

PACS: 78.60.Ya, 78.70.-q

Scintillation characteristics of the single crystalline CdWO_4 and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ compounds doped with mercury-like ions

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Abstract. Investigated are optical, luminescent and light-technical properties of the CdWO_4 and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ single crystals doped with mercury-like Bi^{3+} and Pb^{2+} impurities, respectively, with the aim of ascertaining the possibility to match their spectral characteristics with a spectral sensitivity of semiconductor radiation detectors. It is established that the long-wave shift of the $\text{CdWO}_4:\text{Bi}$ emission spectra and increase of the light yield in the sensitivity region of Si-PD up to 15-20% in comparison with this parameter for the CdWO_4 , occurring at optimal level of the activator concentration 0.025–0.25 mass% Bi_2O_3 in the melt and contents of Li^+ or Ag^+ ions as compensators for providing the ratio of mentioned impurities not less than 1:(1.5÷3), is connected with emission of the (BiO_6^9) complexes with $\lambda_{\text{max}} = 560$ nm and $\tau = 0.8$ – 4.2 μs at 300 K. The shift of the emission spectra of the $\text{Bi}_4\text{Ge}_3\text{O}_{12}:\text{Pb}$ crystals into the red spectral region is caused by emission of the (PbO_6^{10-}) complexes in the bands with $\lambda_{\text{max}} = 570$ and 690 nm and $\tau = 1.0$ μs . In addition, the light yield of the $\text{Bi}_4\text{Ge}_3\text{O}_{12}:\text{Pb}$ single crystals at impurity concentrations of 0.005–0.5 mass% PbO in the melt was not less than 1.0–0.8 in comparison with that of undoped analogs.

Keywords: single crystal, scintillator, impurity, defects, light yield, decay time, photodiode.

Paper received 10.10.99; revised manuscript received 06.12.99; accepted for publication 21.03.00.

1. Introduction

Scintillators based on CdWO_4 (CWO) and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) single crystals are the most effective in the number of the oxide ones widely used at present in the γ -quantum detection blocks. The high values of the density and effective atomic number of CWO ($\rho = 7.9$ g/cm³, $Z_{\text{eff}} = 66$) and BGO ($r = 7.13$ g/cm³; $Z_{\text{eff}} = 83$) ensure great absorption coefficients for γ -quanta and X-rays. The maxima of the emission spectra of these crystals in the 470–500 nm range matches well with the spectral sensitivity region of the standard photomultiplier tube (PMT) what at low afterglow level and light yields of about 35–40% and 10–12% of NaJ:Tl makes it possible to achieve the limit values of the sensitivity and energy resolution of the spectrometrical blocks of the detection on their base [1, 2].

At the same time, in some cases of the practical employment and first of all for X-ray tomography where the

detection blocks of "scintillator-photodiode" (S-PD) – type based on CWO and BGO are used, it is very actual to realize a long-wave shift of the emission spectra of these crystals with the aim of matching scintillation region and spectral sensitivity of the semiconductor PD without reducing their light yield and afterglow level. When carrying out such type investigations for the CWO and BGO single crystals, it is reasonable to dope them with ions which emit in the more long-wave spectral region in comparison with their own emission and parameters of luminescence centers of which are subjected to significant influence of the host crystal field at comparatively low decay times.

In some our previous papers [3, 4], it was shown that for the solution of this problem in the case of CWO it is very perspective to dope them with mercury-like ions, specifically with Bi. Authors [5, 6] established that the doping with Pb ions leads to the appearance of the new emis-

sion component in the red spectral region for the BGO crystals. Proceeding from these data, the purpose of this paper were to investigate CWO:Bi and BGO:Pb single crystals in the wide-range of the dopant concentrations and to establish their optical, luminescent and light-technical characteristics with the aim of optimization their scintillation parameters and matching with spectral characteristics of Si-photodiode for the possible application in the detection blocks of S-PD-type.

2. Particularities of the single crystals CWO and BGO with mercury-like impurities growing

The CWO and BGO single crystals were grown by Czochralsky technique in the oxygen atmosphere ($p_{O_2} = 1.0-1.5$ atm) and in the air, respectively, by using the Pt crucible and charges on the base of CdO, WO₃ and Bi₂O₃, GeO₂ oxides as initial components for the synthesis of compounds (commercial purity materials with iron group impurities content $\geq 10^{-4}$ mass%). The melts for CWO crystals growth contained the excess of CdO in the concentration of about 1.0-1.2 mass% for the compensation of this volatile component loss in the crystallization proc-

ess. The growth of BGO crystals was performed using charges with stoichiometric composition.

The impurities-activators were added into the melts in oxide form in the concentrations of about 0.025-1 mass% Bi₂O₃ and 0.005-2 mass%PbO, respectively. It should be noted that the CWO doping with three-valence bismuth ions was carried out also in the presence of Li⁺, Na⁺ and Ag⁺ ions as charge compensators. There was no pair doping in the case of BGO:Pb single crystals, so the charge compensation, as assumed, was realize by excess content of Ge⁴⁺ ions or by anionic vacancies (V_O²⁻) generated in the lattice.

We established that the segregation coefficient (K_s) for Bi³⁺ ions in CWO essentially depends on availability, type and concentration of the ions-compensators (Fig. 1, Table 1). Thus, for example, co-doping with Li⁺ ions in concentration of about 0.0625–0.125 mass% Li₂CO₃ (in the melt) leads to almost twofold reduction of Bi³⁺ entering¹ into the lattice (Fig. 1, a). The most essential reduction of K_s was observed in the case of introduction of Na⁺ ions as compensator. At the same time, the co-doping with Ag⁺ ions in the concentration range of 0.25–1.0 mass% AgNO₃ was accompanied by increase Bi³⁺ ions segregation coefficient about 1.5 times (Fig. 1, b).

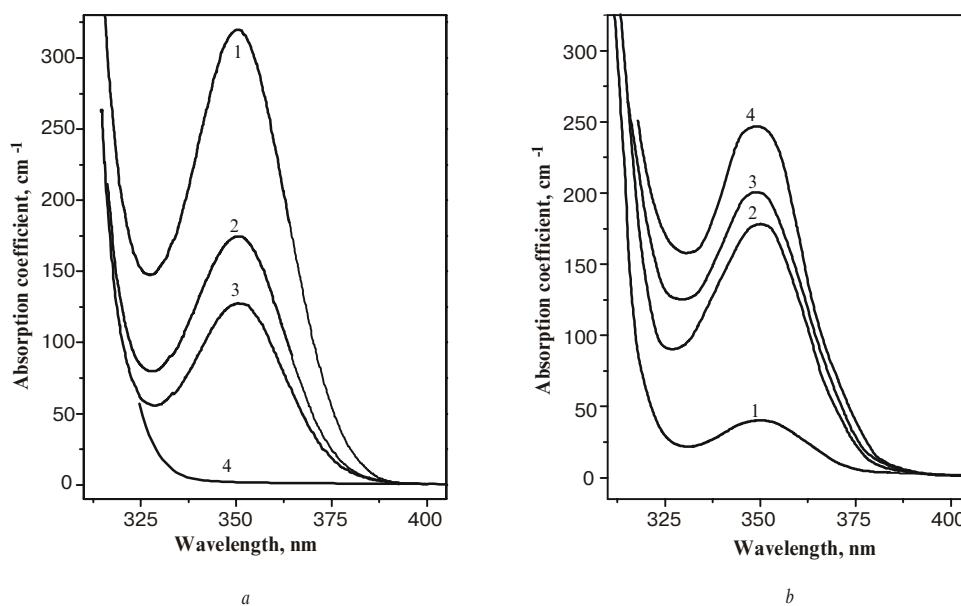


Fig. 1. Absorption spectra of two series CdWO₄ crystals with Bi³⁺ impurity in different concentrations and co-doped with Li⁺ (a) and Ag⁺ (b) ions.

a: 1 - CdWO₄:0.25 mass% Bi₂O₃; 2 - CdWO₄:0.25 mass% Bi₂O₃+0.125 mass% Li₂CO₃; 3 - CdWO₄:0.25 mass% Bi₂O₃+0.0625 mass% Li₂CO₃; 4 - undoped CdWO₄;

b: 1 - CdWO₄:0.05 mass% Bi₂O₃; 2 - CdWO₄:0.25 mass% Bi₂O₃; 3 - CdWO₄:0.25 mass% Bi₂O₃+ 0.25 mass% AgNO₃; 4 - CdWO₄:0.25 mass% Bi₂O₃+ 1 mass% AgNO₃.

¹ The concentration of Bi³⁺ ions in solid has been estimated by using the Smakula-Dexter formula for the oscillator strength $f = 0,1$ [7] of optical transition ¹S₀>³P₁ in Bi³⁺ ion connected with the absorption band (AB) at $\lambda_{max} = 351$ nm (Fig. 1).

Such regularity of Bi³⁺ ion entering in the presence of mentioned above type ions-compensators may be explained by the different values of ion radii for the impurity and substituted Cd²⁺ ions in the regular position of the host matrix ($R = 0.99\text{\AA}$). Evidently, in the case of Na⁺-Bi³⁺ compensation the Na⁺ ion with the ionic radius $R = 0.99\text{\AA}$ which coincides with Cd²⁺ ionic radius creates the essential competition for the substitution processes for Bi³⁺ ions with $R=1.03\text{\AA}$. In the context of these assumption, we believe that the large Ag⁺ ions ($R=1.13\text{\AA}$) promotes entering Bi³⁺ ions and the small Li⁺ ion ($R = 0.63\text{\AA}$) reduces this effect noticeably. So, in the last case for the realization of the complete compensation of the excess Bi³⁺ ion charge in CWO the melts must contain the excess of Li₂CO₃ (as a rule, the calculated value of the Li:Bi ratio was $1,5 \div 3$).

3. Results and discussion

The doping of CWO single crystals with bismuth ions leads to appearance of the intensive absorption band (AB) with $\lambda_{\text{max}} = 351\text{ nm}$ which may be attributed to electro-dipole allowed transition $^1S_0 > ^3P_1$ ($f = 0.1$ [7]) in Bi³⁺ ion. The absorption intensity increases with the rise of activator concentration (Fig. 1, a, b; Table 1) and reaches the value of about 360 cm^{-1} for Bi₂O₃ content in the melt equal to about 0.25 mass%. At the same time, the long-wave part of this AB practically doesn't overlap with the CWO emission spectrum.

The rise of Bi³⁺ ions concentration in the lattice was accompanied by the long-wave shift of CWO emission spectrum (Fig. 2, $\lambda_{\text{max}} = 494\text{ nm}$). For the concentration Bi₂O₃ of about 0.25 mass% in the melt the value of the

shift was 23 nm (0.11 eV) that correlates with the results presented in [3] for the single crystalline films (SCF) CdWO₄:Bi. The co-activation with Li⁺ ions was accompanied by reduction of the emission band shift (Fig. 2, a, curves 2 and 4) connected with the decrease of active impurity concentration (see Fig. 1, a).

With the aim of ascertaining the CWO:Bi emission spectra structure we calculated the difference curves, presented in Fig. 2, a, insert. The form of these spectra which consisted of two bands with $\lambda_{\text{max}} = 560$ and 620 nm permits to suppose that the long-wave shift of CWO emission spectra (Fig. 2, a, curve 1) is caused by the rise of the luminescence intensity in the spectral region of the above mentioned bands. The nature of the observed bands, the position of which within an accuracy of the experiment coincides with that in the spectra of CWO:Bi SCF [3], has been interpreted as connected with radiative transitions in the (BiO₆) clusters and (WO₆-V_{Cd}) complexes where V_{Cd} denotes the vacancy in the Cd²⁺ site.

In favour of this assumption the following data testify:

1. The excitation spectrum of CWO:Bi crystals in the region $\lambda = 560\text{ nm}$ (Fig. 3, curve 1) coincides in a form with the absorption spectrum of such crystals (Fig. 1). The photoluminescence spectrum (PL) of this type crystals under excitation with N₂-laser, $\lambda = 337\text{ nm}$ in the region AB with $\lambda_{\text{max}}=351\text{ nm}$ (Fig. 3, curve 2) has intensive emission band with $\lambda_{\text{max}} = 560\text{ nm}$. The kinetics of PL decay in this band is described by an exponent with $\tau = 4.2\text{-}0.8\text{ }\mu\text{s}$ at 300 K in the dependence on impurity composition for the CWO samples. The temperature dependence of τ is presented in Fig. 3, insert. It should be noted that the τ value and $\tau(T)$ curve form are characteristic for the mercury-like ions emission in the different type oxides [3, 5, 6].

Table 1. Characteristics of series of scintillation detectors based on CdWO₄:Bi and CdWO₄:Bi+Li or Na crystals

Samples	Composition	Dopant (Bi ³⁺) concentration in the crystal, cm ⁻³	Relative light yield	
			η_{PD}	η_{sc}
1	CdWO ₄	-	1.00	1.0
2	CdWO ₄ :0.025 mass% Bi ₂ O ₃ + +0.025 mass% Li ₂ CO ₃ ;	$2 \cdot 10^{17}$	1.09-1.13	0.895
3	CdWO ₄ :0.25 mass% Bi ₂ O ₃ ;	$3.8 \cdot 10^{18}$	0.92-0.84	0.877
4	CdWO ₄ :0.25 mass% Bi ₂ O ₃ + +0.0625 mass% Li ₂ CO ₃	$1.9 \cdot 10^{18}$	0.94-1.17	0.904
5	CdWO ₄ :0.25 mass% Bi ₂ O ₃ + +0.125 mass% Li ₂ CO ₃ ;	$2 \cdot 10^{18}$	1.22	0.944
6	CdWO ₄ :0.42 mass% Bi ₂ O ₃ + +2.8 mass% Na ₂ WO ₄ ;	$> 5 \cdot 10^{18}$	0.66	0.89
7	CdWO ₄ :1.0 mass% Bi ₂ O ₃	$> 5 \cdot 10^{18}$	0.53-0.56	0.53

η_{PD} – measured with typical Si photodiode under electron beam excitation (17 kV, 5 mA);

η_{sc} – measured in spectrometric regime using FEU-110 under Pu²³⁹ excitation.

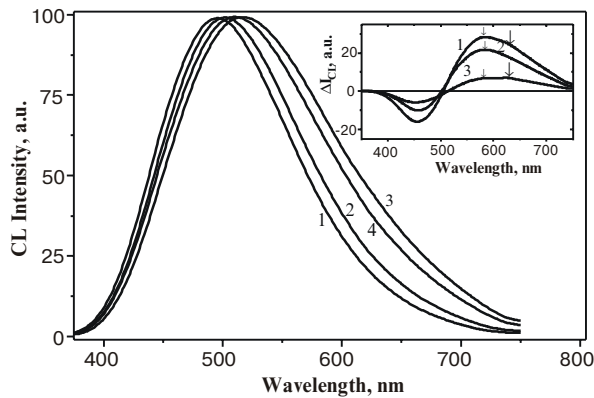


Fig. 2. The effect of CdWO₄ doping with Bi³⁺ and (Bi³⁺-Li⁺)-pair on the cathodoluminescence spectra, T=300 K: 1 – CdWO₄ (undoped); 2 – CdWO₄:0.025 mass% Bi₂O₃; 3 – CdWO₄:0.25 mass% Bi₂O₃; 4 – CdWO₄:0.25 mass% Bi₂O₃+0.125 mass% Li₂CO₃; Insert: difference between curves: 3-1 (1); 4-1 (2) and 3-4 (3).

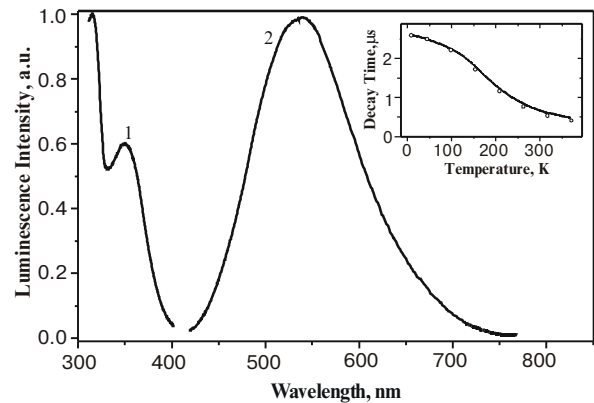


Fig. 3. Excitation (1) and photoluminescence (2) spectra of CdWO₄:0.025 mass% Bi₂O₃ single crystal at 300 K. The emission was excited by N₂-laser ($\lambda = 337$ nm). Insert: temperature dependence of decay of the luminescence in the band with $\lambda_{\text{max}}=564$ nm.

2. The pair doping of CWO crystals with (Bi³⁺-Li⁺) leads to disappearance of the component with $\lambda_{\text{max}} = 620$ nm in the emission spectra of such type crystals. The existence of the red component in the CWO:Bi luminescence spectra is illustrated by curve 2 in Fig. 2, insert (the difference curve of the CWO:Bi³⁺ and CWO:Bi³⁺, Li⁺ emission spectra at ratio Li:Bi = 3:1 in the melt). This result may be explained by the decrease of V_{Cd} concentration in the presence of the compensator.

Thus, in the luminescence of CWO:Bi single crystals in the long-wave region the emission of (BiO₆) and (WO₆-V_{Cd}) complexes predominates, whereas the luminescence of this doped crystals with the ions-compensators is completely determined by the emission of clusters with mercury-like impurity.

Established particularities may be used for the interpretation of the experimental data to the light yield of the CWO:Bi and CWO:Bi, A⁺ (where A⁺=Li⁺, Na⁺) as a function on concentration of the activator and compensator (Table 1). In can be seen that the doping of CWO with Bi³⁺ ions at concentrations up to 0.25 mass% Bi₂O₃ (in the melt) leads to significant (8–16%) decrease of the light yield under scintillation registration with the Si-photodiode as well as scintillation detector on the base of

FEU-110. At the higher activator concentrations it has been observed the essential decrease of the light yield that probably may be connected both with the concentration quenching of the activator luminescence and deterioration the structural perfection of the single crystals.

At the same time, the presence of the compensators in the Li⁺:Bi³⁺ = 1.5:3 ratio in the CWO crystals doped with Bi³⁺ ions in the range concentrations of 0.025-0.25 mass% Bi₂O₃ leads to the noticeable rise of the light yield up to values that exceed this parameter by 15-20% for the scintillators based on the undoped CWO crystals under registration of the scintillation with Si-PD (Table 1). It should be noted that light yield which has been measured in the spectrometrical regime by using FEU-110 is not less than that obtained for the undoped crystals.

This effect is very important from the point of possible application of CdWO₄:Bi single crystals in the detection blocks of S-PD type since the light yield increase, and the decrease of the luminescence decay time values to 1–4 μs must allow to raise the energy resolution and rate response of these blocks to the ionizing radiation.

Some similar effects we observed for BGO crystals doped with mercury-like impurity of the lead. Thus, for example, in the optical spectra of BGO:Pb established

Table 2. Light yield of BGO:Pb scintillators

Samples	Composition	Relative light yield	
		η_{PD}	η_{sc}
1	Bi ₄ Ge ₃ O ₁₂	1.0	1.0
2	Bi ₄ Ge ₃ O ₁₂ :0.005 mass% PbO	1.0	0.998
3	Bi ₄ Ge ₃ O ₁₂ :0.05 mass% PbO	0.8	0.773
4	Bi ₄ Ge ₃ O ₁₂ :0.5 mass% PbO	0.69	0.905
5	Bi ₄ Ge ₃ O ₁₂ :2 mass% PbO	0.49	0.435

was the shift of the absorption edges into the long-wave region (Fig. 4) connected with the rise of the intensive AB with $k \geq 10^{-2} \text{ cm}^{-1}$ which may be assigned to $^1S_0 \rightarrow ^3P_1$ transitions in Pb^{2+} ion and/or to transitions with charge transfer $\text{O}^{2-} \rightarrow \text{Pb}^{2+}$ [8]. The single crystals with activator concentration greater than 0.5 mass% PbO in the melt were noticeably colored. Such an effect is the common characteristic for the number of oxides doped with Pb^{2+} ions and may be considered as a result of the shift of the long-wave part of AB into visible region (see, for example, curve 4 in Fig. 4).

The lead impurities in BGO single crystals are also responsible for the red shift of the long-wave branch of the emission spectra (Fig. 5, a, curve 2, 3) relative to the luminescence spectrum of the undoped sample ($\lambda_{\text{max}} = 470 \text{ nm}$, curve 1). The spectral shift value rises with activator concentration and achieves the saturation at the concentrations of about 0.5 mass% PbO in the melt. Further rise of the Pb^{2+} ions concentration leads to the decrease of the emission intensity in the region $\lambda > 470 \text{ nm}$ (Fig. 5, curve 4) which results from the reabsorption effect in the long-wave part of AB.

The analysis of the structure of BGO:Pb emission spectra (Fig. 5, insert) showed that the increase of the emission intensity of such type crystals at doping level in the 0.005-0.5 mass% PbO range occurs mainly in the orange and red regions of the spectrum corresponding to the emission bands with maxima $\lambda_{\text{max}} = 567 \text{ nm}$ (2.18 eV) and 680-710 nm ($\sim 1.8 \text{ eV}$) that well correlate with the results presented by C. Timmermans [6]. In particular, the author [6] observed the characteristic two-component form emission spectra of the Pb-contaminated germanates, more-over the one of these components has been registered in the red spectral region.

The excitation spectrum for the above mentioned emission components coincides with the long-wave part of the lead ion AB. In particular, under excitation of BGO: 0.5 mass% PbO with N_2 -laser ($\lambda = 337 \text{ nm}$), i.e. in the region of the absorption edge of this sample (Fig. 4, curve 3)

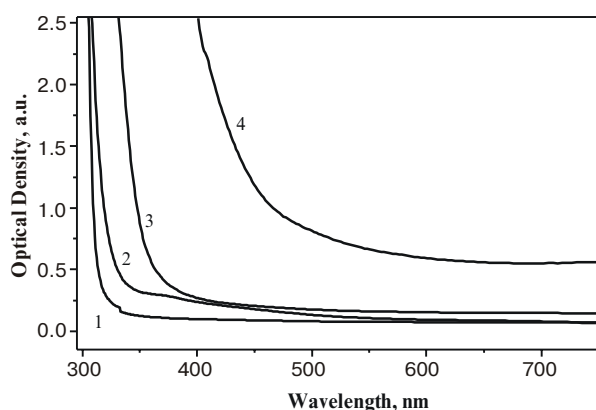


Fig. 4. Evolution of the absorption spectra of Pb doped BGO single crystals: 1 – BGO (undoped); 2 – BGO:0.005 mass% PbO; 3 – BGO:0.5 mass% PbO; 4 – BGO:2 mass% PbO. $T = 300 \text{ K}$, $d = 1 \text{ mm}$.

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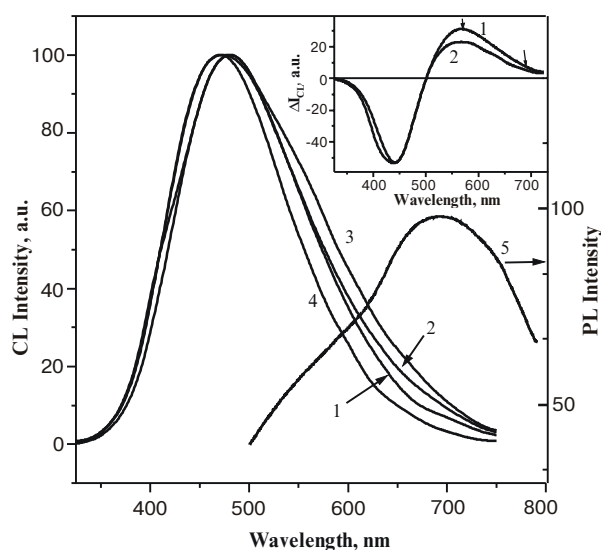


Fig. 5. Cathodoluminescence spectra of BGO crystals doped with lead impurities: 1 – undoped crystals; 2 – 0.005 mass% PbO; 3 – 0.5 mass% PbO; 4 – 2.0 mass% PbO. Photoluminescence spectrum (5) of BGO:0.5 mass% PbO was measured under excitation with N_2 -laser ($\lambda = 337 \text{ nm}$). Insert: difference between curves 2-1 (1) and 3-1 (2).

we measured the PL spectrum with predominant band in the red spectral region and the second band with maxima in the range of 560-580 nm, the position of which in the energy scale coincide with λ_{max} for the components of the difference spectra presented in Fig. 5, insert. This result allows to connect the luminescence bands at 2.18 and 1.8 eV with the emission transitions in Pb-containing complexes of the $(\text{PbO}_6)^{10-}$ -type with the tetrahedral coordination.

The decay of luminescence in the band at $h\nu_{\text{max}} = 1.8 \text{ eV}$ was described by exponent with $\tau = 1 \mu\text{s}$ that has been usually observed for mercury-like ions in oxides [3-6].

The light yield of BGO:Pb crystals in the dopant concentrations range of 0.005-0.5 mass% PbO (in the melt) under emission registration with Si-PD equals 1.0-0.8 of the light yield measured for undoped BGO (Table 2). At higher concentration of Pb ions, the essential (more than twice) decrease of the luminescence output in the PD-region sensitivity takes place, which, probably, is a consequence of reducing quantum yield of BGO:Pb scintillations (Table 2). The possible reason for this effect may be the generation of the point defects, for example V_{O}^{2-} , as a result of heterovalent isomorphism, reabsorption of the emitted light in the region of AB connected with impurities and increase of the decay time caused by components of the $(\text{PbO}_6)^{10-}$ center with $\tau = 1 \mu\text{s}$.

At the same time, the established possibility of the emission spectrum shift at comparatively high intensity of the luminescence in the region of 550-700 nm must stimulate the further investigations dealing with the problem of optimization of the of BGO:Pb crystal growth technology. Alternative methods for eliminating channels of

excitation energy dissipation are the pair doping for the charge compensation and choice of the optimal activator concentration. From the viewpoint of their practical applications, it is of great importance to investigate the possibility to reduce τ for the main emission component, for example, by means of doping with RE ions having allowed $4f-5d$ transitions.

Conclusions

The matching of the characteristics of the scintillators based on the cadmium tungstate single crystals and semiconductor detectors of the radiation, in particular PD, may be achieved by means of CWO doping with Bi³⁺ ions in the concentrations range of 0.025-0.25 mass% Bi₂O₃ (in the melt) in the presence of the Li⁺ or Na⁺, Ag⁺ ions as compensators in the ratio Li:Bi not less than (1.5-3):1. At this condition the light yield of the CWO:Bi crystals in the sensitivity region of Si-PD exceeds that of the undoped analogs by 15–25% at the decay time of the main component $\tau = 0.8-4.2 \mu\text{s}$ at 300 K.

For the single crystals of the bismuth germanate doped with lead ions, it was also observed the shift of the emission spectra in the region of maximum PD sensitivity as a result of the emission of (PbO₆)¹⁰⁻ complexes with $\lambda_{\text{max}} = 570$ and 690 nm at $\tau = 1.0 \mu\text{s}$. Besides, the light yield in the denoted spectral range at activator concentrations of 0.005-0.5 mass% PbO in the melt was not less than 1.0-0.8 in comparison with the corresponding values for the undoped crystals. Further improvement of the scintillators characteristics may be achieved by means of the optimization of the technology of the doped single crystal growth.

Acknowledgments

The work has been fulfilled under financial support of INTAS-Ukraine (project No 95/0166).

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