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Solid-state active media of tunable organic-compound lasers pumped with a laser. I. An XeCl laser

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Abstract. The lasing properties of organic compounds in a polymethylmethacrylate matrix radiating in the blue-green (paraterphenyle and coumarine derivatives) and red (phodamine and phenalemine derivatives) regions of the spectrum pumped by an XeCl laser are studied. The lasing efficiency and photostability of the solid-state active media are compared with corresponding characteristics of the same liquid active media.

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In the last few years the interest in the development and preparation of solid-state active media for tunable organic-compound lasers with lasing characteristics close to solutions has considerably increased. Encouraging results were obtained in the preparation of active laser media (ALM) pumped by 532-nm radiation and lasing in the red region of the spectrum [1–5]. The prospects for preparing solid organic-compound ALM pumped by radiation from an XeCl excimer laser and lasing in the blue and blue-green regions of the spectrum are very good. However, there has been little progress in this direction due to a number of objective difficulties in preparing matrices that exhibit high transparency and radiation resistance and in developing and preparing organic compounds capable of efficient radiation conversion in the matrix without its destruction. A class of molecules capable of lasing in matrices in the blue-green region of the spectrum (coumarins and benzimidazoles) is limited [6, 7]. As a rule, low-power XeCl and N_2 lasers are used to pump them. Shortest-wavelength lasing of the Exalite 377-E solid active medium in a sol-gel matrix pumped by nitrogen-laser radiation ($\lambda = 337$ nm) has been excited at 360 and 378 nm with 1% efficiency and a lifetime of 10^4 pulses [8].

The present work is aimed at studying spectral-luminescent and lasing characteristics of organic compounds emitting in the blue-green and red regions of the spectrum pumped by XeCl excimer laser radiation.

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1 Experiment

Structural formulas of ALM molecules are shown in Fig. 1. Experiments were performed in ethanol solutions and polymethylmethacrylate (PMMA) matrices. All compounds were delivered by the Alpha Akonis Firm. They were very pure and were used further without any additional purification. Polymeric dye blocks were also prepared there; they were homogeneous and exhibited high optical transparency.

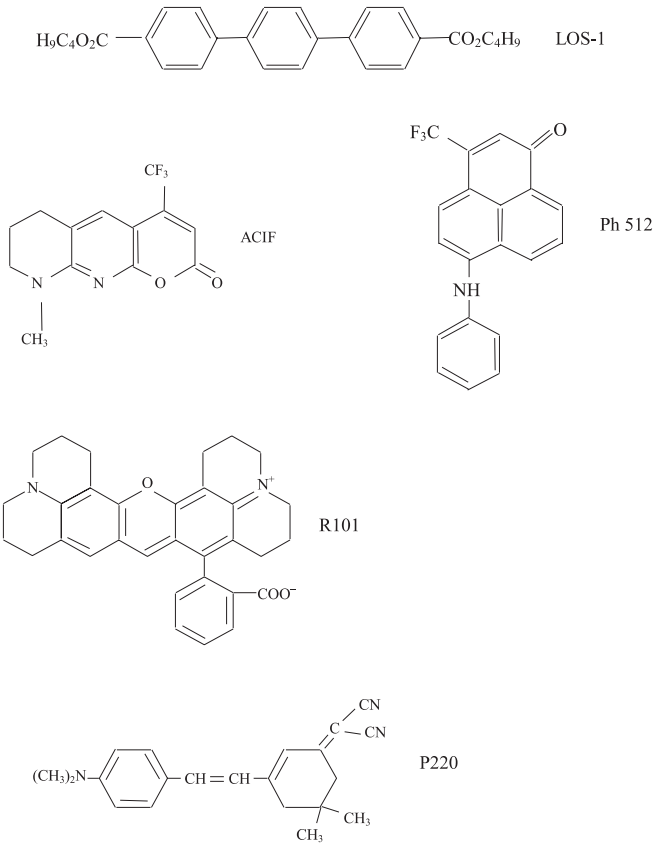

Fig. 1. Structure of the dye molecules

The spectral characteristics were measured with a Specord M40 spectrophotometer and a Hitach 850 spectrofluorometer.

Lasing characteristics of solutions and solid ALM were studied under the same conditions: a transversal pumping configuration and a resonator formed by a non-transmitting mirror and the side of a cell or polymeric sample. The excimer-laser radiation at $\lambda = 308$ nm with energy per pulse from 10 to 100 mJ and 15 ns duration was focused with a lens onto a sample in a spot 8×1 mm. Solid-state samples were rectangular parallelepipeds of 10×10 mm square sections. A laser surface finish was not achieved; therefore, the conversion efficiency of solid samples could be significantly improved.

Phenalemine 512 (Ph512) was investigated not only in the static regime, as described above (the sample was fixed and the irradiated region was not scanned along the sample), but also in the dynamic regime. In this case, the non-transparent mirror and the sample cylinder 40 mm in diameter and 10 mm in length were clamped on the rotating disk axis. The transverse excitation scheme was also employed with radiation incident on the cylinder side. The sample was irradiated with a frequency of 2 Hz. The radiation intensity was 2.5 MW/cm^2.

The integral lasing spectrum was registered with a monochromator, a photoelectric multiplier, and a plotter. Lasing and fluorescence spectra were also recorded for a single pumping pulse with a spectrofluorometer representing an optical system irradiated through a lightguide. The input radiation was split in a Fizeau interferometer and registered with a photodiode matrix. An electric signal from the matrix was fed into a special chip built into a computer, where it was digitized and processed.

The photostability of active media was estimated from their lifetime, $P_{0.5}$ (the energy deposited into the unit volume of an active medium before its efficiency halved), and quantum photodestruction yield (γ), calculated from the formula $\gamma = N_{ph}/N^*$, where N^* is the number of excited molecules and N_{ph} is the number of photodegraded molecules per unit volume. We estimated N_{ph} from changes in the long-wavelength absorption band intensity for low irradiation doses when the influence of photoproduct absorption was insignificant.

2 Discussion of the results

2.1 Blue-green region of the spectrum

In this region of the spectrum, lasing of LOS-1 and AC1F can be excited. The LOS-1 compound ideally matches pumping by an XeCl laser whose radiation falls within the long-wavelength maximum of the absorption band and thereby minimizes Stokes losses. This is especially important for polymeric materials in which local overheating may take place because of low thermal conductivity of their matrix.

Table 1 gives the lasing characteristics of the examined compounds and the lifetime ($P_{0.5}$) of active media prepared. The lasing volume required to estimate the ALM lifetime was calculated for a polymeric matrix from the cross-sectional area of the spot burnt on photographic paper by pumping and lasing radiation.

Table 1. Lasing characteristics of LOS-1 and AC1F in PMMA and ethanol

Compound	Concentration (mmol/ℓ)	λ_{fl} (nm)	λ_{las} (nm)	η (%)	$P_{0.5}$ (J/cm^3)
LOS-1	0.1	365	365	17.6	20
in PMMA	1	367	365	17.5	84
LOS-1	0.1	373	373	25	26
in ethanol	0.5	–	–	40	150
	1	–	–	38	175[1]
AC1F	1	467	465	1.7	20
in PMMA	10	477	475	12.5	87
AC1F	1	480	498	14	48
in ethanol	2.5	–	–	25	250
	10	–	–	–	500[1]

[1] This value corresponds to $P_{0.8}$

Efficiencies of lasing for a LOS-1 concentration in ethanol and PMMA of 0.1 mmol/ℓ differ only slightly (25 and 17.5%, respectively). This concentration corresponds to low coefficient of pump radiation absorption ($K_{308} \approx 5$ cm^{-1}), and lasing is excited not only in the subsurface but also in deeper-lying layers of the sample. For a concentration of 1 mmol/ℓ, K_{308} increased to 50 cm^{-1}; therefore, lasing in the solution and PMMA was excited practically on the surface of the sample. Taking this into account, we suggested that a reason for different lasing efficiencies in ethanol (38%) and PMMA (17.6%) might be the insufficient surface finish.

The maximum lasing efficiency of AC1F in PMMA pumped by the excimer laser was 12.5% (at an AC1F concentration of 10 mmol/ℓ). The low lasing efficiency for a concentration of 1 mmol/ℓ was due to the weak absorption of pump radiation under these conditions. Indeed, the lasing efficiency increased to 19% when the sample was excited by the LOS-1 laser radiation ($\lambda = 373$ nm), because the absorption coefficient at this wavelength was 7 times higher than at $\lambda = 308$ nm.

As follows from Table 1, lifetimes of LOS-1 in ethanol and PMMA are close for a concentration of 0.1 mmol/ℓ. The increase in the concentration to 1 mmol/ℓ resulted in the proportional increase in the lifetime in ethanol, whereas in PMMA the lifetime increased approximately 4 times. This difference is obviously caused by the photolysis of PMMA, exhibiting significant absorption at 308 nm upon exposure to the pump radiation. Photodegradation products of the matrix, in turn, may cause additional decomposition of dye molecules, thereby decreasing the lifetime of the active medium. Analogous dependences of $P_{0.5}$ on the concentration were obtained for the AC1F dye.

Dependences of lasing efficiencies of LOS-1 and AC1F in ethanol and PMMA on the pump power density are shown in Fig. 2. As follows from the results obtained, optimal efficiencies are achieved for sufficiently high intensities of $\approx$ 15–20 MW/cm^2.

Dependences of the position of the emission band maximum and of its half-width as functions of the pump radiation intensity were studied for LOS-1 in ethanol and the matrix. The pump radiation intensity was varied from 0.18 to 27 MW/cm^2. Figure 3 shows the results obtained. Transformations of spectra (Fig. 3a and c) indicate that the fluores-

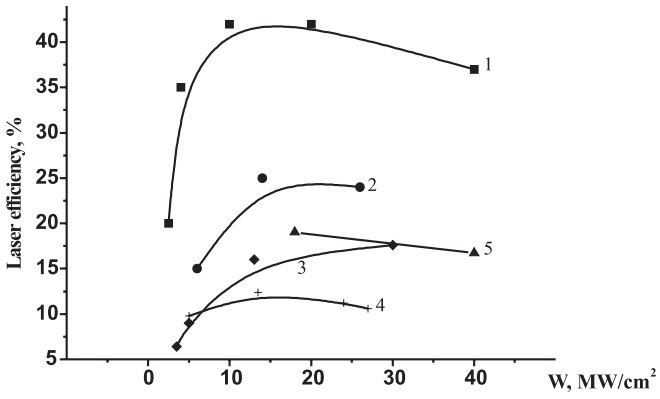

Fig. 2. Dependence of the laser efficiency of LOS-1 (1,3) and AC1F (2,4,5) in ethanol (1,2) and PMMA (3–5) on the pump intensity of radiation with $\lambda = 308$ nm (1–4) and 375 nm (5)

cent radiation is converted into laser radiation with increasing pump radiation intensity. Narrowing of the emission band is illustrated in Fig. 3b and d. We note that the minimum half-width of the emission band in PMMA, equal to 5.5 nm, is achieved for lower pump radiation intensities compared to ethanol. As a whole, the dye behaves similarly in ethanol and PMMA.

Along with the lasing characteristics, we studied the molecular photostability (γ) of LOS-1 and AC1F in ethanol and PMMA. The molecular photostability of dye in the solution and polymeric matrix was studied under very close experimental conditions (irradiated spot area: 0.9×1.3 mm; sample length: 1 and 0.8 mm for liquid and polymeric samples, respectively; XeCl-laser intensity: 0.3 MW/cm^2).

Table 2. Molecular photostability (γ) of the compounds and the absorption coefficients of photoproducts in the lasing (K_l) and pump (K_p) regions

Compound	Solvent	C (mmol/ℓ)	$\gamma = N_{ph}/N^*$	K_l (cm^{-1})	K_p (cm^{-1})
LOS-1	Ethanol	0.1	10^{-4}	~ 0	–
	PMMA		2×10^{-4}	0.62	–
AC1F	Ethanol	1	2×10^{-3}	~ 0	0.4
	PMMA		10^{-3}	0.4	1

Table 2 gives the molecular photostability γ for ethanol solutions and polymeric samples. It follows from the table that LOS-1 in ethanol is more stable than in PMMA. The dependence for AC1F is opposite.

Because the lifetime of an active medium is determined not only by the molecular photostability but also by the absorption of photoproducts in pumping and dye lasing spectral regions, Table 2 tabulates coefficients of photoproduct absorption in lasing (K_l) and pumping (K_p) regions for identical deposited energies. The energies deposited in ethanol and polymeric LOS-1 samples were 90 J/cm^3, respectively. An energy of 60 J/cm^3 was deposited in each AC1F sample. It can be seen that the absorption of photoproducts formed in PMMA is stronger in both the lasing and pumping regions compared to ethanol solutions. Apparently, this fact is the pri-

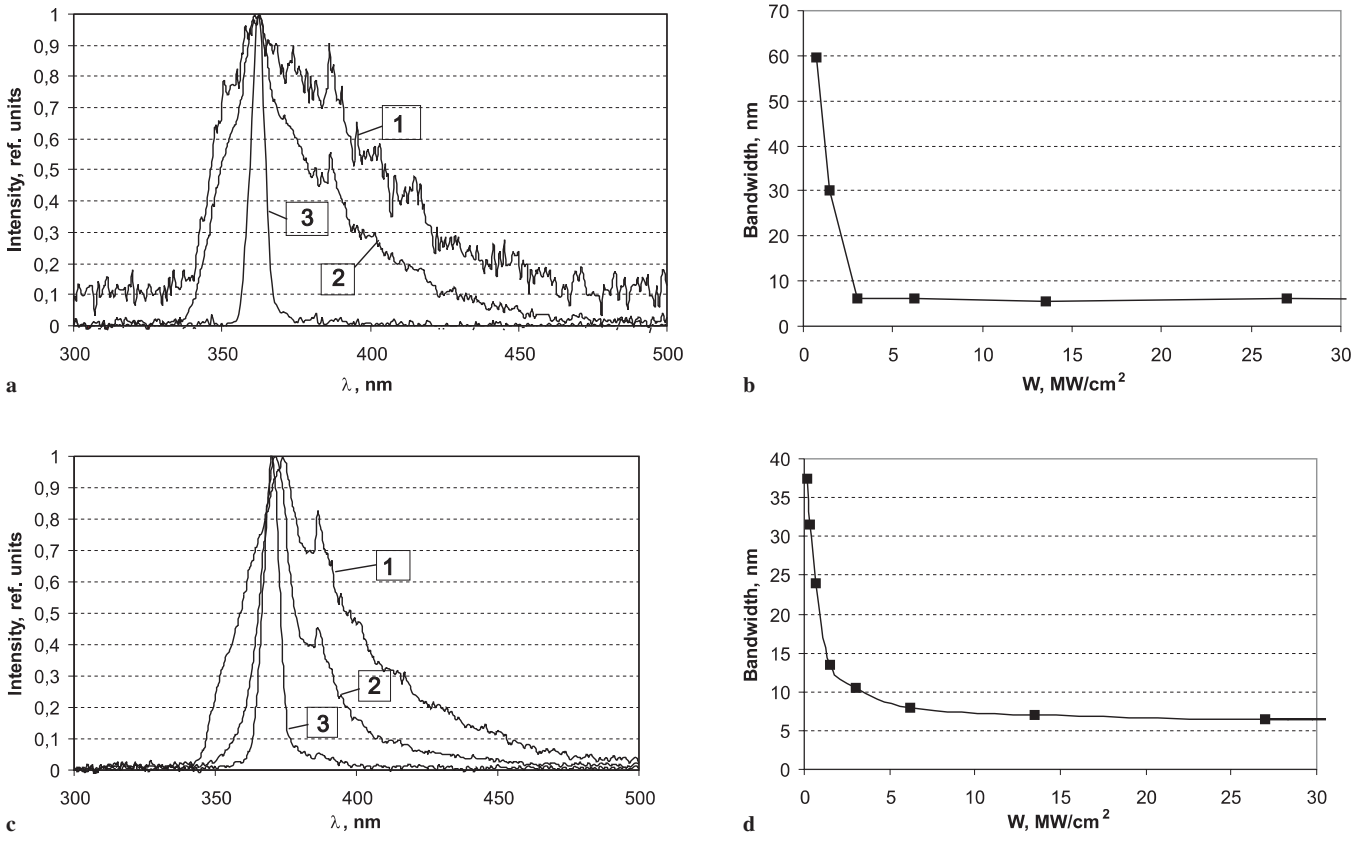

Fig. 3a–d. The dynamic of emitting band changes of LOS-1 ($c = 1$ mmol/ℓ) in **a**,**b** PMMA and **c**,**d** ethanol versus the excitation intensity: (1) 0.7, (2) 1.5, and (3) 27 MW/cm^2

mary cause of a shorter lifetime for the examined compounds in PMMA.

Investigations of the fluorescence of irradiated samples demonstrated that, in addition to the LOS-1 emission, bands of photoproduct fluorescence were observed with maxima at 435 and 480 nm in ethanol and ≈ 430 and 455 nm in PMMA. Positions of photoproduct fluorescence bands in ethanol and PMMA were close. It is possible that their molecular structures are also similar. As to AC1F samples, no fluorescent photoproducts were observed in ethanol upon exposure to the given irradiation dose; however, photoproduct fluorescence bands at 370 and 540 nm were recorded in PMMA.

2.2 Red region of the spectrum

Spectral and lasing characteristics of compounds emitting in the red region of the spectrum are given in Table 3. Measurements were performed for several concentrations; the corresponding absorption coefficients, K_{308}, for the pump radiation wavelengths are also given.

Absorption and fluorescence spectra of Ph512 and P220 in PMMA were shifted toward shorter wavelengths compared to those in ethanol. The dependence was reverse for R101 in PMMA: the spectra were shifted by ≈ 5 nm toward red wavelengths. The displacement of the emission band maximum toward the red region of the spectrum with increasing concentration was typical of all the compounds. Obviously, this is due to the self-absorption effect.

One property in common was a lower lasing efficiency in PMMA compared to ethanol solutions. It should be noted that this difference was not so large for Ph512. Thus, the lasing efficiencies in ethanol and PMMA were 22.5 and 18%, respectively, for a Ph512 concentration of 0.4 mmol/ℓ. R101 in PMMA emitted much worse than in ethanol, irrespective of concentration. P220 is slightly soluble in ethanol, ≤ 0.5 mmol/ℓ. The maximum lasing efficiency in ethanol was 9%. A much better efficiency of 22% was obtained in acetonitrile.

The dependence of lasing efficiency on the pumping intensity was studied for all compounds. It is shown in Fig. 4. As in the case of LOS-1 and AC1F, the maximum lasing efficiency was recorded for sufficiently high pump radiation intensities lying in the range 15–20 MW/cm^2. The lifetime $P_{0.5}$ is tabulated in Table 3 for these intensities. The lifetime of R101 in ethanol solutions was larger than in PMMA; values of $P_{0.5}$ were comparable for Ph512; and P220 in PMMA was more stable than in acetonitrile.

As pointed out above, Ph512 was studied not only in the static regime, but also in the dynamic regime for low pump radiation intensity (2.5 MW/cm^2). The lasing efficiency as a function of the number of pumping pulses is shown in Fig. 5. The experiment was performed with several resting times. The curve has a saw-tooth shape. During the first 5–7 thousand pulses, the lasing efficiency increased after each resting time. Probably this was caused by an increase in the sample temperature due to Stokes losses. Thus, almost 50% of the pump pulse energy (λ = 308 nm) was lost to heat for Ph512 (λ = 601–618 nm). Indeed, when the sample was held in the atmosphere at 30–35 °C, the build-up of lasing was not observed. This effect was also absent when the pump radiation intensity was high (≈ 30 MW/cm^2). In the latter case, local heating was already observed after several pulses. Whether this fact is due to the increasing quantum yield of the Ph512 fluorescence with increasing temperature or due to another reason remains to be elucidated.

As a whole, the lasing efficiency decreased by 36% from its initial value after 75 thousand pulses, and 500 J/cm^3 was deposited into the sample. This value is much higher than the value given in Table 3 (when 240 J/cm^3 was deposited, the ef-

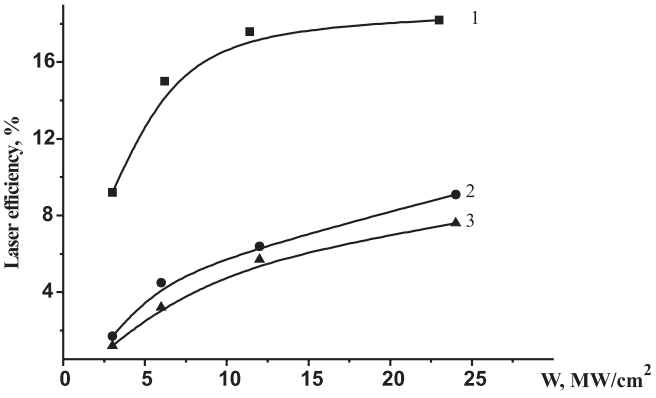

Fig. 4. Dependence of the laser efficiency of (1) Ph512, (2) R101, (3) P220 in PMMA on the pump intensity of radiation. Dye concentrations are equal to 2 mmol/ℓ

Table 3. Lasing characteristics of the compounds emitting in the red region. Et.: ethanol

Compound	C (mmol/ℓ)	K_{308} (cm^{-1})	λ_{fl}, (nm) Et.	PMMA	λ_{las} (nm) Et.	PMMA	Efficiency (%) Et.	PMMA	$P_{0.5}$ (J/cm^3) Et.	PMMA
Ph512	0.5	6.5	605	583	619.8	–	21	–	50[1]	–
	1	13	605	583	619.8	601	23	13.8	–	240
	4	52	605	583	620	611	22.5	18	–	500
	10	130	605	583	620	618	13	9.7	–	420
R101	0.5	7.2	615	620	613	624	25.5	3.8	300	50
	1	15	615	620	617.9	630	27	7.4	–	190
	2.3	33.1	615	620	644	650	25	9	–	120
P220	0.5	5.2	–	610	695	650	3	4.8	–	60
	1	10.5	–	610	–	650	–	2.8	–	330
	2	21	–	610	696[2]	658	22[2]	13.5	75[2]	660

[1] This value corresponds to $P_{0.8}$
[2] In acetonitrile

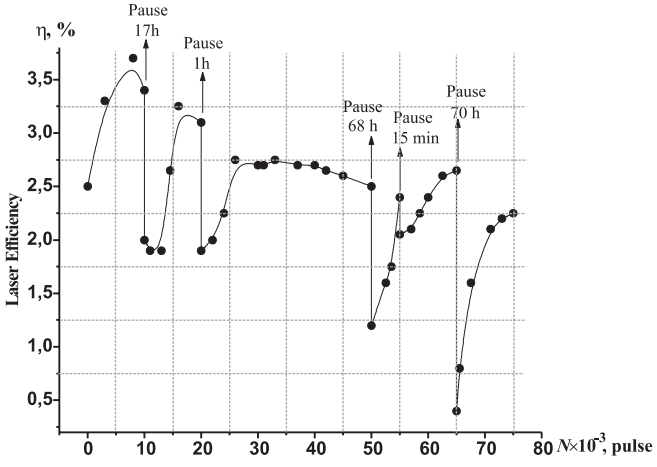

Fig. 5. Laser efficiency of Ph512 in PMMA pumped with an XeCl laser in the dynamic regime

ficiency halved) for the static pump regime with a high pump radiation intensity.

2.3 Concluding remarks

Our investigations of polymeric active media have demonstrated that excitation intensities that are optimal for the lasing efficiency are not optimal for the lifetime. Solid elements pumped with low-intensity radiation have longer lifetimes.

In our opinion, LOS-1 and Ph512 are the most promising of the five molecules examined for use in PMMA pumped by an XeCl laser.

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