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Perylene- and pyrromethene-doped xerogel for a pulsed laser

Michael Canva, Patrick Georges, Jean-François Perelgritz, Alain Brum, Frédéric Chaput, and Jean-Pierre Boilot

Hydrophobic photostable dye molecules such as perylenes or pyrromethenes were trapped in xerogel matrices. Using these new materials as solid-state dye lasers, we have demonstrated efficient laser operation. Slope efficiencies of up to 30% were obtained in the millijoule output-energy range. Tunabilities of up to 60 nm were observed, and more than 150,000 pulses were emitted by the same spot of a given sample when the laser was pumped at millijoule energy levels.

Key words: Dye, xerogel, laser.

Dyes have now been used for many years as gain media of tunable lasers,^{1,2} and until recently dyes represented the sole method of producing tunable optical pulses. Today, similar results may be achieved with nonlinear techniques such as optical parametric oscillation. Yet dye lasers offer many advantages, in particular the fact that the excitation source need not be coherent: compact flash-lamp systems can be easily used. Other advantages include quasi-thresholdless operation and low cost. These organic dye molecules were chosen because of the physical properties they exhibit, in particular, a large spectral absorption band that facilitates pumping conditions, a high fluorescent quantum efficiency that leads to several tens of percents of energy conversion, and a broadband fluorescence spectrum that provides wide tunability. Yet, if organic dye lasers are widely used in the laboratory, to overcome thermal lensing and instability, triplet-state quenching, and photochemical degradation effects, these dyes, when used in solution, must flow through the beam pathway of the laser. This implies that a circulating system (pump, reservoir, etc.) should be

used. These requirements and the extensive maintenance involved have prevented wide use of these dye lasers outside the laboratory. Independently, several research groups have attempted to incorporate these dye molecules into different solid host matrices such as plastics,³ porous glasses,⁴ or solgel matrices.⁵ In some of these solid media, lasing action was obtained⁶⁻¹⁴ after the mechanical requirements necessary for the optical polishing of the material were satisfied. In these cases the optical properties of the organic molecules are retained, and reasonable tunability and slope efficiency have generally been obtained. It appeared that thermal lensing and instability are minimized in the solid matrix compared with a solvent solution used in the same conditions, i.e., without dye circulation, and also that triplet-state quenching and photodegradation arise less often in a good solid matrix than in a solution. However, if the sample remains stationary during the laser operation, the same molecules are always used and finally degrade, thus the energy of the output beam emitted by the sample diminishes toward zero after a certain time of operation. The most commonly used dye is Rhodamine 6G, which is a reference in liquid dye lasers. However, the photochemical stability of this dye is far from being sufficient for use in solid-state dye lasers. For this purpose more stable dyes are required and have been identified, for example, perylenes and pyrromethenes.^{15,16} Unfortunately these molecules are not water soluble, and this has prevented their incorporation into classical xerogel matrices. In this paper we report their introduction into a solid matrix synthesized by the use of the solgel process, which represents a significant step toward stable solid-state dye laser emission.

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A xerogel, which may be of glassy aspect, is a solid gel obtained by gelation of a solution called sol by the use of the sol-gel process, which involves hydrolysis and polycondensation reactions.^{17,18} In some cases these chemical reactions can be performed at room temperature. Any organic optically active molecule may thus be incorporated in a sol in which it is soluble. The dopant molecules are trapped in the structure of the solid obtained at the end of the sample synthesis, without being thermally destroyed in the process.

Our samples were prepared from vinyltriethoxysilane (VTEOS) precursor. Hydrolysis was performed under acid catalysis with acetone as a solvent. The initial molar ratio of VTEOS:water (pH 2.5):acetone was 1:3:3. After 2 h of hydrolysis at room temperature, a small amount of pyridine was added as a basic medium to neutralize the acidity and to increase the condensation reaction rate. Then a solution of doping molecules (pyromethene 567, perylene orange, and perylene red or, for purposes of comparison, Rhodamine 6G) in acetone was added to the previous solution to obtain a doping-molecule concentration between 10^{-5} to 10^{-3} mol l⁻¹. The resulting solutions were subsequently cast into bulk gel disc cylinders. Gelation occurred within 1 week at 40 °C. The samples were left to dry for a further 3 weeks at the same temperature. After the samples were dried, optically clear and dense inorganic-organic hybrid xerogels were obtained.

The colored-glass-like samples were then hard enough to be optically polished with classical techniques. The typical roughness obtained is 4 nm.

For lasing efficiency and sample lifetime measurements, the samples were placed in a 15-cm linear cavity consisting of an 80% transmission flat output coupler and a highly reflective concave mirror with a 2-m radius of curvature. A dichroic flat mirror was used to permit longitudinal pumping. The samples were then optically pumped by a frequency-doubled Q-switched Nd:YAG laser that provided, at 532 nm, pulses of 8 ns duration and 10 mJ energy (E_{max}), at a maximum repetition rate of 50 Hz. The pump beam was focused onto an 800- μ m-diameter surface S on the sample, which was placed 3 cm from the output coupler. Energy measurements were performed with a calibrated photodiode and a joulemeter.

With this cavity, the lasing thresholds obtained were typically approximately 200 μ J, and the slope efficiencies were between 20% and 30% (Table 1),

Table 1. Maximum Slope Efficiencies Obtained with Various Dye-Doped Xerogels in the Laser Cavity Described in the Text

Parameter	Doping Dye			
	Pyromethene 567	Perylene Orange	Perylene Red	Rhodamine 6G
Concentration (mol l ⁻¹)	5.5×10^{-4}	10^{-4}	5.5×10^{-5}	10^{-4}
Slope efficiency (%)	29	25	19	15

with no observed saturation even up to 10 mJ, two orders of magnitude above the threshold (Fig. 1). For comparison we achieved 15% slope efficiency with Rhodamine 6G in this matrix (a 10^{-4} mol/l, 4-mm-thick sample). It should be noted that the maximum fluence (E_{max}/S) of 2 J/cm² that we used approximately corresponds to the damage threshold of the samples. The best result was obtained with a pyromethene 567-doped sample with a concentration of 5.5×10^{-4} mol/l in the initial sol: pulses of 3 mJ energy issued from the cavity when the sample was pumped with 10 mJ/pulse (2 J/cm² fluence), corresponding to a slope efficiency of approximately 30%. These data correspond to a single-shot use of the laser.

To achieve higher energy output, we changed the stable cavity to a plano-plano cavity by the use of two mirrors that were 5 cm apart and increased the pump-beam diameter to a 4-mm spot on the sample to decrease the pump fluence for a given energy. In the 0–10-mJ/pulse range the slope efficiency was only slightly less than in the above case: 25% instead of 30% with pyromethene 567 and 15% instead of 19% in the case of perylene red. Yet the fluence was then only 0.08 J/cm² for 10-mJ pump pulses, which suggests that it is possible to pump at much higher energy levels! We were able to pump our pyromethene 567-doped sample up to 41 mJ/pulse, and we obtained an output energy of 11 mJ/pulse. However, such an unstable cavity leads to a light beam of poor spatial quality and high divergence.

We also studied the evolution of the output energy as a function of the number of pump pulses. As the sample is used, the organic dye molecules are progressively degraded, and the effective concentration of the active species thus diminishes: the laser action is therefore extinguished after a certain number of operating pulses. This behavior may be characterized by the lifetime of the sample, i.e., the number of pump pulses that the sample can withstand on the same spot while still giving rise to emitted pulses of energy greater than a given fraction of the first emitted pulse. If we define this limit fraction as

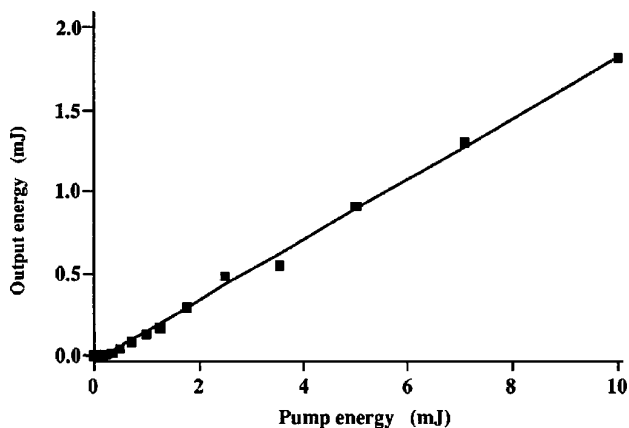


Fig. 1. Conversion efficiency of the laser cavity with a perylene-red-doped sample (concentration 5.5×10^{-5} mol/l, thickness 4 mm).

50%, these lifetimes have, during the past few years, been increased from a few dozen to a few thousand shots. When our sample was pumped with an energy of 1 mJ (0.2 J/cm² fluence) at 1 Hz, the 50% lifetime obtained was approximately 6000 shots for perylene orange and 5000 shots for pyrromethene 567 (in the case of Rhodamine 6G, we had previously obtained only a few thousand shots at best and a few hundred shots with the matrix that we are concerned with in this paper). The best results by far, however, were obtained when the perylene-red-doped samples were used. With such a doped xerogel (concentration 5.5×10^{-5} mol l⁻¹, thickness 4 mm) and with pump pulses of 0.5 mJ energy at a 1-Hz repetition rate, the output is still 62% of the initial value after 38,000 pulses. With a sample doped at 2×10^{-4} mol/l, the lifetime measured with pump pulses of 1 mJ energy at a 1-Hz repetition rate was 100,000 pulses, yet because the dye concentration was too high the slope efficiency was only 6%. However, the sample lifetime is very strongly dependent (more than 1 order of magnitude) on laser beam fluences in the sample and on the operating repetition rate because of both the photodegradation and the thermodegradation processes. This is illustrated by the lifetimes given in Table 2, which summarizes different results obtained with the same doped xerogel in different laser operating conditions: the sample lifetime quickly diminishes when the fluence or the repetition rate of the pumping beam increases. We attribute this phenomenon to the much faster occurrence of thermal degradation as the local temperature rises within the active zone. This means that a key parameter for further improvement of these solid-state dye lasers is the search for and development of more thermally conductive host matrices that are capable of quickly evacuating the hundreds of millijoules that accumulate. This, of course, will not suppress the photodegradation process, but that is not, in our case, the major problem.

One solution would be to increase the sample thickness: a 3.5-cm-thick perylene-red-doped sample with an initial dye concentration of 10^{-5} mol l⁻¹ was synthesized. The lifetimes of this sample were significantly increased compared with the 5-mm-thick sample doped at 5.5×10^{-5} mol l⁻¹: approximately 150,000 emitted pulses instead of approximately 20,000 pulses when the sample was pumped with 1 mJ at 1 Hz and approximately 120,000 pulses instead

of 12,000 pulses when the same pumping-energy level was used at 3.3 Hz!

These results are to our knowledge the best ever obtained with doped xerogels for such a pumping-energy level. They are significantly greater than those we had previously found¹¹ with Rhodamine 6G and those reported by Altman *et al.*,¹² who used Rhodamine B in the same energy range. In the more general field of solid-state dye lasers these performances are only bettered by the recent results of Allik *et al.*,¹³ who used a modified acrylic plastic rod doped with pyrromethene BF2 dye: a useful lifetime of more than 20,000 shots at 3.3 Hz with output energies above 30 mJ was demonstrated. However, because of the unstable plano-plano cavity configuration that was used, the output beam was highly divergent, with a wide spectrum. In Ref. 13, the M^2 parameter¹⁹ was 100, indicating that the beam was far from diffraction limited. In our case the stable cavity that was used led to a near-Gaussian beam with an M^2 of 1.2.²⁰

For tunability measurements, the output coupler of the laser cavity was replaced with a diffraction grating of 2,000 lines/mm used in a Littrow configuration.^{1,2} In the spectral range that we are concerned with (550–650 nm), the diffraction grating may be characterized by a reflection coefficient of approximately 30% (first order) and a transmission coefficient of approximately 40% (zero order). The wavelength measurements were performed with a 25-cm Jobin & Yvon monochromator and an optical multichannel analyzer system.

The results are shown in Fig. 2: with the pyrromethene 567-doped sample, the cavity was continuously tunable over 60 nm, from 543 to 603 nm. This range was 567–594 nm in the case of perylene orange and 595–644 nm in the case of perylene red. It should be noted that these tunabilities are similar to those obtained with a doped solution.

In conclusion, we have been able to trap perylene and pyrromethene dyes, which are known to be chemically more stable than Rhodamine dyes, in xerogel matrices. Using such systems, we have dem-

Table 2. Variations of the Lifetimes at 50% (as Defined in the Text) of a Perylene-Red-Doped Sample (Concentration 5.5×10^{-5} mol/l, Thickness 4 mm) as a Function of Repetition Rate for Different Pumping-Energy Levels

Energy (mJ)	Repetition Rate (Hz)				
	1	3.3	10	16.6	25
0.5	38,000 ^a	18,000	5,000	<1,000	<100
1	20,000	12,000	4,200	1,500	<100
5	5,000	<100	<100	<100	<100

^aLifetime at 62%.

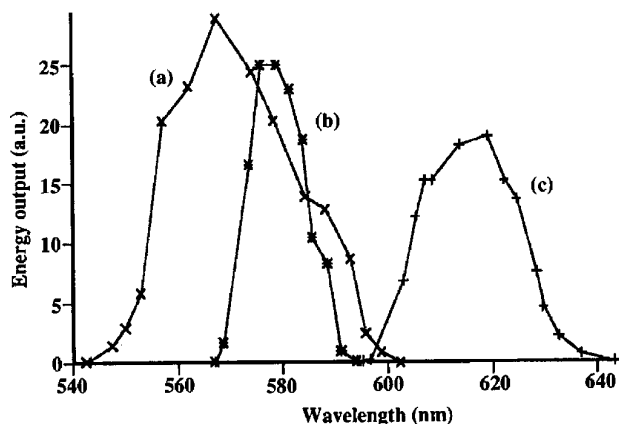


Fig. 2. Tunability obtained with different dyes: (a) pyrromethene 567, (b) perylene orange, (c) perylene red. The cavity is pumped with a fluence level of 0.2 J/cm².

onstrated laser emission of reasonable efficiencies, wide tunabilities, and long lifetimes. These results are, to our knowledge, the best achieved to date with doped xerogels. These results contribute to the progress in terms of performance that has been achieved in the field of solid-state dye lasers in recent years. It is not unreasonable to foresee practical applications in the near future for this new type of gain medium that could lead to compact flash-lamp-pumped solid-state tunable laser systems.

References

1. B. H. Soffer and B. B. MacFarland, "Continuously tunable, narrow band organic dye lasers," *Appl. Phys. Lett.* **9**, 266–267 (1967).
2. F. P. Schäfer, ed., *Dye Lasers*, Vol. 1 of Springer-Verlag Topics in Applied Physics (Springer-Verlag, Berlin, 1989).
3. G. R. Kumar, B. P. Singh, and K. K. Sharma, "Optical phase conjugation in Rhodamine-6G doped boric acid glass," *Opt. Commun.* **73**, 81–84 (1989).
4. A. D. Prishchepov, B. P. Zaripov, and S. Astanov, "Optical properties of Rhodamine-6G monomers and aggregates in polymethyl-methacrylate," *Opt. Spektrosk.* **66**, 763–766 (1989).
5. D. Avnir, D. Lévy, and R. Reisfeld, "The nature of the silica cage as reflected by spectral changes and enhanced photostability of trapped Rhodamine 6G," *J. Phys. Chem.* **88**, 5956–5959 (1984).
6. D. A. Gromov, K. M. Dyumaev, A. A. Manenkov, A. P. Maslyukov, G. A. Matyushin, V. S. Nechitailo, and A. M. Prokhorov, "Efficient plastic-host dye lasers," *J. Opt. Soc. Am. B* **2**, 1028–1031 (1985).
7. G. B. Altshuler, V. A. Bakhanov, E. G. Dulneva, A. V. Erofeev, O. V. Mazurin, V. P. Roskova, and T. S. Tsekhomskaya, "Laser based on dye-activated silica gel," *Opt. Spektrosk.* **62**, 709–710 (1987).
8. F. Salin, G. Le Saux, P. Georges, A. Brun, C. Bagnall, and J. Zarzycki, "Efficient tunable solid-state laser near 630 nm using sulforhodamine 640-doped silica gel," *Opt. Lett.* **14**, 785–787 (1989).
9. R. Reisfeld, D. Brusilovky, M. Eyal, E. Miron, Z. Burstein, and J. Ivri, "A new solid state tunable laser in the visible," *Chem. Phys. Lett.* **160**, 43–44 (1989).
10. E. T. Knobbe, B. Dunn, P. D. Fuqua, and F. Nishida, "Laser behavior and photostability characteristics of organic dye doped silicate gel materials," *Appl. Opt.* **29**, 2728–2733 (1990).
11. M. Canva, P. Georges, A. Brun, D. Larrue, and J. Zarzycki, "Impregnated SiO₂ gels used as dye laser matrix hosts," *J. Non-Cryst. Solids* **147/148**, 636–640 (1992).
12. J. C. Altman, R. E. Stone, F. Nishida, and B. Dunn, "Dye activated ORMOSIL'S for lasers and optical amplifiers," in *Sol-Gel Optics II*, J. D. Mackenzie, ed., *Proc. Soc. Photo-Opt. Instrum. Eng.* **1758**, 507–518 (1992).
13. T. Allick, S. Chandra, R. E. Hermes, J. A. Hutchinson, M.-L. Soong, and J. H. Boyer, "Efficient and robust solid-state dye laser," in *Advanced Solid-State Lasers*, A. A. Pinto and T. Y. Fan, eds., Vol. 15 of OSA Proceedings Series (Optical Society of America, Washington, D.C., 1993), pp. 271–273.
14. R. E. Hermes, T. Allick, S. Chandra, and J. A. Hutchinson, "High-efficiency pyromethene doped solid-state dye lasers," *App. Phys. Lett.* **63**, 877–879 (1993).
15. T. G. Pavlopoulos, J. H. Boyer, K. Thangaraj, G. Sathyamoorthi, M. P. Shah, and M. L. Soong, "Laser dye spectroscopy of some pyromethene-BF₂ complexes," *Appl. Opt.* **31**, 7089–7094 (1992).
16. M. P. O'Neil, "Synchronously pumped visible laser dye with twice the efficiency of Rhodamine 6G," *Opt. Lett.* **18**, 37–38 (1993).
17. F. Devreux, J. P. Boilot, F. Chaput, and A. Lecompte, "Sol-gel condensation of silicon alkoxides," *Phys. Rev. A* **41**, 6901–6909 (1990).
18. C. J. Brinker and G. W. Scherer, *Sol-Gel Science* (Academic, Boston, 1990).
19. T. F. Johnston, "M² concept characterizes beam quality," *Laser Focus World* **26**, 173–183 (1990).
20. M. Canva, P. Georges, J. F. Perelgritz, A. Brun, F. Chaput, and J. P. Boilot, "Improved sol-gel materials for efficient solid-state dye lasers," in *New Materials for Advanced Solid State Laser*; B. H. T. Chai, S. A. Payne, T. Y. Fan, A. Cassanho, and T. H. Allick, eds. (Materials Research Society, Pittsburgh, Pa., 1994), pp. 279–284.