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New inorganic scintillators on the basis of LBO glass for neutron registration

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Undoped lithium borate glasses and those doped with Cu, Ce, Sm, Eu, Tb, Tm, Yb have been synthesized; the optical and luminescence properties thereof have been determined as well as some scintillation characteristics at registration of neutrons ($E_n \leq 10$ MeV) and of the ^{60}Co γ radiation. The lithium borate glassy scintillators have been established in experiment to have a high sensitivity to neutrons and to be suitable to record selectively neutrons in mixed radiation fields. The results obtained evidence that such scintillators can be an alternative of promise to the known neutron detectors based on gases, liquids, plastics, and crystals.

Синтезированы сцинтилляционные литий-боратные стёкла чистые и активированные примесями Cu, Ce, Sm, Eu, Tb, Tm, Yb. Определены их оптические и люминесцентные свойства, а также некоторые сцинтилляционные характеристики при регистрации нейтронов с энергией до 10 МэВ и гамма-излучения ^{60}Co. Экспериментально установлено, что литий-боратные стеклообразные сцинтилляторы имеют высокую чувствительность к нейтронам и эффективны для их селективной регистрации в полях смешанных излучений. Полученные результаты показывают, что сцинтилляторы этого типа могут являться перспективной альтернативой известным детекторам нейтронов на основе газов, жидкостей, пластмасс и кристаллов.

Historically, neutron detecting instrumentation has been based on gas proportional counters. However, it is no doubt that the interest in application of scintillation technologies using neutron-sensitive inorganic scintillators is increasing. The general requirements to these materials have been formulated in [1]. Numerous crystalline neutron scintillators were summarized in review [2]. The possibility of neutron registration by means of these materials is due to (n, α)-type reactions on nuclei of matrix elements followed by the ionization of the medium with energy transfer to light emission centers. Thus, it is especially important for the material to contain a high concentration of elements having large cross sections of (n, α)-reactions as well as intrinsic or extrinsic luminescence centers. Another extremely substantial requirement is a minimal sensitivity of the scintillation material to γ radiation.

The $Li_2B_4O_7$ (LBO) single crystals doped with some activators were recently reported to be an adequate material to these requirements [3, 4]. However, there are essential technological difficulties in the growing of large defect-free $Li_2B_4O_7$ crystals [5] and their doping with activators. At the same time, it is well known that the Li_2O–B_2O_3 oxide system provides a wide range of transparent glasses formation (from 57 to 100 mol.% B_2O_3). The scintillation LBO-glass of the same composition as $Li_2B_4O_7$ crystals were proposed by the authors [6, 7] realizing this trend. In both cases, the scintillator response is due to neutron capture reactions by nuclei of ^{6}Li and ^{10}B isotopes contained in material [2]:

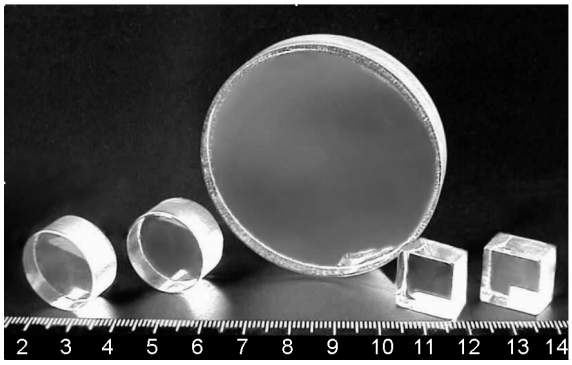

Fig. 1. Samples of LBO glasses.

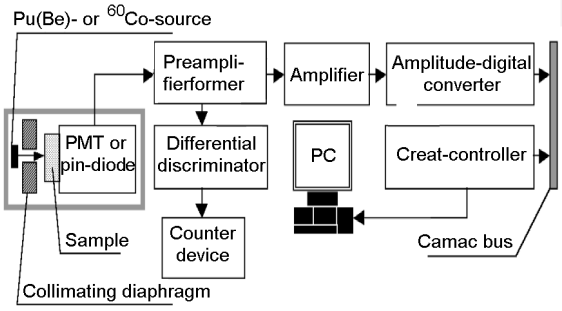

Fig. 2. Measurement system for registration of scintillation characteristics.

$$n + {}^{6}\mathrm{Li} \rightarrow {}^{3}\mathrm{H}(2.75\ \mathrm{MeV}) + {}^{4}\mathrm{He}(2.05\ \mathrm{MeV}), \quad (1)$$

$$n + {}^{10}\mathrm{B} \rightarrow$$

$$\rightarrow \begin{cases} {}^{7}\mathrm{Li}(1.0\ \mathrm{MeV}) + {}^{4}\mathrm{He}(1.8\ \mathrm{MeV}) & (2a) \\ {}^{7}\mathrm{Li}(0.83\ \mathrm{MeV}) + {}^{4}\mathrm{He}(1.47\ \mathrm{MeV}) + \gamma(0.48\ \mathrm{MeV}) & (2b) \end{cases}$$

Here, it is just the reactions (2) that contribute mainly to the response, since the ^{10}B content in initial reagents is much higher than that of ^{6}Li (the natural abundance of boron and lithium isotopes: ^{10}B (19.8 %), ^{11}B (80.2 %), ^{6}Li (7.52 %), ^{7}Li (92.48 %)). Therefore, it is useful to increase the B_2O_3 component content in the glass. Also in comparison with crystals the glassy state of the material provides also much more possibilities of doping to increase light emission and fit its maximum to the maximum sensitivity area of various photoreceivers.

Taking the above as a background, we have synthesized the lithium-borate (LBO) glasses, both pure and doped with some activators. When choosing the activator, we sought to obtain a series of scintillators having light emission maxima in a range from blue to red spectral region. The transmission and luminescence spectra of glasses were investigated as well as their scintillation amplitude spectra under excitation with neutrons and γ-ray sources. A special attention was paid to assess the ability of LBO-scintillators to discriminate the neutron component from attendant γ-radiation and background.

Synthesis of LBO-glasses. $Li_2B_4O_7$, Li_2CO_3, and B_2O_3 reagents of 99.75 % purity were used as starting materials to prepare the LBO glass matrix. The luminescent dopants were introduced in the base blend as Cu_2O, Sm_2O_3, Eu_2O_3, Tb_2O_3, Tm_2O_3, Yb_2O_3 oxides and $Ce(NO_3)_3$ salt. The glasses were synthesized in platinum or porcelain crucibles. The mixtures of initial reagents were melted in air at 875°C and then held for 2–4 h at 975–980°C in to homogenize the melt and to remove gas bubbles therefrom. Then the melt was poured into a mould made of non-wettable material and annealed from 500°C to room temperature for several hours. The obtained glasses contained few defects presented by gas bubbles and cords. The presence of crystalline phases possible in Li_2O–B_2O_3 system was tested by X-ray diffraction and detected ($Li_2B_4O_7$ mainly) in a background level of diffraction patterns in some individual samples only. The samples for measurements were prepared in the form of polished parallelepipeds and disks of 10 to 12 mm thickness (Fig. 1).

Measurements of optical and scintillation characteristics. The optical transmittance spectra were measured in a range up to 900 nm by a double-beam spectrophotometer. The luminescence spectra were registered in 340–800 nm region at room temperature using the excitation at λ_{exc} = 337 nm from nitrogen laser. The scintillation of LBO glasses was measured using a setup shown in Fig. 2 which included a microsecond preamplifier, an active filter amplifier and data collection system comprising an amplitude-digital converter and camac create-controller. The differential discriminator and counting device provided the visual control of measurements. Two types of photoreceivers were used, namely, an AVP-150 photomultiplier (photosensitivity maximum 380–480 nm) and silicon p-i-n photodiodes S 3204-05 of Hamamatsu Co. having the highest sensitivity in the 600–1000 nm range. The amplitude spectra of neutrons and γ-radiation were measured at excitation of LBO-glasses from Pu(Be) and ^{60}Co sources, respectively. The radiation background spectra were also registered.

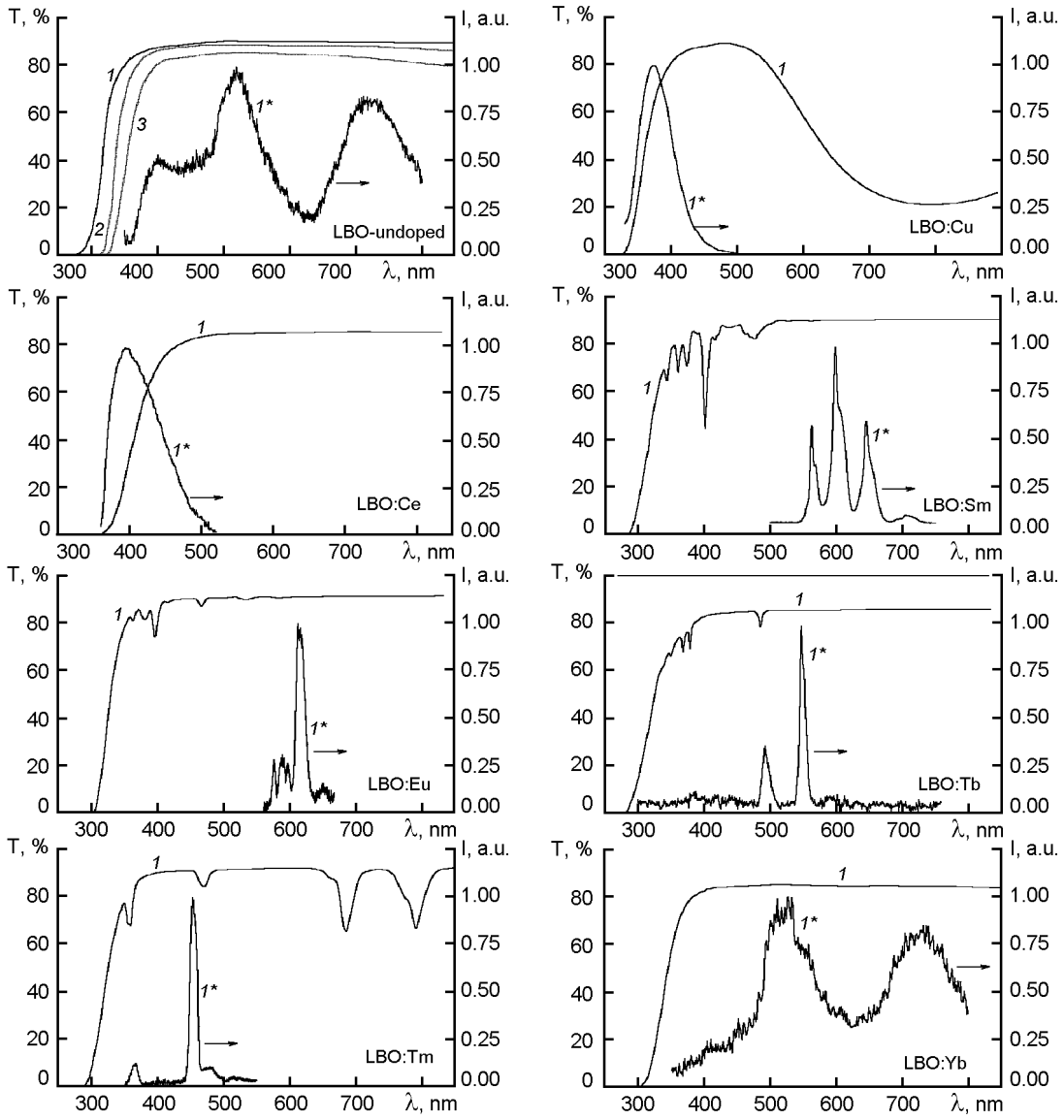

Fig. 3. Transmission (*1*) and luminescence (*1**) spectra of undoped and activated LBO glasses. For undoped LBO glass: *1* — $Li_2O{\cdot}3B_2O_3$; *2* — $Li_2O{\cdot}2B_2O_3$; *3* — $Li_2O{\cdot}1.5B_2O_3$.

The Pu(Be) source had the activity 10^5 n/sec and continuous energy spectrum in 0 to 10 MeV range with weak peaks at 4 and 7 MeV and γ-ray component at 4.43 MeV. The ^{60}Co source activity was $8.7{\cdot}10^4$ sec^{-1}. The distance between sources and samples during the measurements was 10 cm. The amplitude spectra were measured during 10 min using the photomultiplier and during 300 min for photodiodes.

Optical transmission and emission characteristics under UV excitation. The undoped glass samples were synthesized with three Li_2O–$n{\cdot}B_2O_3$ compositions at $n = 1.5$; 2.0, and 3.0. The transmission spectra of these glasses presented in Fig. 3 show the shift of optical transparency edge towards shorter wavelengths while the B_2O_3 content increases. However, B_2O_3 concentration exceeding 75 mol.% causes a strong hygroscopicity of material. Therefore, the matrix of Li_2O–$3B_2O_3$ composition was selected as a basis for the synthesis of LBO glass scintillators. Moreover, it is to note that the use of porcelain crucibles produced 20–30 nm shift of optical transparency edge to long-wavelength side. It is obvious that the reason therefor is some contamination of the glass melt with the crucible material. The density and refractive index of Li_2O–$3B_2O_3$ glass amounted 2.28 g/cm^3 and 1.54, respectively, as measured by of hydrostatic

weighing and an immersion liquid. The effective atomic number of the glass matrix is $Z_{eff} = 7.28$.

The undoped $Li_2O{\cdot}3B_2O_3$-glass shows an intrinsic luminescence with three low-intensity bands as is shown in Fig. 3 and Table 1. This fact indicates that the undoped glass contains emission centers of at least three types. It is known that the intrinsic luminescence of crystalline lithium borates (LiB_3O_5, $Li_2B_4O_7$) is characterized by a broad UV band ($\lambda_{max} = 330–340$ nm at 295 K) and is due to radiative annihilation of the self-trapped excitons or excitons localized at the lattice defects [8, 9]. According to this conception, it is possible to associate the three bands in the LBO glass luminescence spectrum with the intrinsic matrix defects distributed in various fashions in three main structural groups of the glass [10], namely, in triborate and tetraborate complexes and at bridge bonds between those. However, the models of centers and emission mechanism thereof require an improvement.

The transmission and luminescence spectra of doped samples are represented in Fig. 3 and the main characteristics thereof, in Table 1. It is seen that doping with copper, cerium, europium, and ytterbium shifts the optical transparency edge towards longer wavelengths. The reason therefor is obviously the absorption bands of doping ions situated next to the transmittance cutoff wavelength for pure glass. Besides, the

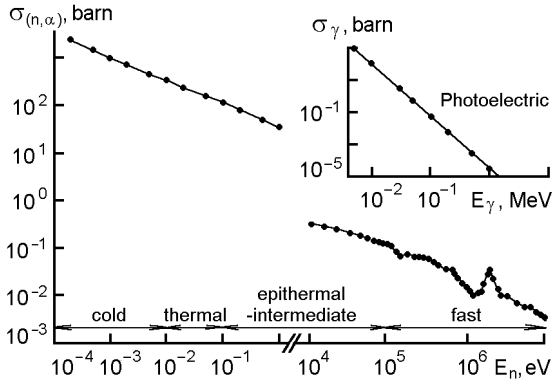

Fig. 4. Total cross section of $^6Li(n,\alpha)$ and $^{10}B(n,\alpha)$ neutron reactions, and cross sections of photoelectric absorption in $Li_2O{\cdot}3B_2O_3$ glass.

glasses containing copper and cerium show additional absorption bands induced by some amounts of Cu^{2+} and Ce^{4+} ions formed in oxidizing conditions of the synthesis. These glasses are colored (Table 1). For LBO:Cu glass, the intensification of absorption next to 300 nm and, moreover, the broad band with a maximum at 800 nm testify to presence of Cu^{2+} ions, while the absorption of Cu^{1+} ions is situated in the fundamental absorption area of glass matrix at 240 and 260 nm ($^1A \leftrightarrow {}^3E$ reversible transition), according to our spectral investigations of $Li_2B_4O_7$:Cu^{1+} crystals and similar data from [3]. The absorption of oxidized

Table 1. Main optical characteristics of LBO glasses

Activator ions, concentration (mass.%)	Glass color	Short-wave edge of optical transparency* (nm)	Main wavelengths of luminescence (nm); emission transitions
Undoped	colorless	281	406; 520;728
Cu^{1+}; 0.25	blue	327	373 $^3E \rightarrow {}^1A$
Ce^{3+}; 1.0	weak yellow	362	395 $^2D_{3/2} \rightarrow {}^2F_{5/2,7/2}$
Sm^{3+}; 2.5	colorless	286	562 $^4G_{5/2} \rightarrow {}^6H_{5/2}$ 598 $^4G_{5/2} \rightarrow {}^6H_{7/2}$ 645 $^4G_{5/2} \rightarrow {}^6H_{9/2}$
Eu^{3+}; 2.5	weak pink	304	612 $^5D_0 \rightarrow$ Б4№ФАО4В$^7F_0$
Tb^{3+};; 0.5	colorless	281	492 $^5D_4 \rightarrow {}^7F_6$ 547 $^5D_4 \rightarrow {}^7F_5$
Tm^{3+}; 2.5	colorless	289	452 $^1G_4 \rightarrow {}^3H_6$
Yb^{3+}; 0.5	colorless	307	527; 728

*) the long-wave edge is found at 2760 nm

Table 2. Efficiency and selectivity coefficients of LBO-glass scintillators

Activator ions, concentration (mass.%)	Source	Detector efficiency for different photoreceiver			
		photomultiplier		p-i-n-photodiode	
		ε_i	K_{discr}	ε_i	K_{discr}
Undoped	Pu(Be)	(2.1±0.1)E-02	50±15	(1.3±0.2)E-03	7±3
	^{60}Co	(4.2±1.2)E-04		(1.9±0.8)E-04	
Cu^{1+}; 0.25	Pu(Be)	(1.5±0.1)E-02	47±18	(1.4+–BR RNºCB0 .2)E-03	8±3
	^{60}Co	(3.2±1.3)E-04		(1.7±0.6)E-04	
Ce^{3+}; 1.0	Pu(Be)	(3.0±0.9)E-02	42±4	(6.4+–BR RNºCB0 .9)E-04	4±2
	^{60}Co	(7.1±2.1)E-04		(1.7±0.7)E-04	
Sm^{3+}; 2.5	Pu(Be)	(8.1±0.1)E-03	22±1	(6.1+–BR RNºCB0 .6)E-04	19±7
	^{60}Co	(3.6±0.1)E-04		(3.2±1.1)E-05	
Eu^{3+}; 2.5	Pu(Be)	(2.2±0.1)E-02	23±8	(1.05+–BR RNºCB 0.03)E-02	19±2
	^{60}Co	(9.5±2.8)E-04		(5.5±0.3)E-04	
Tb^{3+}; 0.5	Pu(Be)	(2.3±0.1)E-02	58±15	(1.5+–BR RNºCB0 .3)E-03	7±3
	^{60}Co	(4.0±1.0)E-04		(2.1±0.8)E-04	

Ce^{4+} ions is not manifested in the optical transparency area of LBO glass, because their absorption band is at 240–250 nm, for example, in silicate and phosphate glasses activated with cerium [11]. The transmittance edge shift by 80 nm to longer wavelengths is caused by Ce^{3+} ion absorption band centered at 310–315 nm ($4f \rightarrow 5d$ absorption transition). For the glass containing ytterbium, the increase of absorption around 300 nm may be due to some amount of Yb^{2+} ions showing a broad absorption band in near UV region.

The luminescence spectra of LBO:Cu and LBO:Ce glasses represented by broad unstructured bands overlapping in short-wavelength parts with edge of the glass optical transparency area. This fact as well as the presence of a fraction of copper and cerium ions in the inactive Cu^{2+} and Ce^{4+} state decreases the luminescence integral output. The main emissive bands of glasses doped with Sm, Eu, Tb, Tm are in the optical transparency region of the material. The bands are relatively broad and their structure is feebly pronounced, what is characteristic for glasses in general. The band positions correspond well to their locations in spectra of other glass types [12]. The luminescence spectrum of LBO:Yb glass contains two bands similar to those centered at 520 and 720 nm in the pure glass spectrum. This fact shows that the main luminescence centers in the range up to 800 nm are the intrinsic centers of the glass matrix. However, the intensity of bands is a little bit higher, also the 520 nm band has a shoulder near 540 nm. It is possible that ytterbium intensifies the emission of intrinsic centers existing in LBO matrix and a fraction of ytterbium in glass is in the abovementioned state of Yb^{2+} ions emitting at 530–550 nm in many materials.

Scintillation by neutron and γ-rays irradiation. The sensitivity of obtained $Li_2O{\cdot}3B_2O_3$ glass to neutrons and γ radiation is characterized by energy dependences of cross sections $\sigma_{(n,\alpha)}$ and σ_γ shown in Fig. 4. The $\sigma_{(n,\alpha)}$ was calculated by us according to data [13] taking into account the natural abundance of ^{10}B and ^{6}Li isotopes. Fig. 4 vindicates in principle the high selectivity of LBO glass scintillator for neutron registration in mixed radiation fields. For example, in the case of attendant γ-radiation of ^{60}Co, the $\sigma_{(n,\alpha)}/\sigma_\gamma$ ratio amounts to 10^7–10^2 within the range from cold to fast neu-

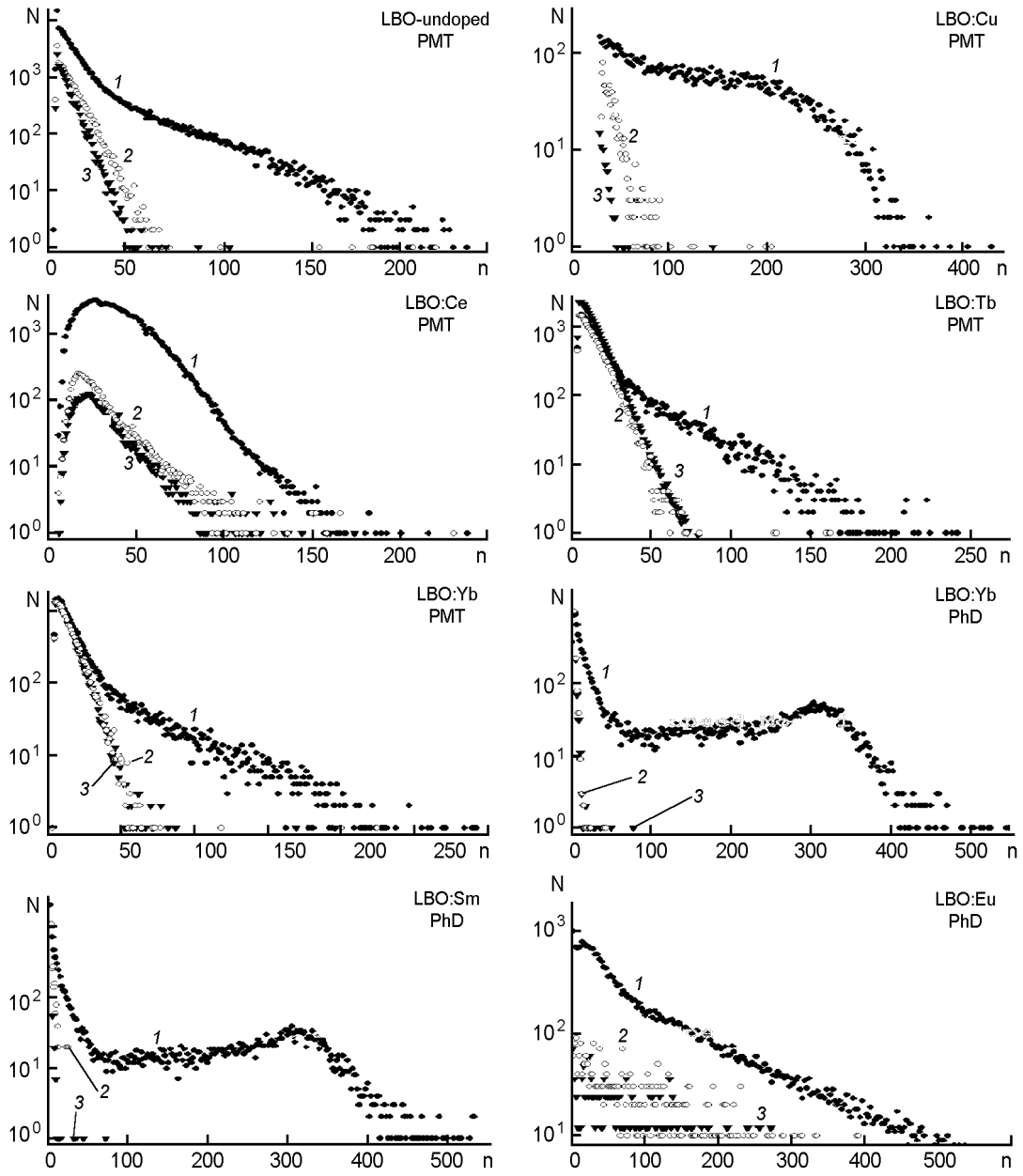

Fig. 5. Amplitude spectra of neutrons from Pu(Be)-source (●), gamma-radiation from ^{60}Co-source (○) and background (▼) obtained by means of LBO glass scintillators and photomultiplier (PMT) or p-i-n-photodiode (PhD). N, total counts per channel; n, number of channel.

trons. Experimentally, the absolute scintillation efficiency of LBO glasses to register neutrons and gamma-radiation was assessed by means of relationship:

$$\varepsilon_i = N_i/(A_i \cdot \Delta\omega \cdot t), \qquad (3)$$

where N_i is a count of events from Pu(Be) or ^{60}Co source registered by the detector; A_i, the source (Pu(Be) or ^{60}Co) activity; $\Delta\omega$, the solid angle of the detector; t, the measurement duration. The selectivity of material to neutrons was characterized by the discrimination coefficient:

$$K_{discr} = \varepsilon_{Pu(Be)}/\varepsilon_{^{60}Co}, \qquad (4)$$

where $\varepsilon_{Pu(Be)}$ and ε^{60}Co are the absolute registration efficiency of events from Pu(Be) and ^{60}Co sources, respectively.

The most typical experimental amplitude spectra obtained by means of LBO glass scintillators are presented in Fig. 5. The spectra of Pu(Be) source have no pro-

nounced photopeaks because the energy spectrum of its neutrons is practically continuous. At the same time, it is seen well that the γ spectra of ^{60}Co source and of background are situated mainly in the region of low channels and do not overlap the main area of neutron spectra. The γ spectra damping is especially effective when a photomultiplier is used as the photoreceiver. The assessments of registration efficiency and discrimination coefficients for both photoreceiver types are presented in Table 2. One can see the values of $\varepsilon_{Pu(Be)}$ and K_{discr} to increase if the emission region of LBO glass coincides with the photosensitivity region of the receiver. These detector parameters of are worse noticeably when a p-i-n photodiode is used instead of photomultiplier. In our opinion, the reason therefor is the high own noise of p-i-n diode, which rises under γ-irradiation from the sources. This result does not close of course the promises of p-i-n-diode use with LBO scintillators. For comparison, the characteristics of traditional organic scintillators (anthracene, polystyrene, stilbene) were measured using a similar photomultiplier and in the same conditions. The obtained discrimination coefficient values do not exceed 6. This result is substantially smaller than K_{discr} shown by investigated LBO-glass scintillators.

Thus, the glasses (pure and doped with some activators) have been synthesized in the $Li_2O–B_2O_3$ oxide system. The optical transmission and luminescence spectra and some scintillation characteristics thereof have been investigated. It was found in experiment that the LBO bglass scintillators have the neutron registration efficiency exceeding that of γ radiation by a factor of 10 to 100. The high selectivity to neutrons gives an advantage to LBO glasses over other scintillators regarding their application in mixed radiation fields. The results obtained demonstrate that the mentioned scintillator type can be a promising alternative for the known neutrons detectors on a basis of gases, liquids, plastics, and crystals. The LBO glasses can be obtained in large volume that is important for making large-size detectors.

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Нові неорганічні сцинтилятори на основі LBO скла для реєстрації нейтронів

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Синтезовано чисті та леговані активуючими домішками Cu, Ce, Sm, Eu, Tb, Tm, Yb літій-боратні стекла та визначено їхні оптичні та люмінесцентні властивості та деякі сцинтиляційні характеристики при реєстрації нейтронів з енергією до 10 МеВ та гамма-проміння ^{60}Co. Експериментально встановлено, що літій-боратні склоподібні сцинтилятори мають високу чутливість до нейтронів і можуть бути застосовані для селективної реєстрації нейтронів у полях змішаних випромінювань. Одержані результати свідчать, що сцинтилятори цього типу можуть бути перспективною альтернативою відомих детекторів нейтронів на основі газів, рідин, пластмас та кристалів.