Spectroscopic, lasing, and photochemical characteristics of organic molecules in silica gel-matrices

R.T. Kuznetsova,[1] Yu.A. Manekina,[1] E.N. Tel'minov,[1] G.V. Mayer,[1] S.M. Arabei,[2] T.A. Pavich,[2] and K.N. Solov'ev[2]

[1] *V.D. Kuznetsov Siberian Physical-Technical Institute at Tomsk State University, Tomsk, Russia*
[2] *Institute of Molecular and Atomic Physics, Belarus National Academy of Sciences, Minsk, Belarus*

Received October 24, 2005

The spectral-luminescent, photochemical and lasing characteristics of some laser dyes: Rhodamine, phenalemine, oxazole, and benzonitrile derivatives, doped into inorganic and hybrid (organic-inorganic) solid silica matrices of different composition and shapes have been studied under conditions of pumping by low-intensity emissions from electron tubes and lasers at different wavelengths and intensities. It has been shown that optical properties of thin silica gel-films (< 1 μm) doped with organic molecules have some peculiarities compared with 3-D gel-matrices. The photostability, lasing efficiency, and spectral characteristics of solid-state matrices doped with dyes have been determined as functions of the pump intensity and absorbed pump energy. It has been shown that the molecular and laser photostability of dyes in gel systems is usually higher as compared with that in ethanol solutions. The proton transfer from solid matrices to the proton-acceptor centers of some dyes is observed in the ground and excited states. The reasons of the changes in molecular spectroscopic characteristics in gel-systems under laser pumping are discussed.

Introduction

The development of modern high technologies is impossible without wide use of tunable lasers, whose best performance characteristics were demonstrated in solutions of organic molecules.[1] However, their application is restricted by the difficult control, large size, and high fire and explosion risk during the operation. The wider application of tunable dye lasers, whose radiation covers almost the entire visible and UV regions and satisfies many tasks of optoelectronics, requires their improvement connected, first of all, with the creation of mini- and microlaser systems, simplification of the pumping system, etc. This stimulates the investigations associated with the development of solid-state active elements for tunable lasers using both luminescent polymers and organic polymers, e.g., polymethylmethacrylate (PMMA), and inorganic, e.g., silica matrices doped with organic molecules.

The advantage of silica matrices like tetraethoxysilane (TEOS) and vinyltriethoxysilane (VTEOS) over matrices of the PMMA is caused by higher threshold of the laser strength of these materials – they stand the laser radiation of the power up to 350 MW/cm^2 without surface damage, as well as by high transmission in the UV region up to 250 nm, which allows the excitation of dyes in these matrices to be performed by the radiation of a XeCl laser (λ_r = 308 nm) – the most versatile source for dye pumping.[2]

It is quite urgent problem now the excitation of electroluminicsence in solid-state film structures with participation of organic luminophores for creation of light-emitting devices, because their obvious advantage over inorganic luminophores is indisputable. Higher efficiency of emission and broadband luminescence in the visible and UV spectral regions[3] are among these properties. It seems very attractive to obtain broadband stimulated emission upon the direct electric excitation of thin-film emitting layers. However, the experimental solution of this problem faces certain difficulties.[4] Therefore, it is worth studying, at the first stage, the properties of the spontaneous and stimulated emission of thin-film layers under optical excitation. In practice of using light-emitting media, a very important role belongs to phototransformations of organic molecules under high-power optical excitation, because they depend on the interaction of excited molecules and determine the service life of such media.

The goals of this study were the stationary and induced absorption spectra and fluorescence spectra of some organic molecules, doped into silica gel-matrices and thin ($\ell \leq 1$ μm) gel-films made from them, as well as to obtain stimulated emission from solid-state samples under laser excitation in the UV and visible spectral regions, and to determine the characteristics of the molecular and lasing photostability of these molecules in gel-systems for different compositions and geometric shapes of the matrix.

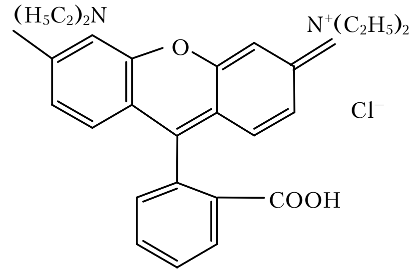
Objects and methods of investigation

The choice of organic dyes, whose structure formulas are given in Fig. 1, for doping into silica gel-systems is caused, first of all, by the fact that earlier we have studied all of them in solutions and that most of them lase in the UV and visible regions.[5]

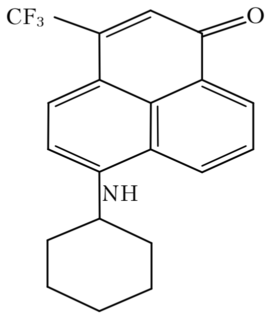
In addition we have studied the molecule of 4-dimethylaminobenzonitrile (DMABN) (Fig. 1), being a model molecule for the study of intermolecular interactions (IMIs), in solutions and used it in this case to investigate the mechanism of interaction of organic molecules with the gel-matrix.

The method of preparation of gel-matrices and gel-films and doping of organic molecules in them has been described in detail in Ref. 2. In this paper, additionally, formamide was added to the initial mixture in some cases. This, ultimately, improved the quality of matrices and prevented them from cracking. In such a case, there was no need in the further mechanical treatment of the sample faces. After polymerization of the sol-solution, placed in a 1×1×3 cm rectangular cell, we obtained a colored solid-state sample shaped as parallelepiped with the dimensions ≈ 0.5–0.6×0.5–0.6×1.5–1.4 cm^3. Thus, once the samples have been dried, their volume decreased 5.5–by 8.5 times depending on the ratio of components in the composition of the gel-matrix. The thickness of the gel-films was measured with a Linnik microinterferometer (MII-4), an MIS-11 double microscope, and an LEF-3M1 ellipsometer. The film thickness was found to be within 0.15–0.3 for the one-layer film, 0.3–0.7 μm for the two-layer film, and 0.8–1.1 μm for the three-layer film, which also depended on the composition, i.e., the viscosity of the sol-solution, the films were made from.

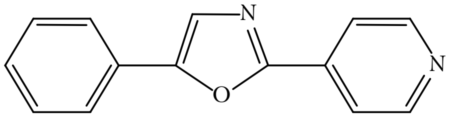
The stationary absorption and fluorescence spectra were recorded with an M40 Specord spectrophotometer, a Hitachi-850 spectrofluorimeter, and an SM2203 Solar (Belarus) spectrometer. The induced short-lived absorption spectra of some samples were recorded with an original setup for laser photolysis, which has been described in detail in Ref. 6. The radiation sources were a XeCl laser (λ_{las} = 308 nm, $\tau_{1/2}$ = 10 ns; E_{las} up to 40 mJ/pulse) and the second harmonic of an Nd:YAG laser (λ_{las} = 532 nm, $\tau_{1/2}$ = 15 ns; E_{las} up to 120 mJ/pulse). The energy characteristics of the excitation and emission were measured with an IMO-2N, KTP-2, and Gentec-E optical power meters. The spectroscopic characteristics of the radiation were determined for one pulse with a Real laser spectrometer (instrumental function broadening the lasing spectra $\Delta\lambda$ = 5 nm; the spectra without correction are shown in Figs. 3, 4, 6, and 7). The lasing spectra were recorded, as a rule, at different positions of a light guide relative to the sample, and therefore the intensities of different spectra in the figures should not be compared.



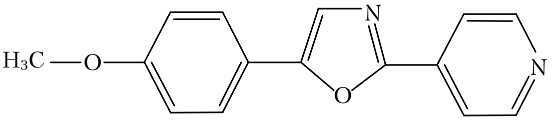
Rhodamine B (RB)



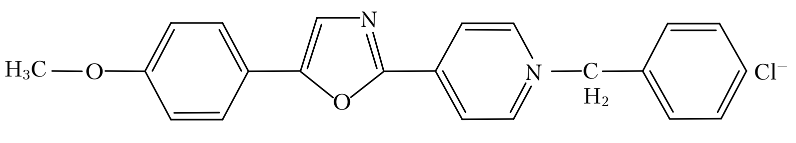
Phenalemine 512 (Ph 512)



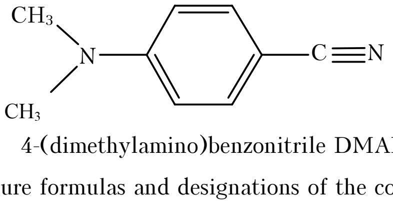
2-(4-pyridil)-5-phenyloxazole (4PyPO)



2-(4-pyridil)-5-oxymethylphenyl-oxazole (4PyOCH$_3$PO)



Quaternized salt 2-(4-pyridil)-5-oxymethyl-phenyloxazole
(4PyOCH$_3$POCH$_2$P$^+$Cl$^-$)



4-(dimethylamino)benzonitrile DMABN

Fig. 1. Structure formulas and designations of the compounds studied.

The stimulated emission of dyes in volume gel-matrices was excited in the transverse geometry in a 1–3 cm long cavity, formed by a 100% reflection mirror and a face of the solid-state sample. In this case, exciting radiation was focused onto a 0.5×0.05 cm strip, which was determined by the sample dimensions and did not satisfy the optimal pump conditions for achieving the maximum efficiency of lasing in each particular case. In the case of thin films, there was no cavity, that is, the stimulated emission took place owing to the single-pass amplification in the excited volume $V \approx 0.05 \times 1.5 \times 10^{-4}$ cm^3 by the method of traveling-wave lasing.[7]

We have developed the spectroscopic method for determination of the photostability characteristics of solutions[5] and modified it for solid samples in this case. The parameters to be determined were the molecular photostability (quantum yield of phototransformations) and the lasing photostability (total specific pump energy, absorbed by the pumped volume until the initial lasing efficiency decreased down to a certain level: 50% for P_{50} and 80% for P_{80}).

The peculiarity of measuring these characteristics in gel-matrices is that the dye concentration and the pumped volume in solid samples should be known. The approach we used to estimate the dye concentration in films yields the maximum possible value of the quantum yield of phototransformations; the error of the method is 10%. The specific pump energy E_{abs} in the case of thin films was determined quite accurately:

$$E_{\text{abs}}^{\text{pulse}} = (E_{\text{inc}} - E_{\text{trans}}/T_{\text{subs}})/V_{\text{pump}},$$

where E_{inc} and E_{trans} are the incident and transmitted pump energies per pulse; T_{subs} is the transmittance of the pure substrate at the pump wavelength; $V_{\text{pump}} = \ell_{\text{film}} S_{\text{pump}}$, and the error in this case does not exceed 10%. In the case of volume gel-matrices, $V_{\text{pump}} = \ell_{\text{p}} S_{\text{pump}}$, where ℓ_{p} is the depth of the pump radiation penetration, was estimated from the value of the 100× attenuation of the pump radiation due to the saturation of the absorption, that is, $T = I/I_0 = 0.01$, where I and I_0 are the intensities of the attenuated and incident radiation, under the condition that the absorption by lasing molecules from the excited state at the pump wavelength is much lower than that from the ground state. Then

$$\ell_{\text{p}} = -\ell g(I/I_0)/C\varepsilon,$$

where C is the concentration of molecules in the gel-matrix; ε is the decimal molar absorption coefficient or the extinction coefficient at λ_{pump}. The estimation made for Ph512, for example, at $W_{\text{pump}} \approx 40$ MW/cm^2, where W_{pump} is the pump power density, gives $\ell_{\text{p}} \approx 0.01$–$0.007$ cm, which is close to the value of ℓ_{p} estimated from the dye lasing area at the transverse excitation geometry. In the following experiments, the value of ℓ_{p} for a dye was determined from the lasing area at the exit from the sample.

The error in the estimation of the volume pumped in this way is rather high, about 25%, which leads to an error of about 30% in the estimation of the lasing photostability for volume gel-matrices P_{50} and P_{80}.

Results and discussion

Tables 1–3 summarize the results of investigation of the spectral-luminescent and lasing properties, as well as photostability characteristics, for laser dyes in solid-state volume gel-matrices and thin gel-films as compared with solutions of the corresponding compounds.

It follows from the Tables that the spectral-luminescent characteristics of the dyes change insignificantly upon the transition from solution to the matrix and more significantly upon the modification of the matrix in both the composition and geometry: volume matrix or thin film.

Table 1. Spectral-luminescent and lasing characteristics and photostability of oxazole derivatives doped into silica gel-matrices and gel-films under the excitation by a XeCl-laser radiation

Medium	$\lambda_{\text{max}}^{\text{abs}}$, nm	$\lambda_{\text{max}}^{\text{fl}}$, nm	W_{pump}, MW/cm^2	$\lambda_{\text{max}}^{\text{em}}$, nm	$\Delta\lambda^{\text{em}}$, nm	φ_{phot}	$P_{50,80}$, kJ/cm^3
4PyPO, ethanol	330	390	30	398	2	$1.6 \cdot 10^{-3}$	$P_{50} = 0.16$
4PyPO, ethanol + HCl	380	460	30	500	2		
4PyPO, TEOS, matrix		470	30	504	58		
4PyPO, TEOS, gel-film, 2 layers	330+380	465	2 45	465 465	75 74	10^{-2}	
4PyOCH$_3$PO, ethanol			30	448	2	$3 \cdot 10^{-3}$	$P_{80} = 0.012$
4PyOCH$_3$PO, TEOS, matrix		520+570	30	579	2		$P_{80} = 0.6$ $P_{50} = 1.6$
4PyOCH$_3$PO, TEOS, gel-film, 2 layers	340+420	535+570	2 30	545 530+550	90 104	$3 \cdot 10^{-3}$ 3–$4 \cdot 10^{-3}$	
4PyOCH$_3$PO, TEOS + VTEOS, gel-film, 2 layers	340+420	450+530	45	450+530	118		
4PyOCH$_3$POCH$_2$P$^+$Cl$^-$ TEOS + VTEOS, gel-film, 3 layers	422	545	2 20	545 547	90 2	$2.3 \cdot 10^{-3}$ $8 \cdot 10^{-5}$	$P_{50} = 64$

Table 2. Spectral-luminescent and lasing characteristics and photostability of Ph512 doped into silica gel-matrices and gel-films under the UV and visible laser excitation

Medium, λ_{pump}, nm	λ^{abs}_{max}, nm	λ^{fl}_{max}, nm	W_{pump}, MW/cm^2	λ^{em}_{max}, nm	$\Delta\lambda^{em}$, nm	φ_{phot} las. (fl)	$P_{50,80}$, kJ/cm^3
Ph512, ethanol, 308	562	602	40	620	3	$3 \cdot 10^{-3}$	$P_{80} = 0.2$
Ph512, ethanol + 0.5%HCl, 308	513	592					
Ph512, TEOS + VTEOS gel-film, 2 layers, 308	575	620	3	620	56	$2 \cdot 10^{-3}$	
			7	618	4		
			40	616	5	$5 \cdot 10^{-4}$	$P_{80} = 1.2$ $P_{50} \geq 2.8$
Ph512, TEOS + VTEOS-gel-film, 2 layers, 532	575	605	5	603	2	$1.5 \cdot 10^{-4}$	
			20	602	4.5		
			40	601	4.5		
			80	601	9		
Ph512, VTEOS-gel-film, 2 layers, 308	540+566	595	7	636	2	$5 \cdot 10^{-4}$	$P_{50} = 0.8$
			15	637	2		
Ph512, TEOS-matrix, 532		660	20	620	58		
			80		58		
			150		55		
Ph512, TEOS + VTEOS-matrix, 532		625	140	620	2		

Table 3. Spectral-luminescent and lasing characteristics and photostability of RB doped into silica gel-matrices and gel-films under the UV and visible laser excitation

Medium, λ_{pump}, nm	λ^{abs}_{max}, nm	λ^{fl}_{max}, nm	W_{pump}, MW/cm^2	λ^{em}_{max}, nm	$\Delta\lambda^{em}$, nm	φ_{phot}	$P_{50,80}$, kJ/cm^3
RB, ethanol, 532	550	580	20	598	1	10^{-5}	$P_{50}{}^{(308)} = 0.1$ $P_{80}{}^{(532)} \gg 0.085$
RB, TEOS-matrix, 308		640	5	629	1		
			10	628	1		$P_{50} = 1.8$
			20	627	1		
			40	626	3		$P_{50} = 1.5$
RB, TEOS-matrix, 532		640	20	627	3		
			40	626	4		$P_{80} > 112$
			60	626	5		
			100	626	7		
			150	626			
RB, TEOS + VTEOS (70:30) gel-film, 3 layers, 308	560	592	3	606	1		
			7	605	1	10^{-3}	$P_{50} = 1.5$
			15	602	2		
			30	600			
RB, TEOS + VTEOS (70:30) gel-film, 3 layers, 532	560	592	15	602	4.5	$5 \cdot 10^{-6}$	$P_{50} > 300$
			25	601			
RB, TEOS + VTEOS (50:50) gel-film, 308	555	587					

In addition, it follows from the value of the dye optical density in thin films (provided that the extinction coefficient does not change upon the transition from solution to the gel-film) that the increase of the dye concentration due to the decreasing volume in the process of synthesis of the gel-matrix is much higher (20–40 times) in the case of formation of the gel-film with $\ell_f \leq 1$ μm than in the case of volume gel-samples (approximately 5–8 times). Similar facts were also noted in other papers, discussing the optical characteristics of organic molecules in thin films.[8–10] These facts are explained either by the increase in the volume of pores, containing the dye, in thin films, as compared to volume matrices[9] or by an increase in the reflection upon the anomalous change of the refractive index in the dye absorption band, which leads to the seeming increase of the optical density of thin films, whose thickness is comparable with the wavelength of the incident radiation.[10] The causes of these changes are still under discussion and call for further investigations. In this connection, the research into the peculiarities of the interaction of organic molecules with a solid matrix is very important.

For this purpose, we have studied the spectral-luminescent characteristics of the model DMABN molecule in volume silica matrices and thin films. As can be seen from Fig. 2, the emission of DMABN in the silica matrix occurs in two bands, as well as in the ethanol solution.

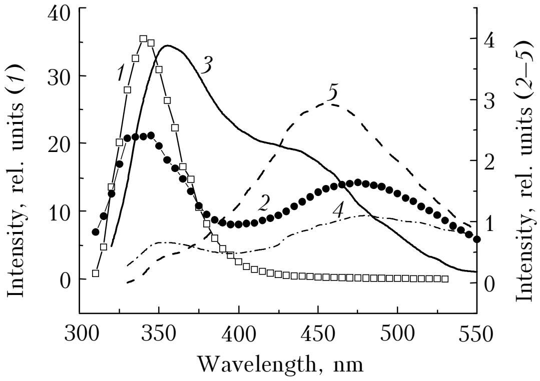


Fig. 2. Fluorescence spectra of DMABN in hexane (*1*), ethanol (*2*), TEOS + VTEOS gel-film (*3*), TEOS gel-matrix (*4*); TEOS + VTEOS gel-matrix (*5*); λ_{pump} = 295 nm.

The decrease in the intensity of the long-wave fluorescence of DMABN with the increasing viscosity of the medium (glycerin, frozen ethanol), which is attributed to TICT conformations[11] occurring in the solid silica matrix is absent. This fact again confirms the specific character of the interaction of organic molecules with OH-groups, paving the nanometer-sized pores of silica matrices, which was noted in Refs. 12 and 13. The change of the intensity ratio between the long-wave and short-wave fluorescence bands (curves *3–5* in Fig. 2) can be caused by the radiation re-absorption in the volume matrix with DMABN, which has the marked absorption nearby 350 nm. The same effect is also observed as the concentration increases from 10^{-5} to 10^{-3} mol/liter in ethanol solutions of DMABN.[14]

The oxazole derivatives, which produce cations and photocations upon the interaction with a proton-donor solvent (addition of mineral acids) as a result of proton attachment to the nitrogen atom of the pyridine cycle,[5] also produce these forms in the silica gel-matrices (see Table 1). As to 4PyPO, it absorbs in the most polar TEOS gel-film, being mostly in the neutral form (λ_{max} = 330 nm) and insignificantly in the cation form (λ_{max} = 380 nm) and fluoresces only in the cation and dication forms, what is indicative of the production of photocations. The lasing of 4PyPO under the XeCl pumping was obtained in neither films nor matrices, since the intense induced absorption,[15] weakening somewhat in the long-wave region (500 nm), is observed in the common emission range of all the forms. This leads to the narrowing of the emission band under the laser pumping to $\Delta\lambda_{1/2}$ = 58 nm owing to the larger fraction of the stimulated emission as compared to the TEOS + VTEOS system ($\Delta\lambda_{1/2}$ = 105 nm), in which 4PyPO emits in the range from 400 to 450 nm [Ref. 2].

The efficiency of phototransformations of, for example, 4PyPO upon the transition from nonpolar pentane, in which the photocation is not produced, to water, in which both neutral and cation forms fluoresce, increases roughly threefold.[5] Unfortunately, it is difficult to compare directly the molecular photostability of 4PyPO in the solution $\varphi = 1.6 \cdot 10^{-3}$ (lasing mode) and TEOS in the gel-film $\varphi = 10^{-2}$ (fluorescence mode), because in this case not only the medium and its polarity, that is, the form of molecular excitation, are different, but also the emission mode is different: it has been shown in Ref. 5 that in the lasing mode the photostability of organic molecules increases as compared to the fluorescence mode.

The metoxyphenyl-derivative of 4PyPO, i.e., $4PyOCH_3PO$, lases in the TEOS gel-matrix in the dication form (579 nm), while its quaternized salt $4PyOCH_3POCH_2P^+Cl^-$ lases in the TEOS+VTEOS gel-film in the cation form (547 nm) (Fig. 3).

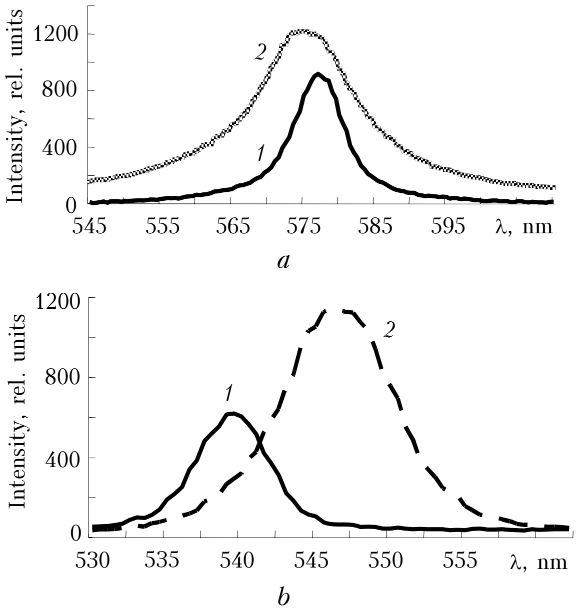


Fig. 3. Lasing spectra: $4PyOCH_3PO$ in TEOS gel-matrix before (*1*) and after (*2*) irradiation with XeCl laser radiation. E_{abs} = 1.5 kJ/cm^3; W_{pump} = 30 MW/cm^2 (*a*); $4PyOCH_3POCH_2P^+Cl^-$ in TEOS + VTEOS (70:30) gel-film (2 layers) – curve *1*, (3 layers) – curve *2* under the XeCl laser excitation (*b*). W_{pump} = 30 MW/cm^2.

The shift of the lasing spectrum for the two- and three-layer films (Fig. 3*b*) is likely connected with the re-absorption of different forms rather than with the re-absorption from the ground state, because the Stokes shift in these compounds is high (≅ 6000–8000 cm^{-1}). The absence of lasing from $4PyOCH_3PO$ in the TEOS and TEOS+VTEOS thin films is connected, as in the case with 4PyPO, with the re-absorption of radiation from different forms by each other: this leads to the broadband fluorescence, covering almost the entire visible region: from 400 to 650 nm ($\Delta\lambda_{1/2}$ = 118 nm). The results obtained indicate that gel-films with oxazole derivatives are highly promising for not only laser active media but also for electroluminescent layers, because not only the broadband photoluminescence is obtained, but it is also shown that these compounds can be charge carriers and this property improves with the excitation of the molecules. The photostability of these media is very high (especially in the lasing mode) and it is accompanied by the spectrum broadening in the process of lasing, which is important for practical use.

The solid gel-samples with Ph512 emit well in the red spectral range from 600 to 700 nm, which is of very important for medical applications. Nearly all samples, except for Ph512 in the TEOS matrix, lase in this range upon the excitation both in the long-wavelength absorption band (532 nm) and in the high-excited state (308 nm). The absence of lasing from Ph512 in the TEOS gel-matrix is explained by the formation of the ion form (interaction with the proton of the OH group of the gel-matrix of the Ph512 nitrogen atom). The fact that the fluorescence spectra of Ph512 in TEOS matrix are shifted to the long-wavelength region and the intensity of this radiation is low can be caused by the formation of the cation in the excited state in the carbonyl group, as was shown in Ref. 5 for aminocoumarin. In the process of lasing, the spectrum of Ph512 in the TEOS+VTEOS gel-films almost does not change in the half-width, only the intensity decreases and an insignificant shift is observed (Fig. 4).

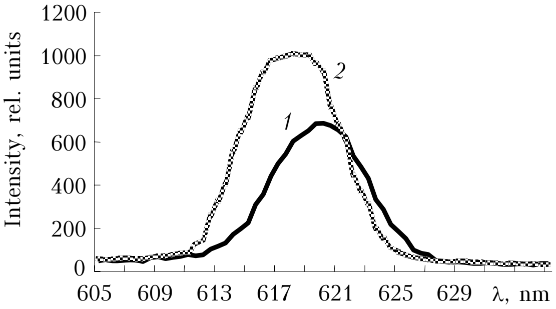


Fig. 4. Lasing spectra of Ph512 in the TEOS + VTEOS (70:30) gel-film (2 layers) before (curve *1*) and after irradiation (*2*) with XeCl laser radiation. $E_{\text{abs}} = 2.7$ kJ/cm^3; $W_{\text{pump}} = 7$ MW/cm^2.

The molecular photostability of Ph512 in the silica films is identical ($\varphi = 5 \cdot 10^{-4}$) and higher than in the ethanol solutions ($\varphi = 2 \cdot 10^{-3}$). However, the lasing photostability of Ph512 in the pure VTEOS gel film is lower than in the hybrid TEOS+VTEOS gel-film. This phenomenon is also connected with the significant shift of the lasing spectrum to the long-wavelength region, although the fluorescence in this sample lies in the shortest-wavelength range (see Table 2). The cause of this phenomenon is still to be understood.

Very interesting results were obtained for the solid gel-matrices and films with RB (see Table 3). All the studied samples lase, as in the previous case, in the red spectral region. However, unlike Ph512, a more significant shift of the spectrum is observed depending on the chemical composition of the gel-system and its geometrical shape, which is connected with the smaller Stokes shift and significant influence of re-absorption on the position of the lasing spectrum of RB in the volume gel-matrix.

The quantum yield of phototransformations, determined for the three-layer TEOS+VTEOS film with RB under the conditions of lasing, amounts to 10^{-3} under the UV excitation (308 nm) and $5 \cdot 10^{-6}$ under the excitation into the long-wavelength absorption band (532 nm) (see Table 3). This agrees with the variation of the molecular photostability of Rhodamine dyes in solutions[5,16] and is explained by the presence of high-excited photochemically active state, in which the proton-acceptor (or electron-donor) capability of the molecule increases significantly,[5] leading to formation of the intermediate photoproduct with its following transformation.

The lasing photostability of the gel-samples with RB also increases considerably upon the excitation in the long-wavelength band as compared to the UV excitation. The exact value of P_{50} is not determined in this case, since after the absorption in the TEOS+VTEOS gel-film $E_{\text{abs}} > 60$ kJ/cm^3, while in the TEOS gel-matrix it is larger than 100 kJ/cm^3 for the radiation with $\lambda = 532$ nm, the efficiency of lasing does not decrease compared to the initial one, as is usually observed in other cases, but continues to increase (Fig. 5).

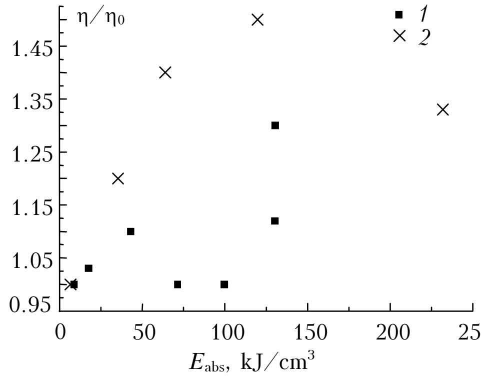


Fig. 5. Relative efficiency of RB lasing in the TEOS gel-matrix (curve *1*) and TEOS + VTEOS (70:30) gel-film (*2*) as a function of the total absorbed specific pump energy of the second harmonic of Nd:YAG laser. $W_{\text{pump}} = 25$ MW/cm^2.

This agrees with the variation of the RB lasing spectrum: short-wavelength shift and broadening of the spectrum are observed, and it is seen that, in the course of irradiation, new lasing centers arise, along with the old ones, in the samples in both a thin gel-film and in a volume gel-matrix (Fig. 6).

The UV irradiation (308 nm) also causes the short-wavelength shift of the lasing spectra, but the spectrum broadening is not observed (Fig. 7), that is, the initial centers disappear immediately, and therefore the service life at such an excitation becomes shorter (see Table 3).

These peculiarities can be connected with the easier formation of the zwitterion form of the molecule $(\text{RCOO}^-)^+$ in the excited S_1 state, well emitting and lasing with the lower threshold, and its photoproducts, lasing in the shorter-wavelength range. The shift of the zwitterion-neutral equilibrium in the S_1 state is partly reversible,[5] and therefore in the silica gel-matrix, capable of specific interactions, under the excitation at $\lambda = 532$ nm simultaneous lasing of many forms is observed (Fig. 6*a*). Under the UV excitation of these samples, RB transforms into the S_4 excited state, in which the interaction occurs through other centers (nitrogen substituted amides).[5] In this case, an irreversible photoproduct is formed immediately, and it decreases the yield of the laser radiation: the shape of the absorption spectrum changes as a result of the UV irradiation (short-wavelength shift and broadening) and does not change upon the excitation in the long-wavelength band (Fig. 8).

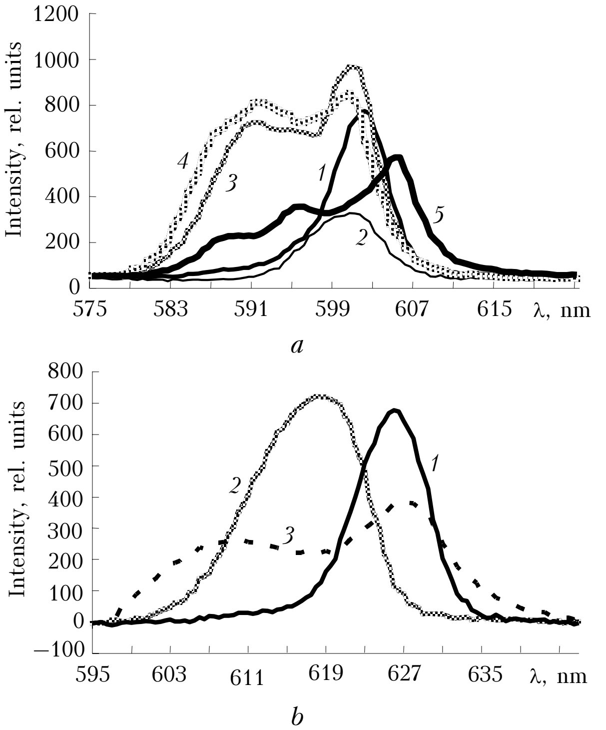


Fig. 6. Lasing spectra of RB: in the TEOS + VTEOS (70:30) gel-film (three layers) before (curve *1*) and after (*2–5*) irradiation by the second harmonic of Nd:YAG laser; W_{pump} = 18 MW/cm^2; E_{abs} = 69 (*2*); 157 (*3*); 229 (*4*); and 293 kJ/cm^3 (*5*) (*a*); in the TEOS gel-matrix before (curve *1*) and after (*2, 3*) irradiation by the second harmonic of Nd:YAG laser. E_{abs} = 89 kJ/cm^3; W_{pump} = 100 MW/cm^2. W_{rec} = 100 (*1, 2*), 3 MW/cm^2 (*3*) (*b*).

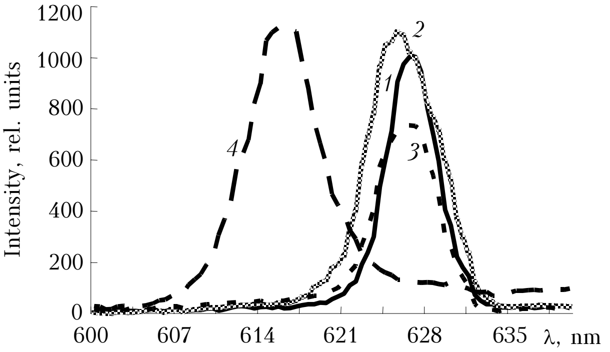


Fig. 7. Lasing spectra of RB in the TEOS gel-matrix before (curves *1*, *2*) and after (*3*, *4*) irradiation with a XeCl laser radiation. E_{abs} = 1.7 kJ/cm^3. W_{pump} = 10 (curves *1*, *3*), 40 MW/cm^2 (*2*, *4*).

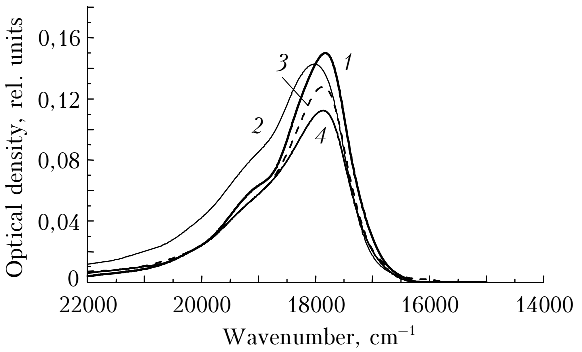


Fig. 8. Absorption spectra of RB in the TEOS + VTEOS (70:30) gel-film before (curves *1*, *3*) and after irradiation with XeCl laser radiation (*2*) and second harmonic of Nd:YAG laser (*4*). E_{abs} = 5 (*2*); 290 kJ/cm^3 (*4*). W_{pump} = 10 (*2*), 20 MW/cm^2 (*4*).

Conclusions

Thus, the investigations carried out have shown that the silica gel-matrices are promising bases for creation of solid-state active media for mini- and micro-lasers, as well as thin-film light emitting devices in a wide spectral range (Δλ > 250 nm).

The long service life (lasing photostability) of active media based on RB in the silica gel-matrix under the excitation by the second harmonic of the Nd:YAG laser and even the increase of the efficiency in the course of lasing are connected with the peculiarities of the molecular structure of RB and its specific interactions with the OH-group of the silica matrix, leading to the formation of ion forms of the RB molecule as an intermediate reversible photoproduct. In this case, the lasing spectrum broadens significantly to the short-wavelength region as compared to the initial one.

The higher stability of organic molecules in the gel-matrices compared to the solutions is likely connected with the fact that the molecules are attached by the strong specific interaction on the pore surfaces with the OH-groups of the silica gel-matrix. This decreases the possibility of their further interaction with the intermediate short-lived products (ion forms), that is, the formation of the irreversible photoproducts.

The existence of several emitting ion forms of the molecules under study in the ground and excited states in the silica gel-matrices allows us to hope for the use of thin silica gel-films with these compounds for electroluminescent devices.

Acknowledgments

This work was supported, in part, by the Russian Foundation for Basic Research (Grant No. 04–02–81002) and Belorussian Foundation for Basic Research (Grant No. F04P–001).

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