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A microporous glass-polymer composite as a new material for solid-state dye lasers: II. Lasing properties

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Abstract. The conversion efficiency and service life of the laser elements based on a polymer-filled microporous glass (PFMPG) composite doped with organic dyes are studied. It is shown that both the conversion efficiency and the service life of the laser elements achieve the values obtained for the same dyes in bulk polymer elements. Good lasing characteristics of the elements studied are advantageously combined with the high mechanical strength and high laser damage resistance and excellent thermooptical properties of the PFMPG composite.

1. Introduction

Attempts to use a microporous glass for fabrication of laser elements have been made many times [1 – 3]. In earlier papers, a dye was adsorbed on the surface of micropores [1]. However, such laser elements had a short service life and have not found practical applications.

Later, solid-liquid laser elements based on a microporous glass impregnated with the dye solution were proposed [2, 3]. In fact, these elements were liquids, with all the disadvantages inherent in liquid elements, but their thermooptical properties were improved [2, 3]. However, their service life was also short and, in addition, the circulation of the dye solution could not be performed by the methods developed for liquid elements. The attempts to perform the dye circulation by other methods have failed [3]. For this reason, solid-liquid laser elements also have not found practical applications.

Efficient solid-state laser elements have been fabricated based on a polymer matrix doped with dyes [4 – 9]. A combination of the properties of a microporous glass and polymers in a polymer-filled microporous glass (PFMPG) composite results in a substantial improvement of a number of characteristics of laser elements (laser damage resistance, mechanical strength, etc. [10]). However, it remains unclear whether the conversion efficiency of dyes and their service life in the PFMPG composite will be as high as in polymers. The specific conditions of formation of polymers in narrow channels of microporous glasses warrant neither an identity of the properties of bulk polymers and polymers imbedded into a microporous glass nor a similar stabilising influence of low-molecular additions on dyes.

The aim of this paper is to study the conversion efficiency and the service life of PFMPG laser elements and to compare the results with similar characteristics of laser elements based on bulk polymers.

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2. Study of lasing properties

2.1. Experimental setups

We studied lasing in a scheme with longitudinal pumping. Dyes were pumped by a frequency-doubled, Q-switched Nd^{3+} : YAG laser. A laser element was placed into a cavity with a dichroic mirror, which was transparent at $\lambda_p = 532$ nm and totally reflecting at the lasing wavelength λ_g. The parameters of experimental setups and their operating regimes are presented below.

	Multimode regime	Single-mode regime
Modulator type	Passive	Electrooptical
Pulse duration/ns	5	5
Beam diameter $(1/e^2)$/mm	1.4	1.3
Cavity length /cm	7	10
Radius of curvature of a totally reflecting mirror/m	0.5	∞
Reflectivity of a flat output mirror R_m (%)	20, 50	62
Pump power density I_p/ MW cm^{-2}	25, 50	9, 22
Pulse repetition rate F/Hz	5	11/3, 33

The lasing wavelength λ_g was measured with a Coherent WaveMate wavemeter and an Optometrics MC1-03 monochromator with an accuracy of ± 1 nm.

2.2. Studies and methods for data processing

We measured the conversion efficiency η of pump radiation by laser elements, their service life $N_{0.7}$ (at the 0.7 level), the dependence of η on the pump intensity I_p over a broad range of intensities, and the dependence of η and $N_{0.7}$ on the pulse repetition rate. The conversion efficiency was determined from the expression

$$\eta = (E_g/E_p)100\ \%$$

where E_p and E_g are the energies of the pump and laser pulse, respectively. The value of $N_{0.7}$ was measured from the relation $\eta(N_{0.7}) = 0.7\eta_0$, where η_0 is the conversion efficiency upon excitation by the first pump pulse.

In measurements of η, one region of the laser element was pumped by a small number of pulses satisfying the condition $N \ll N_{0.7}$. The conversion efficiency was studied by pumping the laser element by a train of pulses of an equal intensity up to the moment when the relation $\eta(N_{0.7}) = 0.7\eta_0$ was obtained. In all measurements, the different regions of the laser element being pumped were separated by a distance of no less than two diameters of the laser beam, so that their mutual influence was excluded.

We calculated η by neglecting the loss of the pump energy caused by the Fresnel reflection from the laser element surface. When the optical density of the laser element was low, a fraction of the pump pulse energy was transmitted through the element, and in this case we calculated η using the absorbed energy of the pump pulse rather than the incident energy.

2.3. Laser elements studied and experimental results

We studied the conversion efficiency of pump radiation in PFMPG using laser elements doped with dyes of the pyrromethene series (PM 580, PM 597, PM 650) and a xanthene dye Rh 11B. Laser elements were fabricated from a monomer composition containing methyl methacrylate and low-molecular additions , which are conventionally used to improve the dye stability in a polymer [4]. Laser elements of size 20 mm ×10 mm × 4 mm were doped with spatially uniformly distributed dyes and were transparent in the visible region. The

Table 1. Conversion efficiency of laser elements.

Dye	C/mmol l^{-1}	R_m(%)	P_0/μJ	η (%)	η_{max} (%)
PM 580	2.4	20	–	–	46
		50	–	–	53
PM 597	1.5	20	150	65	64
		50	130	69	67
	3.0	20	230	73	69
		50	160	65	63
PM650	2.15	20	700	31	28
		50	610	20	18
	4.3	20	670	26	23
		50	290	17	16
Rh 11B	0.2	20	310	56	55
		50	60	52	53
	0.5	20	340	58	54
		50	160	51	50
	1.0	20	450	46	41
		50	100	31	31

Note: η_{max} is maximum conversion efficiency over the entire range of I_p; C is the reduced concentration of the dye equal to the concentration of the dye monomers; P_0 is the lasing threshold.

Table 2. Service life of laser elements.

Dye	C/mmol l^{-1}	R_m (%)	I_p/MW cm^{-2}	F/Hz	$N_{0.7}$/pulses
PM 580	2.4	20	25	1	3300
		20	25	5	2500
PM 597	3.0	20	25	5	60000
		50	50	5	45000
PM 650	4.3	20	25	5	90000
		20	50	5	46000
Rh 11B	1.0	20	25	5	110000
		20	50	5	22000

chosen dyes exhibit the high conversion efficiency of the 532-nm pump radiation and have a large service life in a polymer matrix [6–9].

The values of η and $N_{0.7}$ obtained upon multimode pump are presented in Tables 1 and 2.

3. Experimental results

3.1. Laser element doped with the PM 580 dye

3.1.1 Multimode pumping

Because the 532-nm pump wavelength falls on the wing of the absorption band of the PM 580 dye, the optical density of laser elements doped with this dye is low at the pump wavelength. The transmission of the laser element doped with PM 580 at a concentration of 2.4 mmol l^{-1} was 12 % for I_p = 10 MW cm^{-2} and increased to 27 % for I_p = 50 MW cm^{-2}. The values of η and η_{max} presented in Table 1 were calculated taking into account the absorbed rather than incident pump energy, as was mentioned above.

The dependence $\eta(I_p)$ at $R_m = 20\%$ is shown in Fig. 1. One can see that the conversion efficiency strongly depends on the laser-element region being pumped and virtually does not increase with increasing I_p. Only when $R_m = 50\%$, η slightly increases with increasing I_p. Such a behaviour of $\eta(I_p)$, as well as local variations in η, were observed only for laser elements doped with the PM 580 dye upon multimode pump. The local variations in η cannot be related to the dye distribution in the laser element, because the dye is uniformly distributed over the PFMPG composite volume [10]. It is possible that these variations are related to the generation of parasite modes in the laser element.

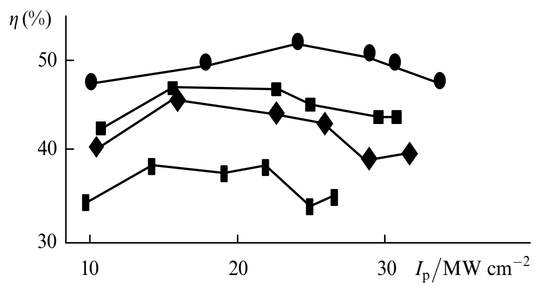

Figure 1. Conversion efficiency η of laser radiation in the PFMPG laser element doped with the PM 580 dye as a function of the pump intensity I_p for different regions of the laser element at $C = 2.4$ mmol l^{-1} and $R_m = 20\%$.

The relatively low service life of the laser element doped with the PM 580 dye upon multimode pump can be also related to the generation of parasite modes.

3.1.2. Single-mode pumping

We failed to obtain stable lasing in a laser element doped with the PM 580 dye at a concentration of 2.4 mmol l^{-1} upon single-mode pumping. This is probably explained by a low optical density of the sample and low I_p. The optical density of the laser element at the pump wavelength increased substantially when the concentration of PM 580 was increased to 6 mmol l^{-1}. In this case, the lasing threshold upon single-mode pumping was 7 mJ cm^{-2}, $\eta_{max} = 46\%$ (for $I_p = 9$ MW cm^{-2}) and $N_{0.7} = 50000$ pulses.

3.2. Laser element doped with the PM 597 dye

3.2.1. Multimode pumping

The PM 597 is known as highly efficient and stable lasing dye [11]. The results presented in Table 2 and in Fig. 2 show that η weakly depends both on the PM 597 concentration in the laser element and R_m (within the dye concentration range studied and under our experimental conditions). Note that the conversion efficiency $\eta_{max} = 69\%$ for the laser element doped with PM 597 at the concentration of 3 mmol l^{-1}

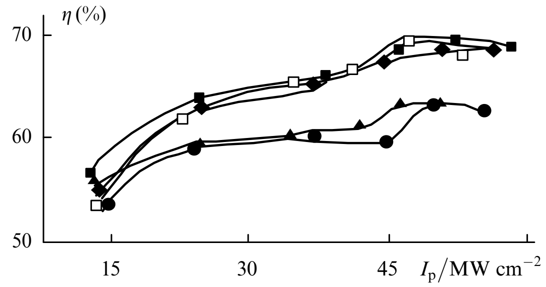

Figure 2. Conversion efficiency η of laser radiation in the PFMPG laser element doped with the PM 597 dye as a function of the pump intensity I_p for different regions of the laser element at $C = 3$ mmol l^{-1} and $R_m = 20$ (■,◆) and 50% (▲, ●); □ reference MPMMA laser element for $R_m = 20\%$.

and at $R_m = 20\%$ coincides with that obtained under the same conditions in the laser element made of modified polymethyl methacrylate (MPMMA) doped with PM 597 at a concentration of 0.1 mmol l^{-1}.

The difference between the dye concentrations in the polymer and composite laser elements is explained as follows. The volume of pores in a microporous glass, which was used in the composite laser element, amounts to 32% of its entire volume and the fill factor of pores in a microporous glass by the dye is 0.2–0.3 [10]. Because the PM 597 dye concentration equal to 3 mmol l^{-1} represents its concentration in the initial monomer composition, taking into account the fill factor, the real concentration is C_{eff}(PM597) = 0.1 mmol l^{-1}.

The conversion efficiency $\eta(I_p)$ of the laser element doped with the PM 597 dye linearly increases with I_p. A similar behaviour of $\eta(I_p)$ take place for the MPMMA laser element (Fig. 2). The service life of the laser element doped with 3 mmol l^{-1} PM 597 was 60 000 and 45 000 pulses for $I_p = 25$ and 50 MW cm^{-2}, respectively. The variation of η upon pumping of the laser element is shown in Fig. 3. This variation is accompanied by a slow decrease in the lasing wavelength from 571 to 568 nm.

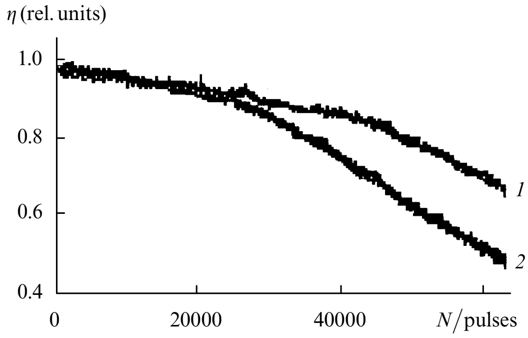

Figure 3. Dependences of the conversion efficiency η on the number N of pulses irradiating the same region of the laser element doped with the PM 597 dye at $C = 3$ mmol l^{-1}, $F = 5$ Hz, and $R_m = 20\%$ for $I_p = 25$ (*1*) and 50 MW cm^{-2} (*2*).

3.2.2. Single-mode pumping

The conversion efficiency upon single-mode pumping of the laser element doped with PM 597 at the concentration of 2 mmol $litre^{-1}$ was $\eta = 52\%$ at $I_p = 9$ MW cm^{-2} and the service life of the element was $N_{0.7} \approx 50000$ pulses. An increase in I_p up to 22 MW cm^{-2} resulted, as was expected, in the increase of η up to 65%. The lasing threshold was 5 mJ cm^{-2}.

3.3. Laser element doped with the PM 650 dye

3.3.1. Multimode pumping

The lasing wavelength of the PM 650 dye is the longest among the dyes studied here and is equal to 625 nm. The specific feature of this dye is a relatively low quantum yield of fluorescence compared to that for other dyes of the pyrromethene series ($\phi = 0.54$ for PM 650 in ethanol, whereas $\phi = 0.90$ and 0.77 for PM 580 and PM 597, respectively). This leads to a lower lasing efficiency and strong heating of the laser element during lasing, resulting in the thermal decomposition of the dye, thereby reducing the service life of the laser element.

A higher heat conduction of the PFMPG composite compared to that of MPMMA allows one to hope that the PFMPG laser element will have a greater service life. The conversion efficiency in the PM 650 dye (Table 1) amounts to 31% at $C = 2.15$ mmol l^{-1}, $R_m = 20\%$, and $I_p = 20$ MW cm^{-2}. Note that this laser element transmitted a small fraction of the pump radiation (about 3–4%), which was taken into account in the calculation of η.

The conversion efficiency $\eta(I_p)$ slowly increased with I_p, as in the case of the PM 597 dye, and was 17 and 26% for the laser element doped with 4.3 mmol l^{-1} of PM 650 (i.e., C_{eff} (PM 650) = 0.2 mmol l^{-1}) for $R_m = 20\%$ and $I_p = 20$ and 50 MW cm^{-2}, respectively. This conversion efficiency is somewhat lower than that for the MPMMA laser element doped with 0.2 mmol l^{-1} of PM 650, which is equal to 32% for $I_p = 35$ MW cm^{-2} and $R_m = 20\%$.

As expected, the service life of the laser element proved to be quite large: $N_{0.7} = 90000$ pulses for $I_p = 25$ MW cm^{-2}, which exceeds that of the laser element doped with the PM 597 dye under the same conditions. During pumping by a train of pulses, as in other cases, the lasing wavelength decreased from 625 to 620 nm.

3.3.2. Single-mode pumping

The conversion efficiency upon single-mode pumping was low and achieved 17% in the laser element doped with 4.4

mmol l^{-1} of PM 650 at $I_p = 22$ MW cm^{-2}. The lasing threshold was 35 mJ cm^{-2}.

3.4. Laser element doped with the Rh 11B dye

3.4.1. Multimode pumping

The Rh 11B dye can be readily impregnated into the composite, which allows us to vary the optical density of the laser element in a broad range and optimise both η and $N_{0.7}$.

For the multimode pumping, an optimal dye concentration in Rh 11B-doped laser element was 0.2 mmol l^{-1} to achieve $\eta = 55\,\%$ at $I_p = 25$ MW cm^{-2} and $R_m = 20\,\%$. Both a decrease and an increase in the concentration of Rh 11B in the laser element reduce η. The increase in the concentration of Rh 11B to 1 mmol l^{-1} reduces η down to 40 %, which is probably caused by the concentration quenching of luminescence of the dye.

We found that the conversion efficiency slowly increased with increasing I_p. No variations in η were observed upon pumping different regions of the laser element. The service life of the laser element doped with Rh 11B (1 mmol l^{-1}) was 110 000 pulses for $I_p = 20$ MW cm^{-2} and $R_m = 20\,\%$. It is important that $N_{0.7}$ greatly decreases with increasing I_p and is equal to 22 000 for $I_p = 50$ MW cm^{-2}. This suggests that nonlinear processes play a substantial role in the decomposition of the Rh 11B dye.

The lasing wavelength of the laser elements decreased during lasing, as in the case of laser elements doped with pyrromethene dyes. Fig. 4 shows this decrease for pump pulses with $I_p = 25$ MW cm^{-2}, a pulse repetition rate of 5 Hz, and $R_m = 20\,\%$. The lasing wavelength shifted by 7 nm to 563 nm after 10^5 pulses.

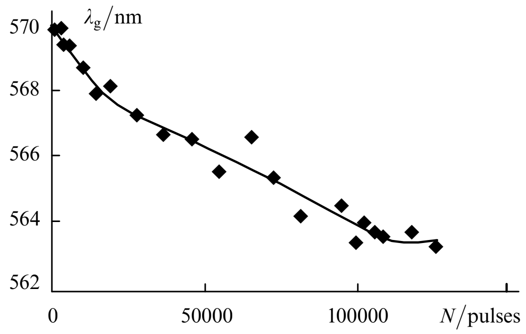

Figure 4. Dependence of the lasing wavelength l_g on the number N of pump pulses for the PFMPG laser element doped with the Rh 11B dye at $C = 1$ mmol l^{-1}, $I_p = 25$ MW cm^{-2}, $F = 5$ Hz, and $R_m = 20\,\%$.

3.4.2. Single-mode pumping

The conversion efficiency of the Rh 11B dye upon single-mode pump was $\eta = 45\,\%$ and the service life was $N_{0.7} =$ 25000 pulses for $I_p = 9$ MW cm^{-2}, $C = 0.1$ mmol l^{-1}.

To estimate the influence of a low-molecular addition on the dye in the PFMPG composite, we fabricated a reference laser element that did not contain the low-molecular additives. The dye concentration in this element was 0.1 mmol l^{-1}. The experiments with this element yielded the same result, $\eta = 45\,\%$ for $I_p = 9$ MW cm^{-2}. However, the service life $N_{0.7}$ of the element decreased by a factor of ten and became as low as 2500 pulses. Therefore, it seems that the mechanism of photobleaching of the dye and the methods of its stabilisation are the same for the polymer and the composite and are governed by processes proceeding in the polymer component of the composite.

4. Discussion

We have shown that the conversion efficiency and the service life of PFMPG laser elements doped with dyes and pumped by the second-harmonic pulses from a Nd^{3+} : YAG laser are comparable with those achieved in MPMMA laser elements. One can see this most clearly for Rh 11B and PM 597 dyes, which have been studied in most detail and have been used for fabrication of laser elements with the optical density that was sufficient for efficient lasing. These results indicate that the microporous glass introduces no special features in the process of doping polymers with dyes. This means that the principles of stabilisation of dyes developed for a polymer matrix can be also applied to their stabilisation in the PFMPG composite, and the radiation conversion efficiency and the service life in the latter case will correspond to those achieved in polymer laser elements.

At the same time, PFMPG laser elements feature important advantages. They have good mechanical and thermooptical characteristics and their laser damage resistance is higher than that of bulk polymer elements. As a result, they have stable characteristics at high pulse repetition rates and exhibit high conversion efficiency both upon single-mode and multimode pump. Note that the parameters of the laser elements did not change over the entire range of pulse repetition rates studied (up to 33 Hz), while their service life was restricted by photobleaching of the dye (the PFMPG composite matrix was destroyed in neither of the experiments at the pump powers used).

During the measurements of the service life of laser elements the lasing wavelength was shifted to the blue. This is explained by the well-known concentration dependence of the lasing wavelength [12]. A fraction of the dye is decomposed during lasing and the dye concentration decreases, resulting in the blue shift of the lasing wavelength. This conclusion is confirmed by the fact that the laser elements doped with the dye at different concentrations produce lasing at different wavelengths. Thus, the laser elements doped with the PM 597 dye at concentrations of 1.5 and 3 mmol l^{-1} emits at 568 and 571 nm, respectively.

A very important parameter of the laser element is its service life. In most papers devoted to the study of solid laser elements, this parameter was determined from the condition $\eta(N_s) = s\eta_0$, where η_0 is the lasing efficiency at the first pump pulse and s is the number, which we set equal to 0.7. The service life found in such a way represents a technical parameter of the laser element. Its main drawback from the point of view of the destruction physics of the laser element is the dependence on a great number of parameters, which precludes the correct comparison of the results obtained by different authors. For this reason, it is difficult to estimate both the stability of a dye in a matrix and their compatibility based on the data on the technical service life.

To understand the mechanism of the dye photodestruction and to compare the stability of the dyes in different matrices under different experimental conditions, a special analysis is required, which takes into account different factors. In particular, the dye stability can be characterised by the energy resource W_s, which represents the energy absorbed by a mole of the dye that reduces the radiation conversion efficiency from η_0 to $s\eta_0$. According to the data presented in Table 2, $W_{0.7}$(Rh 11B) $\approx$ 70 and 15 TJ mol^{-1} at $I_p = 25$ and 50 MW cm^{-2}, respectively; whereas $W_{0.7}$ (PM 597) $\approx$ 30 T mol^{-1} at $I_p = 50$ MW cm^{-2}. It is useful to compare the latter value of $W_{0.7}$ with the corresponding data obtained for this dye in a sol-gel matrix [13]. According to paper [13], $W_{0.7}$ (PM 597) = 0.15 − 1.5 in a sol-gel matrix, which is substantially lower than the value of $W_{0.7}$ obtained for the same dye in the PFMPG composite.

Thus, the PM 597 dye is much more stable in the PFMPG matrix than in the sol-gel matrix. A great technical service life N_s obtained for a sol-gel matrix in paper [13] is probably explained by the fact that the thickness of laser elements studied in [13] (10 mm and above) exceeds that of laser elements investigated by us. In addition, in [13], the service life N_s was measured for $s = 0.5$.

5. Conclusions

We have shown that PFMPG laser elements have good physical characteristics. They possess high mechanical strength, high laser damage resistance, and good thermooptical parameters. In addition, they exhibit stable repetitively pulsed lasing, can be easily doped with dyes, etc. The study of the radiation conversion efficiency and the service life of PFMPG laser elements has shown that the methods of stabilisation of dyes in matrices developed earlier for polymer elements can be applied in full measure to the PFMPG composite. The radiation conversion efficiency and the service life of the laser elements are comparable with those of MPMMA laser elements. Thus, the PFMPG composite is one of the most promising materials for the fabrication of solid laser elements doped with dyes.

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