Features of three red laser dyes and effect on them the adjacency of their molecules

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We have developed and explored laser media on the basis of preliminary annealed xerogel SiO_2 matrices doped with three laser dyes for 600 – 700 nm range of tuning that used actively in biomedical diagnostics and sensory analysis. Spectral, fluorescence, and laser characteristics of the dyes in solutions and matrices have been measured and analyzed. The influence of bulky fragments that may swing within structure of the dye molecule and its nearest adjacency on nonradiative losses in the excited S_1 state of this molecule have been revealed. The specific output laser energy of two laser dyes have appreciably increased in the matrix as compared with their methanol solution. The studied matrices have lasing in a nonselective cavity with red shift relatively the fluorescence maximum by value of 900 – 1700 cm⁻¹ that may extend the penetration depth of laser biosensors radiation into organic tissues.

Keywords: dye, xerogel, red lasing, fluorescence quantum yield, nonradiative losses.

Introduction

Unique spectral properties of laser dyes (LD) and producers of tunable emission on their basis keep them as topical objects of investigations for development of new photonics elements. Therewithal the red spectral region may be especially marked out as very actual for many practical applications [1–4] including the biomedical diagnostics [5]. We have earlier fulfilled a series of studies of laser media on the basis of silica gel matrices doped with the dyes [6–8]. Characteristics of three LD for 600 - 700 nm region have been explored in present paper. The goal of this exploration was to obtain their laser emission in preliminarily annealed SiO₂ matrices and to analyze influence of molecule structure of LD and its nearest adjacency on its spectral and fluorescent properties, and characteristics of stimulated radiation both in solution and in annealed xerogel. We selected for that two oxazine dyes Cresyl Violet (CV) and Nile Red chloride (NRCl), and LD – 4-dicyanmethylene-2-methyl-6-(p-dimethylaminostyryl)-4H–pyran (LC6500) [9]. In this connection we have tested two last dyes under the low-temperature synthesis of laser matrices but have not obtained good results: the NRCl dye was decolorized during the polycondensation process and matrix doped with the LC6500 LD had high lasing threshold that value was close to maximal possible energy of our laser pumping system.

Experimental

Synthesis of silica gel matrices non-activated with the dyes and annealing of them at temperature of 600 °C were fulfilled by the method described in our preceding paper [7]. The saturation of the annealed matrices with the LD was performed by dipping them into methanol solutions of the dyes with concentration 2.0 μ M – 1.1 mM for a time up to 6 hours and afterwards drying in the air at room temperature during 12 – 16 hours.

Methods and instrumentation for measuring spectral, fluorescence and laser characteristics of the dyes in solutions and matrices were described in our previous articles [6–8]. We have used methanol (Met) solutions of the dyes LC6500 and CV as etalons for calculations of their fluorescence quantum yields Q in SiO₂ matrix: for LC6500/Met – $Q_0 = 0.43$ [10] and for CV/Met – $Q_0 = 0.54$ [11]. In case of NRCl its solution in ethyl alcohol was the etalon – $Q_0 = 0.58$ for NRCl /EtOH [11].

When laser characteristics of the matrix were measured, they were put into quartz cuvette (inner sizes ~ $10 \times 10 \times 40$ mm³) filled with immersion liquid – ethylene glycol for the

purpose of reducing optical distortions within the laser cavity by untreated face planes of the matrix. The characteristics of methanol solutions of the dyes were measured in the same cuvette. The studied dyes in matrices and methanol were excited by flashlamp-pumped dye laser (FLPDL) with output energy up to 200 mJ, pulse duration ~1 µs, and half-width of spectrum ~5 nm. Ethanol solutions (EtOH) of three dyes were used in the FLPDL: coumarin C314, iminocoumarin G283, and rhodamine Rh6G. The LC6500 dye was pumped at $\lambda_p = 507$ nm (by C314/EtOH), NRCl – at $\lambda_p = 553$ nm (by G283⁺/EtOH), and CV – at $\lambda_p = 589$ HM (by Rh6G/EtOH). Here λ_p – maximum of the pump spectrum.

Results and discussions

The basic results of our experimental testing of spectral, fluorescent and lasing characteristics of the dyes in alcohol solutions and the pre-annealed matrices and calculated with help of them fluorescence quantum yields Q and rate constants of radiative $k^r = Q/\tau^f$ and nonradiative $k^{nr} = (1-Q)/\tau^f$ transitions are adduced below.

ID/Medium	λa,	$\lambda_{\rm fl}$,	0	τ ^f ,	$k^{\mathrm{r}} \cdot 10$,	$k^{\mathrm{nr}} \cdot 10$,	Δv^{St} ,	$\lambda_{las} \pm \Delta \lambda_{las}$,	Δv^{las} ,	$E_{\rm las}$,
	nm	nm	Q	ns	ns ⁻¹	ns ⁻¹	cm ⁻¹	nm	cm ⁻¹	mJ/cm
LC6500/Met	469	630	0.43	1.23	3.49	4.62	5450	642 ± 5	300	1.1
LC6500/SiO ₂	420	584	0.65	2.28	2.84	1.53	6690	648 ± 5	1690	2.0
NRCl/EtOH	558	645	0.58	3.16	1.84	1.33	2420			
NRCl/Met	557	642	0.54	2.80	1.93	1.64	2370	652 ± 4	240	1.6
NRCl/SiO ₂	590	637	0.60	4.60	1.30	0.87	1230	674 ± 6	880	1.5
CV/Met	596	623	0.54	4.55	1.19	1.01	730	643 ± 5	500	2.1
CV/SiO ₂	585	615	0.57	5.29	1.08	0.81	830	651±5	900	7.3

Table – Characteristics* of the red LD.

* λ_a – maximum of absorption band, λ_{fl} – wavelength of fluorescence maximum, τ^f – fluorescence lifetime, $\Delta \nu^{St}$ – Stokes shift between the absorption and fluorescence maxima, λ_{las} – central lasing wavelength, $\Delta \lambda_{las}$ – halfwidth of laser spectrum, $\Delta \nu^{las}$ – shift between the maxima of fluorescence bands λ_f and lasing spectra λ_{las} , E_{las} – the specific laser energy i.e. output energy normalized to the active element length under pump energy ~150 mJ, and SiO₂-silica gel matrices pre-annealed at 600 °C.

From the data adduced in the Table we accentuate above all the specific output energy of developed solid-state laser elements. So the NRCl dye that have been decolorized during the low-temperature synthesis of the SiO₂ matrix [6] in present study have E_{las} equaled about to one of its methanol solution (within inaccuracy of measurement) and the LC6500 LD that have earlier generated stimulated emission [6] at the highest possible pump energy near oscillation threshold but now its E_{las} is almost twice as much than one in methanol. The specific energy of laser radiation for the matrix saturated with the CV LD is greater by a factor nearly 3.5 than E_{las} of its methanol solution.

In the row of three studied dyes the value of Stokes shift diminishes in the succession of LC6500 - NRCl - CV but for all that at the change-over from methanol to the pre-annealed SiO₂ matrices Stokes shift for LC6500 increases by ~23 %, for Ox17 it diminishes almost in half and for CV – a minor increase by ~14 % is observed. The value of $\Delta v^{St} > 5000 \text{ cm}^{-1}$ for the LC6500 LD testifies considerable increasing the dipole moment of its molecule in the excited S₁ state and strengthening its interaction with the nearest molecular adjacency. In addition in the pre-annealed SiO₂ matrix this process intensifies. For the NRCl LD interaction of the dye molecule with the nearest molecular adjacency relaxes in the row: ethanol – methanol – matrix.

Comparing spectra of oxazine dyes allows to note that substituting small amino group in 9th position of CV by bulky diethylamino group in NRCl and simultaneously imino group in CV by carbonyl oxygen in NRCl produced the short-wave shifting absorption spectrum of NRCl in

methanol by 39 nm and long-wave displacing fluorescence one by 19 nm. At the same time Stokes shift increased more than three times. In the matrix displacing absorption spectrum was counter by 5 nm, but shifting fluorescence spectrum remained long-wave by 22 nm. The laser spectra of NRCl were shifted towards red range relative to CV both in methanol and in matrix. For all studied dyes laser spectrum in the matrix displaced to the red region relative to methanol solution and the value of Δv^{las} increased up to 900 – 1700 cm⁻¹. Such displacement is useful for constructing biomedical sensors on the basis of the studied matrices so far as their emission spectra shift into the range of deeper permeation into organic tissues. Calculated fluorescence quantum yields have showed that its value increases by 51 % for LC6500, by 11 % for NRCl, and by 6 % for CV. It is possible to assume that in pre-annealed SiO₂ matrices microsurroundings of the dye molecule stabilize position of its bulky fragments in excited S₁ state and don't allow them to go out the molecule plane. As a result, the nonradiative losses reduce in this state that confirms by calculations of the rate constants of nonradiative transitions adduced in the Table. As in case of change of τ^{f} maximal decrease of k^{nr} occurred for LC6500 – by three times, for NRCl – by a factor of 1.9, and for CV – by 20 % only.

Conclusion

Thus laser media on the basis of pre-annealed silica xerogel doped with three red dyes with efficient output lasing were explored. Their spectral, fluorescence, and laser characteristics have been detailed studied. The effects of bulky fragments that may swing within structure of the dye molecules and their adjacency in silica matrix on nonradiative losses in the excited state have been revealed.

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