Highly Photostable Solid-state Dye Lasers Based on Mixed Pyrromethene 567 and Coumarin 500

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Abstract—Solid-state dye samples based on polymethyl methacrylate (PMMA) co-doped with pyrromethene 567 (PM567) and coumarin 500 (C500) were prepared. The effects of C500 concentration on the performances of the solid state dye mediums, including spectra property, slope efficiency and photostability were studied. The highest slope efficiency 64.25% was obtained in the sample (PM567 : C500 = 2 : 8). Pumping the samples at a rate of 5 Hz with a pulse energy as high as 100 mJ (the fluence was 0.26 J/cm²), the output energy dropped to half of its initial value after approximate 116130 pulses and the normalized photostability reached 75.48 GJ/mol in the sample (PM567 : C500 = 2 : 1). Our results have shown that it is possible to obtain a high efficiency with a long lifetime for a solid-state dye laser co-doped with PM567 and C500.

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1. INTRODUCTION

Liquid dye lasers are a coherent source of radiation with such advantages as wide tuning range, high output power and high pulse energy and wide choice of pumping sources. The first solid-state dye lasers were reported by Soffer and Mcfarland [1] and Peterson and Snively [2] in the late 1960s. They demonstrated stimulated emission from polymeric matrices doped with organic dyes. However work on solid-state dye lasers was not pursued for over a decade due to low lasing efficiencies and fast photodegradation of the dye. Solid-state dye lasers have several advantages over the conventional liquid dye lasers such as easiness of handling, compactness, low cost, and lack of toxicity [3–7], their applications range over spectroscopy, communications, atmospheric sensing, medical treatment and so on.

In recent years, there are a number of materials which have been used as solid-state hosts for laser dyes such as polymers, porous glasses, organically modified silicates or silicate nano-composites, polycom glass. Polymeric matrices have some important advantages over other host materials because they are simple to prepare and cheap to produce. Polymethyl methacrylate (PMMA) is one of most commonly used polymeric hosts for its optical homogeneity and high transparency in the visible region of electromagnetic spectra; however, it has a relatively low damage threshold and bad photostability [8]. Ahmad et al. obtained a substantial increase in the photostability of PM567 laser dye solutions and in solid polymer media by the addition of Coumarin C540 laser dye [9]. PM567 doped in MTES-derived ORMOSIL with the presence of C440 dye, indicated an enhancement of at least four times in the photostability of PM567 [10]. The photostability of co-doping P-red has been largely improved by the presence of PM567 and C540A, and the laser output decreased less than 30% after 30000 pulses [11]. Compared to solid-state sample doped with pure PM567, at least 5-fold enhancement in the photostability was observed in the sample co-doped with PM567 and C440 [12].

In this letter, C500 was co-doped with PM567 into PMMA. PMMA was used as host matrix because of its excellent optical homogeneity with large volume and easy control of chemical process, which is very important for high pulse energy output. The effects of C500 concentration on the performances of solid state dye mediums, including spectra property, slope efficiency, and photostability were studied.

2. EXPERIMENTAL

2.1. Preparation of Solid-state Dye Samples

The materials under study were two laser dyes, PM567 and C500, in MMA or doped into the solid polymer PMMA. The solid polymer samples were made from MMA monomer which was washed three times with 10% (weight per volume) aqueous sodium hydroxide to remove the inhibitor and then three times with distilled water. After drying over anhydrous CaCl₂, MMA was vacuum distilled [3]. Laser dyes PM567 and C500 were dissolved in the MMA, which were placed in the ultrasonic bath in order to mix the dyes into the MMA. The concentration of PM567 was kept at $2 \times 10^{-4}$ mol/L while the concentration of C500 varied such that the mole ratio of PM567 to...
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C500 was 2 : 0, 2 : 0.5, 2 : 1, 2 : 2, and 2 : 8, respectively. A thermal initiator, $\alpha, \alpha$-azoisobutyronitrile (AIBN) was added, and the mixtures were again sonicated. The resulting solution was filtered into cylindrical molds, and then sealed. Polymerization was performed in the dark in a thermostatic bath at 40–45°C until solidification. The glass tubes were broken to remove the samples, which were cut into cylindrical rods 16 mm in diameter and 20 mm in length, and the ends were polished to obtain reasonably flat, smooth, glass-like surface [13].

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, emitting 15 ns full-width at half-maximum (FWHM) pulses and beam diameter of 7 mm. Details of the measurement setup can be found elsewhere [13]. Longitudinal pump was chosen for laser experiments. The dye laser cavity was a compact plane–plane configuration and with about 5 cm long, which was used to reduce the cavity losses due to a highly divergent output. The cavity consisted of two plane mirrors $M_i$ and $M_0$, a partial output coupler with $T \sim 70\%$ in 500–700 nm and a dichroic mirror with a high transmission ($T > 95\%$) at 532 nm and high reflectance ($R > 95\%$) in 550–590 nm. After the SHG, half-wave-plate and polarizing plate were used to control the intensity of pump beam [14, 15]. The output energy were detected by energy sensor1 J25-MB (Coherent Inc.) and the outputs of energy sensor were recorded by computer through EPM2000 dual-channel energy meter. The energy sensor2 detected the variation of input energy at times.

3. RESULTS AND DISCUSSION

3.1. Spectral Properties

3.1.1. Absorption and fluorescence spectra. The absorption spectra of the samples in MMA and PMMA were obtained by spectrophotometer UV-3010PC (Shimadzu Company) and the fluorescence spectra were measured by the spectrum detector HR4000 (Ocean Optics, 200–1100 nm). The typical absorption and fluorescence spectra of the samples were presented in Fig. 1. The dyes PM567 and C500 in MMA have broad absorption bands: 440–550 nm and 320–430 nm. The solid dye sample doped with PM567 has broad absorption bands: 460–540 nm. It can be seen that the dye C500 has no absorption at 532 nm and the dye PM567 based on PMMA have an intensive absorption at 532 nm, so the absorption in 440–550 nm is mainly contributed by PM567 while the C500 was co-doped with PM567. The solid dye samples all have wide fluorescence band of about 40 nm (FWHM). It can be seen that C500 has little effect on the fluorescence spectra, because C500 dye is almost transparent at 532 nm.

3.1.2. Lasing spectra. Lasing spectra of the samples are presented in Fig. 2. The line width of the lasing spectra varied from 6 to 8 nm, much narrower than the fluorescence spectral width. The maxima of the lasing spectra of the samples range from 558 to 562 nm. It can be seen that C500 has a slight impact on the laser emission of the samples. Spectra and lasing properties of the samples are presented in Table 1.

3.2. Slope Efficiency

Dye laser slope efficiency is very importance for the applications of solid-state dye lasers. The laser effi-