

Microporous glass-polymer composite as a new material for solid-state dye lasers: I. Material properties

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Abstract. The mechanical, optical, and thermo-optical properties of a microporous glass-polymer (MPG–P) composite used as a matrix for solid-state dye lasers are studied. It is shown that the composite has a high mechanical hardness, good transparency, excellent thermo-optical parameters, and high laser damage resistance, and can be also readily doped with various dyes. The analysis of physical properties of the MPG–P composite showed its advantages over other solid matrices (bulk polymers and sol-gel glasses) for applications in efficient solid-state dye lasers.

1. Introduction

Optical elements based on organic dyes are widely used in laser technology. They are applied for lasing, passive Q -switching, and mode locking. The most popular are liquid laser elements based on dye solutions. However, they possess a number of obvious drawbacks such as poor thermo-optical parameters, toxicity of some solutions, etc. For this reason, many attempts have been made to develop laser elements based on solid matrices doped with dyes.

The main requirements imposed upon solid materials used in laser elements is the possibility of their doping with dyes at high concentrations without the destruction and formation of dye aggregates. In addition, these materials must be easily workable and have the mechanical strength and high resistance to the laser radiation damage, as well as good thermo-optical parameters.

Up to now, polymer matrices [1], sol-gel glasses [2–4], and materials based on a microporous glass (MPG) doped with polymers (the MPG–P composite) [5–7] were used as solid matrices. The MPG laser elements with dyes adsorbed in their pores or impregnated with dye solutions have been also investigated [8–10].

Polymer materials that have been used for the development of highly efficient dye lasers (employing dyes of different classes such as xanthenes, pyrromethenes, etc.), optical modulators, etc. [1, 11, 12] are best studied. However, polymer laser elements have a number of disadvantages such as low mechanical strength, the poor thermal conductivity, the large temperature coefficient of the refractive index, etc. These drawbacks restrict the applicability of polymer laser elements, in particular, in the case of high pulse repetition rates and high radiation power.

Another type of materials that are recently extensively studied is sol-gel glasses. However, although considerable efforts have been made to investigate them [2–4], the advantages of this material have not been revealed so far.

As for the MPG laser elements doped with dyes, their substantial drawback is a low stability of dyes in glass pores [8–10]. For this reason, this field was not developed in the last years.

The MPG–P composite most completely satisfies the above requirements imposed upon solid laser materials doped with dyes [5–7]. The advantage of this material is first of all a combination of good thermo-optical properties of a glass component with good solubility and stability of a dye in the polymer. It was shown even in the first studies that this material features good mechanical properties [5, 13] and high damage resistance to the laser radiation both upon single-pulse [5, 13] and repeated pulsed irradiation [5].

The aim of this paper is to study in detail the properties of the MPG–P composite that are important for fabricating laser elements. We investigated mechanical, thermo-optical, and optical properties of the MPG–P composite, as well as lasing parameters of the laser elements made of this composite.

2. Fabrication of the MPG–P composite

2.1. Microporous glass

Microporous plates, which were used as the base of a composite material, were made of an alkali-borosilicate glass by the method of acid leaching. Glasses of two different compositions (types) were used: $6.8\text{Na}_2\text{O} : 20.9\text{B}_2\text{O}_3 : 0.3\text{Al}_2\text{O}_3 : 72.0\text{SiO}_2$ (type 1) and $4.0\text{Na}_2\text{O} : 3.8\text{K}_2\text{O} : 33.2\text{B}_2\text{O}_3 : 59.0\text{SiO}_2$ (type 2). Before leaching, glasses were subjected to thermal treatment, resulting in the formation of two glass phases: a chemically stable enriched SiO_2 phase and an unstable alkali-borate phase.

After thermal treatment, the glass was cut into plates measuring $20 \times 15 \times 4$ mm and was treated in a boiling 3-mol HCl solution during the time required for complete

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leaching. The volume porosity of the obtained MPG samples was 27–30% for a glass of type 1 and 37–40% for a glass of type 2. The pore radius of glasses of types 1 and 2 was 3.25 and 2–7 nm, respectively. The size distribution of pairs was unimodal and narrow in all samples. An example of this distribution for one of the samples obtained by the method of mercury porosimetry [14] is presented in Fig. 1.

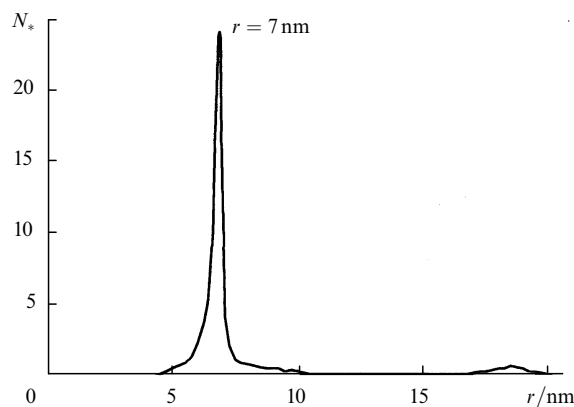


Figure 1. Size distribution of the number N_s of pores in MPG samples of the second type.

2.2. Composite material

To form a polymer component of the composite, we prepared a mixture of a methyl methacrylate (MMA) monomer and a low-molecular modifying additive, in which a dye was dissolved. Before the mixture preparation, a monomer was distilled, while the mixture was filtered through a 0.1- μm porous filter.

Because a MPG is a strong adsorbent, to remove adsorbed substances, the MPG samples were annealed at the temperature 550°C. After annealing, the MPG sample was impregnated with the mixture prepared and free-radical polymerisation was performed at temperatures 30–100°C followed by annealing. After polymerisation, the sample was extracted from a polymer block and was subjected to optical processing.

3. Properties of the MPG–P composite

3.1. Mechanical properties

The microhardness was studied using the Vickers scheme by keeping samples under load of 1 N applied for 40–50 s. The microhardness of the composite and modified polymethyl methacrylate (MPMMA) obtained together with the composite was measured simultaneously. The composite microhardness was between 1500 and 2000 N mm^{-2} and was 15–20 times greater than that of MPMMA. Note that the composite microhardness, in contrast to that of MPMMA, is independent of the composition of the polymer component introduced into the MPG and is determined only by the glass type.

The MPG–P laser elements were polished to the fourth class of purity ($N = 1$, $\Delta N = 0.2$); their surfaces were plane-parallel within 30". Owing to their high microhardness, the samples could be processed using the technology accepted for optical glasses.

3.2. Scattering of radiation

Because the composite is heterogeneous, considerable optical losses caused by scattering of radiation can arise. We studied scattering of light using a setup schematically shown in Fig. 2. As a radiation source, a 633-nm He–Ne laser was used. The laser beam was expanded with a collimator and was limited by an output diaphragm of diameter 1 cm. After a condenser, the laser beam was transmitted through a sample, was focused on a diaphragm of a small diameter ϕ , and detected with a photodetector. The dependences of the transmitted radiation intensity on ϕ obtained for a number of MPG–P samples and a reference MPMMA sample are shown in Fig. 3.

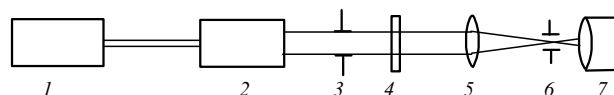


Figure 2. Scheme of the setup for measuring scattering losses: (1) He–Ne laser ($\lambda = 633 \text{ nm}$); (2) collimator; (3) output diaphragm; (4) MPG–P sample; (5) convergent lens; (6) limiting diaphragm; (7) photodetector.

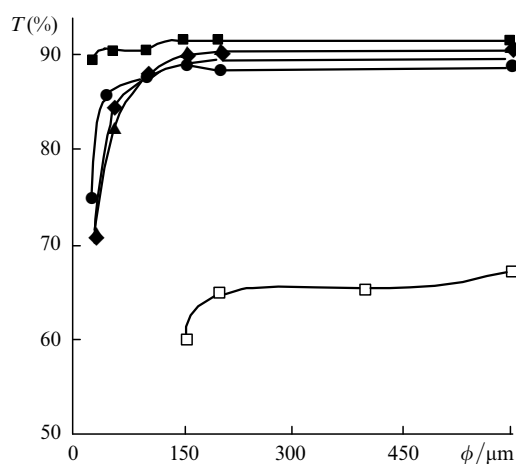


Figure 3. Dependences of the transmission T of laser elements on the limiting diaphragm diameter ϕ (■ – the reference MPMMA sample with the PM 597 dye; ◆ – the MPG–P sample with PM 580; ● – the MPG–P sample with PM 597; ▲ – the MPG–P sample with Rh 11B; □ – a sample fabricated using imperfect technology).

The transmission of MPMMA was 91–92% for all diaphragm sizes, which is explained by Fresnel losses on the sample surface. In the case of the composite, transmission decreases for $\phi \leq 150 \mu\text{m}$, which can restrict the efficiency of radiation conversion upon strong focusing of the laser pump beam. It seems that careful working off of the technology of composite fabrication should eliminate this drawback. One can see this in Fig. 3, which shows that only the first samples, which were fabricated using the imperfect technology, exhibit very strong scattering of light.

3.3. Filling the MPG with the polymer and dye

To control the filling of micropores by the polymer and dye, we performed spectroscopic studies by measuring absorption at a wavelength of 1150 nm for undoped samples and the absorption and fluorescence spectra for samples doped with the dye.

The wavelength 1150 nm corresponds to the second vibrational overtone of the C—H bond in PMMA [15] and lies within the transparency region of the MPG. The degree of filling of the MPG with the polymer can be estimated from the magnitude of absorption at this wavelength. The results of the study of the MPG samples of the first and second types suggest that no microvoids were remained in the MPG after formation of the polymer.

The study of the absorption and fluorescence spectra of dyes revealed specific features of filling of the pore volume with the dye.

The absorption and fluorescence spectra of a pyrromethene 650 dye (PM 650) in the MPG–P composite are shown in Fig. 4. The concentration C of the PM 650 dye in the initial monomer composition was 0.5 mmol l^{-1} for this sample. The absorption and fluorescence maxima of PM 650 in the composite coincide with those for the solution of this dye in ethanol (the absorption and fluorescence maxima are located at 590 and 612 nm, respectively). The extinction coefficient of PM 650 in ethanol at 590 nm is $40500 \text{ l mol}^{-1} \text{ cm}^{-1}$.

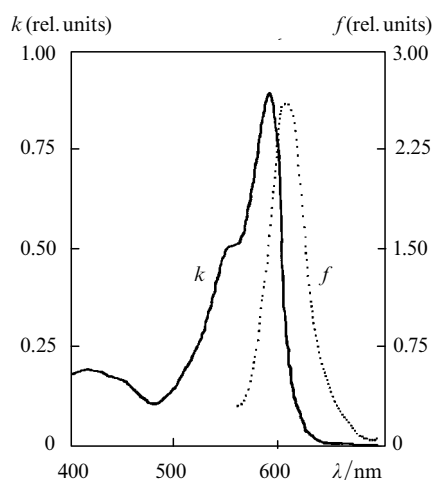


Figure 4. Absorption (k) and fluorescence (f) spectra of the PM 650 dye at the concentration 0.5 mmol l^{-1} in the MPG–P composite.

Assuming that the extinction coefficient of PM 650 in the composite is the same as in ethanol, we obtain that $C(\text{PM650}) = 0.05 \text{ mmol l}^{-1}$. Because $C(\text{PM650}) = 0.5 \text{ mmol l}^{-1}$ in the initial monomer composition and the porosity of the MPG is 30%, the concentration of PM 650 should be 0.18 mmol l^{-1} when micropores are filled completely. A much lower concentration of this dye in the composite compared to the initial concentration for the monomer means that the dye does not fill pores completely during the impregnation of the MPG with the monomer. A similar picture filling of the MPG–P composite was also observed for other dyes of the pyrromethene series (PM 580 and PM 597).

In contrast to pyrromethene dyes, the concentration of rhodamine 11B in the MPG–P composite is, as a rule, higher than in the initial monomer composition. Moreover, when the MPG was kept for a long time in the monomer composition with rhodamine 11B dye, the dye almost completely passed to the MPG volume. The reasons for different filling of glass micropores with different dyes require a special study.

3.4. Distribution of the dye concentration in samples

To study the distribution of the dye concentration in the MPG–P composite, we analysed absorption of radiation from a He–Ne laser in the sample. During the measurements, the sample surface was scanned by the laser beam of 2 mm diameter. This study showed that dyes are uniformly distributed in the samples.

3.5. Thermo-optical effects

We performed a quantitative study of thermo-optical effects and compared them in the composite and MPMMA by measuring the focal distance f_t of a thermally induced lens. The scheme of the experimental setup is shown in Fig. 5. The probe beam from a He–Ne laser at 633 nm was expanded with a condenser consisting of a diverging lens with the focal distance $f_1 = -25 \text{ mm}$ and a converging lens with the focal distance $f_2 = 300 \text{ mm}$. The beam cross section was limited by a diaphragm with diameter 5 mm. The pump beam at 532 nm passed through the same diaphragm. Both beams were incident on a laser element under study. The pump beam transmitted through the laser element was rejected with a filter, while the probe beam was focused with a lens with the focal distance $f_3 = 1000 \text{ mm}$ on a photodetector. A lens with the focal distance f_1 was displaced to obtain the maximum signal from the detector in the absence of the pump.

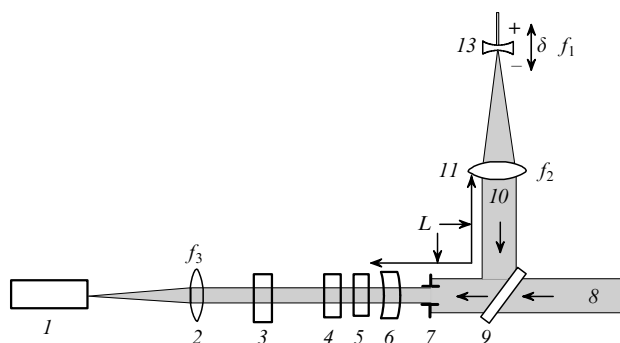


Figure 5. Scheme of the setup for measuring the focal distance of a thermal lens: (1) photodetector; (2) lens with $f_3 = 1000 \text{ mm}$; (3) optical filters; (4) output cavity mirror; (5) element under study; (6) dichroic mirror; (7) diaphragm; (8) pump beam ($\lambda = 532 \text{ nm}$); (9) beamsplitter; (10) collimated beam; (11) lens with $f_2 = 300 \text{ mm}$; (12) probe beam from a He–Ne laser; (13) lens with $f_1 = -25 \text{ mm}$.

Upon pumping, the output signal decreased due to defocusing of radiation by a thermally induced lens. When the f_1 lens was displaced by some distance δ , the signal increased to the maximum. The quantity f_t is related to δ by the simple expression from geometrical optics

$$f_t = (L - f_2) - f_2^2 / \delta, \quad (1)$$

where L is the distance from the f_2 lens to the laser element.

We studied thermo-optical effects in the laser element doped with the PM 597 dye, which absorbs radiation at 532 nm. We measured the dependence of f_t on the average absorbed pump power for the MPG–P laser element and the reference MPMMA element. Our study showed that thermo-optical effects in the MPG–P composite are much weaker than in MPMMA (Fig. 6).

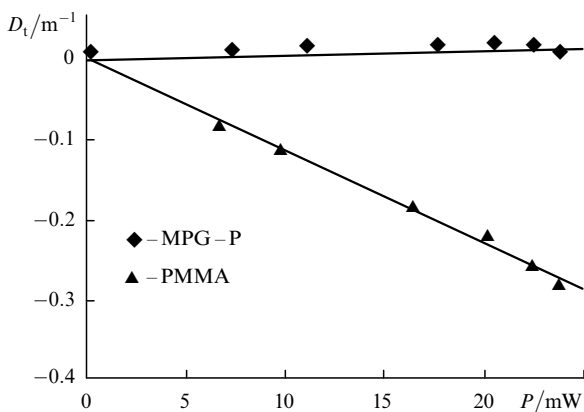


Figure 6. Dependence of the optical power $D_t = 1/f_t$ of the induced thermal lens on the average absorbed power P for the MPG-P and PMMA samples.

3.6. Damage resistance to laser radiation

We studied the laser radiation damage resistance of samples using a 1063-nm multimode Q -switched Nd^{3+} : YAG laser ($\tau_{1/2} = 15$ ns). The laser radiation was focused to samples with a lens with the focal distance $f = 100$ mm. The caustic diameter in the air (at the e^{-1} intensity level) was 500 μm . The sample damage was observed visually by the appearance of a spark. The laser radiation damage resistance was studied both upon single-pulse and repeated irradiation. The damage threshold was estimated as the power density at which the damage was produced with a probability of 0.5. The results of the study of damage thresholds of the composite and bulk MPMMA synthesised simultaneously with the composite are presented in Table 1.

One can see in Table 1 that damage thresholds increase, both upon single-pulse irradiation and irradiation by 200 pulses, in the MPG containing polymer compared to the bulk MPMMA. The maximum increase in the damage threshold (more than by an order of magnitude) was observed upon irradiation by 200 pulses. In this case, the preliminary purification of the monomer did not affect appreciably the damage threshold, whereas the purification of the bulk polymer affected the damage threshold [1].

4. Discussion

4.1. Material transparency

The difference in the refractive indices of the quartz-like frame of a MPG and of MPMMA incorporated into it amounts to $\Delta n \approx (2 - 3) \times 10^{-2}$. Because, however, the size

d of pores filled with the polymer satisfies the inequality $d \ll \lambda$ (in our experiments, $\lambda \sim 500$ nm and $d \sim 5$ nm), it is not surprising that, according to our experiments, the extinction of the MPG-P composite is small despite the great value of Δn .

Talking about the extinction of the MPG-P composite, one should take into account that the optical properties of the polymer incorporated into the composite pores and of bulk polymers can be different. This is confirmed by the fact that the transparency of the MPG-P composite substantially depends on the technology of polymerisation of the polymer incorporated into the MPG. This is not surprising, because polymerisation inside small micropores substantially differs from conventional block polymerisation in macroscopic volumes.

The two most important differences are as follows. Inside micropores, the access of a monomer to the reaction region is strongly hindered. The MMA monomer strongly shrinks during polymerisation, which can induce strains and exfoliation of the polymer from the pore surface. In addition, the formation of the polymer chain inside a narrow channel also has a certain specific nature. One cubic centimetre of a microporous glass that we used for fabrication of the composite has a total surface of pores of the order of 500 m^2 . This volume of pores with a great total surface area contains less than 0.4 cm^3 of monomers, i.e., monomers form in fact a thin layer on the pore surface.

The choice of the optimal regime of thermal treatment of an initial glass is very important for producing an optically homogeneous composite. This regime determines the distribution and sizes of micropores in the MPG obtained upon leaching.

Studies of the MPG-P composites for the two types of glasses showed that the relation between the volume and surface area of pores does not affect appreciably the optical quality of the composite, because there exist other factors related to polymerisation.

4.2. Thermo-optical properties

Thermo-optical effects in a material are determined by the parameter $\mu = \chi(dn/dT)^{-1}$, where χ is the thermal conductivity of the material and dn/dT is the rate of a change in the refractive index n with temperature T .

The advantages of the composite over the bulk PMMA are related to a number of factors. The main one is a considerably lower magnitude of dn/dT . Indeed, according to the Lorentz-Lorentz relation [15], the refractive index is

$$R = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho}, \tag{2}$$

where M is the molar mass and ρ is the material density.

By differentiating (2) with respect to temperature and taking into account that M and R are independent of the temperature, we obtain

$$\frac{dn}{dT} = -\alpha \frac{(n^2 - 1)(n^2 + 2)}{2n}, \tag{3}$$

where α is the linear expansion coefficient of the material.

For PMMA, $\alpha \approx 7 \times 10^{-5} K^{-1}$ [16]. Being incorporated into glass micropores, PMMA cannot expand freely because a rigid frame of micropores restricts it. Since elastic constants of quartz greatly exceed those of PMMA, this means that

Табл.1. Resistance materials to the laser radiation damage

Sample	Monomer filtration	Low-molecular addition	Damage threshold upon irradiation by a single pulse /J cm^{-2}	Damage threshold upon irradiation by a train of 200 pulses /J cm^{-2}
PMMA	-	-	17	1.6-1.9
PMMA	+	-	63	2.2-2.6
MPMMA	-	+	15	5.4-6.3
Composite	-	-	58	31-38
Composite	+	-	76	35-43
Composite	-	+	56	25-28

PMMA incorporated into a microporous glass expands with increasing temperature in the same way as micropores. In this case, to estimate the value of dn/dT of PMMA incorporated into the MPG, one should use in (3) the linear expansion coefficient of fused silica, i.e., take the value $\alpha \approx 0.51 \times 10^{-6} \text{ K}^{-1}$ [16]. Therefore, the value of dn/dT for the MPG–P composite is 100–130 times lower than for bulk PMMA.

The second important factor, which reduces thermo-optical effects in the MPG–P composite compared to PMMA, is the high thermal conductivity of the quartz frame of the composite. The values of thermal conductivity for quartz and PMMA are 1.3 and 0.16 kcal h⁻¹ m⁻¹ K⁻¹, respectively [17], so that their ratio is approximately equal to eight. Taking into account that the glass porosity is 40%, this ratio means that thermo-optical effects should be reduced by a factor of 4–5.

Thus, the parameter μ , which determines thermo-optical properties of a material, is 500–600 times greater for the MPG–P composite than for PMMA.

4.3. Damage resistance to laser radiation

The results of the study of the laser radiation damage resistance of the MPG–P composite can be simply explained. Because a glass is treated with hydrochloric acid during leaching, the inclusions will be probably removed from the glass. The size of micropores is 5–10 nm, so that the inclusions of size 10 nm found in the monomer mixture cannot enter into the composite. When the MPG is impregnated with the mixture obtained, the efficient filtration of the composition occurs, which results, in particular, in a weak dependence of the damage threshold of the composite on the degree of purification of the monomer mixture. These factors increase the damage threshold of the composite caused by absorbing inclusions.

5. Conclusions

Our study of the properties of the MPG–P composite showed that this material is perspective for the fabrication of laser elements doped with organic dyes.

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