

## CHARACTERISTICS OF SOME RED LASER DYES IN ANNEALED SILICA XEROGEL

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The extremely sensitive photosensors on the basis of plasmonic resonances from nanostructures [1] and whisper gallery mode (WGM) resonance [2] are one of the actively developing trends in present-day photonics that employed active laser media. Organic dyes those are able to produce stimulated emission through the all visible region of the spectrum and the contiguous UV and IR ones are often the main element of these sensors. The laser efficiency of the dyes used in the sensor is important for them as well as for dye lasers.

We have earlier studied [3] spectral and fluorescence characteristics of three laser dyes for red and near IR spectral regions that were incorporated into preliminarily annealed silica gel matrices. In these matrices influence of residual moisture organics was excluded. The last changing with time is able to result in undesirable revising of characteristics of the photosensor on the basis of SiO<sub>2</sub> matrices. Our choice of the dyes was determined by the spectral region that is very informative for medical-biological investigations [4].

The aim of the present work was study of laser characteristics of these dyes in preliminarily annealed silica gel matrices and comparison with those in alcohol solutions.

The synthesis of silica gel matrices, the preliminary annealing of them at temperature of 700 °C, and the subsequent deeping with laser dyes were described earlier [3]. The selected laser dyes for 650–750 nm spectral range of lasing were LK678 dye (MCTI) and two oxazine dyes (Aldrich) – Oxazine 170 (Ox170) and Nile Blue Perchlorate A (NBA) [3]. The activated xerogel matrices and initial methanol solutions of the dyes ( $C_0 = 0.13\text{--}0.14$  mmol/l) were tested in laser with right-angled quartz cuvette (internal dimensions –  $10\times10\times40$  mm<sup>3</sup>) and its resonator of 50 mm length was formed by two wide-band dielectric mirrors with reflection coefficients  $R_1 \geq 95\%$  and  $R_2 \approx 60\%$  in the lasing range. Excitation of studied dyes was produced at the short-wave slope of the main band of their absorption near the maximum by transverse scheme with additional flashlamp-pumped laser on ethanol solution of Rhodamine 6G. This laser produced light pulse of  $\sim 1$  mcs duration at 0.5 level with output energy up to 140 mJ at wavelength  $\lambda_p = 588$  nm with half-width of 3.2 nm. The radiation of this laser was focused in a strip of  $\sim 1$  mm height on

lateral surface of the cell with the studied solution or the xerogel matrix along the cavity axis by cylindrical lens with  $F = 110$  mm. The studied pre-annealed matrices (their dimensions  $\sim 5 \times 5 \times 20$  mm<sup>3</sup>) were not exposed to optical processing therefore for the purpose of decreasing the optical distortions in cavity, they placed in the laser cuvette containing immersion liquid – ethylene glycol that did not interact with matrix doped with dye. Output laser energy of tested media and pumping energy were measured with devices of the IMO-2N type (ETALON). Spectra of laser radiation were registered at focal plane of spectrograph based on an UF-90 chamber (LOMO) with 1,200 line/mm diffraction grating.

The main laser characteristics of studied dyes in methanol and annealed xerogel matrices measured in the non-selective cavity under pumping with  $\lambda_p = 588$  nm are presented in the table. In it some spectral characteristics that we have earlier obtained [3] are adduced for obviousness too.

Table

Main characteristics\* of the red laser dyes

Dye	Medium	$\lambda_a$ , nm	$\lambda_{fl}$ , nm	Q	$\Delta\nu^{St}$ , cm <sup>-1</sup>	$\Delta\nu^{las}$ , cm <sup>-1</sup>	$\lambda_{las}$ , nm	$\Delta\lambda_{las}$ , nm	$E_{las}$ , mJ/cm
LK678	SiO <sub>2</sub> -An	600	618	0.72	485	800	652	4	17
LK678	Methanol	605	622	0.67	450	690	650	6	15
Ox170	SiO <sub>2</sub> -An	614	639	0.76	640	750	671	4	7.5
Ox170	Methanol	621	643	0.63	550	580	668	3.7	6.8
NBA	SiO <sub>2</sub> -An	633	663	0.31	715	840;1080	702; 714	3.6; 3.0	3
NBA	Methanol	626	664	0.27	910	No lasing			

\*  $\lambda_a$  – maximum of long-wavelength absorption band;  $\lambda_{fl}$  – wavelength of fluorescence maximum; Q – fluorescence quantum yield;  $\Delta\nu^{St}$  – Stokes shift between the maxima of the absorption and fluorescence bands;  $\Delta\nu^{las}$  – shift between the fluorescence maximum and midpoint of the laser spectrum;  $\lambda_{las}$  – central lasing wavelength;  $\Delta\lambda_{las}$  – halfwidth of laser spectrum;  $E_{las}$  – output laser energy normalized to 1 cm length of active laser element for the same pumping conditions, SiO<sub>2</sub>-An – silica gel matrices preliminarily annealed at 700 °C

The studied dyes in the matrices produced laser emission at long-wavelength slope of their fluorescence spectra with appreciable red shift from the maxima more than 32 nm ( $\Delta\nu^{las} > 750$  cm<sup>-1</sup>). Especially large shift of the lasing spectrum was observed for annealed matrix doped with NBA dye that produced two laser bands in this matrix with maxima at 702 and 714 nm. For the latter band the shift exceeded 50 nm ( $\Delta\nu^{las} > 1000$  cm<sup>-1</sup>). Such a shift of the laser radiation spectrum was caused by its absorption in active medium due to a considerable overlapping of the absorption and the fluorescence spectra. This effect will be useful for biosensors on plasmon and WGM resonances, since it shifts the radiation spectra to the region with large depth of penetration in biological tissues.

In our earlier research [3] we have revealed that application of pre-annealed xerogel not only stabilizes the spectral characteristics of the dye in the matrix in time due to removal of residual moisture organics, but also decreases non-radiative losses in the upper excited state  $S_1$  and increases the quantum yield of the dye fluorescence. The table shows that output laser energy of the studied matrix normalized to the length of the active element (i.e. reduced to 1 cm length) for the same pumping conditions ( $E_p \approx 100$  mJ) exceeds the energy of the corresponding methanol solutions by about 10 – 13 %.

NBA dye is to be note particularly. As shown early [3], “twisted” conformation of the molecule (the so-called TICT-form) may arise in the upper excited state  $S_1$  of this dye due to rotational displacement of  $N(C_2H_5)_2$  – group around single bond leading to disturbance of the molecule planeness. This results in a considerable quenching of fluorescence of this dye; its quantum yield in methanol amounts to 0.27 only. However, in the annealed matrix contribution of TICT-form of the molecule is essentially diminished at  $S_1 \rightarrow S_0$  transition [3]. The mentioned facts may explain the absence of lasing of this dye in methanol solution at the pumping energy up to  $E_p \approx 140$  mJ and the pump duration  $\tau_p \approx 1$  mcs in our study. At the same time, the annealed matrix doped with NBA dye produces (for  $E_p \geq 80$  mJ) two bands of laser radiation shifted by about  $1000\text{ cm}^{-1}$  relative to the fluorescence maximum. The center of the first band corresponds to 702 nm, its half-width is 3.6 nm. The center of the second band is located at 714 nm, the half-width being 3.0 nm.

Note that for LK678 and Ox170 dyes with quantum yields appreciably higher than the one of NBA, at the change-over from methanol to the annealed matrix, there was observed a small ( $\sim 10\%$ ) increase of the Stokes shift of the fluorescence maximum. Thereat, at the value of  $\Delta\nu^{\text{las}}$  (shift of the lasing centre from the fluorescence maximum) increased by  $> 15\%$ . The Stokes shift of NBA fluorescence in the matrix was smaller than the one in methanol, probably due to decrease of the influence of TICT-form of the dye in the matrix.

Thus, the increase of the output laser energy for the dyes in pre-annealed xerogel in comparison with the one in their methanol solutions under the same pumping conditions testifies that stabilization of the molecules in the upper excited state  $S_1$  can be realized not only under spontaneous transitions when non-radiating losses were decrease [3], but also under stimulated transitions.

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