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V.I. BEZRODNYI[1],✉
A.A. ISHCHENKO[2]

High efficiency lasing of a dye-doped polymer laser with 1.06 µm pumping

[1] Institute of Physics NASU, 03022 Kiev, Ukraine
[2] Institute of Organic Chemistry NASU, 02094 Kiev, Ukraine

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ABSTRACT For the first time, tunable lasing from a dye laser with an active polymer medium has been obtained using 1.06 µm pumping. The conversion efficiency of 43% and the tunable range of $\Delta\lambda = 63$ nm have been reached with the use of polymethine dye in a polyurethane matrix.

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1 Introduction

Dye lasers have attractive properties due to their broad spectral range tuning and high quantum efficiency. They are more simple to produce and cheap in comparison with other laser sources. Two types of dye-doped active laser medium are mainly used, namely liquid- and solid-state. The second type has some operational advantages relative to the first. Solid-state media have a lower refractive index temperature dependency, in other words, their thermo-optical characteristics during lasing are better. They can be used over a wider temperature range, including at low temperatures. Second-harmonic generation in a neodymium laser serves as a laser pump for these devices in many cases [1]. Sometimes neodymium laser third-harmonic or XeCl [2] and N_2 [3] laser generation in a neodymium laser is used for pumping.

However, application of these pump sources provides effective lasing mainly in the visible region. There are some fundamental difficulties in shifting the lasing to the near IR range when using such sources in the case of dye-doped active polymer media. To overcome them, it is necessary to create luminophores with large Stokes' shifts, or dyes which intensively absorb light in the near IR and can be pumped in their second or higher electronic transitions. The development of dyes with Stokes' shifts greater than about 500 nm and having a high fluorescence quantum yield is a great problem [4]. Moreover, this shift is decreased in polymer matrices in comparison with liquid dye solutions.

The pumping of higher electronic transitions is of little effectiveness, mainly due to the significant decrease in dye photostability. Therewith the drop of lasing efficiency often takes place. It is caused by the increased probability of radiationless transitions as a result of participation by the highest excited state. In addition, the radiation of UV pump sources is in the absorption region of many polymers. This leads to polymer destruction and the decrease in their conversion efficiency. There are excellent pump sources for producing tunable lasing in the near IR range (1.1–1.5 µm), namely neodymium lasers ($\lambda = 1.06$ µm). However, in this case some difficulties appear in obtaining generation even when liquid solutions such as active media are used [5]. Stable and effective operation of the dyed active medium into the IR region is limited by the small fluorescence lifetime and low photochemical stability of the dyes [4].

In the present paper, we report for the first time how high efficiency lasing in the near IR region from a dye-doped tunable laser with a new dyed active polymer medium has been obtained. A polyurethane composition was used as a polymer matrix, which was synthesized by means of a polycondensation reaction of diol with diisocyanate such as:

$$n\mathrm{HO{-}R{-}OH} + n\mathrm{OCN{-}R'{-}NCO} \rightarrow$$

$$-[-\mathrm{O{-}R{-}O{-}CO{-}NH{-}R'{-}NH{-}CO}-]_n- ,$$

where n is the number of molecules and R, R′ are the aliphatic or aromatic hydrocarbon groups.

The solidification of this polymer composition, as well as epoxy polymers was carried out by a polycondensation reaction. However, unlike epoxy polymers, the reaction proceeded under mild conditions at room temperature in a neutral medium. Thus, dyes of different types could be incorporated in this polymer substance without decomposition (total or partial) during one stage of polymerization. It should be noted that the above-mentioned polymer medium, used as a matrix, allowed the production of stable, passive laser Q-switches with high damage thresholds for the Q-switching of ruby [6] and neodymium lasers with the lasing wavelength of 1.06 µm [7] and even 1.3 µm [8]. We also used this composition to create effective active media based on dyes within the visible range [9]. Excellent results in photostability and lifetime

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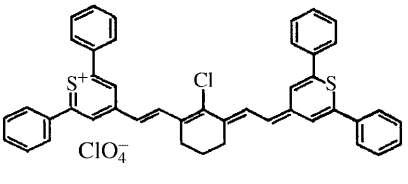
✉ Fax: +380-44/265-1589, E-mail: bezrod@iop.kiev.ua

have been achieved for these media. The chosen polyurethane matrix had highly elastic properties over a wide temperature range. This allowed us to work with pulses of high power without the incorporation of plasticizer in the polymer. The active element was constructed in the form of a triplet. The polymer matrix was placed between the optical substrates. The external surfaces could be covered with antireflective coatings. The high adhesion ($\sim 1000\,\mathrm{N/cm^2}$) between the glass substrates and the polymer used eliminated the need for additional glue to be applied during production of the elements.

2 Results and discussion

Figure 1 shows the spectral transmittance range of the non-dyed polymer matrix of 1 mm thickness. It has been measured using the Shimadzu UV-3100 spectrophotometer. The transmittance curve points out the possibility of using this polymer to create dye lasers using the first-harmonic pumping of a neodymium laser. The damage threshold of the polyurethane polymer matrix has been measured at $\lambda = 1.06\,\mu\mathrm{m}$ using a single-mode YAG laser, working in a single pulse regime. The threshold damage caused by the action of a single pulse with a duration of 20 ns on an irradiated area of 100 μm in diameter is $E_\mathrm{d} \geq 16\,\mathrm{J/cm^2}$.

Active elements for the generation of samples for the spectral study have been produced by methods described in our previous papers [6–8]. The polymethine dye thiopyrylotricarbocyanine which has been used, has a structural formula as follows:



The maximum in its main absorption band in polyurethane lies at 1.079 μm. It has a high absorption cross section in this polymer at $\lambda_\mathrm{p} = 1.064\,\mu\mathrm{m}$ and its value is $6.3 \times 10^{-16}\,\mathrm{cm^2}$. The thiopyrylotricarbocyanine dye has a relatively large excited state relaxation time in liquid solutions of the order of 50 ps [10]. We have measured the relaxation time of the chosen dye in the polyurethane matrix by the method and with the help of equipment described in [11]. The relaxation time was found to be 100 ± 10 ps.

Spectral investigations of the polyurethane composition dyed with the thiopyrylotricarbocyanine dye have been carried out. The absorption shape of this dye in the polymer did not undergo distortions (Fig. 2a) and corresponds to that in the best liquid solvents. Consequently, dye aggregation, responsible for the distortion of the absorption shape, is absent in the polymer used in the operating concentration range of 10^{-5}–0.5×10^{-3} mol/l. The investigation of the fluorescence spectrum has been performed using on the specially constructed equipment. Dye molecule excitation in a sample 1-mm-thick and having $T_0 = 50\%$ initial transmittance at $\lambda = 1.064\,\mu\mathrm{m}$ has been realized in the $S_0 \rightarrow S_1$ transition range using neodymium YAG laser radiation. The fluorescence signal was recorded by a germanium photodetector with the spectral sensitivity range 0.6–1.8 μm. The SPM-2 mirror monochromator was used as a spectral device. The true contour of the fluorescence spectrum presented in Fig. 2b has been calculated with regard to the spectral sensitivity of the photodetector. As can be seen from Fig. 2, the fluorescence band of the thiopyrylotricarbocyanine dye in polyurethane, as well as that of other cation tricarbocyanines in polar liquid solvents, is narrower than the absorption band [12]. According to [12], this is caused by the weakening of electrostatic interactions between the polar groups of the polymer and the distribution charge in the dye chromophore in the excited state in comparison with the ground state. From Fig. 2, it is seen that the ratio between absorption and fluorescence bands allows the pumping of neodymium lasers ($\lambda = 1.06\,\mu\mathrm{m}$) to obtain lasing beyond 1.1 μm.

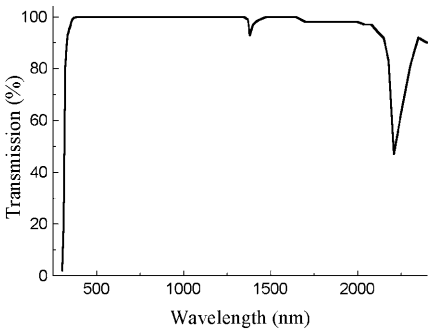


FIGURE 1 Transmission spectrum of the non-doped polymer matrix

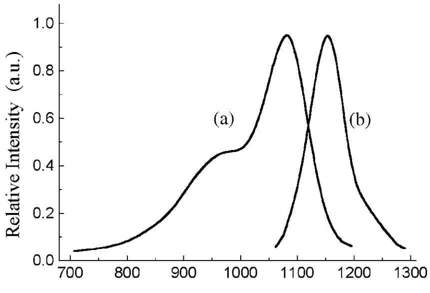


FIGURE 2 Absorption (a) and fluorescence (b) spectra of thiopyrylotricarbocyanine in polyurethane

Active elements with a polymer layer of thickness 2 mm and optical density $D = 5$ have been produced to investigate the dependence of lasing properties on the pumping wavelength. The lasing has been studied in two types of cavities, a non-dispersive cavity (cavity 1, Fig. 3) and a dispersive cavity (cavity 2, Fig. 3). The one marked '1' consists of two flat mirrors of 99.5 and 40% reflectivity respectively, in the spectral region 1.1–1.2 μm. The distance between mirrors was 15 cm. The quasi-longitudinal type of pumping has been achieve using a YAG laser operating in the single-pulse regime ($\tau_\mathrm{p} = 15$ ns) with a repetition rate of 1 Hz. The active element was placed at the Brewster angle to the lasing light near

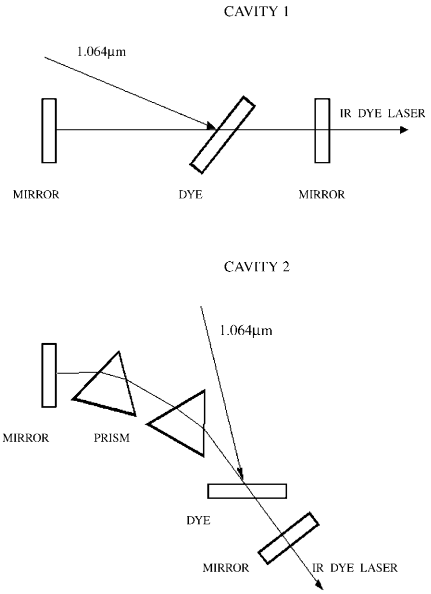


FIGURE 3 Schematic diagrams of experimental set-up

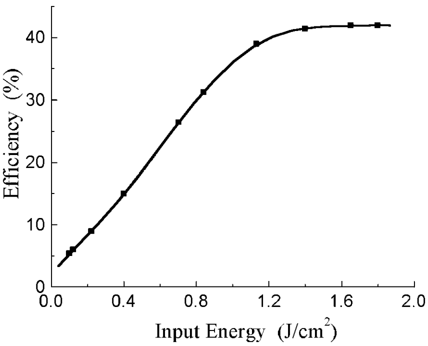


FIGURE 4 Dependence of the conversion efficiency on the pump energy

the output mirror. The pumping light was focused on the active element by the long-focus lens $F = 1$ m. The angle between pumping and lasing beams was 12°. The dependence of the conversion efficiency $\eta = E_g/E_p$ on the excess of the pumping energy E_p over the threshold energy is presented in Fig. 4. After some initial growth with increasing pump energy, the conversion efficiency stops depending on E_p and reaches its maximum value of $\eta_{max} = 43\%$ under the conditions of our experiment. This dye had practically the same efficiency value (44%) in ethanol. The aim of our present paper does not include the investigation of optimal conditions for the conversion efficiency, which depends mainly on the optical density at the pumping wavelength.

The cavity marked as '2' has been used to determine the tuning range of the polymer element. This cavity also consisted of two flat mirrors of 99.5 and 40% reflectivity respectively, in the spectral region of 1.1–1.2 μm. Two 60° angle prisms made of BK-7 glass were used as dispersive elements. In this case, the total length of the cavity was 16 cm. Figure 5 shows the tuning spectrum of the lasing wavelength at the highest possible pumping intensity under our conditions. The tuning range was 63 nm. It should be noted that this conversion efficiency and tuning range are comparable to those of the best active polymer elements for the visible region with 532 nm pumping. For instance, in investigating dye lasers with the polymer polyurethane matrix doped with the rhodamine 590 chloride, we obtained a conversion efficiency of 34% and $\Delta\lambda = 45$ nm [9].

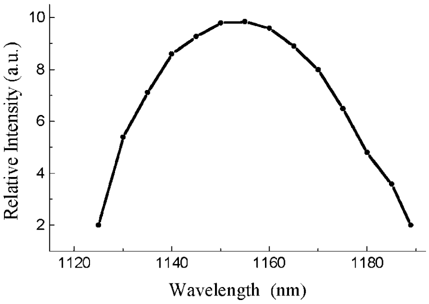


FIGURE 5 Tunable range of the dye-doped laser

We characterised the operation lifetime of the active polymer medium quantitatively by the number of pumping pulses N for a 50% efficiency η drop. The value N was obtained under rigid conditions with the express purpose of obtaining information about lifetime. The irradiation of a sample with the dyed polymer layer thickness of 1 mm between glass was carried out in a local area of 1.3 mm diameter at the following parameters of pumping: pulse energy 20 mJ (which corresponds to 1.5 J/cm^2), duration 12 ns and repetition rate 3 Hz. Under these conditions, the value of the lifetime N was found to be 550. The decrease in η with increasing N was caused by the dye bleaching, without damage to the polymer matrix. The operation lifetime of the active polymer medium can be improved by increasing the dyed polymer layer width, using a laser system based on a dye-doped rotating disk and introducing stabilizing additives to the matrix. However, the aim of the present work did not cover these investigations, which are the object of future studies.

3 Conclusions

In the present work, effective tunable lasing in the spectral range above 1.1 μm has been obtained for the first time in dye lasers using active polymer elements pumped with 1.06 μm light. This demonstrates the potential of these elements for lasing repetition rate tuning not only in the visible region but also in the near IR, which is very important for practical applications.

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