Enhanced laser characteristics of pyrromethene 650 using modified PMMA as solid hosts*

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Solid-state samples based on modified polymethyl methacrylate (MPMMA) with methanol doped with the dye pyrromethene 650 (PM650) are prepared. The effects of a volume percentage of methanol on the laser characteristics of the sample, including spectra properties, slope efficiency, photostability and tunable properties, are investigated. The broadband dye laser output wavelength is around 655 nm and a highest slope efficiency of 32.23% is achieved. Pumping the samples at a repetition rate of 5 Hz with a pulse energy of as high as 100 mJ (the fluence is 0.26 J/cm^2), the longest lifetime (168000 shots) is obtained in the sample (MMA:methanol=18:2), and the corresponding normalized photostability reaches 109.19 GJ/mol. When the sample (MMA:methanol=18:2) is placed in a Shoshan-type oscillator, the narrow-linewidth operation is a continuous tuning range (up to 64 nm). The results indicate that the laser characteristics of solid-state dyes can be greatly enhanced by using modified PMMA with methanol serving as the solid host.

Keywords: solid-state dye laser, modified polymethyl methacrylate, pyrromethene 650, photostability, tunable properties

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1. Introduction

Solid-state dye lasers have been the object of an intense research interest during the past 40 years. The first solid-state dye lasers were reported in the late 1960s by Soffer and Mcfarland[1] and Peterson and Snavely.[2] They demonstrated stimulated emission from polymeric matrices doped with organic dyes. However, the work on solid-state dye lasers has not been pursued for over a decade due to low lasing efficiencies and fast photodegradation of the dye.[3] In recent years, significant breakthroughs have been achieved in the development of practical solid-state dye lasers.[4−8] They have been developed due to their advantages over liquid ones, such as ease of handling, compactness, low cost and lack of toxicity.[9−13]

A solid-state dye laser is a very important laser source for many applications, such as selective photothermolysis in medicine, remote sensing of atmospheric contaminants and underwater communications.[14] Many kinds of dyes, such as Coumarin dyes, Rhodamine dyes and some Pyrromethene dyes, have been investigated. However, the output wavelengths of these dye lasers are less than 600 nm and do not meet some specific demands. Arbeloa *et al.*[15] have used absorption and fluorescence techniques to study the photophysical characteristics of PM650 dye. Fan *et al.*[16] obtained the maxima of lasing spectrum 650 nm, the highest slope efficiency 17.2% and more than 11-mJ laser output energy using the LDS698 dye based on MPMMA as an operating medium. Alvarez *et al.*[17] obtained the highest slope efficiency 20% and a peak wavelength at 600 nm using mixtures of PM597 and PM650 dyes, which allowed laser emission to be tunable over two separate spectral regions up to a wavelength of 619 nm in a solid state. In our previous work,[18] we have obtained a solid-state dye laser output at 653.5 nm with the highest slope efficiency of 27.49% and a laser output energy of 22.0 mJ using PM650 as the doped dye.

In this paper, in order to extend the solid-state dye laser output wavelength to the red region and enhance the photostability of the dye, solid-state dye samples based on modified PMMA with methanol

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doped with PM650 are prepared. Using second harmonic generation of a Q-switched Nd:YAG laser pumping the materials longitudinally, the effects of volume percentages of methanol on the laser characteristics of solid-state dye mediums, including spectra properties, slope efficiency, photostability and tunable properties, are studied.

2. Experiment

2.1. Preparation of solid-state dye samples

Commonly, PM650 is used as laser dye (Exciton Inc.). MMA was chosen as the polymer component and methanol was used as a low-molecular modifying additive. The molecular structures of the compounds used are shown in Fig. 1. MMA was purified with the method mentioned in Ref. [9]. Laser dye PM650 was dissolved in the mixture of MMA and methanol, which was placed in an ultrasonic bath in order to mix the dye into the mixture. The volume percentages of methanol ranged from 0% to 20% and the dye concentration was kept at 2×10^{-4} mol/L. The mixtures were again sonicated after a thermal initiator α and α-azoisobutyronitrile (AIBN) was added. The resulting solutions were filtered into cylindrical molds and then sealed. Polymerization was performed in the dark in a thermostatic bath at 40 °C–45 °C until solidification. The samples were cut into cylindrical rods of 16 mm in diameter and 20 mm in length, and the ends were polished to obtain reasonably flat, smooth, glass-like surface.[19]

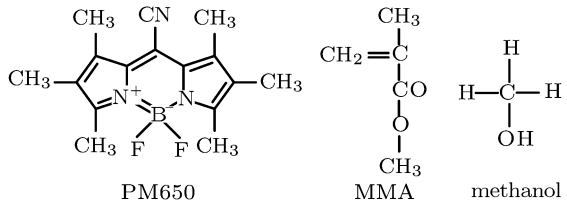


Fig. 1. Molecular structure of the compounds used.

2.2. Measurement setup

The pump source in this work was a Q-switched Nd:YAG laser operating at the second harmonic of 532 nm and emitting 15-ns full width at half-maximum (FWHM) pulses. A simple broadband laser oscillator cavity was composed of two plane mirrors with the solid-state dye samples serving as the gain medium. Details of the experimental setup can be found elsewhere.[16] The dye laser cavity was a compact plane–plane configuration of about 6-cm long, which was used to reduce cavity losses due to a highly divergent output. The cavity was composed of two mirrors M_i and M_o, a partial output coupler with $T \sim 50\%$ in 500 nm∼700 nm and a dichroic mirror with a high transmission ($T > 90\%$) at 532 nm and high reflectance ($R > 90\%$) in 580 nm∼680 nm. The pump laser energy and the output laser energy were both detected by energy meter J-50MB-YAG (Coherent Inc.).

In order to improve the spectral characteristics of the solid-state dye laser and achieve tunability in a wide wavelength region, a tunable narrowband laser oscillator cavity was built by placing the sample in a home-made Shoshan-type oscillator.[6] Details of the experimental setup can be also found elsewhere.[19] The cavity consists of an input mirror M_i (the same as that in the broadband oscillator), a solid-state dye sample, a grating (1200-lines/mm) in grazing incidence and a tuning golden mirror. The first-order-diffracted beam from the grating was reflected back to the cavity by the tuning mirror. The length of the overall cavity was about 20 cm. The laser output was taken directly from the grating in the form of the zero-order beam. The input and the output laser energies were detected by a J-10MB-HE (Coherent Inc.) energy meter.

3. Results and discussion

3.1. Fluorescence spectra

The fluorescence spectra of the solid-state dye samples based on MPMMA doped with PM650 are presented in Fig. 2, which were measured by an HR4000 (Ocean Optics) spectrum detector. The solid-state dye samples each have a wide fluorescence band of

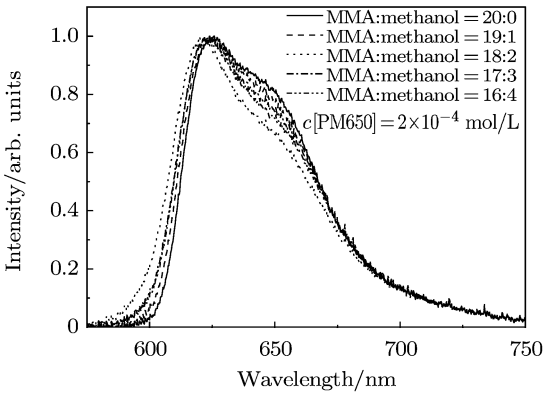


Fig. 2. Fluorescence spectra of solid-state dye samples based on MPMMA doped with the dye PM650.

more than 55 nm (FWHM) which makes possible the realization of tuning on a wide band with solid-state dyes. It can be seen that the volume percentage of methanol has a slight effect on the fluorescent emission from the sample.

3.2. Lasing spectra

The lasing spectra of solid-state dye samples based on MPMMA doped with PM650 are presented in Fig. 3, which were also measured by the HR4000 spectrum detector. The line width of the lasing spectra varies from 8.0 nm to 10.5 nm, much narrower than the fluorescence spectral width. The maxima of the lasing spectra are in a range from 653.0 nm to 655.5 nm, which belongs to the red light region. A summary of the obtained results is shown in Table 1, where data on fluorescence and lasing emission, lasing slope efficiency and lifetime are listed.

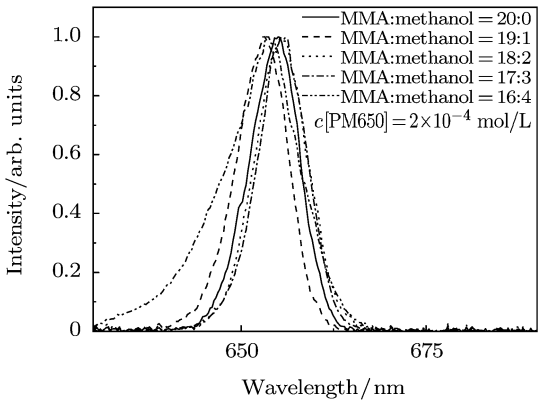


Fig. 3. Laser spectra of solid-state dye samples based on MPMMA doped with dye PM650.

Table 1. Spectra and lasing output properties of solid-state dye samples based on MPMMA doped with the dye PM650.

Material	λ_{FS}/nm	$\Delta\lambda_{FS}$/nm	λ_{LS}/nm	$\Delta\lambda_{LS}$/nm	η/%	Lifetime	Normalized photostability/GJ·mol^{-1}
(MMA:methanol=20:0)	625.5	55.0	655.0	8.0	32.23	51000	33.15
(MMA:methanol=19:1)	625.5	56.0	653.0	8.0	31.17	100000	64.99
(MMA:methanol=18:2)	621.5	56.0	655.5	8.5	29.28	168000	109.19
(MMA:methanol=17:3)	625.5	57.0	655.5	8.0	21.98	82000	53.30
(MMA:methanol=16:4)	624.0	56.5	653.5	10.5 1	8.21	37000	24.05

λ_{FS}: peak of the fluorescence spectrum, $\Delta\lambda_{FS}$: FWHM of the fluorescence spectrum, λ_{LS}: peak of lasing spectrum, $\Delta\lambda_{LS}$: FWHM of the lasing spectrum, η: slope efficiency.

3.3. Slope efficiency

Dye laser slope efficiency is an important parameter for the applications of solid-state dye lasers. The slope efficiency was obtained by averaging several single-shot data points at each input energy. The slope efficiency of the solid-state dye sample was calculated by a simple linear least square fit to the input versus output data. The slope efficiency of solid-state dye sample based on MPMMA doped with PM650 was measured and the results are presented in Fig. 4 as summarized in Table 1. It can be seen that the volume percentage of methanol has an effect on the slope efficiency. When the volume percentages of methanol are 5% and 10%, the samples each have a high slope efficiency of about 30%. With the increase of volume percentage of methanol, the slope efficiency begins to decrease, so there should exist an optimal volume percentage of methanol for obtaining the high slope efficiency.

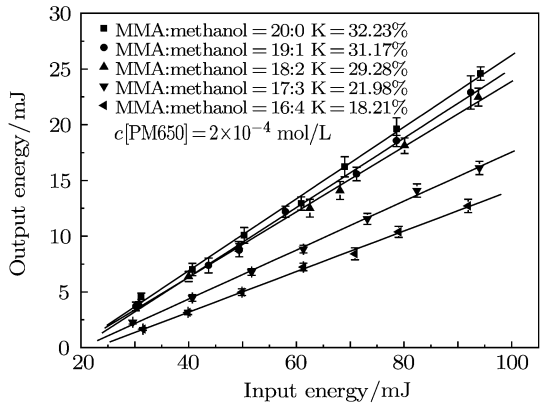


Fig. 4. Slope efficiencies of solid-state dye samples based on MPMMA doped with the dye PM650.

3.4. Photostability

The key performance parameter of a solid-state dye laser, which restricts its applications, is the laser lifetime within which the dye laser works well on a

meaningful energy level or the photostability of the dye is workable. In this paper, we evaluate the photostability of solid-state dye samples by using the lifetime, which is defined as the number of pumping shots at the same point of solid-state dye samples before the dye laser output falls to half of its initial output value.

The second harmonic generation of Nd:YAG laser at 532 nm was used as a pumping source and solid-state dye samples were longitudinally pumped with a pulse energy of as high as 100 mJ (with a fluence of 0.26 J/cm^2) at a repetition rate of 5 Hz. The normalized output energy as a function of number of pump pulses was obtained as shown in Fig. 5 and also listed in Table 1. It can be seen that the volume percentage of methanol plays an important role in enhancing the lifetimes of the samples. The longest lifetime was obtained to be about 168000 shots in the sample (MMA:methanol=17:3) (shown in Fig. 5), but the lifetime of solid-state dye sample only based on PMMA is about 51000 shots.

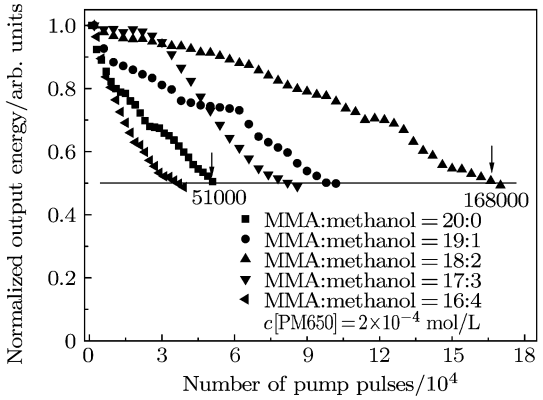


Fig. 5. Normalized laser output energies each as a function of the number of pump pulses at the same position of the samples based on MPMMA doped with dye PM650.

The normalized photostability is defined as the accumulated pump energy absorbed by the system per mole of dye molecules before the output energy falls to half of its initial value,[20] i.e.,

Normalized photostability

$$(\mathrm{GJ/mol}) = \frac{E_{\mathrm{pump}} N_{1/2}}{\pi \times r^2 \times l \times C \times 10^6},$$

where E_{pump} is the pump pulse energy (in joule), $N_{1/2}$ is the total number of pulses before the output energy of pulse has reduced down to half the initial output energy, r is the radius of the pump beam on the surface of the sample, l is the length in unit cm and C is the concentration (molar per liter). The normalized photostability is in GJ/mol. The calculated results are collected in Table 1. It can be seen that the normalized photostability increases dramatically with the increase of the volume percentage of methanol. When the volume percentage of methanol reaches 10%, the maximum normalized photostability 109.19 GJ/mol is obtained. Compared with in the sample based only on PMMA, the photostability increases more than twenty times in the sample (MMA:methanol=17:3). However, too much methanol can cause the photostability to decrease gradually. When the volume percentage of methanol reaches 20%, the normalized photostability drops off to only 24.05 GJ/mol, so there should be an optimal volume percentage of methanol for obtaining the highest normalized photostability.

The reason for the enhancement of photostability could be that low-molecular modifying additives can easily fill the free volumes and preclude the dye from intensively diffusing on the thermal extension of the material. Another important role of these additives is to improve the thermoconductivity of the material and to help cool the lasing material.[21]

3.5. Narrow-line-width operation

It is well known that one of the most important features of dye lasers is their tunability, with the narrow-line-width tuning range of nanometers achieved with a single dye when a wavelength-selective resonator is utilized.

In this experiment, solid-state dye PM650 (MMA:methanol=90:10) was used as an operating medium, the pump laser energy was 0.978 mJ and the angle of grazing incidence was about 85°. A focusing lens was used to focus the pump beam on the surface of solid-state dye sample and the spot diameter on the sample was about 0.4 mm. The first-order-diffracted beam from the grating was reflected by a tuning mirror and the reflected beam was in coincidence with the input beam on the surface of the grating. By rotating the tuning mirror, the tuning laser output of the sample was obtained. Tuning curve of the sample is presented in Fig. 6. It can be seen that more than 64-nm tunable range (from 607 nm to 671 nm) was obtained using the solid-state dye PM650 doped into MPMMA as an operating medium. The narrowband laser linewidths are all about 0.1 nm, which are much narrower than those of the broadband lasing spectra.

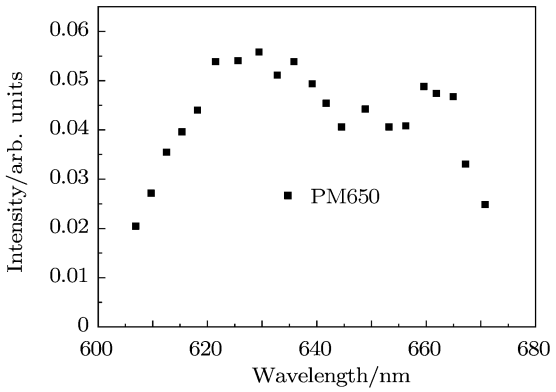


Fig. 6. Tuning curve of solid-state dye of PM650.

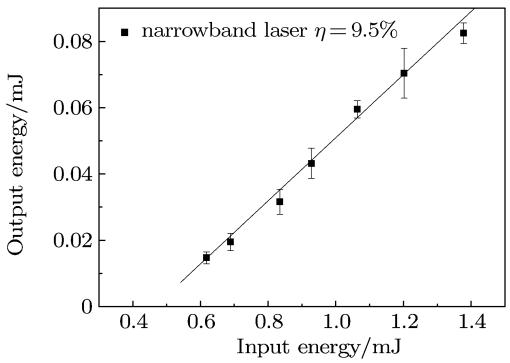


Fig. 7. Narrowband laser slope efficiency of solid-state dye of PM650.

In this experiment, the fixed laser wavelength 635 nm was chosen for measuring the narrowband laser slope efficiency of the sample and the measured result is shown in Fig. 7. It can be seen that the sample has high narrowband slope efficiency (up to 9.5%).

4. Conclusion

In this paper, the laser characteristics of solid-state dye samples based on MPMMA doped with PM650, including spectrum property, slope efficiency, photostability and tunable property, are demonstrated. Each of these samples has a wide fluorescence band and the broadband laser output wavelength is about 655 nm, which is very important for its application to medical treatment. The highest slope efficiency achieved was 32.23%. At a repetition rate of 5 Hz with a pulse energy of as high as 100 mJ (the fluence is 0.26 J/cm^2), the longest lifetime (168000 shots) is obtained in the sample (MMA:methanol=18:2). There exists an optimal volume percentage of methanol for obtaining the higher slope efficiency and better photostability. The narrow-linewidth operation with a continuous tuning range (up to 64 nm) is demonstrated and the narrowband slope efficiency is about 9.5%. The obtained results indicate that the laser performances of solid-state dye samples doped with PM650 can be greatly increased with using MPMMA as solid hosts.

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