TECHNICAL NOTE

Sol-gel silica laser tunable in the blue

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Doped and undoped silica slabs were fabricated through the use of the sol-gel technique. Extended UV transmission was observed for HCl-catalyzed sol-gel silica. Under transverse pumping with a XeCl laser, narrow-linewidth (<0.9-nm) laser oscillation from silica slabs doped with coumarin 460 (C460) was achieved in a grating–resonator cavity configured in the grazing-indicence geometry. Tuning of the C460-doped silica laser extended from 468 to 494 nm. The conversion efficiency of the narrow-linewidth blue laser was 5.5%.

Dye-doped inorganic matrixes derived through the sol-gel route—a new glass-making technology—constitute a new class of tunable solid-state laser materials that offer tuning capabilities ranging from the UV to the near infrared. Previously, polymeric materials such as poly(methylmethacrylate) (PMMA) and modified PMMA (MPMMA) have been used with some success as host materials for organic dyes. Because of the low temperatures that are employed during the sol–gel process, organic dopants, which will otherwise be destroyed in conventional glass-forming processes, can be introduced into sol-gel glasses to serve as optically active centers. In view of the many potentials of dye-doped sol-gel-derived glasses, research interest regarding this class of tunable solid-state-laser materials has been considerable. Rhodamine- and coumarin-doped silicates have been characterized spectroscopically and the mechanical properties ascertained.[1,2] Gain measurements, broadband lasing, and frequency tuning have been performed with a liquid-dye laser or a frequency-doubled YAG laser as the pump source.[3–5] Our group has studied XeF-laser-induced emission properties of 10 dyes in a sol-gel silica matrix that covers the spectral range from 400 to 800 nm.[6,7]

Most of the recent studies on dye-doped sol-gel lasers has been with the green-to-red spectral regions because pumping can be provided conventiently with frequency-doubled Nd:YAG lasers at 532 nm.[8] Recently, Ferrer *et al.*[9] also reported having lased dye-doped PMMA in the blue-green range. Applications in fields like optical storage, underwater communication, etc., however, call for efficient tunable lasers in the blue. Excimer lasers in the UV are powerful pump sources for liquid-dye lasers.[10] They are in fact most useful when one pumps dyes in the blue-to-UV spectral regions. Silica glass formed by means of the sol-gel route, however, usually transmits poorly in the UV. Porous sol-gel silica glass supplied by a commercial vendor (Geltech, Alachua, Fla.), for instance, has UV cutoffs that vary from 300 to 500 nm, depending on the pore sizes. Hence, excimer-laser pumping of dye-doped sol-gel glass that exhibits poor UV transmission could lead to a shortened of laser lifetime and eventually to the destruction of the sample. When HCl was used as the catalyst during the sol-gel process, UV transmission of the undoped sol-gel silica was found to extend down to 260 nm, which thus permitted safe XeCl-laser pumping at 308 nm.[11] Wideband tuning of silica slabs that were doped with coumarin 460 (C460) was demonstrated with a resonator cavity in the grazing-incidence configuration. Narrow-linewidth laser emissions (<0.9 nm) from the C460 slabs were achieved in the 468–495-nm range. For a XeCl laser pump energy of 6.5 mJ, the blue laser output was 0.36 mJ, corresponding to a conversion efficiency of 5.5%.

The C460-doped silica slabs were fabricated in house largely through the sol-gel procedures outlined in Refs. 6 and 7. The only major change was the use of HCl in place of HNO_3 as the catalyst. The initial solutions are typically composed of 15 mL of tetramethoxysilane (TMOS), 12.5 mL methyl alcohol, 18 mL water, 12.5 mL formamide, and 2 mL HCl, which served as the catalyst. We added C460 dyes to the initial solutions using magnetic stirrers until the desired molar concentrations were reached. The

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concentration of C460 is 5.2×10^{-3} M in the initial solutions. The organic dyes and chemicals were procured from commercial vendors (Exciton of Dayton, Oh., and Aldrich of Milwaukee, Wisc., respectively) and were used in the sol-gel process without additional purification. Gelling occurs in hours if the solution is kept at a temperature of 60 °C. After the silica gels are aged and dried for approximately one week, they solidify and are readily removed from the rectangular acrylic cuvettes in which they are formed.

The silica samples typically measure 5 mm × 15 mm × 30 mm (width by height by length) and visually appear to have a good surface finish, with the end faces seeming to be plane parallel. In the laser experiments, such samples were used without their further polishing. The bulk density of the samples is 1.42 g/cm^3. Optically, the undoped silica slabs show excellent UV transmission characteristics (Fig. 1). Excellent transmission deep into the UV for the HCl-catalyzed silica slab is seen. The improved UV transmission is believed to have resulted from smaller pore sizes and a concentrated pore distribution effected through HCl-catalyzed hydrolysis.

Wideband tuning of the dye-doped silica slabs was performed with a grating–resonator cavity in the grazing-incidence configuration (Fig. 2). The grating was ruled at 2400 lines/mm. Wavelength tuning was effected through translation to and from the reflection mirror that was opposite the grating. The output coupler was a flat multilayer dielectric-coated mirror of broadband reflectance. The reflectance *R* has a maximum of 90% near 490 nm, and it drops to 87% near 460 nm. Pumping was provided from a commercial multigas excimer unit that was operated as a XeCl laser (Lumonic of Kanata, Ontario, Canada). The XeCl laser pulse was approximately 10 ns. A Molectron energy meter (Model J3-09) was used for laser-energy measurements. The excitation energy delivered to the samples was approximately 6.5 mJ. The XeCl laser beams were directed transversely at the samples with or without the aid of a cylindrical focusing lens for the laser or fluorescence experiments. The length of gain in the silica slabs as determined by the focused pump beam was 2.5 cm. On-axis emissions from the samples were coupled, by means of an optical-fiber bundle, to a 512-element array detector mounted on a 0.25-m grating spectrograph (Oriel of Stratford, Conn.) for the detection of time-integrated spectra. All the spectra presented in this technical note are uncorrected for the spectral response of the array detector and the fiber bundle. Because of the broadband nature of the detector and the fiber bundle in the visible, however, the effects of the spectral dependence of the detection system on the emission spectra are believed to be slight.

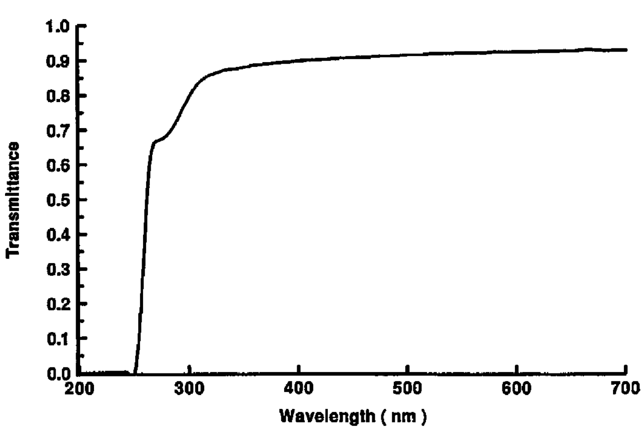

Fig. 1. Transmission trace of an undoped sol-gel silica slab. The sample thickness was 5 mm.

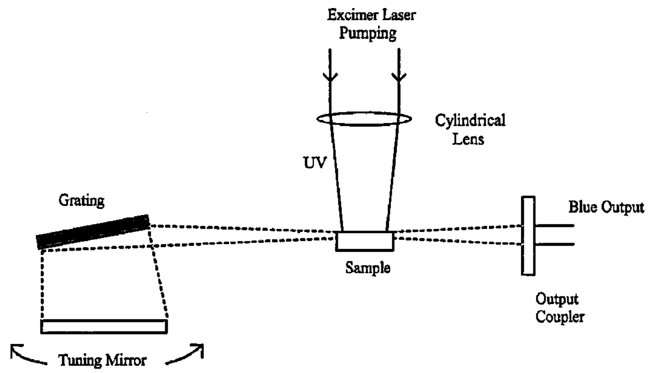

Fig. 2. Experimental arrangement of a narrow-linewidth sol-gel silica laser oscillator.

Fluorescence of silica slabs that are doped with C460 is easily induced when the unfocused XeCl laser beams are pumped. When pumped by a focused beam, narrow-linewidth laser emissions are obtained after the installation of a grating–resonator cavity. Figure 3 shows the laser-output spectra that were obtained as tuning was administered by means of translation of the reflection mirror. The laser linewidth as observed in the emission spectra is approximately 0.9 nm, which is actually the resolution limit of the fiber bundle–array detector–grating spectrograph detection system. The actual laser linewidth should be smaller. In our experiments, narrow-linewidth lasing was demonstrated without the benefit of an intracavity iris. But the signal-to-noise ratio, as defined by the narrow-linewidth output versus the amplified spontaneous emission, is already at 20:1 around, i.e., above and below, 475 nm. The output energy of the sol-gel laser was sampled at 478 nm. A per-pulse energy of 0.36 mJ was measured, and that value corresponds to an UV-to-blue conversion efficiency of 5.5%. An improved output efficiency should be obtainable if an optimized tuning cavity and samples with Brewster-angled end faces are used. Figure 4 shows the tuning range of the XeCl-laser-pumped C460-doped silica-slab laser. A broad range from 468 to 494 nm is observed.

Damage to the porous sol-gel samples caused by the intense UV pump beams was reported in a previous paper.[6] During the present narrow-linewidth laser experiments, the samples were subjected to XeCl laser irradiation for hundreds of pulses at a stretch. The XeCl pump laser was operated at a low repetition

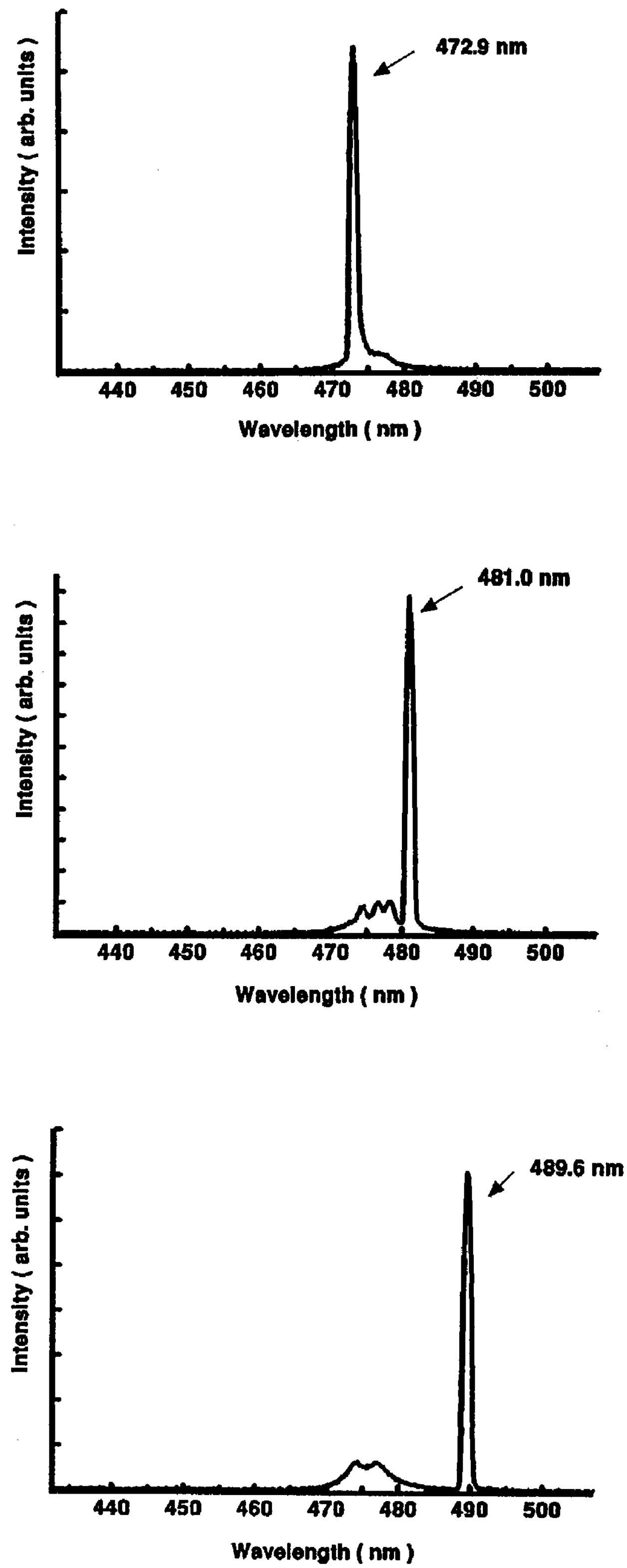

Fig. 3. Narrow-band emission spectra obtained with the C460 laser oscillator for three different wavelengths.

rate ($\sim$0.2 Hz), and NO noticeable dropoff has been observed in blue laser-output energy at the ends of the experiments (i.e., up to several hundred pulses). Indeed, these silica slabs with improved UV transmis-

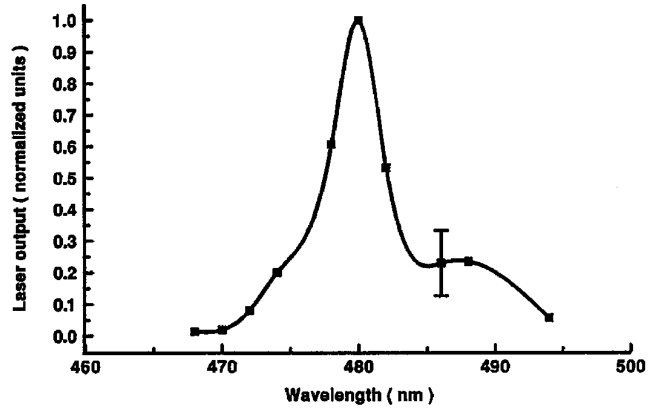

Fig. 4. Tuning range of a C460 silica-slab oscillator with a grazing-incidence grating–resonator cavity.

sion exhibit no surface damage at an XeCl laser incident energy density of the order of 0.03 J/cm^2. We attribute the enhanced durability of the sol-gel samples under UV irradiation to the use of HCl as the catalyst in our preparation procedure. We believe the HCl catalyst to have caused the formation of smaller average pore sizes.[11]

In summary, we have fabricated dye-doped silica slabs that can be pumped with excimer lasers. Narrow-linewidth ($<$0.9-nm) lasing in the blue (468–494 nm) has been demonstrated from these dye-doped silica slabs. Rhodamine 6G-doped MPMMA and organically modified silica lasers that incorporate similar multiprism expanders in the resonator cavities have already yielded narrow-linewidth output with linewidths of 1.1 and 3 GHz, respectively.[12] We anticipate further reductions in the laser linewidths by incorporating our sol-gel samples in grating cavities that have multiprism expanders. Improvements in the output efficiency are also expected if the samples are cut into Brewster-angled wedges and optimized output coupling is used.

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