

## Effect of the growing features on luminescence and thermal glow of $\text{CdWO}_4$ scintillation crystals

*A.P.Luchechko, Ya.M.Zakharko, I.M.Solsky*\*,  
*M.V.Pashkovsky, Yu.V.Zorenko*

Electronics Faculty, I.Franko Lviv National University,  
107 Tarnavsky St., 79017 Lviv, Ukraine  
\*Institute for Materials, SRC "Karat",  
202 Stryiska St., 79031 Lviv, Ukraine

*Received March 2, 2005*

Investigation results of absorption, X-ray-, photo-, and thermally stimulated luminescence spectra of  $\text{CdWO}_4$  crystals are presented as depending on the growing features thereof. Essential changes in relative intensity of some emission bands under X-ray and  $\text{N}_2$ -laser excitation have been observed. The raw material purification in the course of the preliminary recrystallization has been shown to result in an enhanced X-ray luminescence intensity in the blue-green spectral region and in decreased thermal glow peaks responsible for the slow luminescence components.

Представлены результаты исследования спектров поглощения, рентгено-, фото- и термостимулированной люминесценции кристаллов  $\text{CdWO}_4$  в зависимости от технологических особенностей их выращивания. Обнаружены значительные изменения относительной интенсивности отдельных полос свечения образцов при возбуждении рентгеновскими лучами и  $\text{N}_2$ -лазером. Показано, что очистка сырья в процессе предварительной перекристаллизации приводит к повышению интенсивности рентгенолюминесценции в сине-зеленой области спектра и ослаблению пиков термовысвечивания, ответственных за медленные компоненты свечения.

Cadmium tungstate  $\text{CdWO}_4$  (CWO) is used widely in X-ray computer-aided tomographs [1, 3], in nuclear well logging [2], and in low-background scintillation spectrometers [4]. The improved technology of the single crystals made it possible to enhance the scintillation efficiency of dark-yellow CWO samples that was about 18 % relatively to  $\text{NaI-Tl}$  [2] up to 38 % for modern crystals that are almost colorless [3]. The main emission band of CWO at room temperature is at about 480–490 nm and is overlapped with a less intense band peaked at 580 nm [5]. In some crystals, a "red emission" that is believed to be due the structure defects [6] was observed along with the above bands.

The main drawback of CWO scintillators is a rather long decay time (12 to 15  $\mu\text{s}$ ) that limits the maximum possible counting rate [4]. For tomographic measurements where the current recording regime is realized in fact, a long afterglow is of more importance. The afterglow intensity 3 ms after the excitation is over should not exceed  $1 \cdot 10^{-4}$  of the initial value [1]. The detectors of computer-aided tomographs are designed as scintillator/photodiode optoelectronic couples. Since the sensitivity maximum of silicon photodiodes lies in the red spectral region, it is important to elucidate the relation of long-wavelength emission bands and slow decay components with the

Table 1. Characteristics of CWO crystals

Sample No.	Technology features
0	"Old" light-yellow crystal
1	Recrystallized material without CdCO <sub>3</sub> additive
3	Recrystallized blend with 1.1 mass.% of CdO added
4	Mixture of CdCO <sub>3</sub> and WO <sub>3</sub> powders

raw material quality and technology features of the single crystal growing.

The large-size CWO crystals (60 to 65 mm in dia., the cylindrical part length 150 mm) were studied. The crystals were grown by Czochralski technique at SRC "Karat", Lviv, using the equipment from Physiterm, France. The details of the blend preparation and growth procedures were published before [7]. The characteristics of individual crystals wherefrom the samples for the study were cut out are presented in Table 1.

The samples shaped as 10×10×1 mm<sup>3</sup> were cut out of the cylindrical part and polished up to optical quality grade. The facial side of the plate corresponded to the (100) plane of the crystal. The optical absorption of the samples was calculated basing on the transmission spectra measured using a Specord M 40 at room temperature. To examine the X-ray luminescence (XRL) and photoluminescence under N<sub>2</sub>-laser excitation, a setup basing on a quartz monochromator SF-4A was used. The X-ray excitation was done by a microfocussed X-ray tube with copper anticathode through beryllium window of a cryostat, the tube operated at 45 kV, 0.3 mA. The thermal glow (TG) was recorded in linear heating regime at the temperature increase rate of 0.2 K/s. The TG curves were recorded both in the integral mode and at discrimination of individual spectral ranges with monochromator. The luminescence spectra were corrected for the monochromator dispersion and the spectral sensitivity of the PMT.

The absorption spectra of CWO single crystals grown with different technological features are shown in Fig. 1. In the spectrum of the "old" crystal No.0 grown from a mixture of tungsten oxide and cadmium carbonate of 99.99 % purity (curve 1), a broad band peaked at 365 nm is overlapped with a weaker one near 470 nm that is responsible for the appreciable yellowish color of the crystal. The crystal obtained from

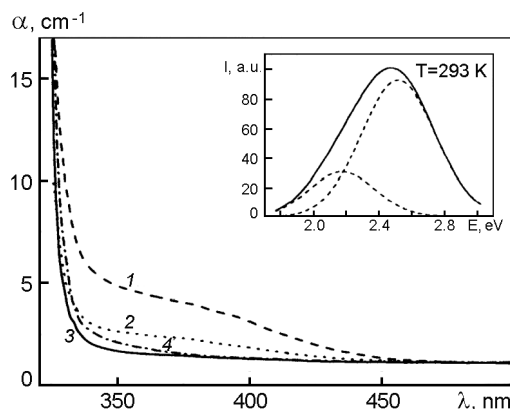


Fig. 1. Absorption spectra of CdWO<sub>4</sub> single crystals Nos. 0(1), 1(2), 3(3), 4(4). Inset; emission spectra of CdWO<sub>4</sub> single crystal No.3 under X-ray excitation.

the recrystallized raw material shows a faint yellowish-green color (curve 2). The Samples Nos.3 and 4 are essentially colorless in the visible spectral region and the absorption coefficient at 365 nm for those crystals does not exceed 0.3 cm<sup>-1</sup>.

The inset in Fig. 1 presents the XRL spectrum of a CWO crystal at room temperature. The dashed lines show the elementary Gaussian bands resulting from the spectrum expansion. The positions of the band maxima were improved by averaging the measured results for crystals of different origins. The maxima of two main bands in the room-temperature XRL spectrum answer to the quantum energy values of 2.51 and 2.17 eV at half-widths of 0.54 and 0.50 eV, respectively. The temperature lowering down to 100 K causes an insignificant shift of the short-wavelength band towards lower energy (2.47 eV) and the band half-width decrease to 0.51 and 0.44 eV, respectively. The data obtained are in a good agreement with literature ones [5, 6]. The intensity ratio of the yellow and blue-green bands in the XRL spectra at room temperature varies for different crystals within limits of 0.31 to 0.39 without any appreciable correlation with technological features. At  $T = 100\text{K}$ , the yellow emission drops by 13 to 20 % relatively to the major band.

Fig. 2 presents the emission spectra of CWO crystals excited by a nitrogen laser ( $\lambda = 337\text{ nm}$ ) at 100 K. In the PL spectra, a new band peaked at 1.81 eV of 0.41 eV half-width is observed along with the two ones observed under X-ray excitation. This "red" band dominates in the emission spectrum of the crystal No.0 where its intensity exceeds almost twice that of the 2.47 eV

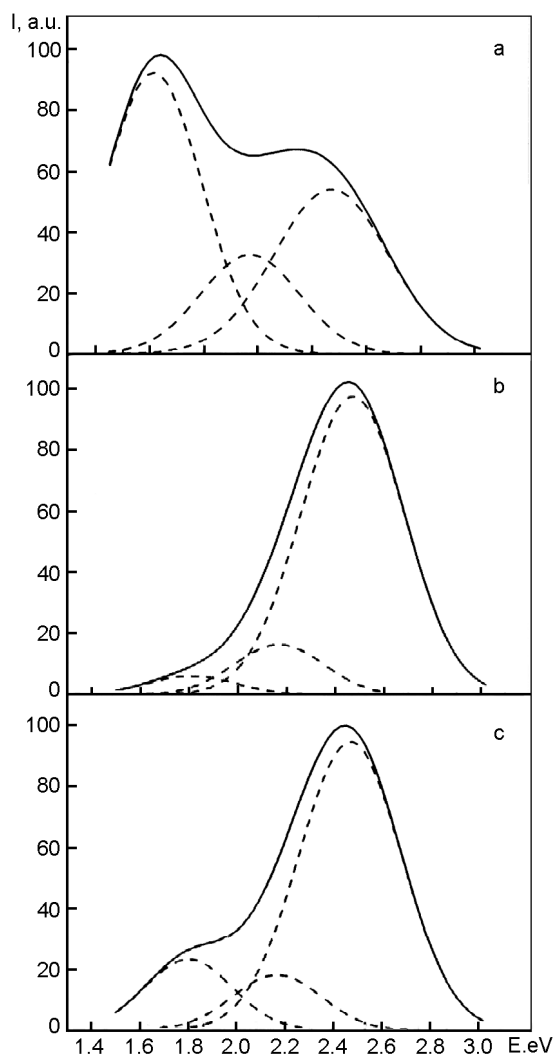


Fig. 2. Emission spectra of  $\text{CdWO}_4$  single crystals Nos.0 (a), 1 (b) and 3 (c) under excitation by  $\text{N}_2$ -laser at 100 K.

band. It is to note that the relative intensity of the 2.17 eV band increases also under the laser excitation. This result is in agreement with literature data on the features of optical excitation of individual CWO bands [5, 6].

In the crystals grown from the recrystallized material, the relative intensities of the long-wavelength emission bands drop sharply. This is true, in particular, for the 1.81 eV band. This fact may be due to the material purification attained by the recrystallization and to the improved scintillator quality as a whole. The data on relative intensity of the 680 and 570 nm emission bands as compared to the major 490 nm one for various CWO crystals excited by nitrogen laser are presented in Fig. 2. The Table 2 shows also

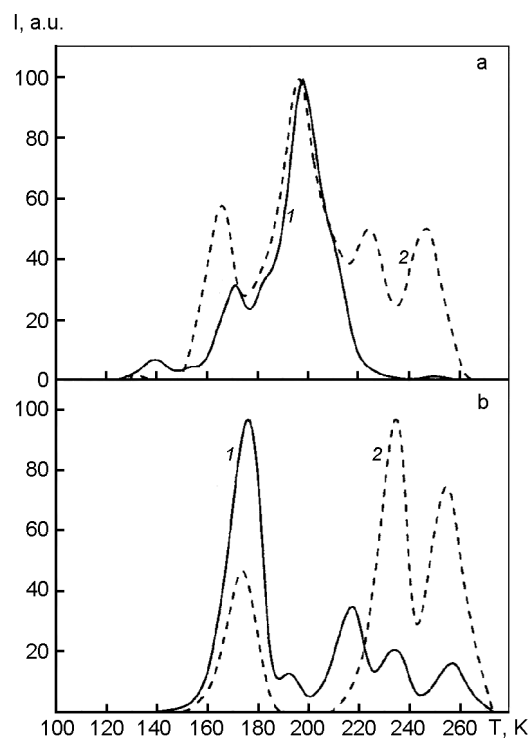


Fig. 3. Thermoluminescence glow curves of  $\text{CdWO}_4$  single crystals No.0 (a) and No.3 (b) after X-ray irradiation at 100 K: 1, integrated intensity; 2, wavelength resolved measurements with  $\lambda_{max} = 670$  nm.

the XRL intensity in the blue-green region at room temperature.

The light yield of the crystals growth by the improved technology is in correlation with the data from [7] that were obtained under excitation with  $^{60}\text{Co}$  gamma quanta and  $\alpha$  particles. The XRL intensity is increased by a factor of almost 1.5 as compared to the "old" crystals.

Fig. 3a shows the thermal glow curve of the crystal No.0. When the integral intensity of TSL is recorded (curve 1), a strong

Table 2. Relative intensities of CWO emission bands under nitrogen laser excitation ( $T = 100$  K) and the intensity of the main band in the XRL spectrum ( $T = 293$  K)

Crystal No.	$I_{570}/I_{490}$	$I_{680}/I_{490}$	XRL intensity at $\lambda_{max} = 490$ nm at 293 K
No.0	0.6	1.72	100
No.1	0.17	0.06	143
No.3	0.19	0.24	168

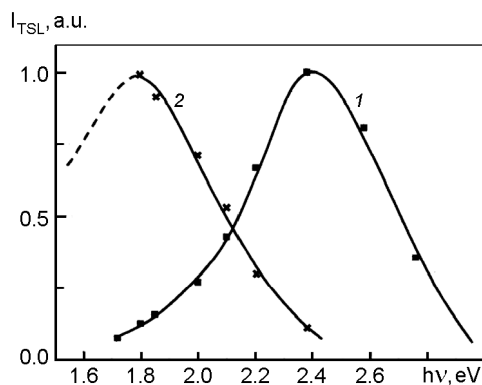


Fig. 4. TSL emission spectra of  $\text{CdWO}_4$  single crystal No.3 at temperatures (K): 174 (1), 255 (2).

overlapping of several TG peaks is observed. The peaks have maxima at 140, 174 and 200 K and an inflection near 210–220 K. The curve 2 in Fig. 3a is obtained when recording the emission passed through the SF-4 monochromator in the spectral region centered at  $\lambda = 668$  nm at the slot width of 1.0 mm. In this curve, there is no peak at 140 K and the relative intensity of the 230 and 255 K TG peaks is increased considerably, while these peaks were almost unobservable in the integral record.

To ascertain the emission spectral composition in the individual TG peaks, the curves were measured at different fixed wavelength values. Fig. 4 presents the TSL spectra in 174 K (curve 1) and 255 K (curve 2) peaks. In low-temperature TG peaks, in particular, in the 174 K one, the stored light sum is emitted mainly in the blue-green spectral region at  $h\nu_{max}$  about 2.4 to 2.5 eV. The long-wavelength emission curves arise when the carriers are released from the traps associated with 235 and 255 K peaks.

Fig. 5 illustrates the effect of annealing in reducing atmosphere on the TG curves of CWO crystals. One of the samples cut out of adjacent crystal area was annealed in vacuum at 400°C for 5 h. The TG curve of the initial untreated crystal No.4 (Fig. 5, curve 1) differs somewhat from those presented above. In this curve, the 170 K peak dominates, the 215 and 235 K peaks are absent while low ones at 135 and 245 K remain. In the TG curve of the vacuum-annealed crystal, almost all the peaks observed for the untreated sample become vanished while a new intense peak at 220 K arises. The total TSL intensity is increased by about one order, the sample is slightly

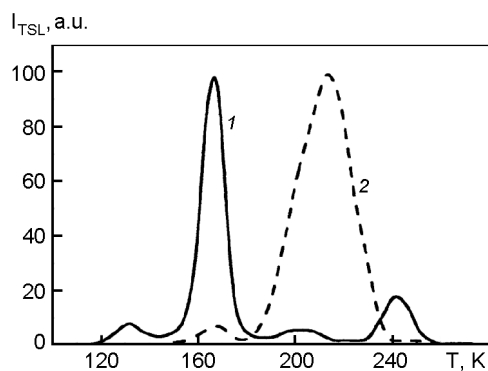


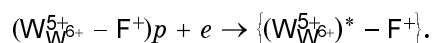
Fig. 5. Thermoluminescence glow curves of  $\text{CdWO}_4$  single crystals No.4 after X-ray irradiation at 100 K obtained in integrated regime of registration: 1, as grown, 2, annealed in vacuum.

darker visually and its emission intensity under X-ray excitation is decreased almost by a factor of 3.

To explain the results obtained let us proceed from the models of the emission centers and the recombination excitation mechanisms thereof proposed in [5, 8]. Let be assumed that the blue-green luminescence results from the recombination of free holes with intrinsic defects related to  $\text{WO}_6$  groups. The yellow luminescence arises at the recombination of free electrons with holes localized at tungstate groups where the oxygen ion is absent [5].

In our opinion, when a vacancy arises at the site of  $\text{O}^{2-}$ , one of  $\text{W}^{6+}$  cations surrounding the anion site may change its coordination and transit into the  $\text{W}_{\text{WO}_6}^{5+}$  state. This corresponds to formation of a donor-acceptor complex that is converted into a neutral center as an electron is localized near to the oxygen vacancy ( $\text{W}_{\text{WO}_6}^{5+} - \text{F}^+$ ). Being in the charge state neutral in relation to the lattice, such a defect is able to capture both an electron and a hole, the capture probability of the one or another charge carrier is defined by the capture cross-section and the free carrier concentration.

The recombination of an electron with the trapped hole can be presented as a reaction



The cation  $\text{W}^{5+}$  transition from the excited state  $5d^1$  into the ground one is accompanied by emission in the yellow spectral region. Recombination of a hole with captured electron results in the blue-green emission peaked at 480 nm. The recombination channel of that emission does not ex-

clude the existence of other ones, e.g., self-localization of elementary excitations. As to origin of the 1.8 eV emission band, it can be assumed to be associated with the iron impurity in the crystal due to raw materials used to synthesize the raw blend. It is just iron that is believed to give rise to similar bands in emission and absorption spectra of the isostructure zinc tungstate [9].

It is known [10] that the slow emission components with decay time exceeding 10 ms at room temperature are possible when the traps are present that are demonstrated themselves in TG peaks at  $T > 200$  K. In our crystals, such traps are visible as TG peaks at 225 and 255 K that emit in yellow and red spectral regions.

The result obtained evidence that the improvement in the raw material purity provides a substantial decrease of thermal glow. The effect of the growing atmosphere and heat treatment on the TSL and afterglow of tungstates is worth to further studies.

*Acknowledgment.* This work has been supported in part by STCU Grant #2042.

## References

1. B.C.Grabmaier, W.Rossner, T.Berthold, Proc. Int. Conf. on Inorganic Scintillators and Their Applications, SCINT95, Delft University Press, 29 (1996).
2. C.L.Melcher, R.A.Manente, J.S.Schweitzer, *IEEE Trans. Nucl. Sci.*, **36**, 1188 (1989).
3. D.R.Kinloch, W.Novak, P.Raby et al., *IEEE Trans.Nucl. Sci.*, **41**, 752 (1994).
4. S.Ph.Burachas, F.A.Danevich, A.Sh.Georgadze et al., *Nucl. Instr. Meth. Phys. Res.*, **A 369**, 164 (1996).
5. M.J.J.Lammers, G.Blasse, D.S.Robertson, *Phys. Stat. Sol.(a)*, **63**, 569 (1984).
6. A.E.Ovechkin, V.D.Ryzhikov, G.Tamulaitis et al., *Phys. Stat. Sol.(a)*, **103**, 285 (1987).
7. V.Nekrasov, Yu.Borodenco, E.Selegenev et al., Proc. Int. Conf. on Inorganic Scintillators and Their Applications (Moscow, 1999), Nauka, Moscow (2000), p.740.
8. M.Springis, V.Tale, I.Tale et al., Proc. Int. Conf. on Inorganic Scintillators and Their Applications (Moscow, 1999), Nauka, Moscow (2000), p.740.
9. L.Grigorjeva, D.Millers, S.Chernov et al., *Radiat. Measur.*, **33**, 645 (2001).
10. B.S.Grabmaier, *IEEE Trans.Nucl.Sci.*, **NS-31**, 372 (1984).

## Вплив особливостей вирощування на люмінесценцію та термовисвічування сцинтиляційних кристалів $\text{CdWO}_4$

*А.П.Лучечко, Я.М.Захарко, І.М.Сольський,  
М.В.Пашковський, Ю.В.Зоренко*

Представлено результати дослідження спектрів поглинання, рентгено-, фото- та термостимульованої люмінесценції кристалів  $\text{CdWO}_4$  в залежності від технологічних особливостей їх вирощування. Виявлено суттєві зміни відносної інтенсивності окремих смуг свічення зразків при збудженні рентгенівськими променями та  $\text{N}_2$ -лазером. Показано, що очистка сировини у процесі попередньої перекристалізації приводить до підвищення інтенсивності рентгенолюмінесценції у синьо-зеленій області спектра та послабленню піків термовисвічування, які відповідають за повільні компоненти свічення.