Scintillators Based on CdWO_4 and $\text{CdWO}_4\text{:Bi}$ Single Crystalline Films

Yuriy Zorenko, Vitaliy Gorbenko, Taras Voznyak, Ivan Konstankevych, Volodymyr Savchyn, Mirosław Batentschuk, Albrecht Winnacker, and Christoph Josef Brabec

Abstract—This research is directed on creating by liquid phase epitaxy the single crystalline film scintillators based on undoped and Bi doped CdWO_4 compounds as well as the phoswich detector based on “ CdWO_4 : Bi or CdWO_4 films/ CdWO_4 or CdWO_4 : Bi crystals” epitaxial structures. The luminescent and scintillation properties of the undoped and Bi^{3+} doped (in a concentration range of 0.04–0.25 at. %) CdWO_4 films, grown by LPE method from Na_2WO_4 flux, were compared with the properties of CdWO_4 bulk crystal analogs, grown from melts by the Czochralski method. Using the traditional luminescence spectroscopy and the luminescence spectroscopy under excitation by pulsed synchrotron radiation with energy in the fundamental absorption range of CdWO_4 host, we have also examined the nature of different emission centers and studied energy transfer processes from tungstate hosts to Bi^{3+} ions and defect centers in CdWO_4 and $\text{CdWO}_4\text{:Bi}$ films and their crystal analogs.

Index Terms—Bi dopant, liquid phase epitaxy, luminescence, scintillators, single crystals and single crystalline films.

I. INTRODUCTION

THE technology of liquid phase epitaxy (LPE) offers now the possibility of obtaining the single crystalline film (SCF) scintillators based on the different high-density oxide compounds [1]. The fields of application of such SCFs include scintillators for registration of α - and β - particles and low-energy quanta, screens for visualization of X-ray images, cathodoluminescent screens, and laser media [1]–[5].

AWO_4 ($A = \text{Cd}, \text{Ca}, \text{Zn}$) tungstates have high densities $\rho = 6.1\text{--}7.4 \text{ g/cm}^3$ and effective atomic numbers $Z_{\text{eff}} = 61\text{--}66$. CdWO_4 , CaWO_4 and ZnWO_4 single crystals (SCs) are the well-

known scintillators for radiation monitoring and computer tomography [6], [7]. Therefore, the tungstates are very promising materials for creation of SCF scintillators emitting in the *blue range*. From activators, which can effectively emit in AWO_4 ($A = \text{Cd}, \text{Ca}, \text{Zn}$) hosts, Bi^{3+} and Pb^{2+} ions can be tested [8], [9].

In this work, we present the first results directed on the development by LPE method of the SCF scintillators based on undoped and Bi-doped CdWO_4 . The luminescent and scintillation properties of undoped and Bi doped CdWO_4 SCF were compared with the properties of their SC counterparts grown by the Czochralski method. We also consider the possibility of creation of phoswich detector [10] based on the mentioned SCF and SCs of undoped and Bi-doped CdWO_4 for simultaneous registration of $\alpha - (\beta)$ and γ -components of mixed ionizing fluxes [1], [8].

II. LPE GROWTH OF UNDOPED AND Bi^{3+} DOPED CdWO_4 SCF

The growth of undoped and Bi^{3+} doped CdWO_4 SCF was performed by the LPE method at 850°C – 860°C from the melt-solution (MS) based on Na_2WO_4 flux onto CdWO_4 substrates, prepared from the respective SC. The thickness of SCF was in the $1.5\text{--}20 \mu\text{m}$ range, and the growth rate was $0.05\text{--}0.1 \mu\text{m/mm}$. The main difficulties in the growth of CaWO_4 SCF by LPE method using Na_2WO_4 flux are low super-cooling rate of MS what lead to high probability of the spontaneous crystallization and non-uniformity of structural and scintillation properties of SCF at thickness of SCF above $20 \mu\text{m}$.

The concentration of Bi_2O_3 dopant in MS was varied in the $1.7\text{--}12$ mole % range for determining the maximum of light yield (LY) of SCF scintillators under excitation of SCF by α -particles of Pu^{239} (5.15 MeV) source. The charge compensation for Bi^{3+} ions in SCF is achieved due to the introduction of Na^+ flux dopant [8]. The undoped and Bi doped CdWO_4 SC were grown by the Czochralski method with the same raw materials in air atmosphere. The peculiarities of growth of these crystals have been recently reported in detail in our previous works [10], [11]. The Bi content in SCF and SC in the $0.04\text{--}0.25$ at. % range was determined using a JEOL JXA-8612 MX electron microscope. We have also determined the segregation coefficient of Bi ions in CdWO_4 SCF ranging from 0.02 to 0.025.

III. LIGHT YIELD AND LUMINESCENT PROPERTIES OF UNDOPED AND Bi^{3+} DOPED CdWO_4 SCF

First, we have studied the luminescent and scintillation properties of undoped CdWO_4 SCF in comparison with their SC

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Fig. 1. (a) Normalized CL spectra of CdWO₄ SC (1), CdWO₄ SCF (2) and CdWO₄:Bi (0.25 at. %) SCF (3), grown by LPE from Na₂WO₄ flux; (b) Difference between the curves 2-1 and 3-2 in Fig. 1(a). The positions of different emission centers from our previous works [8], [11], [12] are indicated in Fig. 1(a) by arrows.

counterpart, as well as the luminescent and scintillation properties Bi³⁺ doped CdWO₄ SCF and SC, depending on Bi³⁺ content under pulsed e-beam excitation (a pulse duration of 2 μ s and a frequency of 30.3 Hz) with an electron energy of 9 keV and a beam current of 100 μ A. The emission spectra were corrected for the spectral dependence of the detection part consisting of DMR-4 monochromator and FEU-106 photomultiplier. The results are presented in Fig. 1.

In previous our works [8], [11], [12], it has been shown that the WO₆²⁻ regular molecular complex acts as a main intrinsic emission center in undoped CdWO₄ SC. Namely, this emission is related to radiative de-excitation of the self-trapped exciton (STE) at molecular WO₆ oxy-anions [13]–[16]. The intrinsic defects also contribute to the luminescence of CdWO₄ SC [8], [12], [14]–[19]. Specifically, the nature of the long-wave components of CdWO₄ SC luminescence is connected with the evaporation of the part of CdO during the crystallization process and the formation of the “defect” of (WO₆-V_{C,A}) luminescent centers [8], [11], [12], [16]–[19]. The luminescence of these centers is related to localized-exciton emission of WO₆ oxy-anions, perturbed by the nearest anion (A) or cation (C) vacancies [14], [15]. In the frame of this assumption, the complex emission spectrum of CdWO₄ SC presents the superposition of the luminescence of WO₆ centers in the main band peaked at 485 nm, as well as the low intensive emission of (WO₆-V_{Cd})

and (WO₅-V_O) centers in the bands peaked at 575 and 650 nm, respectively [8], [11], [12] [Fig. 1(a), curve 1].

The CL spectrum of undoped CdWO₄ SCF [Fig. 1(a), curve 2] shows notable long-wavelength shift (of about 10 nm) in comparison with the spectrum of SC analogue (curve 1). This shift is caused by the incorporation of Na⁺ flux impurity and formation of (WO₆-Na) and (WO₅-V_O) centers [8]. It is necessary to note that the oxygen vacancies V_O provide here the charge compensation for Na⁺ flux impurity in CdWO₄ SCF, grown from Na-based fluxes.

The incorporation of Bi³⁺ ions in the CdWO₄ lattice was accompanied by the long-wavelength shift of the CL spectrum of CdWO₄:Bi SCF [Fig. 1(a), curve 3] in comparison with emission of undoped SCF in the band peaked at 495 nm [Fig. 1(a), curve 2]. The value of the shift was 45 nm for CdWO₄:Bi SCF with bismuth concentration of about 0.25 at. %.

We also calculated the difference of luminescence spectra of undoped and Bi-doped CdWO₄ SCFs with the aim to establish the structure of CdWO₄:Bi emission spectra [Fig. 1(b)]. The shape of these spectra permits to suppose that the long-wave shift of CdWO₄:Bi SCF emission spectra with respect to undoped SCF counterpart (Fig. 1, curves 1 and 2, respectively) is mainly caused by the rise of the luminescence intensity of the two bands peaked approximately at 540 and 620 nm. The position of these bands coincides within an accuracy of the experiment with the position of the analogous bands in the luminescence spectra of CdWO₄:Bi SC. This allows one to assign the observed bands in CdWO₄:Bi SCF to the luminescence of Bi³⁺ ions in the 540 nm band and to the luminescence of (WO₆-Na) centers in the 620 nm band. This assumption is supported by the following data.

- 1) The excitation spectrum of the Bi³⁺ luminescence at 540 nm (Fig. 2, curve 1) coincides with the absorption spectrum of CdWO₄:Bi SCF and contains the intensive band at 350 nm caused by the ¹S₀ → ³P₁ transitions of Bi³⁺ ions [20]. The photoluminescence (PL) spectrum of CdWO₄:Bi SCF under excitation with N₂-laser, $\lambda = 337$ nm in the range of the absorption band at 350 nm shows the dominant emission band of Bi³⁺ centers peaked approximately at 540 nm (Fig. 2, curve 2).
- 2) The decay kinetics of the main component of PL of CdWO₄:Bi SCF registered at 560 nm at 300 K is described by single exponent with the decay time in the microsecond range. The corresponding lifetime values $\tau = 4.2$ – 0.8 μ s depend on the dopant content in CdWO₄:Bi SCF samples in the range 0.025–2.5 at. %. The temperature dependence of the decay time of the Bi³⁺ luminescence in CdWO₄:Bi (0.25 at.%) SCF is presented in Fig. 2, inset. It should be noted that τ values in the microsecond range and temperature dependence $\tau(T)$ are typical for the luminescence of the mercury-like ions (ns²-electronic configuration) in the different oxide hosts [9], [21]–[25], particularly in CaWO₄:Bi SC [9].

We have also performed the time-resolved spectral-kinetic luminescence investigations of CdWO₄ and CdWO₄:Bi SCFs in comparison with their SC analogs at the Superlumi station (HASYLAB at DESY) under excitation by pulsed synchrotron radi-

Fig. 2. Excitation spectra of luminescence at 540 nm (1) and PL (2) spectra of CdWO₄:Bi (0.25 at.%) SCF at 300 K. The emission was excited by N₂-laser ($\lambda = 337$ nm). Inset: temperature dependence of decay of the Bi³⁺ luminescence in CdWO₄:Bi (0.25 at.%) SCF at 300 K registered at 560 nm.

ation (pulse duration of 0.127 ns) with an energy of 3.7–25 eV at 10 K. The main goal of this research was confirmation of the nature of different emission centers in SCF and studies of the energy transfer processes from tungstate hosts to Bi³⁺ ions and defect centers in SCF and their SC analogs. The obtained results are presented in Figs. 3 and 4.

Under excitation by SR with energy of 7.94 eV in the range of interband transitions of CdWO₄ host the luminescence of WO₆ regular centers is dominated in the emission spectra of CdWO₄ SC [Fig. 3(a), curve 1]. Some elongation of the emission spectra of CdWO₄ SC in the long-wavelength range is observed under excitation by SR in the onset of CdWO₄ absorption edge at 330 nm. This elongation can be caused by contribution of the luminescence of defect WO₆-V_{Cd} and WO₆-V_O centers in the bands peaked approximately at 2.155 eV (575 nm) and 1.9 eV (650 nm), respectively [8], [11], [13]. At the same excitation at 330 nm, the emission spectra of undoped CdWO₄ SCF [Fig. 3(b), curves 1 and 2] show notable long-wavelength shift with respect to their SC counterpart caused by the emission of WO₆-Na centers in the band peaking at 2.1 eV (590 nm) and the emission of WO₅-V_O centers in the band peaking at 1.9 eV (650 nm).

The luminescent properties of CdWO₄:Bi SCF at 10 K (Fig. 4) under excitation by SR with different wavelength in the edge of CdWO₄ host are mainly determined by the luminescence of WO₆ centers in the bands peaked at 2.45 eV (505 nm), the luminescence of Bi³⁺ ions in the band peaked at 2.2 eV (560 nm), and the luminescence of WO₆-Na centers in the band peaked at 2.1 eV (590 nm).

The LY of undoped and Bi³⁺ doped CdWO₄ SCF was measured depending on Bi³⁺ content under excitation by α -particle of Pu²³⁹ source (5.15 MeV) and compared with the LY of their SC counterparts. For LY measurements, we have used detector based on FEU-110 photomultipliers, which have the maximum sensitivity in the 440–450 nm range and multichannel single-photon counting systems working within a time interval of 0.5 μ s. The results are presented in Table I.

The LY of CdWO₄ SCF and CdWO₄:Bi SCF reaches the values equal to about 50% and 45% of those for their best SC

Fig. 3. Emission spectra of (a) CdWO₄ SC and (b) CdWO₄ SCF under excitation by SR with different wavelengths at 10 K.

Fig. 4. Emission spectra of CdWO₄:Bi SCF at 10 K under excitation by SR with different wavelengths.

analogs (Table I). The lower LY of CdWO₄ and CdWO₄:Bi SCFs with respect to the SC counterparts is caused by quenching

TABLE I
LY OF CdWO_4 AND $\text{CdWO}_4\text{:Bi}$ SCFs IN COMPARISON WITH THEIR SC
ANALOGS UNDER EXCITATION BY α -PARTICLE OF Pu^{239} SOURCE (5.15 MeV)

Samples	LY, %
CdWO_4 SC	100
CdWO_4 SCF	52
$\text{CdWO}_4\text{:Bi}$ (0.1 at. %) SC	87
$\text{CdWO}_4\text{:Bi}$ (0.25 at. %) SCF	37

Fig. 5. Decay kinetics of SC (1) and SCF (2) components of combined scintillators based on $\text{CdWO}_4\text{:Bi}$ SCF ($h = 20 \mu\text{m}$) / CdWO_4 SC epitaxial structure under excitation by pulsed X-ray radiation at 300 K.

induced by Na^+ flux dopant, specifically, by the $\text{WO}_6\text{--Na}$ and $\text{WO}_5\text{--V}_\text{O}$ centers formation with lower luminescent efficiency in comparison with the efficiency of WO_6 and Bi^{3+} centers.

We have also compared the decay kinetics of the luminescence of $\text{CdWO}_4\text{:Bi}$ SCF / CdWO_4 SC epitaxial structure under excitation by pulsed X-ray radiation ($\text{CuK}\alpha$, $E_{\text{eff}} = 8 \text{ keV}$) at 300 K from both sides of SCF and SC scintillators (Fig. 5). Due to high of X-ray absorption coefficient of CdWO_4 matrix, more than 90% of X-ray quanta are deposited in films with thickness of about $20 \mu\text{m}$. The typical decay curves for CdWO_4 SC (Fig. 5, curve 1) are related to radiative de-excitation of the STE at molecular WO_6 oxy-anions with triplet radiative level [14], [15]. This STE luminescence can be considered in the framework of conventional tree-level model describing the emission centers in tungstates [15]. The decay kinetics of the main component of the luminescence of $\text{CdWO}_4\text{:Bi}$ SCF (Fig. 5, curve 2) is notably faster than that in CdWO_4 SC (Fig. 5, curve 1) due to contribution of the faster Bi^{3+} luminescence. The average decay times $\tau(1/e)$ of the corresponding decay curves for $\text{CdWO}_4\text{:Bi}$ SCF and CdWO_4 SC are equal to 8.0 and 12.9 μs , respectively.

Such a difference in the decay time of SCF and SC scintillators in principle can be used for separation of signals coming from the different parts of phoswich detector based on $\text{CdWO}_4\text{:Bi}$ SCF/ CdWO_4 SC or CdWO_4 SCF/ $\text{CdWO}_4\text{:Bi}$ SC epitaxial structures. Namely, the SCF scintillators can be used for detection of α - and β -particles or low-energy γ -quanta, when the SC scintillators can be applied for detection of high-energy γ -quanta. The nontrivial advantage of such type phoswich detector is absence of losses of light at the border of

SCF and SC scintillators due to close values of their refraction indexes.

IV. CONCLUSION

The luminescent and scintillation properties of the undoped and Bi^{3+} doped (in a concentration range of 0.04–0.25 at. %) CdWO_4 single crystalline films grown by LPE methods from Na_2WO_4 flux were compared with the properties of CdWO_4 crystal counterparts grown from the melts by Czochralski method. We found that the main emission centers both in crystal and film forms is the luminescence of regular WO_6 centers in the band peaked approximately at 485 nm. We also observed the long-wavelength shift of the emission spectra of CdWO_4 film with respect to undoped CdWO_4 crystal. This shift is connected with the emission of $\text{WO}_6\text{--Na}$ centers and the luminescence of $\text{WO}_5\text{--V}_\text{O}$ centers (V_O is oxygen vacancy) in the bands peaked approximately at 590 and 650 nm, respectively.

We have found that the luminescence of Bi^{3+} ions in the band peaked at 540 nm with $\tau = 0.8 \mu\text{s}$ at 300 K is dominated in the in the emission spectra of $\text{CdWO}_4\text{:Bi}$ films and crystals. The decay time of the Bi^{3+} luminescence in $\text{CdWO}_4\text{:Bi}$ depends on the Bi content and varies in the 4.2–0.8 μs range when the activator concentration varies in the 0.025–2.5 at. % range. Apart from the Bi^{3+} luminescence, the luminescence of $\text{WO}_6\text{--Na}$ centers in the band peaked at 590 nm is also detected in the emission spectra of $\text{CdWO}_4\text{:Bi}$ films.

The above-mentioned luminescent and scintillation properties of undoped and Bi-doped CdWO_4 films allow in principle to create the phoswich detector based on the $\text{CdWO}_4\text{:Bi}$ film/ CdWO_4 crystal or CdWO_4 film/ $\text{CdWO}_4\text{:Bi}$ crystal epitaxial structures and to perform the separate registration of low-penetration particles or quanta by film scintillators together with the registration of high-energy quanta by crystal parts of the mentioned phoswich detector.

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Index Terms—Bi dopant, liquid phase epitaxy, luminescence, scintillators, single crystals and single crystalline films.

I. INTRODUCTION

THE technology of liquid phase epitaxy (LPE) offers now the possibility of obtaining the single crystalline film (SCF) scintillators based on the different high-density oxide compounds [1]. The fields of application of such SCFs include scintillators for registration of α - and β - particles and low-energy quanta, screens for visualization of X-ray images, cathodoluminescent screens, and laser media [1]–[5].

AWO_4 ($A = \text{Cd}, \text{Ca}, \text{Zn}$) tungstates have high densities $\rho = 6.1\text{--}7.4 \text{ g/cm}^3$ and effective atomic numbers $Z_{\text{eff}} = 61\text{--}66$. CdWO_4 , CaWO_4 and ZnWO_4 single crystals (SCs) are the well-

known scintillators for radiation monitoring and computer tomography [6], [7]. Therefore, the tungstates are very promising materials for creation of SCF scintillators emitting in the *blue range*. From activators, which can effectively emit in AWO_4 ($A = \text{Cd}, \text{Ca}, \text{Zn}$) hosts, Bi^{3+} and Pb^{2+} ions can be tested [8], [9].

In this work, we present the first results directed on the development by LPE method of the SCF scintillators based on undoped and Bi-doped CdWO_4 . The luminescent and scintillation properties of undoped and Bi doped CdWO_4 SCF were compared with the properties of their SC counterparts grown by the Czochralski method. We also consider the possibility of creation of phoswich detector [10] based on the mentioned SCF and SCs of undoped and Bi-doped CdWO_4 for simultaneous registration of $\alpha - (\beta)$ and γ -components of mixed ionizing fluxes [1], [8].

II. LPE GROWTH OF UNDOPED AND Bi^{3+} DOPED CdWO_4 SCF

The growth of undoped and Bi^{3+} doped CdWO_4 SCF was performed by the LPE method at 850°C – 860°C from the melt-solution (MS) based on Na_2WO_4 flux onto CdWO_4 substrates, prepared from the respective SC. The thickness of SCF was in the $1.5\text{--}20 \mu\text{m}$ range, and the growth rate was $0.05\text{--}0.1 \mu\text{m/mm}$. The main difficulties in the growth of CaWO_4 SCF by LPE method using Na_2WO_4 flux are low super-cooling rate of MS what lead to high probability of the spontaneous crystallization and non-uniformity of structural and scintillation properties of SCF at thickness of SCF above $20 \mu\text{m}$.

The concentration of Bi_2O_3 dopant in MS was varied in the $1.7\text{--}12$ mole % range for determining the maximum of light yield (LY) of SCF scintillators under excitation of SCF by α -particles of Pu^{239} (5.15 MeV) source. The charge compensation for Bi^{3+} ions in SCF is achieved due to the introduction of Na^+ flux dopant [8]. The undoped and Bi doped CdWO_4 SC were grown by the Czochralski method with the same raw materials in air atmosphere. The peculiarities of growth of these crystals have been recently reported in detail in our previous works [10], [11]. The Bi content in SCF and SC in the $0.04\text{--}0.25$ at. % range was determined using a JEOL JXA-8612 MX electron microscope. We have also determined the segregation coefficient of Bi ions in CdWO_4 SCF ranging from 0.02 to 0.025.

III. LIGHT YIELD AND LUMINESCENT PROPERTIES OF UNDOPED AND Bi^{3+} DOPED CdWO_4 SCF

First, we have studied the luminescent and scintillation properties of undoped CdWO_4 SCF in comparison with their SC

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Fig. 1. (a) Normalized CL spectra of CdWO₄ SC (1), CdWO₄ SCF (2) and CdWO₄:Bi (0.25 at. %) SCF (3), grown by LPE from Na₂WO₄ flux; (b) Difference between the curves 2-1 and 3-2 in Fig. 1(a). The positions of different emission centers from our previous works [8], [11], [12] are indicated in Fig. 1(a) by arrows.

counterpart, as well as the luminescent and scintillation properties Bi³⁺ doped CdWO₄ SCF and SC, depending on Bi³⁺ content under pulsed e-beam excitation (a pulse duration of 2 μ s and a frequency of 30.3 Hz) with an electron energy of 9 keV and a beam current of 100 μ A. The emission spectra were corrected for the spectral dependence of the detection part consisting of DMR-4 monochromator and FEU-106 photomultiplier. The results are presented in Fig. 1.

In previous our works [8], [11], [12], it has been shown that the WO₆²⁻ regular molecular complex acts as a main intrinsic emission center in undoped CdWO₄ SC. Namely, this emission is related to radiative de-excitation of the self-trapped exciton (STE) at molecular WO₆ oxy-anions [13]–[16]. The intrinsic defects also contribute to the luminescence of CdWO₄ SC [8], [12], [14]–[19]. Specifically, the nature of the long-wave components of CdWO₄ SC luminescence is connected with the evaporation of the part of CdO during the crystallization process and the formation of the “defect” of (WO₆-V_{C,A}) luminescent centers [8], [11], [12], [16]–[19]. The luminescence of these centers is related to localized-exciton emission of WO₆ oxy-anions, perturbed by the nearest anion (A) or cation (C) vacancies [14], [15]. In the frame of this assumption, the complex emission spectrum of CdWO₄ SC presents the superposition of the luminescence of WO₆ centers in the main band peaked at 485 nm, as well as the low intensive emission of (WO₆-V_{Cd})

and (WO₅-V_O) centers in the bands peaked at 575 and 650 nm, respectively [8], [11], [12] [Fig. 1(a), curve 1].

The CL spectrum of undoped CdWO₄ SCF [Fig. 1(a), curve 2] shows notable long-wavelength shift (of about 10 nm) in comparison with the spectrum of SC analogue (curve 1). This shift is caused by the incorporation of Na⁺ flux impurity and formation of (WO₆-Na) and (WO₅-V_O) centers [8]. It is necessary to note that the oxygen vacancies V_O provide here the charge compensation for Na⁺ flux impurity in CdWO₄ SCF, grown from Na-based fluxes.

The incorporation of Bi³⁺ ions in the CdWO₄ lattice was accompanied by the long-wavelength shift of the CL spectrum of CdWO₄:Bi SCF [Fig. 1(a), curve 3] in comparison with emission of undoped SCF in the band peaked at 495 nm [Fig. 1(a), curve 2]. The value of the shift was 45 nm for CdWO₄:Bi SCF with bismuth concentration of about 0.25 at. %.

We also calculated the difference of luminescence spectra of undoped and Bi-doped CdWO₄ SCFs with the aim to establish the structure of CdWO:Bi emission spectra [Fig. 1(b)]. The shape of these spectra permits to suppose that the long-wave shift of CdWO₄:Bi SCF emission spectra with respect to undoped SCF counterpart (Fig. 1, curves 1 and 2, respectively) is mainly caused by the rise of the luminescence intensity of the two bands peaked approximately at 540 and 620 nm. The position of these bands coincides within an accuracy of the experiment with the position of the analogous bands in the luminescence spectra of CdWO₄:Bi SC. This allows one to assign the observed bands in CdWO₄:Bi SCF to the luminescence of Bi³⁺ ions in the 540 nm band and to the luminescence of (WO₆-Na) centers in the 620 nm band. This assumption is supported by the following data.

- 1) The excitation spectrum of the Bi³⁺ luminescence at 540 nm (Fig. 2, curve 1) coincides with the absorption spectrum of CdWO:Bi SCF and contains the intensive band at 350 nm caused by the ¹S₀ → ³P₁ transitions of Bi³⁺ ions [20]. The photoluminescence (PL) spectrum of CdWO:Bi SCF under excitation with N₂-laser, $\lambda = 337$ nm in the range of the absorption band at 350 nm shows the dominant emission band of Bi³⁺ centers peaked approximately at 540 nm (Fig. 2, curve 2).
- 2) The decay kinetics of the main component of PL of CdWO:Bi SCF registered at 560 nm at 300 K is described by single exponent with the decay time in the microsecond range. The corresponding lifetime values $\tau = 4.2\text{--}0.8$ μ s depend on the dopant content in CdWO₄:Bi SCF samples in the range 0.025–2.5 at. %. The temperature dependence of the decay time of the Bi³⁺ luminescence in CdWO₄:Bi (0.25 at.%) SCF is presented in Fig. 2, inset. It should be noted that τ values in the microsecond range and temperature dependence $\tau(T)$ are typical for the luminescence of the mercury-like ions (ns²-electronic configuration) in the different oxide hosts [9], [21]–[25], particularly in CaWO₄:Bi SC [9].

We have also performed the time-resolved spectral-kinetic luminescence investigations of CdWO₄ and CdWO₄:Bi SCFs in comparison with their SC analogs at the Superlumi station (HA-SYLAB at DESY) under excitation by pulsed synchrotron radi-

Fig. 2. Excitation spectra of luminescence at 540 nm (1) and PL (2) spectra of CdWO₄:Bi (0.25 at.%) SCF at 300 K. The emission was excited by N₂-laser ($\lambda = 337$ nm). Inset: temperature dependence of decay of the Bi³⁺ luminescence in CdWO₄:Bi (0.25 at.%) SCF at 300 K registered at 560 nm.

ation (pulse duration of 0.127 ns) with an energy of 3.7–25 eV at 10 K. The main goal of this research was confirmation of the nature of different emission centers in SCF and studies of the energy transfer processes from tungstate hosts to Bi³⁺ ions and defect centers in SCF and their SC analogs. The obtained results are presented in Figs. 3 and 4.

Under excitation by SR with energy of 7.94 eV in the range of interband transitions of CdWO₄ host the luminescence of WO₆ regular centers is dominated in the emission spectra of CdWO₄ SC [Fig. 3(a), curve 1]. Some elongation of the emission spectra of CdWO₄ SC in the long-wavelength range is observed under excitation by SR in the onset of CdWO₄ absorption edge at 330 nm. This elongation can be caused by contribution of the luminescence of defect WO₆-V_{Cd} and WO₆-V_O centers in the bands peaked approximately at 2.155 eV (575 nm) and 1.9 eV (650 nm), respectively [8], [11], [13]. At the same excitation at 330 nm, the emission spectra of undoped CdWO₄ SCF [Fig. 3(b), curves 1 and 2] show notable long-wavelength shift with respect to their SC counterpart caused by the emission of WO₆-Na centers in the band peaking at 2.1 eV (590 nm) and the emission of WO₅-V_O centers in the band peaking at 1.9 eV (650 nm).

The luminescent properties of CdWO₄:Bi SCF at 10 K (Fig. 4) under excitation by SR with different wavelength in the edge of CdWO₄ host are mainly determined by the luminescence of WO₆ centers in the bands peaked at 2.45 eV (505 nm), the luminescence of Bi³⁺ ions in the band peaked at 2.2 eV (560 nm), and the luminescence of WO₆-Na centers in the band peaked at 2.1 eV (590 nm).

The LY of undoped and Bi³⁺ doped CdWO₄ SCF was measured depending on Bi³⁺ content under excitation by α -particle of Pu²³⁹ source (5.15 MeV) and compared with the LY of their SC counterparts. For LY measurements, we have used detector based on FEU-110 photomultipliers, which have the maximum sensitivity in the 440–450 nm range and multichannel single-photon counting systems working within a time interval of 0.5 μ s. The results are presented in Table I.

The LY of CdWO₄ SCF and CdWO₄:Bi SCF reaches the values equal to about 50% and 45% of those for their best SC

Fig. 3. Emission spectra of (a) CdWO₄ SC and (b) CdWO₄ SCF under excitation by SR with different wavelengths at 10 K.

Fig. 4. Emission spectra of CdWO₄:Bi SCF at 10 K under excitation by SR with different wavelengths.

analogues (Table I). The lower LY of CdWO₄ and CdWO₄:Bi SCFs with respect to the SC counterparts is caused by quenching

TABLE I
LY OF CdWO_4 AND $\text{CdWO}_4\text{:Bi}$ SCFs IN COMPARISON WITH THEIR SC
ANALOGS UNDER EXCITATION BY α -PARTICLE OF Pu^{239} SOURCE (5.15 MeV)

Samples	LY, %
CdWO_4 SC	100
CdWO_4 SCF	52
$\text{CdWO}_4\text{:Bi}$ (0.1 at. %) SC	87
$\text{CdWO}_4\text{:Bi}$ (0.25 at. %) SCF	37

Fig. 5. Decay kinetics of SC (1) and SCF (2) components of combined scintillators based on $\text{CdWO}_4\text{:Bi}$ SCF ($h = 20 \mu\text{m}$) / CdWO_4 SC epitaxial structure under excitation by pulsed X-ray radiation at 300 K.

induced by Na^+ flux dopant, specifically, by the $\text{WO}_6\text{-Na}$ and $\text{WO}_5\text{-V}_\text{O}$ centers formation with lower luminescent efficiency in comparison with the efficiency of WO_6 and Bi^{3+} centers.

We have also compared the decay kinetics of the luminescence of $\text{CdWO}_4\text{:Bi}$ SCF / CdWO_4 SC epitaxial structure under excitation by pulsed X-ray radiation ($\text{CuK}\alpha$, $E_{\text{eff}} = 8 \text{ keV}$) at 300 K from both sides of SCF and SC scintillators (Fig. 5). Due to high of X-ray absorption coefficient of CdWO_4 matrix, more than 90% of X-ray quanta are deposited in films with thickness of about $20 \mu\text{m}$. The typical decay curves for CdWO_4 SC (Fig. 5, curve 1) are related to radiative de-excitation of the STE at molecular WO_6 oxy-anions with triplet radiative level [14], [15]. This STE luminescence can be considered in the framework of conventional tree-level model describing the emission centers in tungstates [15]. The decay kinetics of the main component of the luminescence of $\text{CdWO}_4\text{:Bi}$ SCF (Fig. 5, curve 2) is notably faster than that in CdWO_4 SC (Fig. 5, curve 1) due to contribution of the faster Bi^{3+} luminescence. The average decay times $\tau(1/e)$ of the corresponding decay curves for $\text{CdWO}_4\text{:Bi}$ SCF and CdWO_4 SC are equal to 8.0 and $12.9 \mu\text{s}$, respectively.

Such a difference in the decay time of SCF and SC scintillators in principle can be used for separation of signals coming from the different parts of phoswich detector based on $\text{CdWO}_4\text{:Bi}$ SCF/ CdWO_4 SC or CdWO_4 SCF/ $\text{CdWO}_4\text{:Bi}$ SC epitaxial structures. Namely, the SCF scintillators can be used for detection of α - and β -particles or low-energy γ -quanta, when the SC scintillators can be applied for detection of high-energy γ -quanta. The nontrivial advantage of such type phoswich detector is absence of losses of light at the border of

SCF and SC scintillators due to close values of their refraction indexes.

IV. CONCLUSION

The luminescent and scintillation properties of the undoped and Bi^{3+} doped (in a concentration range of 0.04–0.25 at. %) CdWO_4 single crystalline films grown by LPE methods from Na_2WO_4 flux were compared with the properties of CdWO_4 crystal counterparts grown from the melts by Czochralski method. We found that the main emission centers both in crystal and film forms is the luminescence of regular WO_6 centers in the band peaked approximately at 485 nm. We also observed the long-wavelength shift of the emission spectra of CdWO_4 film with respect to undoped CdWO_4 crystal. This shift is connected with the emission of $\text{WO}_6\text{-Na}$ centers and the luminescence of $\text{WO}_5\text{-V}_\text{O}$ centers (V_O is oxygen vacancy) in the bands peaked approximately at 590 and 650 nm, respectively.

We have found that the luminescence of Bi^{3+} ions in the band peaked at 540 nm with $\tau = 0.8 \mu\text{s}$ at 300 K is dominated in the emission spectra of $\text{CdWO}_4\text{:Bi}$ films and crystals. The decay time of the Bi^{3+} luminescence in $\text{CdWO}_4\text{:Bi}$ depends on the Bi content and varies in the 4.2–0.8 μs range when the activator concentration varies in the 0.025–2.5 at. % range. Apart from the Bi^{3+} luminescence, the luminescence of $\text{WO}_6\text{-Na}$ centers in the band peaked at 590 nm is also detected in the emission spectra of $\text{CdWO}_4\text{:Bi}$ films.

The above-mentioned luminescent and scintillation properties of undoped and Bi-doped CdWO_4 films allow in principle to create the phoswich detector based on the $\text{CdWO}_4\text{:Bi}$ film/ CdWO_4 crystal or CdWO_4 film/ $\text{CdWO}_4\text{:Bi}$ crystal epitaxial structures and to perform the separate registration of low-penetration particles or quanta by film scintillators together with the registration of high-energy quanta by crystal parts of the mentioned phoswich detector.

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