition to the lowest excited electron state takes place, followed by emission of a long-wavelength light, often in IR region.

In the studied samples with  $\text{Me}^{3+}$  type impurities, the slow "red" XRL centers similar to above-mentioned ones in Mo- and Fe-doped crystals not are observed. The study of TSL spectra of the samples containing  $\text{Ho}^{3+}$  have revealed two thermoluminescence peaks differing in the spectral compositions namely, at  $T_{max} = 130$ – $140$  K (510–515 nm) and at  $T_{max} = 230$  K (540 nm), see Fig. 4. The low-temperature TSL peak intensity becomes reduced after the sample annealing in an oxygen-containing medium. For CWO crystals with Bi impurity, typical is a high TSL maximum in the 180–190 K range and that at 240–250 K emitting in the 520–550 nm range [9]. The thermostimulated conductivity is absent for some CWO:Bi samples, thus evidencing the intra-center relaxation charac-

Table. Light yield and afterglow characteristics of CWO crystals

No.	Purity	Concentration, mass. %	Light yield, %	Afterglow after 20 ms, %
1	undoped	—	100	0.014
2	Cd	0.25	98	0.013
3	Li	0.1	107	0.008
4	Na	0.01	99	0.008
5	Zn	0.1	90	0.026
6	Pb	0.1	64	0.03
7	Bi	0.025	50	1.5
8	Bi/6Li	0.025	95	0.2
9	Cr	0.025	20	0.018
10	Fe	0.005	41	0.03
11	Fe	0.0005	98	0.03
12	Fe/5Li	0.0005	99	0.03
13	Fe/5Li	0.005	41	—
14	Ho	0.0025	45	0.6
15	Ho (after annealing)	0.0025	50	0.2
16	Gd	0.05	49	0.09
17	Hf	0.03	47	0.033
18	Zr	0.003	98	0.019
19	Nb	0.01	8	0.035
20	Ta	0.03	74	0.02
21	Mo	0.05	38	0.05
22	Mo	0.5	35	0.1

ter. The decay of the stored light sum in those samples may cause an additional XRL component.

Thus, the Mo and Fe impurities in cadmium tungstate crystals can be concluded to form specific "slow" emission components in the "red" spectral range. In the studied CWO crystals containing  $Me^{3+}$  impurities, the additional slow XRL components may be due to the decay of the stored light sum.

Table presents the light yield and afterglow characteristics of CWO crystals with various impurities. The consideration of those data makes it possible to conclude that in most cases, introduction of univalent and bivalent impurities does not influence the light yield as compared to nominally pure (n.p.) crystals. It is just the doping with trivalent impurities (Gd, Ho, Sm, Bi, etc.) that influences most strongly. Since the main charge compensating structure defects in CWO crystals are oxygen vacancies, the doping with  $Me^{3+}$  seems to cause formation of complex color centers containing the dopant ions, reduced tungsten ( $W^{5+}$ ) or F centers [9].

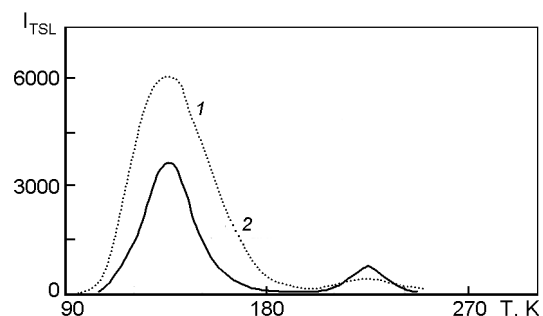


Fig. 4. Curves of the TSL of CWO crystals doped with Ho ( $5 \cdot 10^{-2}$  mass. %): 1 — prior to annealing, 2 — after annealing.

It is to note that the introduction of singly charged alkali cations into CWO crystals results in most cases in increased light yield and decreased afterglow. This may be associated, as was mentioned above, with the charge compensation of uncontrollable impurities. In those cases, a fraction of the deep traps formed by trivalent dopants is converted into shallower ones, thus reducing the contribution from the millisecond

emission component. A similar effect is typical of the annealing of crystals with some impurities in an oxygen-containing atmosphere.

In conclusion, the results presented show that the intrinsic luminescence of cadmium tungstate should not be related with emission of any tungstate groups, but only with those interacting with the lattice distortions or associated with defects. The possible variety of the latter gives rise to several types of emission characterized by individual spectral characteristics. The luminescence characteristics of CWO crystals are influenced to the greatest extent by trivalent impurities. Those form the color centers and deep traps of charge carriers, thus resulting in the absorption of the intrinsic emission, the light sum storage, and the slow decay component. The univalent alkali impurities, as well as annealing in oxygen in some cases, favor the conversion of the complex defects formed by  $\text{Me}^{3+}$  and so improve the performance parameters of CWO crystals. Mo and Fe in CWO crystals are responsible for specific "red" emission components with decay times of several hundreds of microseconds and more. The results obtained were used in the CWO crystal growing technology and have provided the

samples with afterglow of less than 100 ppm after 20 ms and light yield of about 20,000 photons per MeV.

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## Люмінесценція монокристалів CWO з різними дефектами

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Вивчено вплив домішкових дефектів на люмінесцентні і функціональні характеристики кристалів CWO. Показано, що Mo і Fe утворюють в кристалах CWO специфічні "червоні" компоненти свічення з часами висвічення декілька сотень і більше мікросекунд, тривалентні домішки приводять до утворення глибоких пасток носіїв заряду, відповідальних за післясвічення у мілісекундному діапазоні. Ці дефекти також відповідальні за утворення центрів забарвлення, поглинаючих в області власного свічення, що погіршує сцинтиляційні характеристики кристалів. Проведені нами дослідження дозволили розробити технологічний процес отримання великогабаритних кристалів CWO поліпшеної якості. Томографічні елементи, виготовлені з цих кристалів, мали післясвічення менше 100 ppm через 20 мс, світловий вихід ~ 20000 фотон/MeV.