

Laser and Fluorescence Properties of Dye-Doped Sol-Gel Silica from 400 nm to 800 nm

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Abstract. Lasing and fluorescence properties of ten dyes covering the spectral range from 400 nm to 800 nm were studied in a silica matrix prepared by the sol-gel technique. The dye-doped sol-gel silica samples fluoresced strongly under laser excitation. Many of the samples were also induced to superradiate. In comparison to dyes in alcohol solvents, significant red-shifting was observed in the sol-gel silica fluorescence spectra. Plausible causes of the red-shift are discussed.

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The use of the low temperature sol-gel technique to prepare solid-state laser materials has become of interest recently. Earlier, rhodamine dye-doped sol-gel silica was successfully prepared [1] and tunable laser action was achieved [2]. A study of laser-relevant properties of neodymium-doped sol-gel silica was also reported [3]. We reported in a recent article [4] the demonstration of multi-megawatt superradiant emission from coumarin-doped sol-gel silica. The great promise of the sol-gel technique notwithstanding, there appears in the literature the results of only a few dyes and one rare earth element as dopant materials. Laser action was achieved mainly in the green (around 530 nm) and red (around 630 nm). In view of the versatility of sol-gel silica as solid-state laser host material, the need to further explore the spectral coverage range of this class of laser material is obvious.

Partly because of the extensive coverage of rhodamine-related dye-doped sol-gel silica already extant in the literature, we concentrated our efforts more on dyes in the blue-green and near-infrared. Also, since one of the motivations of this research endeavor is to find new laser material in the deep blue, preferably with emission lines matching the transition wavelengths of atomic filters (i.e. cesium at 455/459 nm [5], or calcium at 422.7 nm [6]), dyes in the blue have been preferentially chosen. In this paper, exper-

imental results of fluorescence and laser characteristics are reported for stilbene 420, coumarin 440, coumarin 460, coumarin 521, coumarin 540, rhodamine 560 (chloride), rhodamine 640 (perchlorate), and the styryl dyes: LDS 759 and LD 800, roughly covering the spectral region from 400 nm to 800 nm. The molecular structure of nine dyes are shown in Fig. 1. The molecular structure of LDS 759 is not available because it is proprietary information of Exciton Inc. (We follow in this paper the dye nomenclature of the vendor – Exciton Inc.) Strong fluorescence emissions are observed for all the dyes under investigation. Coherent superradiant emissions are also induced in several of the dyes.

1 Experimental

Preparation procedures for the dye-doped samples follow the well known sol-gel route [7] and are identical to those in [4] except that the exact amount of formamide (drying control chemical additive, DCCA) added was finely adjusted for each individual dye to achieve optimum pore size distribution and consequently the mechanical strength. The molar concentration of the dye solutions are normally maintained between $0.5\text{--}5 \times 10^{-4}$, roughly following the guidelines suggested by the vendor. During the sample preparation, we made slight deviations from the guidelines as some of the suggested concentration levels were found to be not compatible with the typical sol-gel procedures. We did not find the concentration levels employed in our experiments in any way affect the general shapes and peaks of the emission spectra. The doped samples so prepared are cylindrical rods of various colors, typically 2.5 cm in length and 1.5 cm in diameter. Final finishing of the sample can be carried out by diamond sawing and hand sanding. When examined under a high-power microscope, the surface quality of the samples appears to exceed the commercial cosmetic standard (scratch and dig better than 80–50).

We also find in the course of sample preparation that dye molecules can be introduced into the undoped sol-gel silica rods by immersing the rods in methanol/formamide solutions of suitable dyes; immersion of the samples in pure

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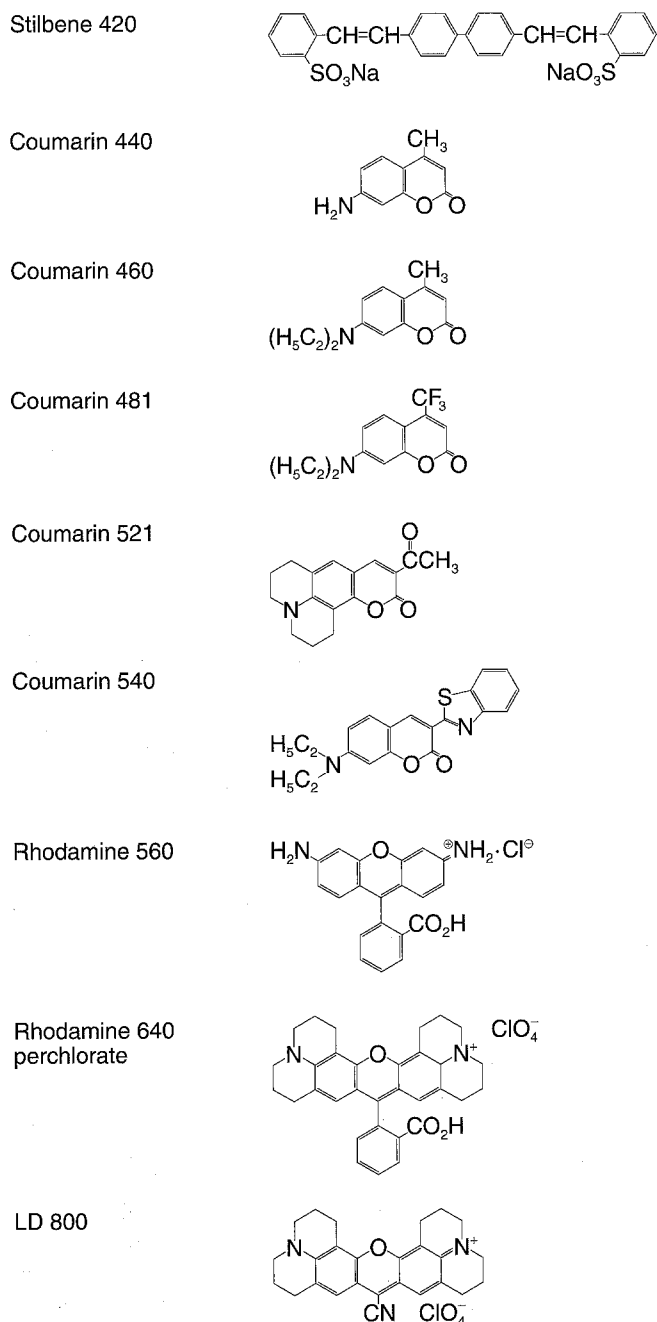


Fig. 1. Molecular structure of nine of the dyes used in this paper. (Courtesy of Exciton Inc.)

methanol solution causes complete fragmentation. Since dye molecules lodge themselves in pore sites in the silica by diffusion, the concentration level is readily controlled by time duration of the immersion.

Laser and fluorescence characteristics were studied by observing the emission spectra of the dye-doped silica samples. The excitation source for the visible dyes was a XeF laser operating at 351 nm (Lambda Physik EMG 201 E). The per pulse energy was about 200 mJ and the laser duration was 20 ns. Both focused and unfocused beams were used to excite the samples. The two near-infrared dyes (LDS 759 and LD 800) were excited by a prism-tuned flashlamp-pumped dye laser operating at 540 nm (Candela LFDL-6). The laser energy was about 40 mJ and the duration

was 1 μ s. Fluorescence or superradiant emissions along the axial direction of the sample rods were directed to and dispersed by a 0.275 m focal length monochromator (Acton Research). Two pieces of broadband mirrors (> 95% reflectivity from 370 nm to 900 nm) were used as light-steering optics to direct emission signals to the Acton monochromator. Time-integrated signals were detected by an intensified diode array (Princeton Instruments IRY-700G) mounted at the exit port of the monochromator and displayed on the PC monitor as emission spectra. All the emission spectra presented here are not corrected for the variations in the spectral dependence of the transmission and diffraction optics. Similarly, the spectral sensitivity of the diode array has not been accounted for. In view of the broadband nature of the optics and the array detector over the spectral range under study here, however, the effect of the spectral dependence of the detection instrumentation on the emission spectra is believed to be slight.

2 Emission Spectra of Dye-Doped Silica

2.1 Stilbene 420 and coumarin 440, 460

One of the motivations of this research endeavor is to investigate suitable blue-green dye-doped sol-gel silica for possible applications as transmitters for selected atomic filters. One of the more developed atomic filters has been the cesium filter at 455/459 nm. Our earlier work [4] had indicated that, at least for some coumarin dyes, emission peaks tended to red-shift in sol-gel silica. Experiments showed coumarin 481, which was reported to have a fluorescence peak at 509 nm in methanol [8], peaked at 520 nm in sol-gel silica. Bearing in mind the red-shifting of dyes, we proceeded to prepare samples using dyes in the short-wavelength side of 455/459 nm in the hope of matching the cesium filter.

Fluorescence and superradiance experiments were carried out using a XeF laser as the excitation source, with a fused silica cylindrical lens for line-focussing purpose. Emission spectra of stilbene 420 in methanol and sol-gel silica are illustrated in Fig. 2. Superradiant emission of stilbene 420 in methanol induced by line-focused beam excitation appeared at 425 nm, in apparent good agreement with the maximum laser wavelength reported in the literature [8]. By contrast, the superradiant emission from the sol-gel silica is at 440 nm, confirming the anticipated red-shifting of sol-gel samples. The fluorescence spectrum of the same sample has a peak farther to the long-wavelength side at 460 nm and the halfwidth amounts to 30 nm. The spectra of superradiant and fluorescence emission of coumarin 460 in sol-gel silica are shown in Fig. 3. The superradiant emission peaks at 475 nm, while that of fluorescence is at 478 nm, comparing with maximum laser wavelength and fluorescence wavelength in ethanol solution at 454 nm and 451 nm, respectively [8]. Sol-gel silica doped with coumarin 440 was also prepared. The fluorescence peak was found at 474 nm. However, superradiance experiments were attempted without success. The fluorescence spectra of coumarin 440- and 460-doped sol-gel silica appear similar, while coumarin 460-doped silica seems so much easier to lase, we did not pursue the study of coumarin 440 samples further.

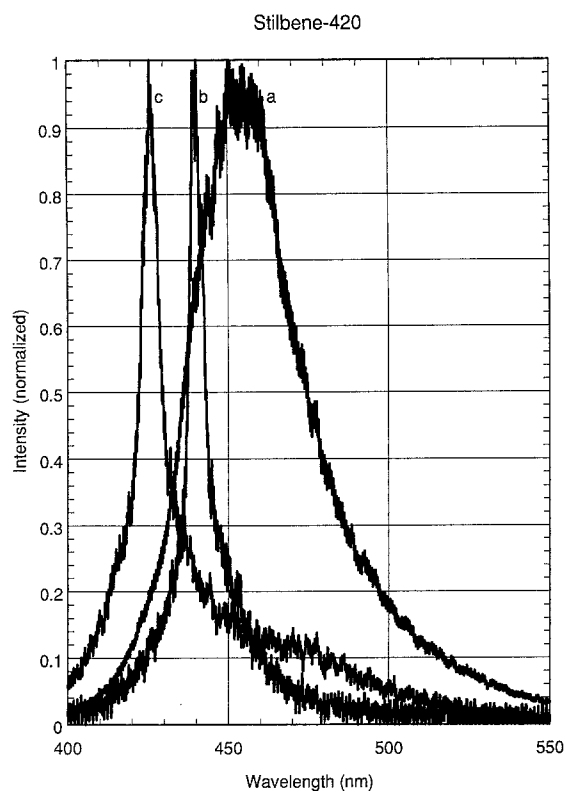


Fig. 2. *a* Fluorescence and *b* superradiance emission spectra of stilbene 420 in sol-gel silica; *c* superradiance spectrum of stilbene 420 in methanol

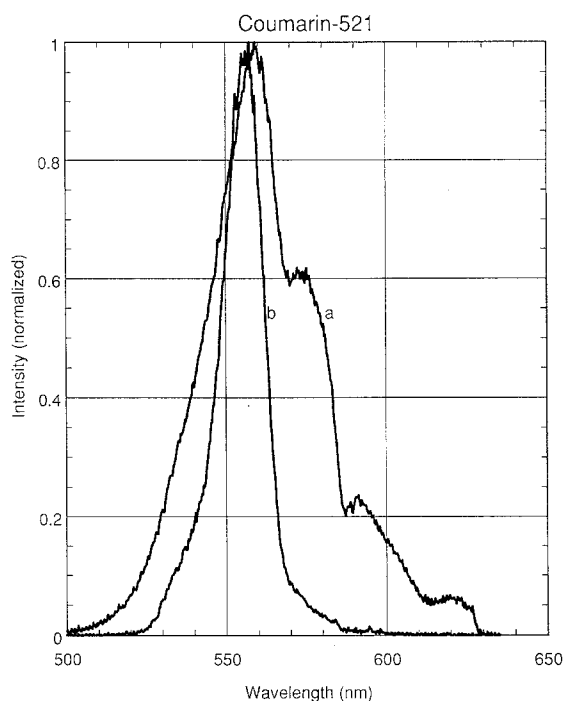


Fig. 4. *a* Fluorescence and *b* superradiance emission spectra of coumarin 521 in sol-gel silica

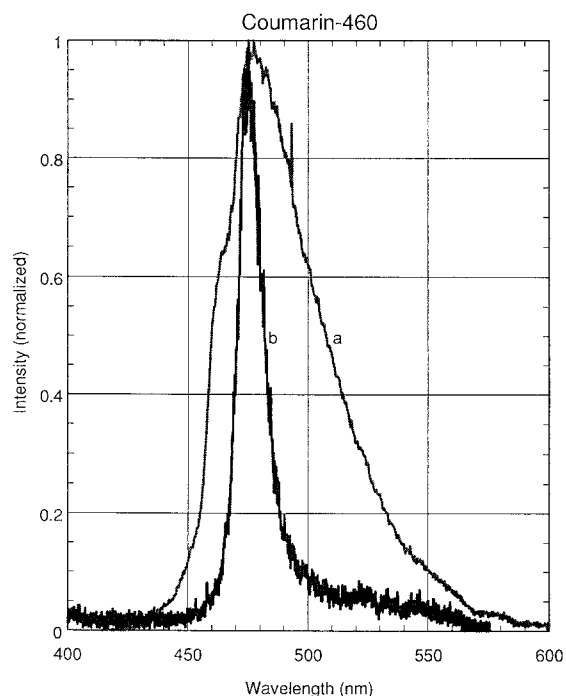


Fig. 3. *a* Fluorescence and *b* superradiance emission spectra of coumarin 460 in sol-gel silica

Although the superradiant lines of stilbene 420- and coumarin 460-doped sol-gel silica do not exactly match the cesium lines, in view of the broad fluorescence halfwidths (~ 30 nm) of these two dyes and the ease with which superradiant emissions were induced, it seems highly likely

that narrow linewidth laser action can be achieved by installing tuning elements in a resonator cavity. Matching laser lines at 455 nm and 459 nm should thus be obtained.

2.2 Coumarin 521, 540 and rhodamine 560, 640

A number of widely-used green and red dyes are also investigated to determine their compatibility with the sol-gel technique. In Figs. 4–6, we show the XeF-laser excited fluorescence and superradiance spectra of coumarin 521, rhodamine 560, 640, respectively, at 558, 625, and 655 nm, and the fluorescence peaks at 560, 638, and 660 nm, respectively. It is worth noting that the corresponding numbers for alcohol solutions in the literature [8] are, in the sequence of coumarin 521, rhodamine 560 and 640, 514 nm, 555 nm and 650 nm for maximum laser wavelength, and 495 nm, 532 nm, and 594 nm for maximum fluorescence wavelength. We tried, without success, to induce superradiance in coumarin 540-doped sol-gel silica. But fluorescence spectra were readily obtained. For a 2.5×10^{-4} molar concentration sample, the fluorescence peak was at 520 nm. (The corresponding maximum fluorescence wavelength in alcohol solution is 505 nm [8].) Upon doubling the dye concentration and the amount of formamide used, the fluorescence peak shifted to 540 nm (Fig. 7). Based on this observation of formamide dependence, one may come to appreciate the influence of residual chemicals on dye molecules. Since the dye molecules are actually embedded in a silica matrix in the sol-gel silica samples, the recurrent red-shifting of the emission spectra indicates some combined effect of the local environment

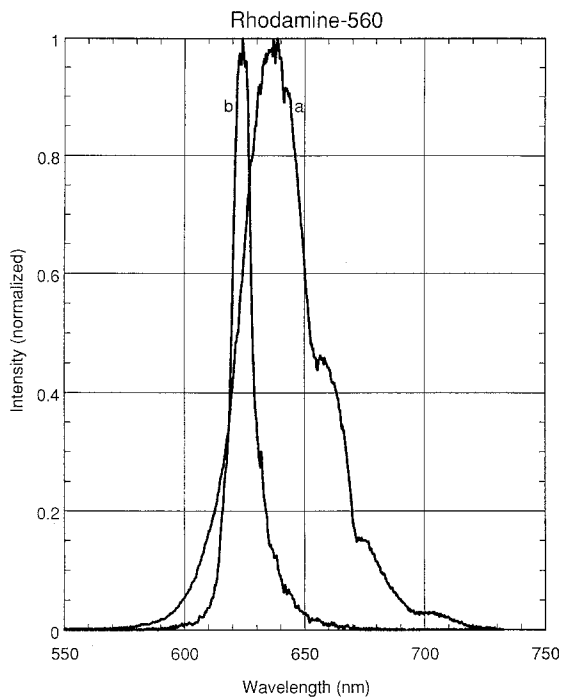


Fig. 5. *a* Fluorescence and *b* superradiance emission spectra of coumarin 560 in sol-gel silica

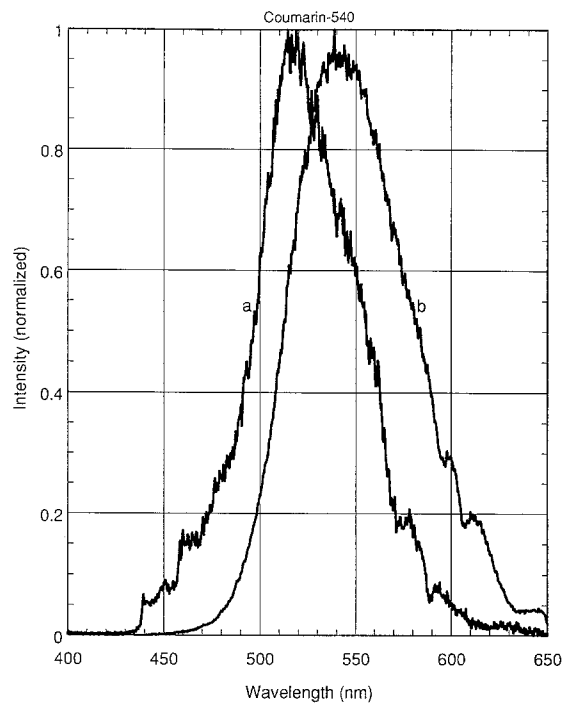


Fig. 7. Fluorescence emission spectra of coumarin 540 in sol-gel silica prepared by: *a* formamide-lean procedures; *b* formamide-rich procedures

consisting of the rather porous silica matrix and whatever residual chemicals or precursors (formamide, methanol, water, TMOS) left in the pores; an effect not unlike the solvatochromic effect (solvent influencing emission spectra) in liquids. More discussion of the shifting of the fluorescence peak will be presented in a later section.

2.3 LDS 759 and LD 800

There exists interest for the development of pump sources, for Nd:YAG lasers. The absorption band accessible to the Nd³⁺ transition of $^4F_{3/2} - ^4I_{11/2}$ around 1.064 μm lies between 740 and 820 nm. An exceptionally strong absorption

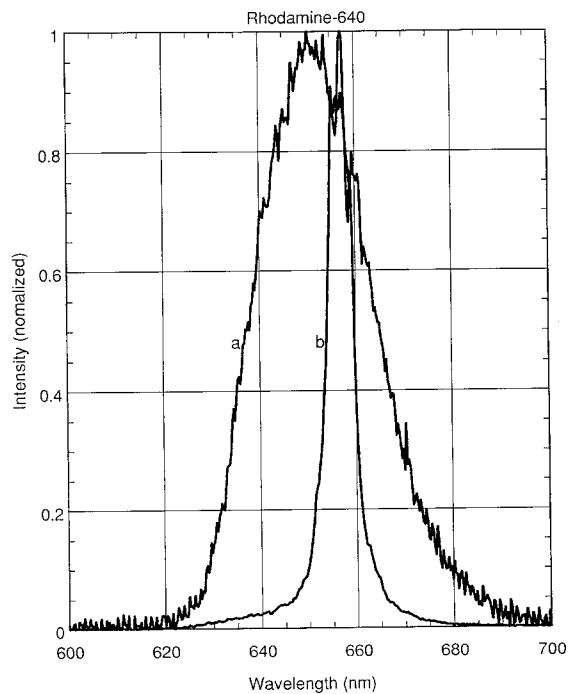


Fig. 6. *a* Fluorescence and *b* superradiance emission spectra of rhodamine 640 in sol-gel silica

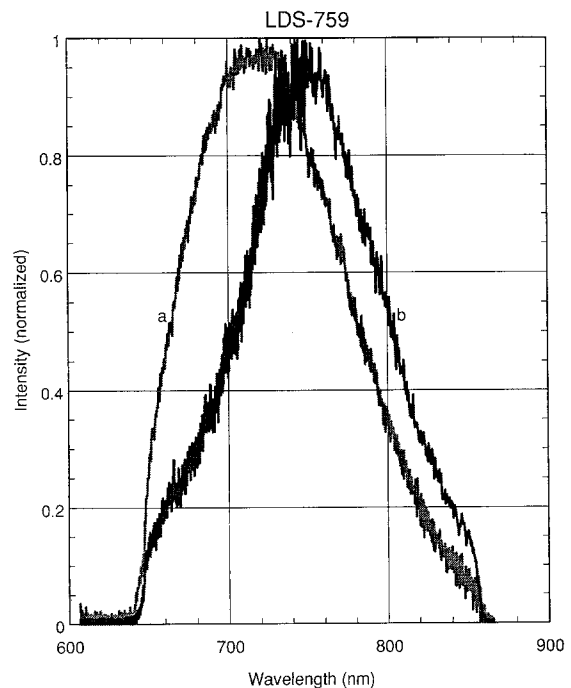


Fig. 8. Fluorescence spectra of LDS 759 in: *a* ethanol; *b* sol-gel silica

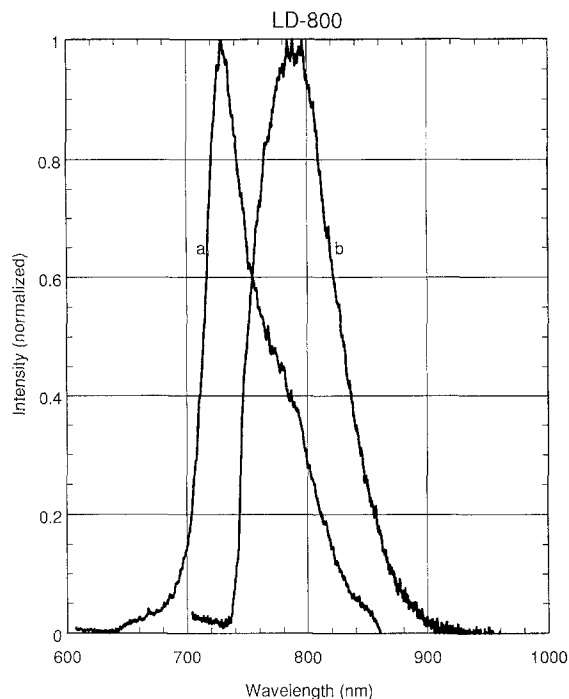


Fig. 9. Fluorescence spectra of LD 800 in: *a* ethanol; *b* sol-gel silica

line is that of ${}^4I_{9/2} \rightarrow {}^4F_{5/2}$ at around 800 nm. LDS 759 and LD 800 were selected as pump source candidates. To excite LDS 759- and LD 800-doped sol-gel silica samples, a prism-tuned dye laser operating at 540 nm was used. The fluorescence spectra of these two dyes with silica and ethanol as host materials are shown in Figs. 8 and 9. The peaks are 745 nm for LDS 759 and 790 nm for LD 800 in silica, and 730 nm for LDS 759 and 730 nm for LD 800 in ethanol. The corresponding numbers in the literature are 736 nm for LDS 759 and 704 nm for LD 800 in methanol [8]. Superradiance action for both dye-doped samples were attempted without success by means of line-focused beam excitation, probably because of the meager excitation power provided by the dye laser ($\sim 0.4 \text{ MW/cm}^2$) compared to 90 MW/cm^2 by the excimer laser.

Based on the observations of strong fluorescence and induced superradiance action under laser excitation, quenching effects should not be severe. As the excitation beam was also observed to be completely absorbed a few mm into the sample rods, dyes in sol-gel silica appear to retain their absorption characteristics. A complete understanding of the photochemistry of dyes in sol-gel route requires further study. However, it is safe to say now that silica derived along the sol-gel route appears to be a suitable host material for many dye molecules.

3 The Effect of Host Material on Emission Spectra

Our experimental investigation of doped sol-gel silica indicated a persistent red-shifting of emission peak for all dyes under study (Table 1). Early studies of dye lasers already revealed that the choice of solvents affected fluorescence yield, lifetime and, hence, laser properties [9, 10]. The more subtle effect of solvents in influencing emission spectra (solvatochromic effect) was also observed for rhodamine [9] and coumarin-derived dyes [11]. Specifically, it was found that the emission peaks tended to shift to the long-wavelength side of the spectrum and the fluorescence band also broadened as the polarity of the solvent increased. The contribution due to hydrogen-bonding which accounts for dipole-dipole association with the solute must also be considered if, in addition, the solvent is a hydrogen-bond donor (HBD) or acceptor (HBA). The red-shifting of emission was contemplated useful for expanding the tuning range of some dyes.

Following Kamlet et al. [12], the solvatochromic effect for most solvents is summarized in the following equation of fluorescence frequency:

$$\nu_F = \nu_0 + s(\pi^* d\delta) + a\alpha, \quad (1)$$

where s, d, δ are constants of the dye under study; π^* is the empirically derived parameter accounting for polarity-polarizability of the solvent, and α is the empirically derived parameter accounting for the susceptibility of the dye molecule to changes of HBD acidity. The π^* values of ethanol and formamide, for example, are 0.54 and 1.118, respectively [13], while the α values are 0.827 and 0.721 for ethanol and formamide, respectively [14]. Hence, it is to be expected that for certain dyes, solution in formamide should exhibit a red-shifted emission peak with respect to that in ethanol.

The silica samples used in the experiments were dried gel. Heat treatment has not been performed on the dye-doped gel for fear of destroying dye molecules. Residual chemicals and unreacted precursors (viz. water, TMOS) must hence remain inside the porous structure of the doped silica. Water and formamide both possess large π^* and α values [13, 14]. We therefore theorized that if sufficient amount of formamide is present in the vicinity of the embedded dye molecules, significant red shifting may result for sol-gel silica. The results of Fig. 7, which show increased red-shift for sol-gel silica derived from the process employing twice the amount the formamide, tended to lend credence to this speculation. Further study, however, uncovered additional complications to the effect of host material on the emission spectra.

Table 1. Fluorescent (F)/superradiance (SR) emission maxima (in nanometers) of several dyes

	Stilbene 420	C 440	C 460	C 481	C 521	R 540	R 560	R 640	LDS 759	LD 800
Ethanol/Methanol	425(SR)	430(F) ^a	451(F) ^a	510(F) ^b	495(F) ^a	505(F) ^a	532(F) ^a	594(F) ^a	730(F)	730(F)
Sol-gel silica	440	474	478	530 ^b	560	520	638	660	745	790

^a Exciton dye catalog [8]

^b D. Lo et al. [4]

^c Data not otherwise specified are from present experiments

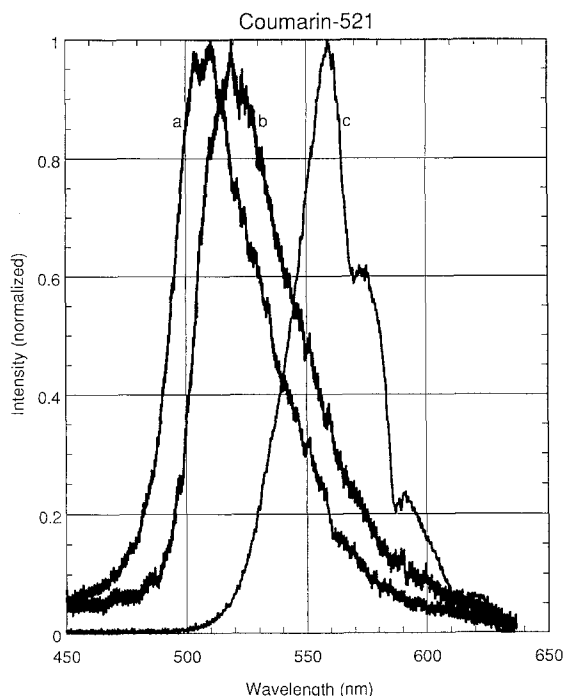


Fig. 10. Fluorescence spectra of coumarin in: *a* ethanol; *b* formamide; *c* sol-gel silica

The one obvious test of the effect of formamide on dye-doped sol-gel silica is to compare dye solutions in formamide with those in alcohol. (Most dyes do not readily dissolve in aqueous solution). Such a test was performed and the results are shown in Fig. 10. It is seen that the emission spectrum of coumarin 521 in pure formamide does indeed shift to the long-wavelength side (peak at 520 nm compared to peak at 505 nm in ethanol). A far larger shift, however, is experienced by the emission spectrum of the doped sol-gel silica which should contain a lesser amount of formamide (peak at 560 nm compared to 520 nm). It therefore seems certain that, in addition to the residual chemicals trapped in the pores, the local environment of dye molecules in silica must have played a role. Different structure of active centers in host materials have been known to cause shifting of emission-peak position as in the case of Nd ions in various glasses [15]. The structure of dye molecules in our sol-gel silica would be more difficult to understand however, because the samples tend to become more dense with time as residual chemicals continued to evaporate and pores shrunk. Indeed, Pope and Mackenzie [16] observed that the absorption peaks of neodymium-doped silica experienced shifting to long wavelengths as the samples went through a heat treatment cycle. The final position of the absorption peak was established at 200° C.

To gain understanding of the shifting of the emission peak, careful study of the structure of dye molecules in sol-gel silica appears to be in order. Heat treatment processing of dye-doped silica could yield useful information. But the use of lower temperature would be necessary to avoid destruction of the dye molecules.

4 Summary

An experimental investigation of laser and fluorescence properties of dye-doped sol-gel silica was performed. Superradiance emissions were induced in a number of dye-doped silica samples, including a few that covered the cesium lines. It is believed that tunable laser action should be readily demonstrated in these samples. Fluorescence spectra were obtained for all the dye-doped samples studied and compared with dye solutions in alcohol. A persistent red-shifting in the sol-gel silica spectra was observed. Solvatochromic and local environmental effect were invoked to explain the red-shifting.

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