Far-red polyurethane-host solid-state dye laser

S.V. Nikolaev, V.V. Pozhar, M.I. Dzyubenko, A.O. Doroshenko

Abstract. **The output energy and emission spectrum of a solid-state dye laser using Oxazine 1 in polyurethane as the gain medium have been measured. Under microsecond pumping, efficient lasing has been obtained in the range 700–745 nm. The highest conversion efficiency and output energy achieved are 23 % and 127 mJ, respectively.**

1. Introduction

Recent years have seen increasing interest in the development of efficient solid-state dye lasers (SSDLs), motivated by the fact that SSDLs are viewed as an attractive alternative to conventional liquid dye lasers (LDLs) because they offer the advantages of compact design and, more importantly, environmental safety and nonflammability [1, 2].

The materials most widely used to produce gain media of SSDLs are polymers. The active elements of SSDLs may have the form of polymer matrices or matrices made of polymer-filled nanoporous materials [3–6]. To date, the most detailed information has been reported about efficient operation of polymer dye lasers (PDLs) pumped by nanosecond laser pulses [7–11]. At the same time, many potential applications of SSDLs require longer pulse durations, in particular in the order of microseconds.

To create polymer gain media capable of operating under high-power microsecond pumping, materials having considerable elasticity are needed. As shown earlier [12–14], attractive polymers for use under such conditions are polyurethane and its derivatives. Detailed studies of the chemical, thermophysical and optical properties of polyurethane media have shown that they have a high optical damage threshold, in particular in the UV spectral range, can be doped with a variety of dyes and can be used to produce both intracavity passive *Q*-switches and active

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elements of PDLs. The main drawbacks of polyurethane are its relatively low shape stability, rather high shrinkage during polymerisation and considerable thermal expansion coefficient. Moreover, polyurethane matrices are inferior in optical homogeneity to other polymers. These drawbacks hinder the development of sufficiently long active elements. To overcome them, efforts have been focused on the fabrication and testing of efficient cylindrical polyurethane matrices more than 1 cm in length, suitable for transverse excitation [15]. In this way, lasing has been obtained with the dyes Rhodamine 6G and Oxazine 17 under microsecond pumping, and narrowing and tuning of the output spectrum of the PDLs have been achieved. The results prompted us to continue our studies in this direction, with major attention focused on raising the efficiency of a laser with a cylindrical polyurethane active element. This issue is addressed in the present paper.

The key steps in solving the problem in hand were to improve the process for the fabrication of polyurethane matrices and to select a dye with good lasing properties in such media. Our attention was attracted by results of Russell et al. [16, 17], who successfully used the dye Oxazine 725 (Oxazine 1) to dope modified poly(methyl methacrylate) matrices and observed a low lasing threshold under excitation with microsecond pulses. One characteristic feature of Oxazine 1 is that embedding it in a viscous solvent increases the quantum yield of its fluorescence. Therefore, this dye would be expected to be efficient as well in a polyurethane matrix. All the above led us to select Oxazine 1 as a dopant for polyurethane matrices, whose lasing performance was studied in this work.

2. Characterisation of polyurethane matrices and experimental procedure

We prepared a series of polyurethane matrices differing in Oxazine 1 concentration: from 10^{-3} to 1.25×10^{-4} M. The matrices had the form of quartz cylinders 2 cm in length and 1 cm in radius, with plane-parallel faces, filled with doped polyurethane. Oxazine 1 was readily incorporated into polyurethane, without bleaching during the polymerisation process. The spectral characteristics of the resultant gain medium are illustrated in Fig. 1, which shows its normalised absorption, $A(\lambda)$, and fluorescence, $F(\lambda)$, spectra.

Note that the length-to-radius ratio of the cell determines to a significant extent the optical quality of the polyurethane matrix. This is related to the properties of polyurethane, which not only shrinks but also has a

tendency to experience internal stress during polymerisation in a closed space. Our experiments show that the resulting stress has the least effect on the optical quality of the gain medium when the matrix is cylindrical in shape and has the above dimensions.

The lasing properties of the cylindrical polyurethane matrices were studied with the same setup as in an earlier study [15]. We used transverse pumping of the polyurethane matrices. The excitation source used was an LDL (ethanolic solution of Oxazine 17) which generated $\sim$ 5-µs pulses up to 1.5 J in energy in the range 660–670 nm, close to the maximum absorption wavelength of Oxazine 1 (Fig. 1).
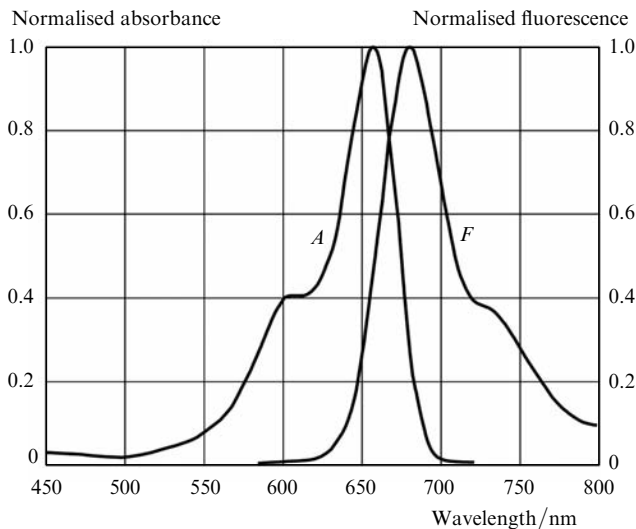
Figure 1. Normalised absorption, $A(\lambda)$, and fluorescence, $F(\lambda)$, spectra of Oxazine 1 in polyurethane.

In our experiments, the output energy, E_e, and emission spectrum of the polyurethane matrices in cavities with different reflectances of the output coupler, R, were measured at a variable pump energy, E_p. To maintain the pump pulse shape unchanged, the LDL was operated at a constant voltage across the storage capacitor, and the pump energy was controlled by a reflecting plate.

3. Results and discussion

The most illustrative data on the energy efficiency of four matrices differing in dye concentration, C, are presented in Fig. 2 as plots of output energy [curves ($1-4$)] and laser efficiency [curves ($1'-4'$)] against pump energy. The efficiency was evaluated as the percent ratio of the PDL output energy to the incident pump beam energy. Curves ($1, 1'$) and ($2, 2'$) were obtained in a cavity with $R = 0.04$ for the matrices with dye concentrations $C = 10^{-3}$ and 5×10^{-4} M, respectively. When a glass substrate was used as the output coupler, those matrices were most efficient almost throughout the range of pump energies studied, except for the lowest energies. Curves (3) and ($3'$) were obtained at $C = 2.5 \times 10^{-4}$ M and $R = 0.22$. At these values of C and R and a pump energy of 560 mJ, we achieved the highest output energy, 127 mJ. Curves (4) and ($4'$) were obtained at $R = 0.3$ for the matrix with $C = 1.25 \times 10^{-4}$ M. That matrix ensured the highest conversion efficiency, $\sim 23\,\%$. Note that all the polyur-
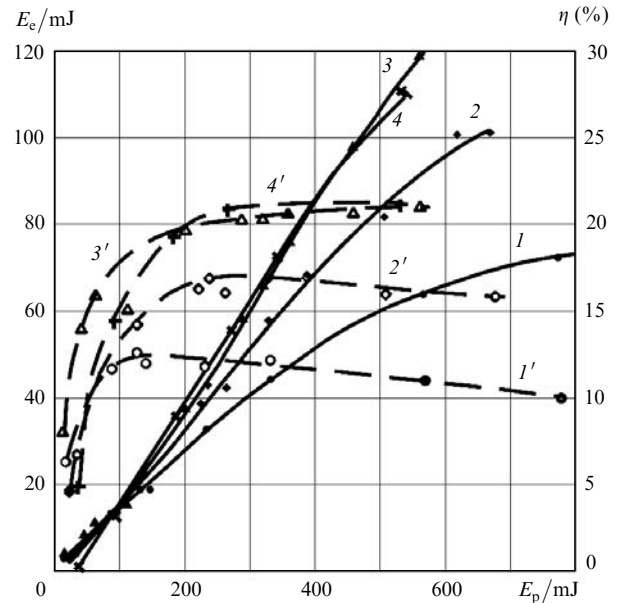
Figure 2. ($1-4$) Output energy E_e and ($1'-4'$) laser efficiency η vs. pump energy E_p at Oxazine 1 concentrations of ($1, 1'$) 10^{-3}, ($2, 2'$) 5×10^{-4}, ($3, 3'$) 2.5×10^{-4} and ($4, 4'$) 1.25×10^{-4} M.

ethane matrices studied withstood high pump energy densities without visible damage.

The lasing spectra of the matrices show that a given matrix may lase on either one or two bands, depending on experimental conditions. This is illustrated in Fig. 3, which presents the lasing spectra of the matrix with $C = 1.25 \times 10^{-4}$ M at different pump energies and two values of R. Shown at the bottom of Fig. 3 are the Hg lines used as references. When the output coupler had a reflectance $R = 0.22$ and the pump energy was 230 mJ, lasing on two bands was observed (top spectrum). As seen, the shorter wavelength band lies near 700 nm, and the longer wavelength band, near 745 nm. When the cavity finesse was increased ($R = 0.65$) and the pump energy was reduced to 160 mJ, lasing was observed only at the longer wavelength. One possible reason for this is that the shape of the gain spectrum is influenced by induced thermo-optic losses in the active element, characteristic of asymmetric microsecond pumping. Oxazine 1 has a well-defined vibrational structure in the long-wavelength part of its fluorescence spectrum, and its absorption and fluorescence bands overlap considerably, which would be expected to result in two maxima in its gain spectrum, with relative heights dependent on the total losses in the cavity. This can be demonstrated by calculating the spectral distribution of the relative gain coefficient of the active medium, $K(\nu)$, for steady-state lasing, i.e., for
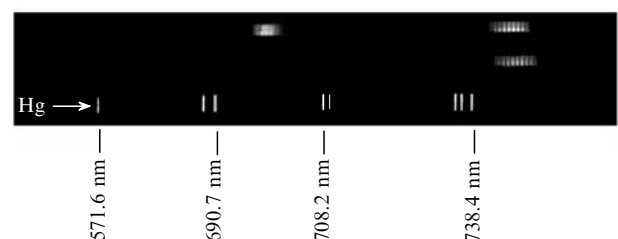
Figure 3. Time-integrated lasing spectra of Oxazine 1.

$K(v) = \rho$, where ρ is the total cavity loss coefficient and v is the frequency, related to the wavelength by $v = c/\lambda$. The total losses comprise the useful losses through the output coupler and the parasitic losses due to thermal distortion of the active element. The thermo-optic loss is unsteady state and increases with pump intensity.

For simplicity, the energy spectrum of the dye molecule is assumed to comprise two broadened singlet electronic levels: the ground and first excited levels. Designating the populations of these levels as N_0 and N_1, respectively, and describing the absorption and emission processes in this system with the effective absorption and stimulated emission cross sections, $\sigma_{ab}(v)$ and $\sigma_{em}(v)$, respectively, we obtain

$$K(v) = N_1\sigma_{em}(v) - N_0\sigma_{ab}(v). \tag{1}$$

The spectral distribution of the gain can be represented as the $K(v)/K(v^*)$ ratio, where v^* is a predetermined frequency. In our case, it is convenient to select v^* corresponding to the wavelength λ^* of the second (longer wavelength) maximum in the fluorescence spectrum of Oxazine 1. In addition, the effective absorption and emission cross sections are assumed to be related by the equation that follows from the principle of detailed balancing [18]:

$$\sigma_{ab}(v) = \sigma_{em}(v) \exp\left[\frac{h}{kT}(v - v_{el})\right],$$

where v_{el} is the frequency of a purely electronic transition. Designating $f(v) \equiv \exp[h(v - v_{el})/(kT)]$ and introducing the threshold population inversion $\delta = N_1/N_0$, for $K(v)/K(v^*)$, we obtain the simple relation

$$\frac{K(v)}{K(v^*)} = \frac{\sigma_{em}(v)}{\sigma_{em}(v^*)}\left[\frac{\delta - f(v)}{\delta - f(v^*)}\right]. \tag{2}$$

The ratio of the effective emission cross sections in (2), $\sigma_{em}(v)/\sigma_{em}(v^*)$, can be determined from the measured fluorescence spectrum, $F(\lambda)$, because the stimulated emission cross section is proportional to the fluorescence intensity.

The spectral distributions of the gain, $K_g(\lambda) = K(\lambda)/K(\lambda^*)$, calculated by Eqn (2) for different threshold population inversions, δ, are displayed in Fig. 4. The frequencies v^* and v_{el} were taken to correspond to the wavelengths $\lambda^* = 730$ nm and $\lambda_{el} = 625$ nm. Also shown for reference in Fig. 4 is the spectral dependence of the stimulated emission cross section for Oxazine 1, normalised to the 730-nm cross section [curve (6)]. It is well seen that the spectral dependences of the gain each have two maxima, with different heights. If cavity losses are not very high, lasing occurs at low population inversion, and the gain coefficient has a maximum in the longer wavelength band [curve (1)]. With increasing losses, including the thermo-optic one, the threshold population inversion increases. As a result, the shorter wavelength maximum rises, while the longer wavelength maximum decreases [curves (2–5)]. Note that, at some values of δ, the gain spectrum may have two maxima of the same height. Under such conditions, lasing may occur at the wavelength of either maximum or the laser may switch between them. Switching between two wavelengths was reported, e.g., by Russell et al. [17].
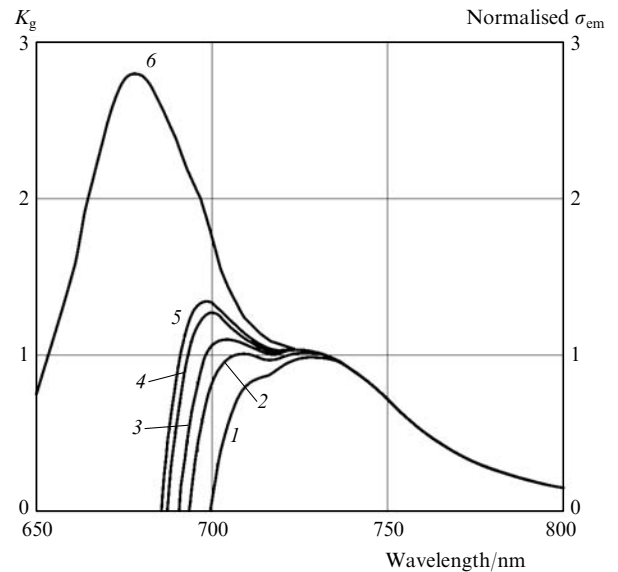
Figure 4. Spectral dependences of the gain coefficient at population inversions $\delta = 0.005$ (1), 0.009 (2), 0.012 (3), 0.017 (4) and 0.020 (5); (6) is the fluorescence spectrum of Oxazine 1.

4. Conclusions

The output energy and emission spectrum of polyurethane matrices doped with the dye Oxazine 1 were measured under excitation with microsecond laser pulses. The polymer matrices showed efficient lasing under transverse pumping, with a conversion efficiency of up to 23 %. The matrices were demonstrated to have a high optical damage threshold, which allowed us to use high pump energy densities and to obtain output energies in excess of 120 mJ. The time-integrated lasing spectra of the matrices show one or two bands, depending on the pump intensity and the reflectances of the cavity mirrors. The present results suggest that polyurethane is an attractive host material for active elements of SSDLs pumped with high-power microsecond pulses.

References

1. Kranzeilbinder G., Leising G. *Rep. Prog. Phys.*, **63**, 729 (2000).
2. Zemskii V.I., Kolesnikov Yu.L., Meshkovskii I.K. *Fizika i tekhnika impul'snykh lazerov na krasitelyakh* (Physics and Technology of Pulsed Dye Lasers) (St. Petersburg: SPb GUITMO, 2005) p. 176.
3. Sunita Singh, Kanetkar V.R., Sridhar G., et al. *J. Lumin.*, **101**, 285 (2003).
4. Gromov D.A., Dyumaev K.M., Manenkov A.A., et al. *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **48**, 1387 (1984).
5. Costela A., Garcia-Moreno I., Gomez C., et al. *Proc. SPIE-Int. Soc. Opt. Eng.*, **5460**, 44 (2004).
6. Anufrick S.S., Koldunov M.F., Kuznetsov Yu.M., et al. *Proc. SPIE Int. Soc. Opt. Eng.*, **6054**, 60540V (2005).
7. Kopylova T.N., Mayer G.V., Reznichenko A.V., et al. *Appl. Phys. B: Lasers Opt.*, **73**, 25 (2001).
8. Kopylova T.N., Sukhanov V.B., Mayer G.V., et al. *Appl. Phys. B: Lasers Opt.*, **74**, 545 (2002).
9. Kravchenko Ya.V., Manenkov A.A., Matyushin G.A. *Kvantovaya Elektron.*, **23**, 1075 (1996) [*Quantum Electron.*, **26**, 1045 (1996)].
10. Belichenko A.S., Matyushin G.A., Matyushin T.G. *Lazernaya Med.*, **4**, 25 (2000).
11. Costela A., Garcia-Moreno I., del Agua D., et al. *J. Appl. Phys.*, **101**, 731 (2007).

12. Bezrodnyi V.I., Ishchenko A.A. *Kvantovaya Elektron.*, **30**, 1043
     (2000) [*Quantum Electron.*, **30**, 1043 (2000)].
13. Bezrodnyi V.I., Ishchenko A.A. *Appl. Phys. B: Lasers Opt.,* **73**,
     283 (2001).
14. Bezrodnyi V.I., Derevyanko N.A., Ishchenko A.A. *Zh. Tekh.
     Fiz.*, **71**, 72 (2001).
15. Nikolaev S.V., Pozhar V.V., Dzyubenko M.I. *Kvantovaya
     Elektron.*, **36**, 758 (2006) [*Quantum Electron.*, **36**, 758 (2006)].
16. Russell J.A., Pacheco D.P., Russell W.H., Aldag H.R.,
     Manenkov A.A. *Proc. SPIE Int. Soc. Opt. Eng.*, **4630**, 24
     (2002).
17. Russell J.A., Pacheco D.P., Aldag H.R. *Proc. SPIE-Int. Soc.
     Opt. Eng.*, **5707**, 217 (2005).
18. Tikhonov E.A., Shpak M.T. *Nelineinye opticheskie yavleniya v
     organicheskikhk soedineniyakh* (Nonlinear Optical Phenomena in
     Organic Compounds) (Kiev: Naukova Dumka, 1979) p. 138.