Silica matrices doped with red laser dyes

I.M.Pritula, O.N.Bezkrovnaya, V.M.Puzikov, V.V.Maslov[*], A.G.Plaksiy, A.V.Lopin, Yu.A.Gurkalenko

Institute for Single Crystals, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine
[*]Usikov Institute of Radiophysics and Electronics, National Academy of Sciences of Ukraine, 12 Proskura Str., 61085 Kharkiv, Ukraine

Sol-gel SiO_2 matrices activated with laser dyes for the red spectral region DCM, LK678 and benzopyran derivatives LD1 and LD2 were synthesized. Pyridine was used to prevent bleaching of the dyes during the synthesis of the matrices. Studied were the spectral and luminescent characteristics of the laser dyes in SiO_2 matrices. Laser pumping of DCM and LK678 made it possible to obtain stimulated emission. The laser efficiency of LK678 dye in the matrix was 1.5 times as high as that of rhodamine 6G. The absence of lasing radiation of the benzopyran derivatives LD1 and LD2 in the synthesized matrices was explained.

Синтезированы золь-гель SiO_2-матрицы, активированные лазерными красителями для красной области спектра DCM, LK678 и производными бензопирана LD1 и LD2. Для предотвращения обесцвечивания красителей в процессе синтеза матриц использовался пиридин. Исследованы спектрально-люминесцентные характеристики лазерных красителей в SiO_2-матрицах. На DCM и LK678 при лазерной накачке получено вынужденное излучение. Лазерная эффективность красителя LK678 в матрице в 1.5 раза выше, чем у родамина 6G. В работе объясняется отсутствие генерации производных бензопирана LD1 и LD2 в синтезированных матрицах.

1. Introduction

For many years, organic dye molecules are being used in lasers and amplifiers with optical pumping. The lasers tuned in the red spectral region and the dyes-sensitizers for this range are widely applied for investigations of different objects in biology and medicine. The urgency of the creation of laser radiation sources for the red and near-IR ranges is due to the fact that this radiation deeply penetrates into living tissues; for instance, oxazine derivative [1] is used for early diagnostics of Alzheimer's disease. As is known, liquid dye lasers have wide radiation tuning band. However, for practical purposes solid active media are most promising [2–4], since they do not require bulky systems for the laser dyes solution circulation, and no toxic and inflammable solvents. Such media comprise e.g. dye-activated matrices based on different polymers, silica gels synthesized by the sol-gel method, or porous glasses. The matrices based on SiO_2 possess high thermal conductivity and low temperature coefficient of the change of the refractive index [5]. For a number of efficient laser dyes, photostability in inorganic matrices is higher in comparison with that in organic polymer media. In particular, the photostability of rhodamine 6G in sol-gel matrix by 2.7 times exceeds the corresponding value for polymethylmethacrylate matrix [3]. Moreover, sol-gel matrices have higher laser damage threshold as against polymer media [3], due to higher thermal conductivity of silica in comparison with that of polymer materials [5]. High efficiency and photostability in liquid media are characteristic of iminocou-

marin derivatives and benzopyran derivatives with a condensed benzimidazole ring [6, 7] and of the dye LK678 [8] which lasing in 600−630 and 640−660 nm regions, respectively. The standard laser dye is 4-Dicyanomethylene)-2-methyl-6-(4-dimethylamino-styryl)-$4H$-pyran (DCM) [9]. The obtaining of laser radiation of the said dye in ORMOSIL matrices based on TiO_2 was reported in [2]. However, in a solid matrices based on acryle copolymers, laser generation of the dye DCM was not obtained [9].

For creating laser media based on SiO_2 matrices for the red region of the spectrum we synthesized and investigated matrices doped with a number of dyes effectively generating in 600−660 nm range in alcoholic solutions.

2. Experimental

The silica gels were synthesized using tetraethoxy- and tetramethoxysilane (TEOS and TMOS, respectively; Aldrich), additionally purified ethyl alcohol, formamide (FA, chemically pure) and twice distilled water, as well as the dyes rhodamine 6G (Rh6G, Aldrich), the benzopyran derivatives with a condensed benzimidazole ring LD1 and LD2 (synthesized at the V.Karazin Kharkiv National University [6]), DCM (Aldrich) [10] and LK678 (synthesized at D. Mendeleev Chemical Technology University, Moscow [8, 11]). Presented below are the structural formulas of some dyes:

LD1   LD2

DCM
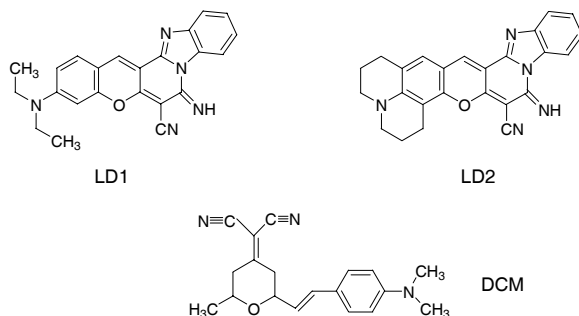
SiO_2 matrices were synthesized by means of the sol-gel method by the hydrolysis of alkoxysilanes (TEOS or TMOS) in water-alcoholic solutions according to the procedure described in [12−14]. As a catalyst, there was added nitric acid. The alcoholic dyes solutions (LD1, LD2 and LD678 in ethanol solutions; DCM in methanol solution; LD2 in ethanol solutions with added 1 mM HNO_3) were introduced after 30-minute mixing of alkoxysilane in ethanol (or in methanol for the matrices based on TMOS). Then we added twice distilled water and FA (as dry-

ing control chemical additives), and the resulting mixture was stirred during hour; and then pyridine was added to the mixture. The synthesized sol was placed into plastic cuvette, hermetically sealed and stored till the gel was formed. Afterwards the plastic cuvette were opened and dried for 3−4 weeks at room temperature and for 7−10 days at 60°C. The density of the obtained SiO_2 matrices was 1.4−1.6 g·cm^{-3}.

The absorption and luminescence spectra of the samples were measure on a Lambda 35 (Perkin-Elmer, USA) spectrophotometer and a FluoroMax-4 (Horiba Jobin Yuon, USA) fluorimeter, respectively. The luminescence of the dyes in the solutions was excited near their absorption bands maxima.

The matrices were tested in the capacity of active media in a laser with non-selective resonator (LNSC), formed by two planar wideband dielectric mirrors with reflection coefficients $R_1 \approx 99$ % and $R_2 \approx 60$ %. The LNSC excitation was carried out on the transverse scheme performed with flash-lamp-pumped dye laser (FLPDL). Matrices with DCM and Rh6G dyes were pumped by the FLPDL with ethanol solution of coumarin 314 ($\lambda_p = 507$ nm), and that with LD678 by one with — rhodamine 6G ($\lambda_p = 588$ nm). The output energy of FLPDL for pumping the matrices did not exceed 230 mJ with the pulse duration — $\tau_{0.1}$ ~ 1.5 µs and the half-width of the spectrum $\Delta_{0.1}$ ~ 3 nm. The output laser energy for FLPDL and LNSC was measured by a device of IMO-2 type. The laser spectra were registered by a spectrograph based on UF-90 camera with 1200 line/mm diffraction grating and captured by EOS 400D DIGITAL camera. The surfaces of the examined samples were not subjected to optical treatment. To reduce the losses in the LNSC resonator the samples were placed into a rectangular quartz dish containing immersion liquid (ethylene glycol). The radiation of FLPDL was focused on the cuvette by a cylindrical lens with $F = 110$ mm in strip with heights ~ 1 mm.

3. Results and discussion

We synthesized transparent SiO_2 matrices on the base of TEOS and TMOS with incorporated molecules of the laser dyes LD1, LD2, DCM and LK678 (Fig. 1). There was established an essential contribution of micro-environment (the matrix) on the spectral properties of the incorporated dye mole-

Table 1. Spectral characteristics of LD1 and LD2 in liquid and solid media

Medium	C_{HCl}, mM	λ_a, nm	λ_L, nm
LD1			
Ethanol	–	549	572
Ethanol	0.15 (HCl)	552[*]	574[*]
Ethanol	1.5 (HCl)	571[*]	594[*]
Ethanol	15 (HCl)	572[*]	595[*]
Ethanol	–	–	571
Ethanol	0.44 (HNO₃)	–	592
SiO₂ gel	1.33 (HNO₃)	564	586
SiO₂ matrices (60°C)	–	566	582
LD2			
Ethanol	–	567[*]	586[*]
Ethanol	0.15 (HCl)	576[*]	602[*]
Ethanol	1.5 (HCl)	582[*]	603[*]
Ethanol	15 (HCl)	583[*]	603[*]
SiO₂ gel	1.33 (HNO₃)	–	598
SiO₂ matrices (20°C)	–	–	592
SiO₂ matrices (60°C)	–	575	587

λ_a is the absorption maximum wavelength; λ_L, the luminescence maximum wavelength; luminescence of LD1 and LD2 dyes in SiO₂ matrices was excited at 530 nm, in the solutions it was excited at 520 nm (LD1) and 530 nm (LD2); [*] — reference [6].
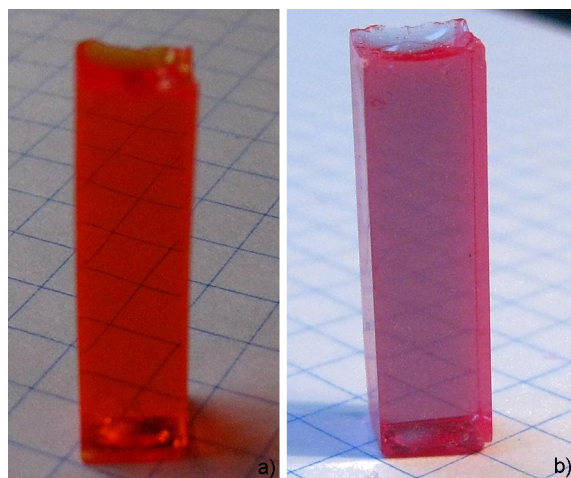

Fig. 1. Photographs of SiO₂ matrices with DCM (a) and LD678 (b) dyes.

Fig. 2. Luminescence spectra of $1.8 \cdot 10^{-7}$ M LD1 in: ethanol solution (*1*), ethanol solution with $0.44 \cdot 10^{-3}$ M HNO₃ (*2*) and $1.1 \cdot 10^{-5}$ M LD1 in SiO₂ matrix (*3*).

cules. The structure of the molecules of the LD1 and LD2 benzopyran derivatives contains the imino-group possessing strong proton acceptor properties and the amino-group fixed by two six-member cycles in LD2. In proton-donor solvents the imino-group present in such dyes may lead either to the formation of a complex with hydrogen bond, or to protonation of the molecule (in the case of strong acids) [15]. In the gel the
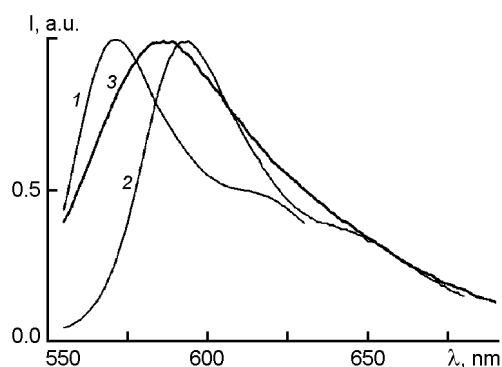
absorption and luminescence maxima of the dye LD1 correspond to 564 and 586 nm, respectively (Table 1, Fig. 2), but after drying of SiO₂ matrix at 60°C the luminescence maximum becomes shifted to 582 nm. The influence of the medium on the LD2 molecules in SiO₂ matrix manifests itself in the short-wavelength shift of the luminescence maximum from 598 nm (gel) to 592 nm and 587 nm while the samples are dried at 20°C and 60°C, respectively (Fig. 3). The position
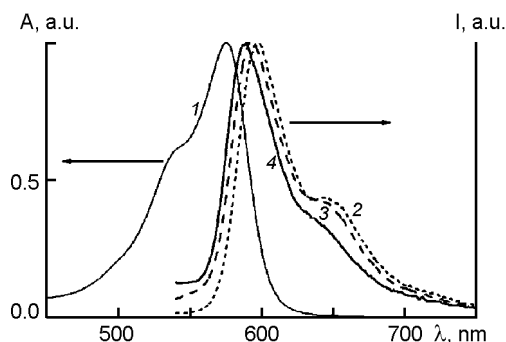
Fig. 3. Absorption (*1*) and luminescence (*2–4*) spectra of LD2 dye ($3.5 \cdot 10^{-4}$ LD2/1 Mole TEOS) in SiO_2 matrix: gel (*2*), xerogel dried at 20°C (*3*) and 60°C (*4*).

of the absorption and luminescence maxima of the LD1 and LD2 dyes caused by the fact that the dye molecules are in the solvation shell of solvent molecules in the liquid-impregnated silica gel, and are prone to protonation in the presence of acid. In the process of drying the solvent and water are practically removed from the matrices and the dye molecules enter the silica gel pores. Moreover, is obvious that the molecules of LD1 and LD2 dyes undergo partial deprotonation while interacting with the surface of the SiO_2 nanoparticles which form the silica gel skeleton.

The absorption and luminescence maxima of LD1 dye in ethyl alcohol are 549 and 572 nm, respectively. The addition of nitric acid to the LD1 and LD2 ethanol solutions leads to the bathochromic shift of the luminescence maxima (Table 1, Fig. 2, Fig. 3) similar to the one observed at the addition of HCl [6]. Such a shift is caused by the

appearance of the protonated form of the dyes due to the presence of a strong proton-acceptor imino group in their molecular structure. Thereat, the increase of the content of HCl acid in the ethanol solutions of LD1 and LD2 dyes from 1.5 to 150 mM does not change the luminescence maximum [6, 7]. The matrices were prepared using the ethanol solution of the dye LD2 with the addition of the acid, whereas in the sol gel medium the dye is contained in the protonated form (the absorption maximum is located at 575 nm, as in the alcohol solution with the addition of the acid) (Table 1, Fig. 3).

As we have established, the process of drying is accompanied with bleaching of LD1 and LD2 in SiO_2 matrices. The observed effect seems to be caused by protonation of nitrogen in the 7-th position of the benzopyran base of the dyes. It is more noticeable for LD1 in which diethylaminogroup in the 7-th position may leave the plane of the benzopyran base at protonation, thus sharply diminishing the probability of the transition $S_1 \rightarrow S_2$ and leading to luminescence quenching [6, 16]. Therefore, while creating the active media on the base of SiO_2 matrices we added pyridine to reduce the acidity in the process of sol synthesis. However, we did not manage to obtain laser radiation on the matrices with these two dyes due to their essential bleaching. The effect of complete bleaching of the dye was also observed at the synthesis of the matrices with LK678 not using pyridine. As is known, the luminescence intensity of the dye DCM in SiO_2 matrices also diminishes under the influence of nitric acid [17]. This

Table 2. Spectral characteristics of DCM and LD678 dyes in liquid and solid media

Medium	λ_a, nm	λ_L, nm	Δv^{St}, cm^{-1}	$\lambda_{las} \pm \Delta\lambda_{las}$, nm
DCM				
Acetonitrile	463	622	5500	632±6
Methanol	472	630	5280	635±+4
SiO_2 matrices (60°C)	–	610	634±2**	
LD678				
Methanol	609*[8]	626*[8]	450	650±+10
SiO_2 matrices (60°C)	608	620	320	654±4**

λ_a i the absorption maximum wavelength; λ_L, the luminescence maximum wavelength; Δv^{St}, the Stokes shift between the maxima of the absorption and luminescence bands; λ_{las}, the central wavelength of the laser spectrum; $\Delta\lambda_{las}$, the halfwidth of the spectrum; luminescence of DCM and LD678 dyes in SiO_2 matrices was excited at 460 nm and 590 nm, respectively, in the solution it was excited at 500 nm (DCM) and 530 nm (LD678); ** SiO_2 matrices synthesized on the basis of TMOS.
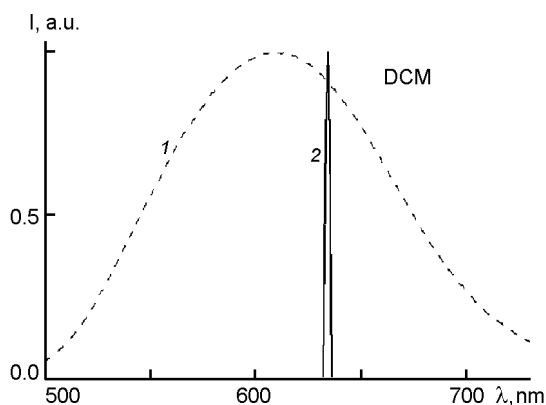
Fig. 4. Luminescence spectrum of $1.08 \cdot 10^{-4}$ M DCM (*1*) and laser emission spectrum of $1.10 \cdot 10^{-3}$ M DCM (*2*) in SiO_2 matrices. Luminescence and laser emission of DCM in SiO_2 matrices were excited at 460 nm and 507 nm, respectively.

obviously explains the fact that the matrices with DCM synthesized without pyridine does not laser radiation.

The solvate environment exerts a considerable influence on the molecules of the dye DCM (Table 2, Fig. 4) defined by the electrical parameters of the solvents: μ (the dipole moment of the solvent molecule) and ε (the dielectric constant). For the solvents methanol and acetonitrile $\mu = 1.664$ D and 3.37 D; $\varepsilon = 32.63$ and 37.5, respectively (at $20-25°C$). At the transition from acetonitrile to methanol the maxima of the absorption and luminescence bands of DCM undergo bathochromic shifts (Table 2). Thereat, for methanol possessing low μ and ε values such a shift is connected with "specific" intermolecular interactions [18] which may give rise to the formation of complexes owing to hydrogen bonds or donor-acceptor interaction. At the transition from methanol to SiO_2 matrix there is observed the shift of the luminescence matrix from 630 nm to 610 nm. This seems to be caused by a lesser polarity of the medium in SiO_2 matrix and by its lesser influence on DCM dye molecules in comparison with the alcohol solution. The Stocks shift Δv^{St} between the maxima of the absorption and luminescence bands for DCM in the solvents is more than by an order greater in comparison with the one for LK678. This is explained by the fact that in the first excited state S_1 the dipole moment μ_{S1} of DCM molecule essentially rises, whereas for LK678 it changes slightly.
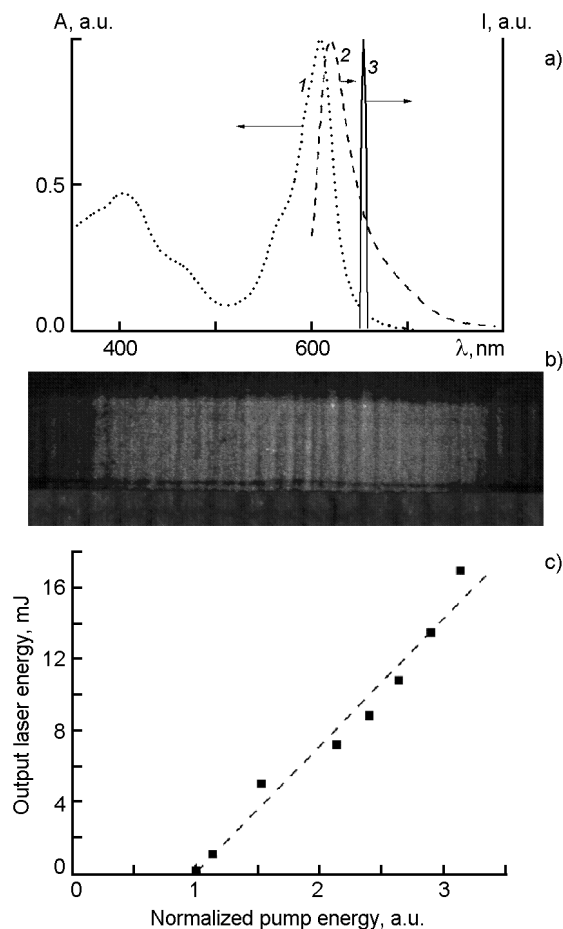

Fig. 5. a) Absorption (*1*), luminescence ($\lambda_{ex} = 590$ nm) (*2*) and laser emission spectra of LD678 dye in SiO_2 matrices (*3*) (with the dye concentrations $3.1 \cdot 10^{-4}$ M, $9.14 \cdot 10^{-6}$ M and $1.08 \cdot 10^{-3}$ M, respectively); b) spectrogram of laser emission of this sample (the reciprocal dispersion ~6.2 Å/mm); c) dependence of the laser output energy on the pumping pulse energy (588 nm) for SiO_2 matrices with LD678.

The laser radiation of the dyes DCM and LK678 was obtained on the SiO_2 matrices synthesized with the addition of pyridine for reducing the acidity of the medium (Fig. 4, 5). In the process of this synthesis there were used both TEOS and TMOS. Was found that the SiO_2 matrices with these dyes are more transparent when used as a precursor TMOS compared with TEOS. This is caused by the decrease of the aggregation of SiO_2 nanoparticles in the silica gels based on TMOS.

On these TMOS matrices activated with LK678 dye we obtained effective laser radiation at 654 nm wavelength (Fig. 5a, b). Presented in 5c is the graph of the dependence

of the laser output energy of the matrix with the dye LK678 on the value of normalized pumping energy (the pumping energy is normalized to the value of the threshold pumping $E_{th} \sim 70$ mJ). At the threefold increase of the pumping energy the output laser energy of the active media rises linearly.

The central wavelength of the laser radiation spectrum λ_{las} of DCM in acetonitrile and methanol is 632 nm and 635 nm, respectively. Thereat, for DCM with large Stokes shift $\Delta\nu^{St}$ and small overlap of the absorption and luminescence spectra the laser radiation spectrum is located close to λ_L. For LK678 dye with small $\Delta\nu^{St}$ this spectrum is shifted towards the long-wavelength wing of the luminescence spectrum, due to the self-absorption in the active medium. While comparing the spectral parameters of DCM and LK678 dyes one can see that the influence of the SiO_2 matrices on the laser dye molecules is approximately similar to the influence of the solvate environment in methanol. For LK678 its lasing spectrum the matrix is bathochromically shifted by 4 nm with respect to that of methanol solution.

The output laser energy by the matrices with LK678 at a pumping energy of about 200 mJ was by 1.5 higher than the one of the matrix with $1.9{\cdot}10^{-3}$ M Rh6G. At the maximal pumping energy the matrix with $1.08{\cdot}10^{-3}$ M LK678 the output laser energy was 17 mJ (λ_{las} =654±5 nm). For the matrices with DCM the threshold pumping energy was approximately twice as high as the analogous value for LK678, therefore for the used FLPDL energy laser radiation of the DCM in matrices has been registered with a small excess over E_{th}. The half-width of the laser radiation spectrum of the SiO_2 matrix with DCM (~2 nm) is considerably less than that in the solutions (Table 2). The measured spectral, luminescent and energy characteristics of the DCM and LK678 dyes testify to their sufficiently high effectiveness in the red spectral range which presumed its perspective use for creation of the active media for solid-state dye lasers.

4. Conclusions

SiO_2 matrices with the laser dyes DCM, LK678 and the benzopyran derivatives LD1 and LD2 which emit in the red spectral range, are synthesized. Studies are the spectral properties of these dyes in SiO_2 matrices. The spectral properties of these dyes in SiO_2 matrices were studied. The luminescence spectra of the dyes LD1 and LD2 in

SiO_2 gels are similar to those in polar media with low pH. Blue shifts of the absorption and luminescence maxima of LD1 and LD2 dyes in SiO_2 matrices compared to the gels are due to changes in the microenvironment of dyes. Significant bleaching of the LD1 dye and LD2 at least during the synthesis of matrices, probably connected with the protonation of the nitrogen in the 7th position of their benzopyran basis.

In the SiO_2 matrices with DCM and LD678 dyes, synthesized on the basis of TMOS with the addition of pyridine, obtained by a laser radiation. SiO_2 matrices with incorporated dyes DCM and LD678 for the red spectral region can be used as active media for solid-state dye lasers.

References

1. 1.M.Hintersteiner, A.Enz, P.Frey et al., *Nature Biotechnology*, **23**, 577 (2005).
2. A.Dubois, M.Canva, A.Brun et al., *Appl. Opt.*, **35**, 3193 (1996).
3. M.D.Rahn, T.A.King, *Appl. Opt.*, **34**, 8260 (1995).
4. W.Hu, H.Ye, C.Li et al., *Appl. Opt.*, **36**, 579 (1997).
5. W.Koechner, *Solid-State Laser Eng.*, **4**, 400 (1996).
6. V.V.Maslov, M.I.Dzyubenko, S.N.Kovalenko et al., *Zh. Kvantovoy Electroniki*, **7**, 998 (1987).
7. V.V.Maslov, in: Proc. 2nd International Workshop on Laser and Fiber-Optical Networks Modeling, Kharkov, Ukraine (2000), p.83 [in Russian].
8. V.V.Maslov, *Functional Materials*, **13**, 13, 419 (2006).
9. M. Alvarez, F.Amat-Guerri, A.Costela, *Opt. Commun.*, **267**, 469 (2006).
10. P.R.Hammond, *Opt. Communs.*, **29**, 331 (1979).
11. B.I.Stepanov, N.N.Bychkov, V.G.Nikiforov et al., *Pis'ma v Zh. Technicheskoy Fiziki*, **14**, 650 (1980).
12. F.Salin, G.Le Saux, P.Georges, A.Brun, *Opt. Lett.*, **14**, 785 (1989).
13. M.Sharma, D.Mohan, R.D.Singh, N.Singh, *Opt. Mater.*, **30**, 1273 (2008).
14. O.N.Bezkrovnaya, I.M.Pritula, V.V.Maslov et al., *Functional Materials*, **17**, 537 (2010).
15. V.V.Maslov, M.I.Dzyubenko, V.M.Nikitchenko, *Zh. Kvantovoy Electroniki*, **19**, 463 (1989).
16. G.Jones II, W.R.Jackson, Chol-yoo Choi, W.R.Bergmark, *J. Phys. Chem.*, **89**, 294 (1985).
17. G.Hungerford, M.R.Pereira, J.A.Ferreira et al., *J. Fluorescence*, **12**, 397 (2002).
18. N.G.Bakhshiev, Spectroscopy of Intermolecular Interactions, Nauka, Leningrad (1972) [in Russian].

Матриці на основі кремнезему, активовані червоними лазерними барвниками

І.М.Притула, О.Н.Безкровна, В.М.Пузіков, В.В.Маслов, А.Г.Плаксій, А.В.Лопін, Ю.А.Гуркаленко

Синтезовано золь-гель SiO_2-матриці, активовані лазерними барвниками для червоної області спектра DCM, LK678 і похідними бензопірану LD1 і LD2. Для запобігання знебарвлення барвників у процесі синтезу матриць використовувався піридин. Досліджено спектрально-люмінесцентні характеристики лазерних барвників у SiO_2-матрицях. На DCM і LK678 при лазерному накачуванні отримано вимушене випромінювання. Лазерна ефективність барвника LK678 у матриці в 1,5 разів вище, ніж у родаміну 6G. В роботі пояснюється відсутність генерації похідних бензопірану LD1 і LD2 у синтезованих матрицях.