LUMINESCENCE CENTERS IN THIN FILMS OF BISMUTH-CONTAINING TUNGSTATES

O.M. BORDUN, A.T. STETSKIV, T.M. YAREMCHUK

Ivan Franko Lviv National University
(1, Universitetska Str., Lviv 79000, Ukraine; e-mail: bordun@wups.lviv.ua)

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The photo-excitation spectra and spectra of the luminescence of Bi_2WO_6, $Bi_2W_2O_9$, and $CdWO_4$:Bi thin films have been investigated. A decomposition of the luminescence spectra into elementary components has been carried out using the Alentsev–Fock method. The bands with the maxima at 2.93 eV in the spectrum of the luminescence of Bi_2WO_6, 2.43 eV in that of $Bi_2W_2O_9$, and 2.47 eV in the spectrum $CdWO_4$:Bi are assigned to the emission of the self-trapped Frenkel excitons. The bands with the maxima at 2.35 and 1.90 eV in the spectrum of Bi_2WO_6, 2.10 and 1.90 eV in that of $Bi_2W_2O_9$, as well as 2.15 and 1.88 eV in the spectrum of $CdWO_4$:Bi, respectively, are concluded to be associated with oxygen vacancies.

The problems concerned with individual, technical and reactor dosimetries, as well as those accompanied with the application of the nuclear physics methods in geophysics, medicine, and other branches of science and technology, have imposed stricter and stricter requirements on solid-state scintillators. Recently, the investigation of bismuth-containing materials, namely Bi_2WO_6 and $Bi_2W_2O_9$ tungstates, have been prevalent in this regard [1, 2]. As concerns the scintillation parameters, these materials are inferior to the traditional ones based on alkali-halide crystals, but they have an advantage of the thermal and chemical stability. In addition, thanks to the high values of density and effective atomic number $Z_{\rm eff}$, they provide a high efficiency in the ionizing radiation registration. However, the spectral kinetic characteristics of tungstates are extremely sensitive to the defects arising in a crystal lattice, particularly, in consequence of a deviation of a crystal composition from the stoichiometric one [1]. As a result, the studies of the tungstate compounds of bismuth in various states, namely in the single crystalline, thin-film, or ceramic ones, are rather topical. The aim of the present work is to study the luminescence of Bi_2WO_6, $Bi_2W_2O_9$, and $CdWO_4$:Bi thin films.

Thin films of Bi_2WO_6, $Bi_2W_2O_9$ and $CdWO_4$:Bi with a thickness of 0.5—1.5 μm were fabricated by the method of discrete evaporation in air on the substrates from melted quartz. After the deposition, the films were subjected to heat treatment in air at 800 °C. X-ray diffraction studies revealed an oriented polycrystalline structure with a preferred orientation in (113), (020), and (220) planes for Bi_2WO_6 films, and in (111), (021) and (002) for $CdWO_4$:Bi films. The content of the Bi^{3+} activation dopant was found to equal 0.5 mol. %. The polycrystalline structure of $Bi_2W_2O_9$ films is in compliance with the perovskite-like structure of $Bi_2W_2O_9$ described in [3].

A URS-55A setup with a copper anticathode (40 kV, 2—12 mA) served as an X-ray excitation source. The investigation of laser-stimulated luminescence was carried out in the impulse excitation regime using an LGI-21 laser with an excitation light wave-length of 337.1 nm (3.68 eV). A source of optical excitation was a DksEl-1000 lamp with a ZMP-3 monochromator. A luminosity of the samples was analyzed with the use of an SF-4A monochromator and registered with a FEU-51 photomultiplier whose signal was transmitted through an amplifier to a PDA-1 analog data recorder. The luminescence spectra were corrected for a spectral sensitivity of the photomultiplier and dispersion of the monochromator.

The studies of Bi_2WO_6 and $Bi_2W_2O_9$ polycrystals [4, 5], as well as Bi_2WO_6 thin films [6] have demonstrated that the luminosity of these specimens constitutes a wide non-elementary band, whose form depends on both the excitation conditions, and the time of the delay in measurements, with respect to the excitation onset. Such spectra are poorly informative, since the important information can only be obtained by means of a careful analysis of the parameters of separate bands, the complex spectra consist of. As a result, there appears a necessity to decompose the complex spectra into elementary constituents, and to determine the number of elementary bands, and their form and position on a frequency scale. The most widespread method of the spectra decomposition is the Alentsev–Fock one [7], as well as the methods of correlation spectroscopy and factor analysis, which are similar to the former. In this paper, the decomposition of the spectra into individual bands is carried out making use of the Alentsev–Fock's method. In calculations, the standard programs for the

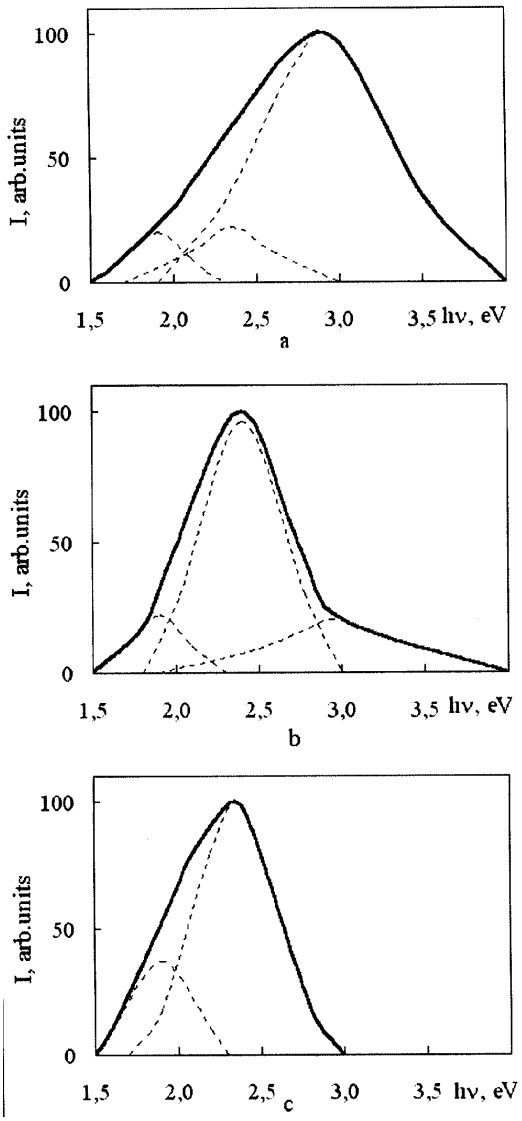

Fig. 1. Spectra of the X-ray (a), photoluminescence at $h\nu_{ex} = 5.17$ eV (b), and luminescence at the laser excitation ($h\nu_{ex} = 3.68$ eV) (c) for the Bi_2WO_6 thin films, $T = 80$ K. Dashed lines — elementary constituents

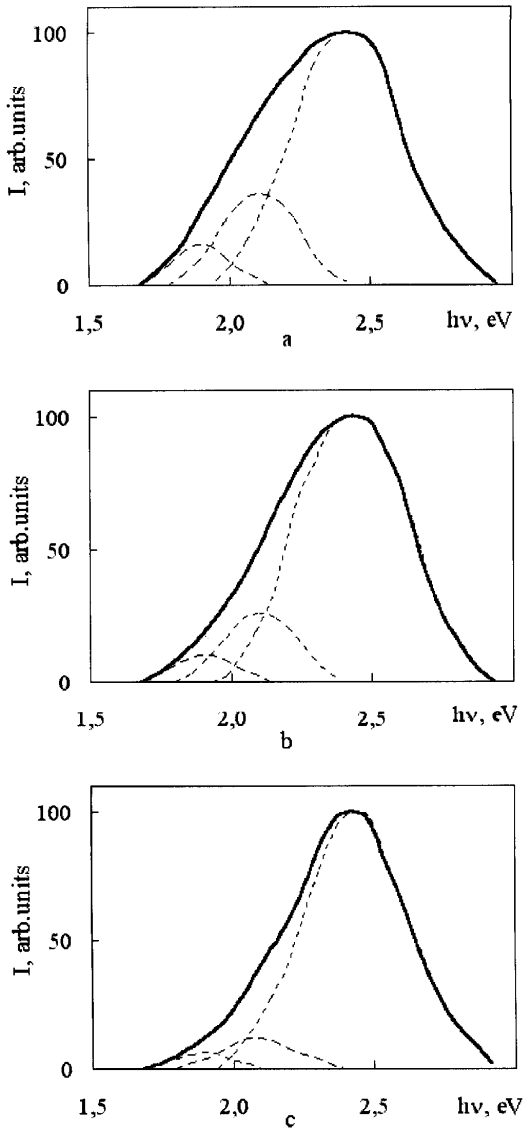

Fig. 2. Spectra of $Bi_2W_2O_9$ thin films at the excitation in a regions of 4.4 eV (a), 3.4 eV (b), and at the laser excitation ($h\nu_{ex} = 3.68$ eV) (c), $T = 80$ K. Dashed lines – elementary constituents

optical spectra processing are used, like those described in [8]. For the most part, the studies of the spectra measured at 80 K have been performed, since at low temperatures the bands usually becomes narrowed, and their mutual overlap decreases.

The studies performed on the Bi_2WO_6 thin films have shown that, when excitation is carried out with the light of more than 5.0 eV in energy, the X-ray- as well as photoluminescence spectra consist of three individual bands with the maxima at 2.93, 2.35, and 1.90 eV. At the same time, in the case of the laser excitation, there are only two bands with the maxima at 2.35 and 1.90 eV (Fig. 1).

As can be seen from Fig. 2, the spectra of the $Bi_2W_2O_9$ thin films consist of three individual bands with the maxima at 2.43, 2.10, and 1.90 eV for both the laser excitation as well as photo excitation with the energy of more than 3.3 eV. Unfortunately, at excitation energies $h\nu < 3.3$ eV, the intensities of both the X-ray- as well as photoluminescence spectra are so small that the decomposition of spectra is difficult.

The luminosity of the Bi_2WO_6 luminophor is suggested to be associated with the emitting de-excitation of the WO_4^{2-} anionic complex [4]. Such complexes are well studied in the MWO_4 (M = Pb, Ca, Zr) compounds with the scheelite structure [8]. The results obtained by us confirm such a suggestion. The parameters of the bands isolated in the Bi_2WO_6 films as well as those obtained with the help of kinetic studies of $PbWO_4$ [9], are presented in the Table.

The results obtained upon the investigation of the luminescence of $Bi_2W_2O_9$ thin films with the perovskite-like structure are in compliance with those obtained for A_2MgWO_9 (A = Ca, Sr, Ba) and Ba_2BWO_6 (B = Mg, Zn, Cd, Ca, Si, Ba) ordered perovskites [10]. In particular, the luminescence spectra of the latter consist of the luminescence bands located just in the same spectral regions of the emission. Luminescence of such compounds is usually associated with the emitting processes in the constituents of the crystalline lattice — WO_6^{6-} groups.

The $Bi_2W_2O_9$ crystalline lattice contains Bi_2O_2 layers and W_2O_7 complexes [3], and the latter are composed of WO_6^{6-} octahedrons, with their vertices being connected with one another.

As follows from the analysis of the $Bi_2W_2O_9$ crystalline structure, the luminescence of this compound may be caused by the radiation of both the Bi_2O_2 groups and WO_6 ones. The measurements of the luminescence extinction time, performed in [5], have lead to a conclusion that the radiation of $Bi_2W_2O_9$ originates from the WO_6 groups, rather than from Bi_2O_2 layers. As was noted above, this also agrees with the results obtained upon comparison of our data with the luminescence of the ordered perovskites [10].

Holding the opinion that the radiation of $Bi_2W_2O_9$ is associated with the emitting processes in WO_6^{6-} octahedrons, it is interesting to compare our results with those obtained upon the investigation of the luminescence spectra in MWO_4 (M = Cd, Zn) compounds with the tungstate structure. Radiation of these tungstates is believed to be associated with the emission of WO_6 groups. In particular, the luminescence spectra of the $Bi_2W_2O_9$ films consist of almost the same bands, as those contained in the spectra of $CdWO_4$ and $ZnWO_4$ [11]. The parameters of the bands singled out from the luminescence spectra of $Bi_2W_2O_9$ films, as well as $CdWO_4$ and $ZnWO_4$ crystals [11], are presented in the table as well. Negligible deviations in the spectral composition of the luminescence bands of the WO_6^6 complexes in $Bi_2W_2O_9$ films and in $CdWO_4$ and $ZnWO_4$ crystals are thought to result from a weak modification

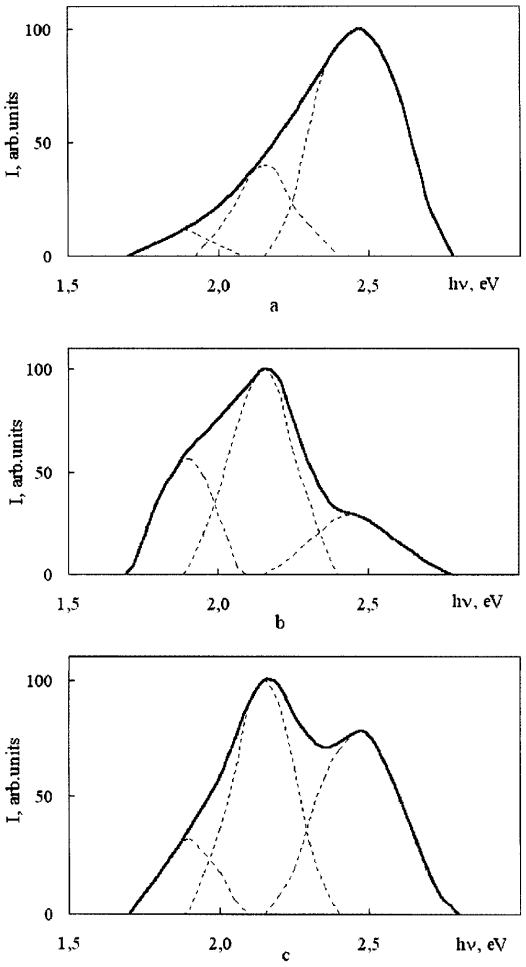

Fig. 3. Luminescence spectra of $CdWO_4$: Bi thin films at the X-ray (*a*), laser- ($h\nu_{ex}$ = 3.68 eV) (*b*), and photoexcitation in a region of 4.1 eV (*c*), T = 80 K. Dashed lines — elementary constituents

of the wave functions of such complexes due to admixing the Bi^{3+} wave functions.

Such a modification may be revealed in experiments at the analysis of the luminescence spectra of $CdWO_4$:Bi thin films. The results obtained by us show that the luminescence spectra of these films consist of three elementary bands with the maxima at 2.47, 2.15, and

Emission bands in the luminescence spectra of the tungstates

Compound	Emission bands maxima, eV		
Bi_2WO_6	2.93	2.35	1.90
$PbWO_4$[9]	2.80	2.35	1.75
$Bi_2W_2O_9$	2.43	2.10	1.90
$ZnWO_4$ [11]	2.55	2.14	1.80
$CdWO_4$ [11]	2.50	2.17	1.80
$CdWO_4$:Bi	2.47	2.15	1.88

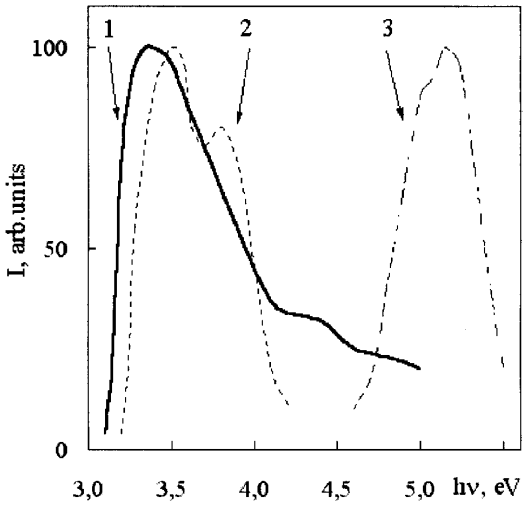

Fig. 4. Spectra of the luminescence excitation for $Bi_2W_2O_9$ (*1*), $CdWO_4$:Bi (*2*) and Bi_2WO_6 (*3*) thin films recorded with the use of a ZhS-12 color filter

1.88 eV (Fig. 3). In comparison with the luminescence of non-activated $CdWO_4$, there are both a slight low-energy shift of two high-energy luminescence bands and a high-energy shift of the low-energy luminescence band. Under the assumption that the luminescence originates from both the WO_6^{6-} complexes of $CdWO_4$ and those modified with the Bi^{3+} activation dopant, the situation becomes clear, and all the results may be easily explained. As follows from the analysis of the spectra of the tungstate-like $Bi_2W_2O_9$, just the given kind of the modification should result in the above character of luminescence bands shift: the low-energy shift for two high-energy luminescence bands and the high-energy shift for the low-energy band.

It is worth noting that the common features of the luminescence of $Bi_2W_2O_9$ and $CdWO_4$:Bi thin films also become apparent at a consideration of the luminescence excitation spectra for these films (Fig. 4). These spectra consist of the similar excitation bands in the low-energy region near 3.4 eV, have a developed structure, and completely differ from those observed in Bi_2WO_6 thin films.

Great values of both the Stokes shift (more than 2.0 eV for Bi_2WO_6 and 1.0 eV for $Bi_2W_2O_9$ and $CdWO_4$:Bi thin films) and the half-width (more than 0.5 eV for Bi_2WO_6 and 0.4 eV for $Bi_2W_2O_9$ and $CdWO_4$:Bi films at 80 K) for the bands singled out are the evidence for the existence of the strong electron-phonon interaction, which itself testifies to a local character of the electron excitations resulting in an emitting decay. This allows us to suggest that the luminescence bands singled out are caused by the radiation decay of the excitations, which are localized at WO_4^{2-}complexes in the Bi_2WO_6 films and at WO_6^{6-} complexes in the $Bi_2W_2O_9$ and $CdWO_4$:Bi films, and relaxed to the lowest oscillation states. In this case, according to the studies [12, 13], the high-energy luminescence bands with the maximum at 2.93 eV for Bi_2WO_6, and at 2.43 and 2.47 eV for $Bi_2W_2O_9$ and $CdWO_4$:Bi, respectively, are associated with the self-trapped Frenkel's excitons which describe the excited states of the $(WO_4^{2-})^*$ and $(WO_6^{6-})^*$ complexes.

When an excitation is performed with the use of an LGI-21 laser, the appearance of the luminescence bands with the maxima at 2.35 and 1.90 eV, which are located in the forbidden band of Bi_2WO_6, makes it possible to assert that these bands originate from the local levels situated in the forbidden band. In this case, the process of energy transmission to the defect levels, following by a subsequent radiation, may occur, that becomes more evident in the X-ray luminescence spectra of the films under study. As the direct excitation of the defect centers is carried out with the light whose spectrum belongs to that of the own transmission of the Bi_2WO_6 films, the luminescence spectra only consist of the aforementioned bands, whereas the luminosity of the band with the maximum at 2.93 eV does not occur. A similar situation seems to occur in $Bi_2W_2O_9$ spectra, since a long-wave shift of the photoluminescence spectrum maximum is registered, when the excitation is performed with the light whose spectrum belongs to that of the own transmission $h\nu < 3.4$ eV. The weak luminosity intensity, however, makes it difficult to perform any quantitative investigations.

As follows from a comparison of the intensities of the luminescence bands singled out for the films annealed in air and in oxygen, the luminescence bands with the maxima located at 2.35 and 1.90 eV in Bi_2WO_6, and 2.19 and 1.90 eV in $Bi_2W_2O_9$ thin films, respectively, are supposed to be associated with defects in the oxygen sublattice. In this case, the mechanism suggested in [9] is suitable for the transmission of the excitation energy from an exciton to either a couple "vacancy — WO_3-group" for Bi_2WO_6, or a couple "vacancy — WO_6-group" for $Bi_2W_2O_9$ thin films, with the subsequent emission of green and red light.

In summary, the use of the Alentsev–Fock method for the decomposition of the luminescence spectra of the Bi_2WO_6, $Bi_2W_2O_9$ and $CdWO_4$:Bi thin films shows that these spectra consist of the three individual bands. The emission bands with the maxima located at 2.93 eV in

the luminescence spectrum of Bi_2WO_6, 2.43 eV in that of $Bi_2W_2O_9$, and 2.47 eV in the spectrum of $CdWO_4$:Bi, respectively, are interpreted as the luminosity of self-trapped Frenkel's excitons. The luminescence bands with the maxima at 2.35 and 1.90 eV in the spectrum of Bi_2WO_6, 2.19 and 1.90 eV in that of $Bi_2W_2O_9$, as well as at 2.15 and 1.88 eV in the spectrum of $CdWO_4$:Bi, respectively, are associated with oxygen vacancies.

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ЦЕНТРИ ЛЮМІНЕСЦЕНЦІЇ В ТОНКИХ ВІСМУТВМІСНИХ ВОЛЬФРАМАТНИХ ПЛІВКАХ

О.М. Бордун, О.Т. Стецьків, Т.М. Яремчук

Р е з ю м е

Досліджено спектри фотозбудження та люмінесценції тонких плівок Bi_2WO_6, $Bi_2W_2O_9$ і $CdWO_4$:Bi. Методом Аленцева—Фока проведено розклад спектрів на елементарні складові. Смуги випромінювання з максимумом при 2,93 еВ в спектрі люмінесценції Bi_2WO_6, при 2,43 еВ в спектрі люмінесценції $Bi_2W_2O_9$ і при 2,47 еВ в спектрі люмінесценції $CdWO_4$:Bi віднесено до свічення автолокалізованих екситонів Френкеля. Смуги з максимумами при 2,35 і 1,90 еВ в спектрі Bi_2WO_6; 2,10 і 1,90 еВ в спектрі $Bi_2W_2O_9$ та 2,15 і 1,88 еВ в спектрі $CdWO_4$:Bi пов'язані з кисневими вакансіями.