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PM567-Doped solid dye lasers based on PMMA*

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Polymers are a kind of attractive hosts for laser dyes due to their high transparency in both pumping and lasing ranges and superior optical homogeneity. In this paper solid dye samples based on polymethyl methacrylate (PMMA) doped with different concentrations of 1, 3, 5, 7, 8 -pentamethyl-2, 6-diethylpyrromethene-BF_2 (PM567) are prepared. The absorption, fluorescence and lasing spectra of the samples are obtained. Wide absorption and fluorescence bands are obtained and a red shift of the maxima of the lasing emission spectra is observed. With the second-harmonic generation of Q-switched Nd:YAG laser (532 nm, ∼20 ns) pumping the samples longitudinally, the slope efficiencies of the samples are obtained. There is an optimal dye concentration for the highest slope efficiency when the pumping energy is lower than some typical value (∼250 mJ), and the highest slope efficiency 35.6% is obtained in the sample with a dye concentration of 2×10^{-4} mol/L. Pumping the samples at a rate of 10Hz with a pulse energy as high as 200 mJ (the fluence is 0.2 J/cm^2), the output energy drops to one-half of its initial value after approximate 15500 pulses and the normalized photostability is 5.17 GJ/mol. A kind of solid dye laser which could have some applications is built.

Keywords: solid dye laser, PMMA, slope efficiency, photostability
PACC: 4200, 4255Q, 4270J

1. Introduction

The liquid dye laser is a coherent source of radiation with such advantages as wide tuning range, high power output and high pulse energy and wide choice of pumping sources. However, liquid dye lasers have some disadvantages such as large circulation and flow system and the use of toxic and expensive dyes and organic solutions. Solid dye lasers have some advantages which can make up for the disadvantages of liquid ones, including ease of handling, low cost, compactness, and lack of toxicity.[1−7] Since the first realization of solid dye lasers by Soffer with Mcfarland[8] and Peterson with Snavely[9] in the 1960s, many kinds of materials have been used as solid dye hosts, including polymers,[1−3,8−10] sol-gel silicates,[11] inorganic glasses,[12] organic modified silicates[12,13] and so on. Polymers are a kind of attractive hosts for laser dyes because they have some advantages over other hosts, such as high transparency in pumping and lasing ranges, superior optical homogeneity, better chemical compatibility with organic dyes, easy control of the chemical process and so on. Polymethyl methacrylate (PMMA) is one of most commonly used polymeric hosts, and it has high transparency in visible region of electromagnetic spectrum. 1, 3, 5, 7, 8 -pentamethyl-2, 6-diethylpyrromethene-BF_2 (PM567) is a kind of very efficient dye with a high quantum efficiency of 99.5% and a triplet excitation coefficient that is one-fifth of rhodamine560's. Solid dye samples based on PMMA doped with different concentrations of PM567 are prepared. The absorption, fluorescence and lasing spectra of the samples are studied. Using the second harmonic generation of Q-switched Nd:YAG laser pumping the materials longitudinally, the slope efficiency and photostability of the samples are also studied.

2. Materials

Methyl methacrylate (MMA) was purified by using the method mentioned in Ref.[1]. An adequate amount of PM567 was dissolved with sonication in the freshly prepared PMMA and the initial concentrations were 5×10^{-5}–2×10^{-3} mol/L. A thermal initiator α, α-azoisobutyronitrile (AIBN) was added, and the mixture was again sonicated. The resulting solution

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was filtered into cylindrical moulds, and then sealed. Polymerization was performed in the dark in a thermostatic bath at 40–45°C until solidification (which took at least 5 days). The samples were cut into cylindrical rods 18 mm in diameter and 30 mm in length, and their ends were polished to obtain reasonably flat, smooth, glass-like surface.

3. Methods

The absorption spectra were obtained by spectrophotometer UV-3010PC (Shimadzu Company), and the fluorescence and lasing spectra were measured by the spectrum detector HR4000 (Ocean Optics). For the laser experiments, a longitudinally pumped solid dye laser system was built. The pumping source was the second-harmonic generation of Nd: YAG laser emitting pulses with a 20 ns full-width at half-maximum (FWHM) at 532 nm. The dye laser cavity was about 10cm long, and it comprised two plane mirrors $M_{\rm i}$ and $M_{\rm o}$. $M_{\rm i}$ had a high transmittance at 532nm and high reflectivity in a wide band of 550–590 nm. $M_{\rm o}$ was a 50% broadband output coupler. Filter 1 was used to filter out the 1064 nm light. Filter 2 was to filter out the residual pumping light in case it interferes with the results. The output energy is detected by the energy meter. The experimental setup is presented in Fig.1.

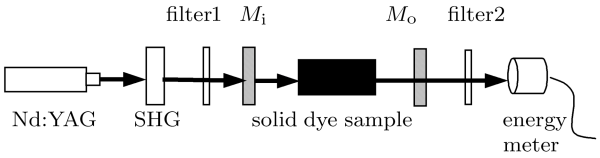


Fig.1. Schematic of the laser system.

4. Results and discussion

4.1. Spectral properties

4.1.1Absorption and fluorescence spectra

The typical absorption and fluorescence spectra of the solid dye samples are presented in Fig.2. The absorption spectrum was obtained from the samples with 5 mm in size and, two ends polished manually. The solid dye samples doped with PM567 have two broad absorption bands: 325–375 nm and 450–550 nm. It can be seen that the samples have an intensive absorption at 532 nm, so we choose the frequency-doubled Q-switched Nd:YAG laser as the pumping source. The solid dye samples all have a wide fluorescence band of about 40 nm (FWHM) which makes possible the realization of tuning in a wide band with solid dyes.

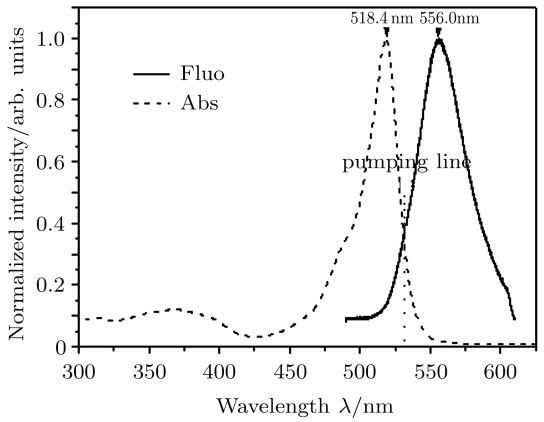


Fig.2. Absorption and fluorescence spectra of the solid dye sample.

4.1.2Lasing spectra

Dye concentration has an important influence on the lasing spectra (see Fig.3). The spectra all have a wide band-width of about 6 nm which is much narrower than that of the fluorescence spectra. The maxima of the lasing spectrum has a red shift, with the increase of dye concentrations, from 556.2 nm to 582 nm. This is caused by the reabsorption and re-emission effects of dye molecules, which become more obvious when the dye concentration is higher.[10]

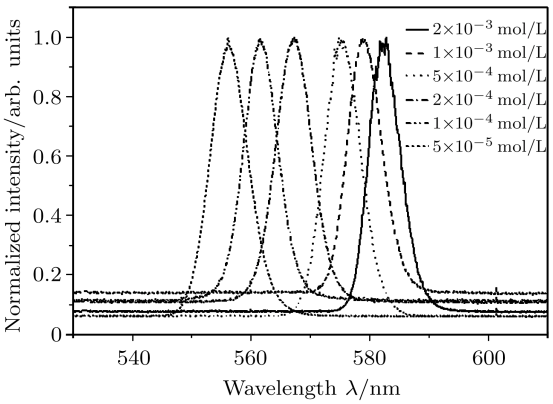


Fig.3. Lasing spectra of solid dye samples with different dye concentrations.

4.2. Slope efficiency

Efficiency is of great importance to the applications of solid dye lasers. The slope efficiencies of the samples were measured, and the results are presented in Fig.4.

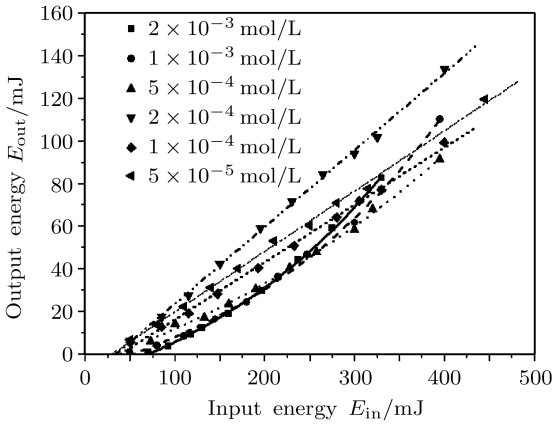


Fig.4. Laser efficiencies of solid dye samples with different dye concentrations.

We can see that the dye concentration has an important influence on the slope efficiency of the samples. The output pulse energy increases with the increase of input energy in quite different ways when the dye concentrations are in different regions. When the dye concentration is high enough (higher than 5×10^{-4} mol/L), the output energy increases exponentially with the input energy increasing; when the dye concentration is low enough (lower than 2×10^{-4} mol/L), the output increases linearly with the increase of input energy. We can give some qualitative explanations. Since our samples are a bit long (∼30 mm), for the samples with high dye concentrations, when the pumping energy is low, only a small portion of the dye molecules are excited to higher state level while the others remain in the ground state, so the absorption to the lasing radiation is very intensive; when the pumping energy becomes higher, a large portion of the dye molecules are excited by the pumping source and the absorption to the lasing radiation is not so intensive. It is more excited dye molecules and less absorption dye molecules that make the output increase exponentially with the input energy. For the efficiency, we can reach the same conclusion as that given by other authors when the input energy is lower than some typical value (about 250 mJ). Namely, there exists an optimal dye concentration, at which the slope efficiency can attain to a maximum. In our experiment, the optimal concentration is 2×10^{-4} mol/L, and the corresponding slope efficiency is 35.6%. However when the input energy is higher than a typical value, it seems that there is no definite relationship between the efficiencies of solid dyes and the dye concentrations, and the result is quite different from the other authors'.

4.3. Photostability

Another factor restricting the application of solid dye laser is fast dye photodegradation. So photostability is very important to solid dyes. We use longevity of the sample to evaluate the photostability of the samples. We define the longevity as the number of pumping shots at the same point of the solid dye samples before the lasing output falls away to one-half of its initial value. Pump the samples longitudinally with second harmonic generation of Q-switched Nd:YAG laser (532 nm, 200 mJ/pulse, with a fluence of 0.2 J/cm^2) at a frequency of 10 Hz and record the output with energy meter, then the ratio of the output energy to its initial value as a function of the number of pumping shots will be obtained, and it is shown in Fig.5. By the definition, longevity of about 15500 pulses was obtained. To make a comparison in a way independent of experimental setup, Rahn and King[14] introduced a normalized photostability defined as the accumulated pump energy absorbed by the system per mole of dye molecules before the output energy falls away to one-half of its initial value. The normalized stability of the samples we prepared is 5.17 GJ/mol.

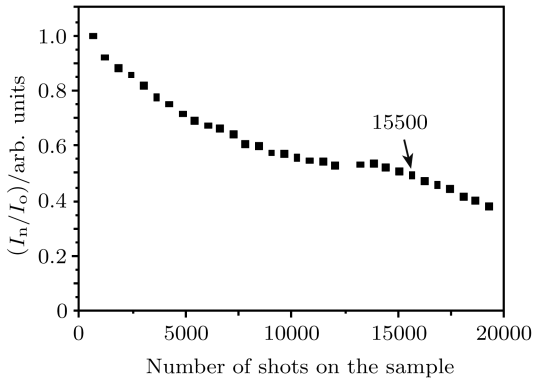


Fig.5. Photostability of solid dye sample.

5. Conclusions

In this paper, the absorption, fluorescence and lasing spectra of solid dye lasers based on PMMA with different concentrations of PM567 have been demonstrated. Broad absorption and fluorescence spectra are obtained and a red shift of the maxima of the lasing spectra is observed. The slope efficiency and photostability of the samples are obtained. There is an optimal dye concentration for the highest slope efficiency when the input energy is lower than some typical value, and the highest slope efficiency in our ex-

periment is 35.6% which is achieved in a sample with a dye concentration of 2×10^{-4} mol/L. The normalized photostability is 5.17 GJ/mol. It is obtained with input pulse energy as high as 200 mJ, the highest input pulse energy used to study the longevity of the solid dye samples. The obtained results indicate that solid dye samples which can have some applications are prepared.

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