

## SPECTRAL-LUMINESCENT, PHOTOCHEMICAL, AND LASING CHARACTERISTICS OF BORON DIPYRRROMETHENE DIFLUORO (III) DERIVATIVES IN LIQUID AND SOLID-STATE MEDIA

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UDC 535.37; 539.19

*Optical properties of some boron dipyrromethene difluoro (III) (BF<sub>2</sub>-dipyrromethene) derivatives are studied depending on the ligand structure, the medium in which they are incorporated, irradiation time, and radiation wavelength. Prospects for application of the prepared solid-state media painted by the examined compounds in various optical devices used in modern technologies are demonstrated. These are active laser media in the range 550–565 nm based on three-component silicate matrices with high laser damage threshold and sensor media based on boron difluoride complexes of halogen-substituted dipyrromethenes incorporated into an organic polymer for the determination of oxygen concentration in a gas mixture. Spectral, energy, and resource characteristics of lasing of solid-state elements are presented. The effect of reversible dye photo-unpainting in three-component silicate matrices with subsequent restoration in the darkness is discovered. Possible reasons for this effect are discussed with allowance for which laser media with increased photostability can be prepared. A high sensitivity of the sensor medium based on diiodinated complex of BF<sub>2</sub>-dipyrromethene incorporated into polyvinyl butyral is obtained. Reasons for the increase in the response time to the change of the gas mixture when going over to neutral argon and possibilities of its elimination are discussed.*

**Keywords:** dipyrromethenes, BODIPY, coordination complexes, photonics of complex compounds, laser media, sensor materials.

One of the fundamental problems of natural sciences is the establishment of a relationship between the structure of the substance and its properties; exactly this problem is studied in the present paper. The last decades were characterized by increased interest in the development of various optical devices based on complex molecular compounds. Depending on the structure, they were used as active laser media of tunable lasers, sensor media for the determination of the oxygen concentration in a gas mixture, and photosensitizers of singlet oxygen necessary for the development of catalysts of many chemical reactions and agents of photodynamic therapy in treatment of virus and oncological diseases. Example of such compounds are coordination boron dipyrromethene difluoro (III) (BF<sub>2</sub>-dipyrromethene or BODIPY) complexes having different structures [1–3] whose sufficiently easy synthesis, essentially

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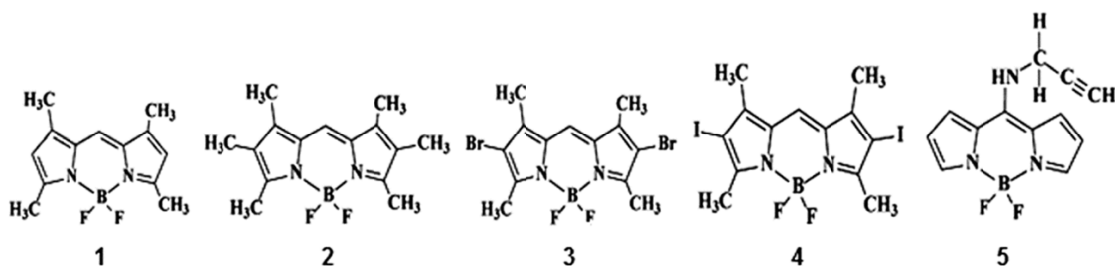


Fig. 1. Structural formulas and designations of the examined complexes. Here **1** shows  $(\text{CH}_3)_4\text{BODIPY}$  – tetramethyl BODIPY, **2** shows  $(\text{CH}_3)_6\text{BODIPY}$  – hexamethyl BODIPY, **3** shows  $\text{I}_2(\text{CH}_3)_4\text{BODIPY}$  – diiodo-tetramethyl BODIPY, **4** shows  $\text{Br}_2(\text{CH}_3)_4\text{BODIPY}$  – dibromo-tetramethyl BODIPY, and **5** shows *ms*-(NH-CH<sub>2</sub>-C≡CH)BODIPY – meso-propargylamino BODIPY.

advancing the study of their photophysics and photochemistry, slows down their practical application, because requirements to the creation of concrete structures for solving specific problems have not yet been formulated. Spectroscopic investigation of the photonics of these compounds depending on the ligand substitute and the medium in which they are incorporated is extremely urgent in this stage, since it allows media to be predicted for concrete optical devices used in modern technologies [1]. The use of miniature solid-state matrices painted by complex molecules stable in the ground and electronically excited states radiating in the entire optical range is characteristic for these technologies. Since lasers with high light flux intensity ( $>20 \text{ MW/cm}^2$ ) are used for excitation in these devices, it is necessary to create solid-state matrices with high radiation damage threshold and increased photostability of dyes painting this matrix. It was established that for a number of painting compounds, higher radiation damage threshold in comparison with organic polymers into which they are incorporated possess solid-state silicate matrices based on alkoxysilanes [4]. In the present work, results of spectroscopic investigation of the optical characteristics of some BODIPY derivatives in ethanol, solid matrices, and films of different natures are presented based on which recommendations on their application in different optical devices are formulated.

## OBJECTS AND METHODS OF RESEARCH

Figure 1 shows structural formulas and designations of the examined BODIPY. Ethanol (undried), cyclohexane, and ethyl acetate (chemically pure) were used as solvents. Organic polyvinyl butyral (PVB) polymer and silicate matrices were chosen to synthesize solid-state matrices 1 mm thick in 1-millimeter quartz cells and films 140 and 700  $\mu\text{m}$  thick. The PVB polymer films 700  $\mu\text{m}$  thick were prepared by the method of pouring ethanol PVB solution painted by BODIPY derivatives on glass substrates and their subsequent drying at room temperature. Solid-state hybrid sol-gel matrices with incorporated different BODIPY were synthesized from a two-component mixture of alkoxysilanes: tetraethoxysilane (TEOS) and vinyltriethoxysilane (VTEOS) in the ratio 70:30 wt.%. After the termination of the hydrolysis process, the BODIPY solution was added to the sol so obtained. Since not all BODIPY were painted by two-component silicate matrices for the reason discussed below, painted films and matrices based on complex three-component mixtures of substituted alkoxides were prepared: aminopropyltriethoxysilane (APTEOS), phenyltriethoxysilane (PTEOS), and methyltriethoxysilane (MTEOS) taken in the volume ratios (1:1:1). For these gel materials, the following technique was used: after the process of hydrolysis of the three-component mixture in an aqueous-alcoholic medium, the saturated solution of the corresponding BODIPY in dimethylformamide (DMFA) was added, and then the painted gel solution was either poured into cells ( $l = 0.1 \text{ cm}$ ) or deposited on quartz substrates with subsequent thermal treatment at  $100^\circ\text{C}$ . By this method, well fluorescing organo-inorganic gel materials painted at  $C \approx 5 \cdot 10^{-4} \text{ M}$  only by compounds **1**, **2**, and **5** were synthesized. Compounds **3** and **4** gradually unpainted in the three-component matrix (the same as in the two-component TEOS + VTEOS silicate matrix) in the course of polymerization.

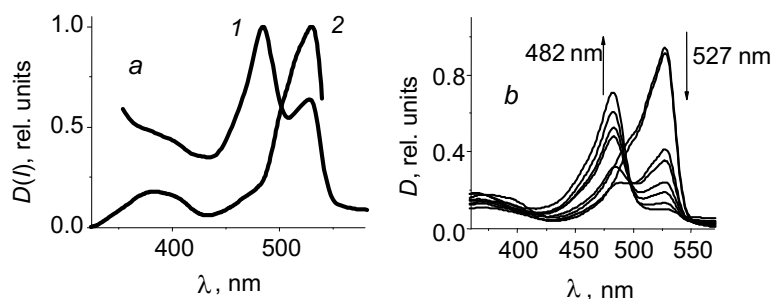


Fig. 2. Normalized absorption (curve 1) and fluorescence excitation spectra (curve 2) of  $(\text{CH}_3)_6\text{BODIPY}$  in TEOS + Pluronic F-127 ( $\lambda_{\text{rec}} = 550 \text{ nm}$ ) (a). Change of the absorption spectra of  $(\text{CH}_3)_6\text{BODIPY}$  in ethanol ( $10^{-5} \text{ M}$ ) after addition from 1 to 20% of the 33 % (10.6 M) solution of HCl (b).

The silicate matrices do not retain incorporated BODIPY compounds because of the acidified water-ethanol medium required in the first stage for the process of sol-gel synthesis and the presence of residual silanol groups in pores of the synthesized matrix. In such excited media, as shown in [5, 6], the BODIPY complexes can associate or decompose with escape of the complexing agent and formation of the protonated ligand. We have undertaken an attempt of preliminary solubilization of the BODIPY complexes on neutral micelles formed by Triton X100 and Pluronic F-127 detergents with subsequent incorporation of such colored micelles into the TEOS matrices. The results presented in [6] demonstrated that in aqueous-ethanol solutions with addition of Pluronic F-127 with concentration exceeding its critical value of micelle formation ( $2 \cdot 10^{-3}$ ), only neutral monomer BODIPY were presented. However, this method does not protect the BODIPY complexes from destruction when painted micelles are incorporated into the TEOS matrix. A considerable part of them is transformed into a protonated ligand right after synthesis with continued decoloration during drying (Fig. 2a). This conclusion was made based on the study of acidified ethanol solutions: the acidified solutions were irreversibly decolorated (a slight yellowish tint remained) and did not fluoresce (Fig. 2b). The use of BODIPY solutions in DMFA reduced the influence of the acidified medium, and addition of this solution to TEOS + VTEOS sol slightly reduced the influence of silanol groups (their concentration decreased), but the concentration of the remaining neutral form of complexes was insufficient, especially for excitation of lasing of stimulated radiation.

It seems likely that qualitatively the same effect, but less pronounced, is observed in three-component media where the substitution of one of the TEOS ethoxy groups by aminopropyl, phenyl, or methyl group also reduces the influence of acidification and silanol groups in a polymer. Therefore, even  $(\text{CH}_3)_6\text{BODIPY}$  most unstable in proton donor media [5] was not destroyed in such matrices and films together with more stable tetramethyl and meso-propargylamine BODIPY (see Table 1). It is important to note that the addition of the acid catalyst during sol-gel synthesis of two-component matrices was insignificant, and the initial liquid reaction medium approached neutral one after termination of hydrolysis (in this stage, the reaction mixture had intense color corresponding to the neutral complex). However, in the process of formation of the solid silicate skeleton with nanopores both two- and three-component matrices with BODIPY compounds 3 and 4 gradually unpainted. In this case, it was obtained that halogen derivatives of BODIPY which should be more stable in such media, according to [5] became colorless, that is, not only the content of complexes, but also the content of dipyrromethenes formed in exchange reactions with acids of protonated ligands decreased. Probably, the formation of protonated ligand was followed by its interaction with singlet oxygen generated by halogen BODIPY absorbing visible light and having a high yield of T-states [7] with the subsequent formation of colourless UV photoproducts [8]. Additional investigations are required to establish unambiguously the mechanisms of BODIPY interaction with silicate matrices to prepare samples painted by neutral complexes.

Lasing of stimulated radiation by solutions and solid-state matrices painted by the BODIPY complexes was excited by the 2<sup>nd</sup> and 3<sup>rd</sup> harmonics of a Nd:YAG laser (LQ215 or LQ529, SOLAR, Belarus:  $E_p$  up to 25 mJ,  $\lambda = 532$

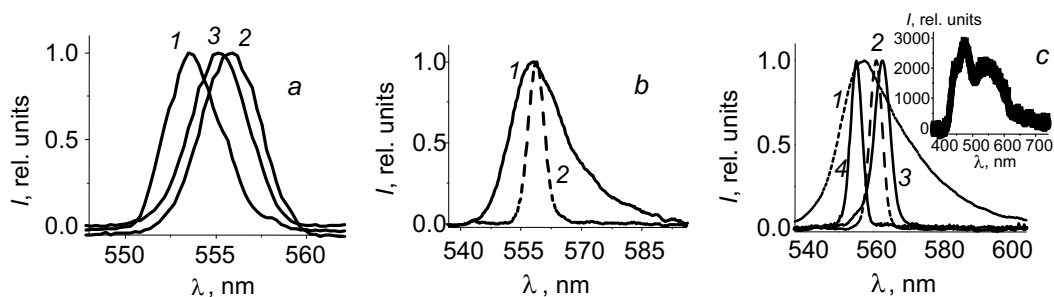


Fig. 3. Lasing spectra of  $(\text{CH}_3)_6\text{BODIPY}$  in ethanol (*a*), solid-state PVB film (*b*), silicate APTEOS + PTEOS + MTEOS matrix (*c*, curves 2 and 4), and film (*c*, curves 1 and 3) for  $W_{\text{pump}} = 0.3$  (*a-c*, curves 1), 16 (*b*, curve 2), 30 (*c*, curves 2–4), and 40  $\text{MW}/\text{cm}^2$  (*a*, curves 2 and 3). Spectra *a*, curve 3 and *c*, curve 4 were registered after resource measurement. In the insert: emission spectrum of *ms*-propargylamine BODIPY excited by the 3<sup>rd</sup> harmonic (355 nm) ( $W_{\text{pump}} = 40 \text{ MW}/\text{cm}^2$ ).

or 355 nm, and  $\tau_p = 10\text{--}13 \text{ ns}$ ). The transverse pumping scheme was used, and the solution was excited in the plane-parallel resonator having a base of 2 cm formed by a nontransmitting mirror and an external side of the cell ( $l = 1 \text{ cm}$ ). Lasing of solid-state samples was excited in a mirrorless resonator operating on the principle of a planar waveguide at the expense of the total internal reflection (TIR) with two-side radiation output. To measure the energy characteristics, an OPHIR NOVA II power meter (Israel) and a pyroelectric detector (Gentec-EO Inc., ED100AUV) model DUO (Canada) with sensitivity to 8–9  $\mu\text{J}$  were used. The lasing spectra were measured with an AVANTES spectrometer (the Netherlands). The experimental setup for measuring the lasing characteristics, including photochemical and resource ones, was described in detail in [9]. As resource characteristics, the specific pumping energy absorbed by 1  $\text{cm}^3$  of the lasing volume (in  $\text{J}/\text{cm}^3$ ) was used; therefore, the initial efficiency decreased to a conditional value ( $P_{90}$ ,  $P_{80}$ ,  $P_{50}$ , etc.).

The sensor characteristics of a number of solid-state matrices painted by halogen BODIPY were measured using the original setup [10] comprising a CM2203 spectrometer with a special cell compartment and device for forming gas mixture flows controlled by a computer.

## RESULTS AND DISCUSSION

### Spectral and lasing characteristics

The influence of the medium (solutions, solid-state matrices, and films of different natures) on the spectral-luminescent, lasing, and resource characteristics was studied on an example of hexamethyl BODIPY. For a comparison, tetramethyl and *ms*-propargylamine BODIPY were used in some cases.

Table 1 presents the obtained characteristics from which it follows that hexamethyl BODIPY is one of the typical alkyl BODIPY well fluorescing (well fluor.) and lasing stimulated radiation with efficiency up to 70% in solutions excited into a long-wavelength absorption band. Because of the small Stokes shift, the fluorescence maximum of saturated solutions is displaced toward longer wavelengths when the concentration increases, and the halfwidth of the fluorescence band decreases because of the reabsorption. The displacement of the lasing spectra (Fig. 3*a*) demonstrates the change of the reabsorption with changes of the excitation intensity and during irradiation, the same as in a number of other alkyl BODIPY. The photostability characteristics in the ethanol solution are slightly lower ( $\varphi_{\text{phot}}^{532} = 1.3 \cdot 10^{-4}$  and  $P_{80} = 245 \text{ J}/\text{cm}^3$ ) in comparison with other alkyl derivatives [11] that is explained by lower stability of hexamethyl BODIPY in proton-donor media in comparison with other BODIPY [5].

This compound is well incorporated into the neutral PVB film, well fluoresces in it, generates stimulated radiation without external resonator (based on the TIR principle) with a low lasing threshold. For  $W_{\text{pump}} < 0.3 \text{ MW}/\text{cm}^2$ , the emission band is narrowed by 2–3 times in comparison with the fluorescence spectrum, and when pumping

TABLE 1. Spectral-Luminescent, Lasing, and Photochemical Characteristics of BODIPY Complexes in Solutions and Polymer Matrices

Compound, medium, concentration, M	$\lambda_{\text{abs}} (\epsilon)$ , $\text{M}^{-1}\cdot\text{cm}^{-1}$ $A_{532}, A_{355}$	$\lambda_{\text{fl}}, \Delta\lambda$ ( $\lambda_{\text{exc}}$ ), nm	$\gamma_{\text{fl}}$ ( $\lambda_{\text{exc}}$ ), nm	$\lambda_{\text{las}}, \Delta\lambda$ ( $\lambda_{\text{exc}}$ ), nm [ $W_{\text{pump}}, \text{MW}/\text{cm}^2$ ]	Lasing efficiency, % ( $W_{\text{pump}},$ $\text{MW}/\text{cm}^2$ )	$\Phi^{532}_{\text{phot}} \cdot 10^5$ , ( $W_{\text{pump}}, \text{MW}/\text{cm}^2$ ) [ $P_{90}, P_{80}, P_{50}$ $\text{J}/\text{cm}^3$ ]
(CH <sub>3</sub> ) <sub>6</sub> BODIPY, Ethanol, 10 <sup>-3</sup>	527 (61710) $A_{532} = 65$	538, 45 (532) 574, 43 (532)	0.9 (500)	553, 3.5 (532) [1] 556, 5 (532) [40]	60–70 (25)	13 (40) [ $P_{80} = 240$ ]
(CH <sub>3</sub> ) <sub>6</sub> BODIPY, cyclohexane, 10 <sup>-5</sup>	531 (56250)	539 (10 <sup>-5</sup> )	0.9 (500)			
(CH <sub>3</sub> ) <sub>6</sub> BODIPY, PVB film, $l = 0.7$ mm, 5·10 <sup>-4</sup>	531 $A_{532} = 2.3$	547, 45 (500)	Well fluor.	557, 10 (532) [0.3] 559, 5 (532) [16]	12–13 (10–20)	[ $P_{55} = 494.6$ ]
(CH <sub>3</sub> ) <sub>6</sub> BODIPY, matrix, APTEOS + PTEOS + MTEOS (1:1:1), $l = 1$ mm, 5·10 <sup>-4</sup>	532 $A_{532} > 3$	553, 38 (355, 500)	Well fluor.	562, 5 (532) [25]	11.5 (10–20)	[ $P_{90} = 250$ ] (with allowance for transmission)
(CH <sub>3</sub> ) <sub>6</sub> BODIPY, film, APTEOS + PTEOS + MTEOS (1:1:1), $l = 0.14$ mm, 5·10 <sup>-4</sup>	532 $A_{532} = 0.41$	549 (355, 500)	Well fluor.	557, 21 (532) [0.6] 557, 10 (532) [2] 563, 5 (532) [25]		
(CH <sub>3</sub> ) <sub>4</sub> BODIPY, matrix, APTEOS + PTEOS + MTEOS (1:1:1), $l = 1$ mm, 5·10 <sup>-4</sup>	502 $A_{502} > 3$ $A_{532} = 0.1$ $A_{355} = 0.45$	526 (355, 420)	Well fluor.			
(CH <sub>3</sub> ) <sub>4</sub> BODIPY in ethanol, 10 <sup>-5</sup>	504 (70000)	514 (490)	1 (490)			
( <i>ms</i> -NH-CH ≡CH)BODIPY), matrix, APTEOS + PTEOS + MTEOS (1:1:1), $l = 1$ mm, 5·10 <sup>-4</sup>	404 $A_{404} = 0.76$ $A_{355} = 0.71$	445 (355, 400)				
( <i>ms</i> -NH-CH <sub>2</sub> -C ≡CH)BODIPY), ethylacetate	409 (37400)	470 (355)	0.9 (370)			

increases to 10–16 MW/cm<sup>2</sup>, a narrow lasing band ( $\Delta\lambda_{\text{las}} = 5$  nm) is observed in the long-wavelength edge of the fluorescence band with the maximum displaced toward longer wavelengths in comparison with the solution, which is characteristic for all BODIPY (see Table 1 and Fig. 3b).

Since this compound is excited practically to the maximum of the intense absorption band, with insignificant linear transmission ( $T_{532} < 1\%$ ), the transmission of this film during the exciting pulse increased with pump density to 18% (at 25 MW/cm<sup>2</sup>) due to molecules that escape from the ground state. Figure 4 and Table 1 illustrate the dependence of the lasing efficiency on the excitation power density with allowance for the change in the transmission. The lasing process is important in spite of the fact that the efficiency of solid-state samples is much lower than that of the solution. This is explained by low (not laser) quality of these samples, strong radiation scattering on optical inhomogeneities in the lasing volume, and measurement of the output energy on one side of the TIR resonator, whereas radiation is emitted from both sides of the system with mirrorless resonator, and so on. It should be noted that opacification (microcracks) is

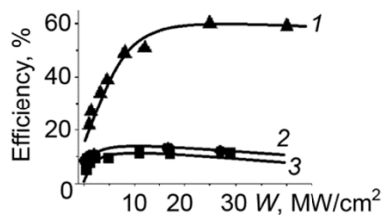


Fig. 4

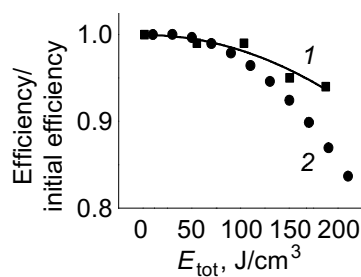


Fig. 5

Fig. 4. Dependences of the lasing efficiency of  $(\text{CH}_3)_6\text{BODIPY}$  on the power density of pumping radiation for ethanol solution (curve 1), PVB film ( $l = 0.7$  mm) (curve 2), and three-component silicate matrix ( $l = 1$  mm) (curve 3).

Fig. 5. Dependence of the relative decrease in the lasing efficiency on the total specific absorbed pumping energy for the three-component silicate matrix ( $l = 1$  mm) painted by  $(\text{CH}_3)_6\text{BODIPY}$  (curve 1) and for its ethanol solution (curve 2).

formed in the lasing volume of the PVB film at pumping density of 15–25 MW/cm<sup>2</sup> because of the low radiation damage threshold of the PVB matrix; therefore, we further studied silicate three-component matrices (1 mm thick) and films (0.14–0.15 mm thick).

As follows from the results obtained, the lasing spectra in solid-state media experience a bathochromic shift compared to the spectra in ethanol (by 3 nm in the PVB film and by 6 nm in the silicate matrix), which is in agreement with the results obtained for other polymer matrices (PMMA) and others alkyl BODIPY [9, 11]. The hypsochromic displacement of the lasing spectrum after irradiation during lasing is explained by the decrease of the reabsorption with decreasing absorption.

Since the thin film of the three-component silicate polymer painted by  $(\text{CH}_3)_6\text{BODIPY}$  has sufficiently high linear transmission ( $T_{532} = 0.4$ ) that increases even more with pumping, the lasing efficiency of a thin silicate film ( $l = 0.14$  mm) could not be estimated, since the lasing energy was below the sensitivity threshold of the setup. Nevertheless, the fact of lasing of stimulated radiation was confirmed by measurement of the spectra (Table 1 and curves 1 and 3 in Fig. 3c). These results demonstrate that in silicate polymers, the bathochromic shift of the spectral-luminescent and lasing band of  $(\text{CH}_3)_6\text{BODIPY}$  subsequently increases together with the nonlinear transmission of the 0.1-cm matrix that increases from 1 to 20% for  $W_{\text{pump}} = 25$  MW/cm<sup>2</sup> (Table 1 and Fig. 3). For this pumping intensity, the APTEOS + PTEOS + MTEOS matrix, unlike the PVB film, remains transparent, that is, its radiation damage threshold is sufficiently high; therefore, we further estimated the resource characteristics of the solid-state silicate sample.

Measurement of the output lasing energy of the painted solid-state samples depending on the irradiation time (the number of pulses at a frequency of 2 Hz) demonstrated that the initial lasing energy is halved for 3–5 min, and the irradiated volume is significantly unpainted. Consideration of the change in the transmission of the three-component silicate sample demonstrated that the transmission in such experiment increased, and 3 min after the irradiation onset reached 20%; therefore, the lasing efficiency, taking into account the change of the transmission, decreases depending on the total specific absorbed pumping energy, almost the same as in the solution (Fig. 5). The lasing spectrum obtained after measurement of the resource experienced hypsochromic displacement compared to the spectrum of unirradiated volume, which is caused by the decrease of the reabsorption because of the decrease of the BODIPY concentration under irradiation. The subsequent observation demonstrated that in the absence of excitation, gel-matrix painting in the unpainted zone was restored with time. Measurement of the resource characteristics in about 70 h (without changing the parameters of excitation adjustment on the previously irradiated zone) demonstrated that the transmission was restored to its reference value (2%), and the lasing energy that decreased in the previous experiment from 0.4 to 0.07 mJ

increased again to 0.32 mJ, that is, partial restoration of the spectral and lasing characteristics of the sample was observed. As a whole, determination of the resource characteristics of the solid-state matrices painted by  $(\text{CH}_3)_6\text{BODIPY}$  showed minor alterations in comparison with the resource in the solution (Fig. 5), which is also in agreement with analogous results obtained for other BODIPY [11]. The sample in the PVB film exhibits no such restoration, but measurement of the output lasing energy depending on the number of pulses demonstrates that during the first minute of irradiation the energy almost halved (cracks appeared in the lasing volume); however, during subsequent 4 min, after absorption of  $495 \text{ J/cm}^3$ , the lasing energy remained at the same level as after the 1<sup>st</sup> minute. The small irradiation time at which the energy significantly decreased compared to the solution is explained by the small absorbing (lasing) volume:  $0.004 \text{ cm}^3$  for the three-component matrix and  $0.003 \text{ cm}^3$  for the PVB film in comparison with the  $0.5 \text{ cm}^3$  lasing volume for the solution.

The results obtained demonstrated that the photodestructed  $(\text{CH}_3)_6\text{BODIPY}$  complexes under high-power ( $16\text{--}25 \text{ MW/cm}^2$ ) laser excitation in solid-state silicate APTEOS + PTEOS + MTEOS matrices were partially restored in the darkness within several hours when surrounded by a silicate local medium, that is, the characteristics of the neutral monomer BODIPY complex were restored. Probably, unpainting of dye observed in this matrix under high-power laser excitation is due to the effective intramolecular electron density (electron) transfer from the double bond of the methine bridge of the ligand to electron accepting fluorine atoms that caused partial violation of conjugation of aromatic pyrrole systems and decrease of the probability of radiation absorption in the visible range of the spectrum. The restoration of conjugation in the darkness is accompanied by the restoration of the chromophore properties of the compound. Such intramolecular electron transfer can be stimulated by the structure of the three-component silicate matrix.

Further investigations are required to understand mechanisms of the observed phenomenon, special features of the influence of the matrix nature on the behavior of BODIPY luminophors in it, and study of the possibility of creation of solid-state matrices painted by the BODIPY complexes and photostable under laser excitation.

In addition to the  $(\text{CH}_3)_6\text{BODIPY}$  complex,  $(\text{CH}_3)_4\text{BODIPY}$ , and *ms*-propargylamine derivative analog: *ms*( $-\text{NH}-\text{CH}_2-\text{C}\equiv\text{CH}$ )BODIPY (see Fig. 1) were incorporated into the three-component APTEOS + PTEOS + MTEOS matrix. These compounds do not absorb radiation at 532 nm; therefore, they were excited by radiation of the 3<sup>rd</sup> harmonic (355 nm). The obtained absorption and fluorescence spectra indicated the retention of the molecular form of these complexes in the APTEOS + PTEOS + MTEOS matrix (Table 1); however, the absorption at 355 nm was too low (far from the maxima):  $A_{355} = 0.35$  for  $(\text{CH}_3)_4\text{BODIPY}$  and 0.47 for *ms*( $-\text{NH}-\text{CH}_2-\text{C}\equiv\text{CN}$ )BODIPY; therefore, no inverse population density was formed. Moreover, in addition to the fluorescence band with maximum at 478 nm belonging to *ms*( $-\text{NH}-\text{CH}_2-\text{C}\equiv\text{CH}$ )BODIPY, broadband radiation with maximum at 540 nm arose under UV excitation, and after irradiation of this sample by 355 nm in the attempt to obtain stimulated radiation, a bright yellow band arose in the irradiated region against the background of almost colorless sample. Apparently, this is a reason for long-wavelength (540 nm) radiation (see the insert in Fig. 3c). Introduction of additives increasing the photostability of BODIPY derivatives under UV excitation is required [11].

### Sensor characteristics of solid-state films painted by halogen BODIPY

As shown in [7, 12], halogen BODIPY badly fluoresce, but have good triplet yields and noticeable phosphorescence in frozen solutions according to the effect of *heavy* atom [13]. Therefore, these compounds in solid-state samples at room temperature were tested for the possibility of their application as sensor media for oxygen in a gas mixture. Oxygen whose ground state is triplet forms complexes with triplet excited BODIPY in which the excitation energy is transferred to oxygen translating it into the singlet excited state  $^1\text{O}_2$ , and triplet excited BODIPY is translated into the ground state, that is, phosphorescence quenching occurs. The quality of the sensor media is determined by the structure of the phosphorescing compound, quantum phosphorescence yield, interaction constant of triplets with oxygen, relationship between the concentration of the sensor and analyte, as well as by the structure of the solid-state matrix and its permeability for molecules of the quencher. These qualities are characterized by the sensor sensitivity which is the ratio of the phosphorescence intensity without quencher (for example, in the 100% argon medium) to the intensity in the 100% oxygen medium. The higher this ratio, the more reliable and more qualitative is the sensor medium. In addition, the response time to the change of the gas medium (the time of signal rise and fall when going

TABLE 2. Spectral-Luminescent Characteristics of Halogen BODIPY in Solid State Media

Compound, medium	$\lambda_{\max \text{ abs.}}$ , nm	$\lambda_{\max \text{ fl.}} (\lambda_{\text{exc}})$ , nm	$\lambda_{\max \text{ ph.}}$ , nm	$\gamma_{\text{ph}}$ (ethanol, 77 K)	$I_{\text{Ar}}/I_{\text{O}_2}$
$\text{I}_2(\text{CH}_3)_4\text{BODIPY}$ in the PVB film	540 ( $A_{540} = 1.1$ )	557 (535)	805	0.6	29
$\text{Br}_2(\text{CH}_3)_4\text{BODIPY}$ in the PVB film	532 ( $A_{532} = 0.4$ )	547 (530)	798	0.006	4.2
$\text{I}_2(\text{CH}_3)_4\text{BODIPY}$ in TEOS + VTEOS (7:3) matrix	537 ( $A_{537} = 0.17$ )	553 (532)	794	0.6	2.5

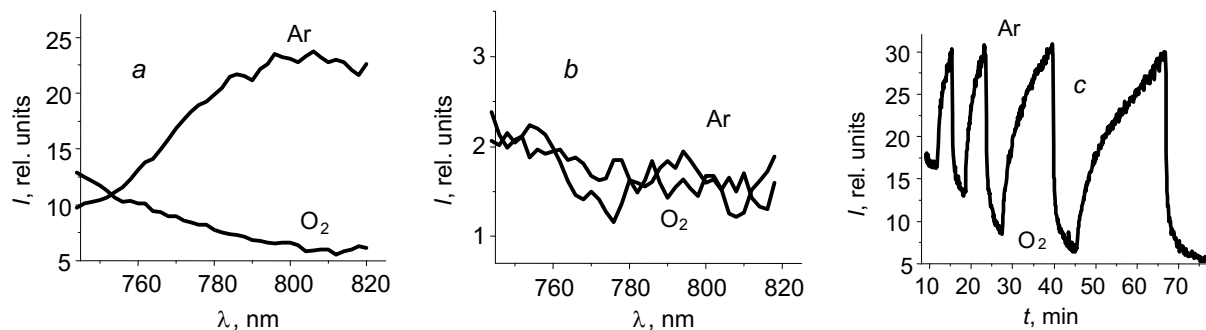


Fig. 6. Phosphorescence spectra of  $\text{I}_2(\text{CH}_3)_4\text{BODIPY}$  in the PVB film (*a*) and TEOS + VTEOS (7:3) matrix (*b*) together with the change in the phosphorescence intensity of  $\text{I}_2(\text{CH}_3)_4\text{BODIPY}$  in the PVB film depending on the composition of the gas mixture (Ar +  $\text{O}_2$ ): intensity maxima in the 100% Ar atmosphere (*c*). Here minima correspond to Ar +  $\text{O}_2$  in the ratios 90:10, 80:20, 50:50, 20:80, and 0:100% in the cell compartment.

over to pure argon or pure oxygen) is important. In the event that this time does not exceed 3–5 min, this sensor is considered suitable for practical application [10].

As already mentioned above, we failed to incorporate neutral forms into halogen BODIPY in silicate matrices in sufficient concentration, which is confirmed by the spectral characteristics. On the other hand, sufficient amount of halogen BODIPY was incorporated into the PVB film. Low radiation damage threshold does not allow the PVB films to be used as laser media, but this polymer is quite suitable for the sensor media with low light fluxes. Table 2 presents the spectral-luminescent properties and the sensor sensitivity of the solid-state samples painted by halogen BODIPY derivatives.

From Fig. 6 it can be seen that the sensitivity sufficiently high for practical applications is characteristic for the PVB film with  $\text{I}_2(\text{CH}_3)_4\text{BODIPY}$  (Table 2 and Fig. 6*a* and *c*). The response time when going over from neutral argon to active oxygen quencher is 2–3 min, whereas the transition to argon takes 10–30 min. Such difference can be caused by intensive interaction of the luminophore with the polymer or increased time of destruction of the intermediate complex formed by triplet molecules with subsequent removal of oxygen, actively interacting with BODIPY, from pores of polymer materials and its substitution by argon. The same  $\text{I}_2(\text{CH}_3)_4\text{BODIPY}$  complex in small concentration incorporated into the silicate TEOS + VTEOS matrix (Fig. 6*b*) and  $\text{Br}_2(\text{CH}_3)_4\text{BODIPY}$  complex incorporated into the PVB film (Table 2) practically do not feel oxygen, which can be caused by insufficient permeability of nanopores in the silicate matrix for the quencher and weak quenching of the inefficient luminophore – dibromo BODIPY [12] in the PVB film.

## CONCLUSIONS

Our investigations have demonstrated the possibility of synthesis of solid-state laser media for the visible range of the spectrum (550–564 nm) based on alkyl BODIPY derivatives incorporated into the three-component silicate



APTEOS + PTEOS + MTEOS gel matrix having high laser damage threshold. Further investigations of the role of the hybrid silicate matrix in reversible photo-unpainting of incorporated alkyl BODIPY derivatives and restoration of their painting in the darkness aimed at creation of photostable solid-state laser media with high damage threshold to laser radiation are required.

The possibility of the development of high-sensitive solid-state sensor materials based on halogen derivative of  $I_2(CH_3)_4BODIPY$  in the PVB films intended for optical determination of the oxygen content in a gas mixture was demonstrated. Investigations will be continued aimed at reduction of the response time of the optical sensor, that is, elimination of time delay of destruction of the active oxygen complex with phosphorescing compound and its subsequent substitution by an inert gas.

This work was supported in part by the Russian Foundation for Basic Research (Grant No. 14-03-90011-Bel\_a), Belorussian Republican Foundation for Fundamental Research (Grant No. F14R-096), and the President of the Russian Federation (Grant No. NSh-1305.2014.2).

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