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Output performance of a dye-doped sol-gel silica laser in the near UV

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Visibly transparent near-UV dye (Exalite 377E)-doped silica in the form of parallelepiped were prepared by the low-temperature sol-gel process. The laser output performance of dye-doped sol-gel silica samples pumped by a short pulse (1 ns) N_2 laser at 337 nm was reported. With a grating as the wavelength selection element, the laser was tuned from 367 to 387 nm with a laser linewidth of 2 nm. Using a resonator cavity consisting of two flat mirrors, the sol-gel laser showed a slope efficiency of 34.7% and a pump energy threshold of 20 μJ. The variation of sol-gel laser energy output as a function of the number of pulses under repetitive N_2 laser excitation was investigated. The laser output energy decreased initially with the number of shots. The output energy recovered to its original intensity after a ten minute interruption in pumping. In this way, the dye-doped samples showed no signs of long term degradation after being irradiated at 337 nm for tens of thousand shots. © *1996 American Institute of Physics.* [S0003-6951(96)04551-2]

Considerable interest has been renewed in the area of tunable solid state dye lasers in recent years. One of the main reasons of this surge in interest has been the rapid development of solid state host materials for the laser active dye molecules. Polymeric host based on modified poly(methyl methacrylate) (MPMMA) and/or 2-hydroxyethyl methacrylate (HEMA) appears to have the high homogeneity, laser damage resistance, and reasonable photostability that are required of good solid state laser materials.[1,2] Useful lifetimes of 20 000 shots have been obtained from pyromethene dye-doped polymer lasers pumped at 532 nm[3] and from a modified rhodamine 6G-doped polymer laser pumped at 337 nm.[4] Another class of solid state host material for dye molecules is sol-gel glass which promises better photo- and chemical stability. A number of dye molecules have been successfully incorporated into silica matrices using the low temperature sol-gel process. Relevant fluorescence and laser emission properties of these dye-doped sol-gel silica have been studied.[5–8] Recently, Canva *et al.* reported that 150 000 laser shots were emitted from the same spot of a perylene red-doped inorganic-organic hybrid silica xerogel sample when pumped by a frequency-doubled Nd:Yag laser at 532 nm.[9] Such results compare well with polymeric dye lasers and stimulate further work on sol-gel dye lasers.

We previously fabricated sol-gel silica slabs with UV transmission down to 260 nm, thus making possible effective pumping by a number of UV lasers. Subsequent experiments using a XeCl laser as pump source demonstrated wide-band tuning laser action from rhodamine and coumarin-doped sol-gel silica.[10] In order to extend the spectral range of solid state dye lasers, we incorporated several UV laser dyes into sol-gel silica matrices. Intense superradiance emissions were observed.[11] In this letter, we report laser output performance of Exalite 377E (E377)-doped sol-gel silica samples pumped by a 1 ns N_2 laser. A slope efficiency of 34.7% and tuning from 367 to 387 nm were achieved from a sample of an initial dye concentration of 2×10^{-4} molar. Laser output energy dropped off under uninterrupted repetitive N_2 laser excitation. After a respite of some 10 min, the laser output regained its original strength. The sample showed no sign of long lasting degradation after being subjected to tens of thousands of N_2 laser shots.

The UV dye doped-silica samples were fabricated following largely the sol-gel process of acid catalyzed hydrolysis/polycondensation as outlined in Ref. 7. The main difficulty involved in the sample preparation is that most of the commercially available UV dyes dissolve poorly in the initial solutions of the sol-gel process. After vigorous mixing at elevated temperatures to promote solubility, we succeeded in making some doped sol-gel samples which were initially transparent after gelation. As the aging progresses, however, the samples turned turbid. Fluorescence emissions from these samples as induced by laser excitation were weak.

The UV dye E377 obtained from Exciton Inc. dissolves readily in the initial solutions. (The chemical formula and structure of E377 are not available as E377 is claimed to be proprietary information of the vendor, Exciton Inc.) Sol-gel samples doped with E377 yielded intense fluorescence emissions under XeCl laser excitation.[11] A detailed report of laser experiments on E377-doped sol-gel samples is presented in this letter.

In the following sentences, we review briefly the sample preparation procedures. The initial solutions were typically composed of 15 ml of tetraethoxysilane (TEOS), 11 ml of ethyl alcohol, 9 ml of water, 10 ml of formamide, and 1.5 ml of hydrochloric acid serving as catalyst. E377 dyes were added to the initial solutions under magnetic stirring until the desired molar concentrations were reached. The organic dyes and chemicals used in these experiments were procured from commercial vendors without further purification (Exciton Inc. and Aldrich, respectively). Maintained in a thermostat at 60 °C, gelling occurs in hours. After aging and dying for about one week, the silica gels solidify and are readily removed from acrylic cuvettes. The silica samples typically

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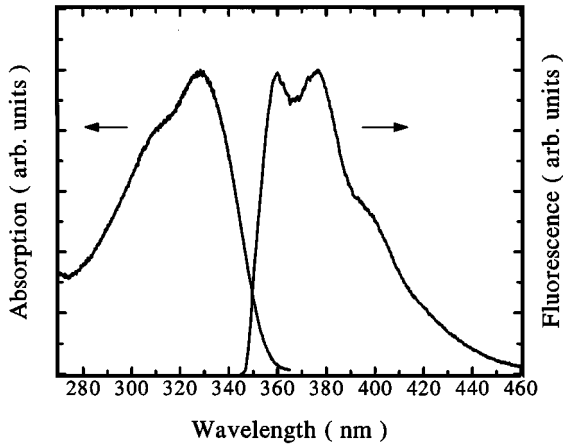

FIG. 1. Absorption and fluorescence (induced by the N_2 laser) spectra of E377-doped sol-gel silica.

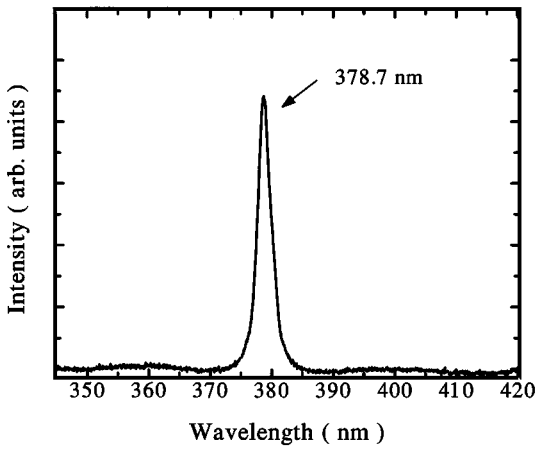

FIG. 2. E377-doped sol-gel silica laser emission spectrum.

measured at $6(w)\times6(h)\times12(l)$ mm^3 were visually of good surface finish with end faces appearing to be plane parallel. In the laser experiments, such samples were used without further polishing. The bulk density of the samples was 1.25 g/cm^3.

Absorption measurements of the E377-doped samples were performed using a Hitachi Spectrophotometer. The peak of the absorption was at 328 nm. The absorbance at 308 and 337 nm, the two wavelengths of importance to pumping consideration, was roughly equal. The fluorescence spectrum of the samples induced by 337 nm pumping showed a two-peak structure at 360 and 375 nm for the concentration (2×10^{-4} M) used in the laser experiments. The 360 nm peak was lower in intensity. The 360 nm peak was further diminished while the 375 nm peak gained in prominence as the concentration was increased. At low concentrations ($\sim8\times10^{-5}$ M), the 360 nm peak was equal or slightly higher than the 378 nm peak (Fig. 1). The shifting of fluorescence intensity from the shorter wavelength peak to the longer wavelength peak at increased concentration could be caused by the formation of dimers in the sample. Details of the absorption and fluorescence emission spectral characteristics will be reported elsewhere.

Tuning of the dye-doped silica samples was performed using a 1800 grooves/mm grating blazed at 300 nm as the back reflector set in the Littrow configuration. The output coupler was a flat multilayer dielectric-coated mirror of 90% reflectance at 380 nm. The reflectance drops to 60% at 360 nm. For samples with a concentration of 1×10^{-3} M as suggested by the vendor for use in liquid solutions, only superradiance emissions (SE) were observed. The SE signals (centered at 376 nm) were so strong that tuning was not possible. In subsequent laser experiments, samples of 2×10^{-4} M concentration were used exclusively. For slope efficiency measurements, a flat-flat resonator cavity was used. The same 90% reflectance mirror was used as the reflector and a 10% reflectance mirror (also measured at 380 nm) served as the output coupler.

Pumping was provided by a short pulse (1 ns) N_2 laser (Photon Technology International). Waveforms of the N_2 laser, the fluorescence, and the sol-gel laser pulses were measured with a calibrated fast phototube (Hamamatsu R1 193U-02) and processed with a wide-bandwidth digital signal analyzer (Tektronix 602A) with a single-shot bandwidth of 1 GHz. The excitation energy delivered to the samples was 90 μJ as determined by time integrating the N_2 laser waveforms. The N_2 laser beams were directed transversely at the samples with or without the aid of a cylindrical focusing lens for laser or fluorescence experiments. The gain length gain was simply the sample width of 6 mm. Laser and fluorescence emission spectra were directly detected by an intensified/gatable array detector (Princeton Instruments IRY-700) mounted on a 1/4 m grating spectrograph (Oriel Multispec 257). All of the spectra presented in this letter were uncorrected for the spectral response of the array detector. On account of the broadband nature of the detector from 350 through 450 nm, however, the effects of the spectral dependence of the detection system on the emission spectra were believed to be slight.

To be successful in tuning the sol-gel laser, care must be taken in suppressing parasitic oscillations and superradiance emissions (SE). The sample was heavily tilted with respect to the optical axis defined by the grating and the output coupler to avoid its side surfaces to act as reflecting surfaces. The focused spot of the excitation beams on the sample often needs fine adjustment so as to prevent the occurrence of SE. When lasing, a bright laser spot of diameter, ~3 mm was observed on a screen placed approximately 200 mm from the output coupler. The screen was illuminated by a bluish diffuse glow when the grating was blocked. Figure 2 shows the laser output spectrum. The laser linewidth as observed in the emission spectrum is about 2 nm full width at half-maximum (FWHM). The maximum of the tuning curve (Fig. 3) is at 376 nm which roughly corresponds to the long wavelength peak in the fluorescence spectrum. For the sample concentration of 2×10^{-4} M, tuning is achieved from 367 to 387 nm (Fig. 3).

For slope efficiency measurements, the flat-flat resonator cavity described earlier was used. Variation of the pump laser energy was achieved by inserting calibrated quartz plates in the beam path. Laser oscillation of the flat-flat cavity was verified by blocking and unblocking the back reflector.

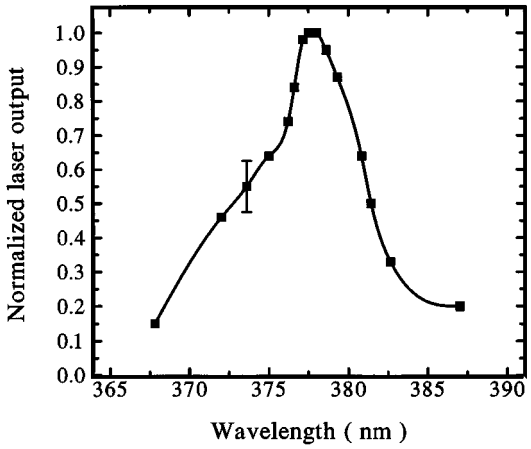

FIG. 3. Tuning range of E377-doped sol-gel silica laser at a concentration of 2×10^{-4} M.

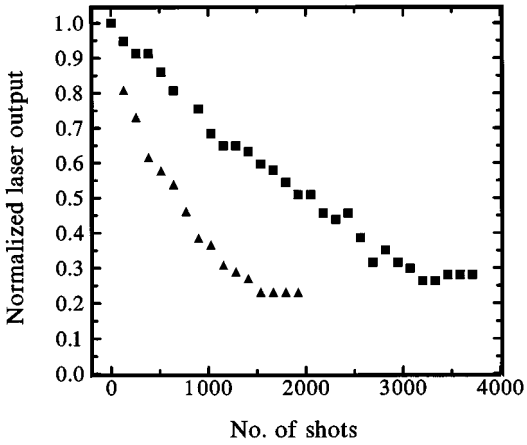

FIG. 5. Laser output energy (relative units) as a function of the number of pump shots at 1 Hz rep. rate (squares), at 3.5 Hz rep. rate (triangles).

Whenever the reflector was blocked, no directional emissions could be observed on the screen, implying that parasitic oscillations or SE signals were not present. The laser output from this flat-flat cavity was centered at 377.5 nm with a width (FWHM) of 2.5 nm. Figure 4 shows the results of the slope efficiency measurements. The straight line represents a 34.7% slope efficiency as calculated by a linear curve fitting routine (AXUM Software). A pump threshold energy of 20 μJ is also observed from Fig. 4. The flat-flat cavity has not been optimized to achieve higher efficiency.

To evaluate the practicality of the E377-doped sol-gel silica laser, we measured the laser output energy as a function of the number of excitation pulses. In these experiments, the excitation energy was kept at 90 μJ. Figure 5 summarizes the results at pump repetition rates of 1 (squares) and 3.5 Hz (triangles). At rep. rate of 1 Hz, the laser output dropped to 50% after 2000 shots, while 700 shots was the 50% drop off point at 3.5 Hz. In both cases, the laser output seemed to level off to some asymptotic values of, 30% for the 1 Hz case and 25% for the 3.5 Hz case. Indeed, laser output energy regained its highest value at the first shot when pumping was stopped for 10 min and then resumed. For all the laser experiments reported in this letter (results shown in Figs. 2 through 5), only one sol-gel sample was used. It showed no signs of long term degradation that could possibly be resulted by the irradiation of tens of thousand of N_2 laser pulses. We believe that the drop in laser output as the number of shots accumulates is mainly due to the slow removal of the waste heat. The E377-doped sol-gel silica sample seemed to have suffered no photodegradation.

In summary, we have fabricated and lased E377-doped sol-gel silica pumped by a 1 ns N_2 lasers. Wavelength tuning was achieved from 367 to 387 nm. Measurements of laser output energy versus pump energy revealed a slope efficiency of 34.7%, which compared reasonably well with polymeric dye lasers and sol-gel dye lasers in the visible spectral region. Study of the laser output as a function of shots indicates that short term useful lifetimes were at least 2000 and 700 shots at 1 and 3.5 Hz, respectively. Since no provisions were made to remove waste heat in the sample and the same focused spot was used throughout, improved short term lifetimes should be expected by better heat removal through the combined use of heat sink/ external cooling and a larger size sample[9] or a rotating system.[12]

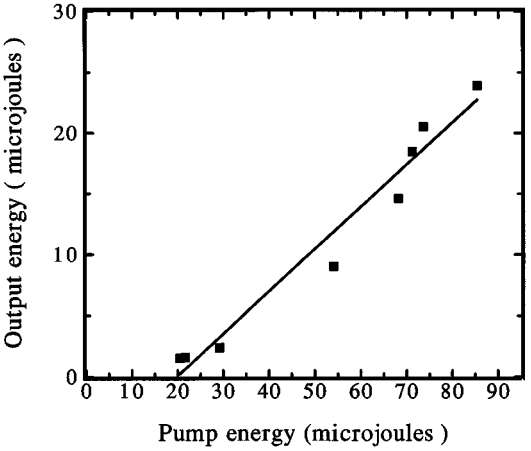

FIG. 4. Output energy (in μJ) of E377-doped sol-gel silica laser as a function of pump energy, showing a slope efficiency of 34.7%.

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