

Silicate-matrix active media for tunable solid-state lasers

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Abstract. The lasing characteristics of solid active media based on laser dyes (rhodamines, coumarin 2, paraterphenyl) doped into silicate bulk matrices and thin films of different compositions are studied upon optical excitation. The lasing efficiency, photostability, and spectral parameters of laser media are investigated as functions of the excitation wavelength and intensity. Variations in these parameters due to the interaction of organic luminophores with a silicate matrix and radiation are discussed.

Keywords: solid-state laser media, thin gel films, organic luminophores, silicate matrices, photostability, spectra, lasing, radiation.

1. Introduction

Recent studies have shown that the use of solid-state elements based on polymer matrices doped with organic luminophores instead of liquid solutions of these luminophores is more promising for the improvement of tunable lasers emitting in a broad spectral range. It has been found that inorganic polymers prepared by the sol–gel method based on tetraethoxysilane (TEOS) doped with luminophores have advantages over organic polymers, for example, polymethyl methacrylate due to their high strength and transparency in the UV region [1]. The outlook for using light-emitting thin-film devices in large-area screens and broadly tunable lasers directly excited by the electric current require the increase in the yield of electroluminescence of thin ($d < 1 \mu\text{m}$) films [2, 3]. This in turn is impossible without the fundamental study of the interaction of such elements with radiation at different wavelengths and different intensities and the interaction between the components contained in a solid-state element. In addition, some spectral and luminescent parameters of organic luminophores doped into thin films differ from

those in bulky matrices [1, 4, 5]. Therefore, it is necessary to study the interaction of organic luminophores with inorganic matrices of different compositions and geometrical shape. In this paper, we report the manufacturing of solid-state laser elements for optical excitation in the visible and UV regions and study the dependence of their parameters on the interaction of luminophores in the ground and excited states with solid silicate matrices and thin films.

2. Experimental

Solid-state polymer elements, bulky ($V = 0.5 \times 0.5 \times 1.5 \text{ cm}$) and thin-film ($d = 0.4 - 1 \mu\text{m}$), were fabricated by the sol–gel synthesis from reaction mixtures including TEOS, vinyltriethoxysilane (VTEOS), ethanol, and water with additions of mineral acids and formamide as a catalyst for the sol–gel synthesis. The gels obtained in this way were dried by the method described in [1, 5].

The introduction of some amount of VTEOS along with TEOS reduces the fraction of the OH groups on the surface of pores of a prepared gel matrix and should change the interaction of impurity organic molecules with the matrix. The prepared polymer elements differ in the composition of the reaction components – the ratio of the amounts of TEOS and VTEOS and concentrations of doped dyes, as well as by the shape of samples. Films were deposited on quartz substrates by the centrifugation [1], and bulky elements were used without any additional mechanical processing of their sides.

We used the following organic molecules: p-terphenyl (p-TP), coumarin 2 (C2), and a series of rhodamine dyes [rhodamine 19 (R19), rhodamine C (RC), and rhodamine 101T (R101T)]. All rhodamines have the same non-esterified carboxyphenyl substituent, but different substituents on symmetric amino groups: NHC_2H_5 in R19, $\text{N}(\text{C}_2\text{H}_5)_2$ in RC, and the $\text{NCH}_3\text{C}_3\text{H}_4(\text{CH}_3)_2$ group fixed on the xanthene nucleus in R101T. Such a substitution leads to the red shift of the absorption and fluorescence spectra and changes the interaction of dyes with matrices. These dyes were chosen because their ethanol solutions are laser-active media for the UV, blue, and red spectral regions and their parameters are well studied [6]. To study the influence of rare-earth ions on the physical and chemical characteristics of rhodamines, we prepared gel films doped with RC with the addition of the 2% weight amount of $\text{Ce}(\text{NO}_3)_3$.

Solid-state elements were excited by 308-nm, 10-ns, 20-mJ pulses from a XeCl exciplex laser and by the second-harmonic 532-nm, 15-ns, 70-mJ pulses from a Nd:YAG

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laser in the transverse scheme. The resonator of length 1–1.5 cm was formed by a highly reflecting mirror and the output face of a bulky element. In the case of thin films, the external mirrors were absent and lasing was produced in the ‘zigzag’ resonator due to multiple reflections of super-radiation from air layers and quartz substrates with the refractive index lower than that of the doped film [1]. All the samples were pumped in the same excitation scheme without any optimisation of each of the dyes and the exciting laser, and without the additional mechanical processing of faces and the film surface. Such an approach allows us to observe the influence of the matrix composition on the emission parameters of dyes, while the use of mechanical processing in the future can considerably reduce losses and increase the output power. We measured the output energy (IMO-2H, KTP2, Gentec-E) and spectral characteristics of the exciting and laser radiation (Specord M40 spectrophotometer, Solar CM2203 spectrofluorimeter, Angstrom laser spectrometer with the instrumental function width 6 nm), and determined from them the lasing efficiency, the operating resource, and the quantum yield of phototransformations of organic molecules in silicate matrices with an accuracy of 30%. The operating resource P (J cm^{-3}) was defined as the specific energy absorbed in the lasing volume resulting in the decrease in the lasing efficiency by 20% (P_{80}) and 50% (P_{50}). The lasing volume in a solid element was estimated by the saturation of the optical density with decreasing the pump energy E_{pump} down to its threshold due to absorption, as described in detail in [7]. The thickness of films was measured with a MII4M interference microscope with accuracy of 20%.

3. Results and discussion

Figures 1–4 and Tables 1 and 2 present the spectral, lasing and photochemical parameters of the dyes in hybrid silicate matrices and thin films, which show that such matrices are promising even without any additional processing for the development of tunable miniature lasers.

We obtained for the first time lasing of p-TP and C2 in a solid silicone matrix pumped by a XeCl excimer laser. In the first case, lasing occurs on the most intense vibrational transition of the fluorescence band (Fig. 1) and lasing parameters correspond to the results obtained in [8] for

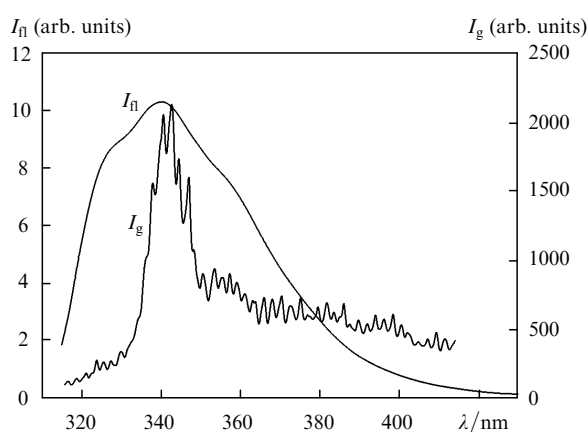


Figure 1. Fluorescence and lasing spectra of p-TP in a bulky TEOS:VTEOS = 7:3 matrix for $\lambda_{\text{exc}} = 308$ nm and the pump power density $W_{\text{exc}} = 40$ MW cm^{-2} .

p-TP lasing in another matrix at different pumping. The resource parameters of p-TP were estimated qualitatively: lasing disappeared after three–five pulses and only a broad fluorescence band remained. To obtain lasing again, it was necessary to pump another region of the element. This can be caused by the lower concentration of p-TP in the silicate TEOS/VTEOS matrix compared to other luminophores due to its poor solubility in the gel solution. To enhance the resource of the p-TP laser, it is necessary to optimise the matrix structure.

The lasing of C2 in a thin film occurs in the long-wavelength wing of the fluorescence band (Fig. 2), which corresponds qualitatively to the lasing of these molecules in solution [6]. The resource P_{50} for C2 in the TEOS:VTEOS = 7:3 film is 1430 J cm^{-3} , which exceeds the resource of coumarines in ethanol and water–ethanol solutions [6]. The output energy decreases during the laser operation due to phototransformations and the laser spectrum shifts to the red (Fig. 2). This type of lasing also agrees qualitatively with lasing of C2 in solutions [6]. On the other hand, no lasing of C2 was observed in TEOS films where the intensity of coumarin fluorescence is decreased due to interaction with the OH groups of matrix pores. Note that no lasing of C102 was also observed in silicate matrices of different compositions [1]. It should be pointed out that the difficulties of obtaining lasing of coumarin derivatives in polymers related to their emission properties in solid matrices were reported in papers [9–11]. These facts show that it is necessary to study the influence of intermolecular interactions of luminophores with silicate matrices on their emission parameters.

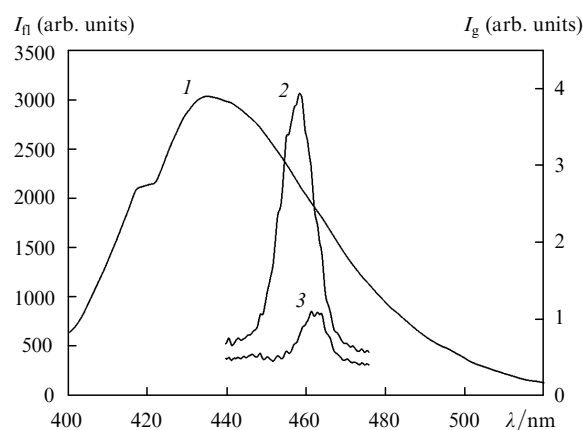


Figure 2. Fluorescence (I) and lasing (2, 3) spectra of C2 in a TEOS:VTEOS = 7:3 gel film ($d = 0.9$ μm , $\lambda_{\text{exc}} = 308$ nm) before (2) and after irradiation (absorption of the energy by the active medium corresponding to the resource P_{50}) (3); $W_{\text{exc}} = 40$ MW cm^{-2} .

The influence of such interactions on the spectral, luminescent, lasing, and photochemical properties have been studied in more detail for rhodamine dyes (Tables 1 and 2), for which the parameters of the ionic molecular forms produced upon interaction with proton donors and acceptors are well known [6]. It follows from Tables 1 and 2 that the lasing efficiency, resource, and phototransformation efficiency considerably decrease upon excitation to the high-energy S_3 state compared to excitation into the long-wavelength absorption band, which is typical for rhodamine solutions [6]. In addition, the lasing spectrum and even fluorescence spectrum shifts depending on the wavelength

Table 1. Spectral, luminescent, lasing, and photochemical parameters of solid-state laser elements based on bulky silicate matrices doped with rhodamines at the concentration $C = 9 \times 10^{-3}$ M.

Dye	Matrix	λ_{exc}/nm	λ_{fl}^{max}/nm	$W_{exc}/MW\ cm^{-2}$	λ_{las}^{max}/nm	Lasing efficiency (%)	$W_{th}/MW\ cm^{-2}$	$P_{50}(P_{80})/kJ\ cm^{-3}$	
R19	TEOS:VTEOS = 7:3	532	553	10	589	7	0.8	1210	
				40	593(592)	10–12			
				80	593	8			
R19	TEOS:VTEOS = 7:3	308	569	4	589	7.2	1	0.9	
				30					
				70					
RC	TEOS:VTEOS = 7:3	532	587	15	620	8	0.8	480	
				30	621	8.5			
				95	622(618)	6.5			
RC	TEOS:VTEOS = 7:3	308	589	10	628	4.6	0.8	1.7	
				100	625(619)				2.1
RC	TEOS:VTEOS = 1:1	532	589	20	608 + 627	5.2	0.6	1025	
				40	627(624)	6–8.5–3			
				75	627(619)	5			
RC	TEOS:VTEOS = 1:1	308	593	40			0.4		
				80	628(625)	12		3	

Note: In parentheses are presented the values of λ_{las}^{max} after irradiation (absorption of the energy by the active medium corresponding to the resource P_{50}); W_{exc} is the pump radiation power density; W_{th} is the threshold power density.

and intensity of exciting radiation and the sample shape (Fig. 3, Tables 1 and 2), which is typical for solid-state elements. This is explained by the excitation and emission of the so-called inhomogeneous solvates, i.e. luminophore molecules located in different environments and differently interacting with a silicate matrix. Inhomogeneous solvates in solutions are quenched due to collisions, so that the equilibrium solvates emit predominantly. For this reason, the dependence of the fluorescence parameters on the excitation parameters is weak or absent at all. The high yield of fluorescence and the values of λ_{fl}^{max} coincide with those for diluted (10^{-6} M) ethanol solutions. For example, for the zwitterion and neutral forms of R19 in ethanol, we

have $\lambda_{fl}^{max} = 555$ and 560 nm, respectively (cf. values $\lambda_{fl}^{max} = 553 - 558$ nm for $\lambda_{exc} = 532$ nm in Tables 1, 2 and Fig. 3).

This suggests that even rhodamine dyes, which are capable of association at high concentrations in solutions, do not form associates in pores of silicate matrices, which agrees with the results presented in [4] and means that organic molecules in pores more efficiently interact with a silicate matrix than with each other. In accordance with the spectral parameters of the dyes, we observed the specific interaction of the carboxyl of rhodamines with proton-acceptor siloxane ($\equiv Si-O-Si \equiv$) groups of the matrix and the substituted amino group with proton-donor silanol

Table 2. Spectral, luminescent, lasing, and photochemical parameters of thin TEOS:VTEOS = 7:3 films doped with rhodamines.

Dye	C/M	d/ μm	λ_{exc}/nm	λ_{abs}^{max}/nm	λ_{fl}^{max}/nm	$W_{exc}/MW\ cm^{-2}$	λ_{las}^{max}/nm	Lasing efficiency (%)	$W_{th}/MW\ cm^{-2}$	$P_{50}, P_{80}/kJ\ cm^{-3}$	$\varphi_{phot} \times 10^5$
R19	7×10^{-2}	1.05	532	532	558	10	587	2	0.5		23
						30	589(587)	2.5			
						75	590	6			
R19	7×10^{-2}	1.05	308	532	559	7	593	2.2	0.85	12.7	110
						30	595(597)				
RC	6×10^{-2}	0.56	532	549	586	8	615	3.3	0.4	(1620)	0.3
						20	616				
						30	617(607)	3			
RC	6×10^{-2}	0.56	308	549	586	7	616	0.5	0.7	13.1	50
						30	614				
RC+ Ce(NO ₃) ₃	1.4×10^{-1}	0.61	532	549	590	8	626 + 630	5	0.2	1543	7
						20	609 + 626				
						30	609 + 626 (600 + 619)				
RC+ Ce(NO ₃) ₃	1.4×10^{-1}	0.61	308	549	589	8	633	0.5	0.8	41.6	30
						15	632				
						30	632				
R101T	3×10^{-1}	0.44	532	583	604	30	634(617)	3	0.8	268	10
R101T	3×10^{-1}	0.44	308	583	614	30	632		3	5.1	62

Note: In parentheses are presented the values of λ_{las}^{max} after irradiation (absorption of the energy by the active medium corresponding to the resource P_{50}).

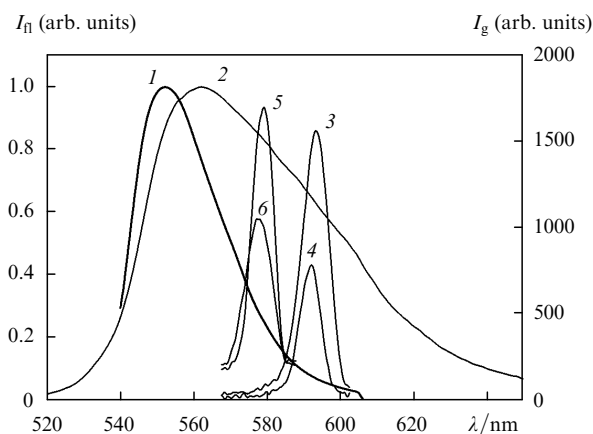


Figure 3. Fluorescence (1, 2) and lasing (3–6) spectra of R19 in a bulky TEOS:VTEOS = 7:3 silicate matrix (1, 3, 4) ($\lambda_{\text{exc}} = 532$ nm) and a film ($d = 1.05$ μm , $\lambda_{\text{exc}} = 308$ nm) (2, 5, 6) before (1, 3, 5) and after irradiation (absorption of the energy by the active medium corresponding to the resource P_{50}) (4, 6); $W_{\text{exc}} = 40$ MW cm^{-2} .

($\equiv\text{Si}-\text{OH}$) groups. The absorption spectra of films doped with rhodamines exhibit, along with bands corresponding to the neutral and zwitterion forms of monomer molecules, a noticeable increase in absorption in the short-wavelength region, which is typical for the interaction of rhodamines with proton-donor centres [6] (Fig. 4). The spectral parameters of fluorescence and lasing weakly change with increasing the VTEOS fraction in the matrix (see Table 1) due to the relative decrease in the fraction of silanol groups, i.e. the decrease of interaction involving proton-acceptor centres of rhodamine dyes.

Note that the lasing and absorption spectra of solid samples doped with rhodamines shift to the blue due to phototransformations during lasing (Figs 3, 4). This is caused by the ‘burning out’ of low-threshold solvates in a solid matrix and the involvement of high-threshold solvates to lasing, which emit at shorter wavelengths. The low-threshold solvates are formed in the case of non-esterified rhodamines under study due to specific interactions of the carboxyphenyl substituents, while the high-threshold ones are formed due to interactions of the substituted amino groups with the OH groups ‘lining’ pores

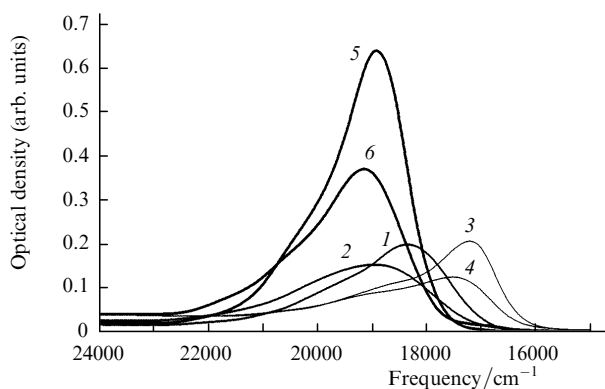


Figure 4. Absorption spectra of RC (1, 2), R101T (3, 4), and R19 (5, 6) in a TEOS:VTEOS = 7:3 film before (1, 3, 5) and after irradiation (2, 4, 6) by a XeCl laser.

of silicate matrices. As a result, such interactions can lead to the formation of ionic molecular forms.

These conclusions were made based on the study of the acid-base interaction of rhodamines in solutions [6], the spectral shifts, and the relative increase in absorption in the short-wavelength wing of the absorption band of irradiated solid samples (Fig. 4). Because the fraction of high-threshold RC solvates in the TEOS:VTEOS = 1:1 matrix decreases, the resource of such elements is higher than that in the TEOS:VTEOS = 7:3 matrix. The higher photostability of laser dyes in solid-state elements compared to that in solutions is explained by the recombination of the primary photoproducts in immobile solvates, which is negligible in solutions due to their chaotic motion.

In addition, the dependence of the relative change in the lasing efficiency on the energy absorbed in a sample, from which the operating resource is determined, upon excitation into the long-wavelength band has another characteristic feature, which is absent upon UV excitation of solid-state elements and any excitation of the solutions of dyes under study. As the pump energy absorbed in the lasing volume is increased, the lasing efficiency first increases and then decreases, resulting in the increase in the resource. Similar properties were observed for solid-state elements doped with dyes in [5, 7, 12]. In this case, the lasing parameters also change. For example, the lasing efficiency of RC in the TEOS:VTEOS = 1:1 matrix increased from 1% to 8.5% and the lasing spectrum shifts from 627 to 624 nm. After the passage through the maximum of the lasing efficiency, the maximum of the spectrum returns to the initial value, and only after the absorption of the ‘resource’ energy, when the lasing efficiency decreases down to 3%, the maximum of the spectrum shifts to 621 nm. This means that during excitation, first the low-threshold solvates, consisting of neutral and zwitterion molecular forms, exhibit lasing, and then the high-threshold solvates, related to the interaction involving amino groups, begin to dominate. The two- and even three-band lasing of rhodamines in silicate matrices (Tables 1 and 2) is explained by the simultaneous lasing of different solvates, which increases the operating resource of the lasers and extends their tuning range compared to that of lasers based on organic dye solutions.

The additions of rare-earth ions during the sol-gel synthesis of samples doped with RC act ambiguously. The photostability upon UV excitation increases (Table 2) due to a decrease in the fraction of solvates facilitating the formation of an irreversible photoproduct involving the interaction of rhodamines over amino groups in the high excited state due to the competition with positively charged rare-earth ions doped into the matrix. On the other hand, these additions extend the tuning range and lead to the increase in the lasing efficiency upon excitation into the long-wavelength band of rhodamines due to a high yield of low-threshold solvates in the form of neutral molecules, the efficiency of their formation in the S_1 state increasing compared to that in the ground and high excited states [6]. In this case, rare-earth ions do not compete with the low-threshold solvates, but on the contrary, facilitate their stabilisation. The photostability decreases in this case because the mechanism of phototransformations of rhodamines upon long-wavelength excitation is probably related to the interaction involving the carboxyl substituent, i.e. it differs from that upon UV excitation [6]. These effects require further investigations.

The difference in the lasing stability of the same dye in bulky matrices and thin films can be related to the inhomogeneities of bulky elements and different concentrations of dyes. This concentration in films is higher, probably due to their higher porosity compared to bulky elements [4].

The results presented in the paper have shown that solid-state elements based on silicate matrices of different compositions doped with organic luminophores are promising for the development of miniature active media for tunable lasers and light-emitting thin-film devices. The laser element containing RC in the TEOS:VTEOS = 1 : 1 matrix is the most stable upon pumping by the second harmonic of a Nd:YAG laser. This element also most efficiently converts radiation from a XeCl laser to the red region. The lasing efficiency of the film doped with R101T upon UV excitation is lower than that for other samples, which can be explained by the fact that this film has the smallest thickness and high transmission of the pump radiation, i.e. the absorption of pump radiation is insufficient. In addition, silicate matrices should be optimised in the future for improving the lasing parameters of solids doped with coumarin dyes and para-terphenyl emitting in the blue and UV spectral regions.

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