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Solid State Dye Lasers from Stereospecific Host−Guest Interactions

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For some time it had been tacitly assumed that the low thermal stability of organic molecules precluded their incorporation into inorganic matrices. This view did not survive the invention of sol−gel glasses whose relatively cold processing temperatures enabled the entrapment of dyes as well as other organic molecules.[1] These doped aluminosilicate glasses have shown a wide range of optical properties,[2] including laser action.[3] We have been studying not glasses but single crystals of simple salts that contain oriented inclusions of organic dyes.[4] These materials have a longer history[5] than doped sol−gel glasses, although their uses as optical materials have not been previously considered. Herein, we describe a simple preparation of single K_2SO_4 crystals doped with pyrene and rhodamine derivatives and their operation as blue, green, and red solid state dye lasers.[6,7]

We recently described a procedure for choosing organic guests for simple salts which involved the matching of anionic functionalities on chromophores with the anion spacings in simple salt lattices such as K_2SO_4.[4a] The structures of several doped K_2SO_4 crystals, containing triarylmethyl (**1**) or pyrene (**2**) dyes, were determined through absorption studies with polarized light. For example, crystals containing pyranine (**2a**, 8-hydroxy-1,3,6-pyrenetrisulfonate)[8] were typically grown by evaporating water solutions (5×10^{-5} M **2a**, 0.5 M K_2SO_4). Crystals in excess of 1 cm^3 were grown from seeds suspended in aqueous solutions. The yellow dye was principally adsorbed in the {010} growth sectors (Figure 1).[9] The green luminescence was polarized parallel to [001]. This is consistent with our model in which the sulfonate groups substitute for sulfates in the lattice that are related to one another by the *a* and *c* lattice translations.

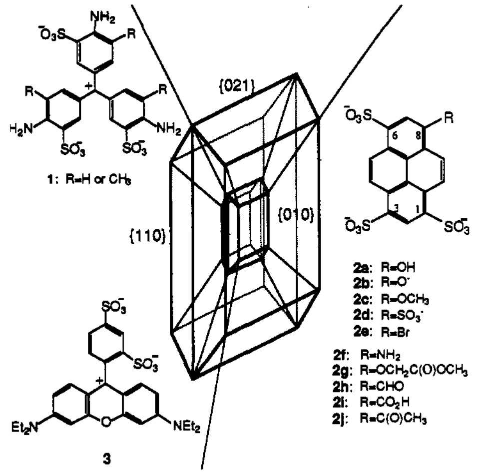

Figure 1. Idealized habit of K_2SO_4 crystal. Boundaries between "inner nucleus" and out polyhedron delineate growth sectors. This drawing indicates that **1** and **3** color the {110} growth sectors, while **2** principally colors the {010} growth sectors.

The 1,3,6-trisulfonated pyrene moeity can tolerate a variety of substituents in the 8-position without interrupting the

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(1) Avnir, D.; Levy, D.; Reisfeld, R. *J. Phys. Chem.* **1984**, *88*, 5956−5959. Avnir, D.; Braun, S.; Ottolenghi, M. In *Supramolecular Architecture*; Bein, T., Ed.; ACS Symposium Series 499; American Chemical Society: Washington, DC, 1992; pp 384−404.

(2) Klein, L. C., Ed. *Sol−Gel Optics: Processing and Applications*; Kluwer: Boston, 1994.

(3) Dunn, B.; Knobbe, E.; McKiernan, J. M.; Pouxviel, J. C.; Zink, J. I. *Mater. Res. Soc. Symp. Proc.* **1988**, *121*, 331−342. Kobayashi, Y.; Kurokawa, Y.; Imai, Y.; Muto, S. *J. Non-Cryst. Solids* **1988**, *105*, 198−200. Sasaki, H.; Kobayashi, Y.; Muto, S.; Kurokawa, Y. *J. Am. Ceram. Soc.* **1990**, *73*, 453−456. Knobbe, E. T.; Dunn, B.; Fuqua, P. D.; Nishida, F. *Appl. Opt.* **1990**, *29*, 2729−2733. For contemporary reviews, see: Dunn, B.; Nishida, F.; Toda, R.; Zink, J. I.; Allik, T. H.; Chandra, S.; Hutchinson, J. A. In *New Materials for Advanced Solid State Lasers;* Chai, B. H. T., Payne, S. A., Fan, T. Y., Cassanho, A., Allik, T. H., Eds.; Materials Research Society Sypmosium Proceedings 329; MRS: Pittsburgh, 1994; pp 267−277. Canva, M.; Georges, P.; Perelgritz, J.-F.; Brun, A.; Chaput, F.; Boiot, J.-P. Ibid.; pp 279−284.

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(5) First example: de Sénarmont, H. *Ann. Phys. (Leipzig)* **1854**, *167*, 491−494. Reviews: Kahr, B.; Chow, J.; Peterson, M. *J. Chem. Educ.* **1994**, *71*, 584−586. Buckley, H. E. *Crystal Growth*; John Wiley: New York, 1951.

(6) For general references to solution dye lasers, see: Schafer, F. P., Drexhage, K. H., Eds. *Dye Lasers*; Springer-Verlag: Berlin, 1990. Duarte, F. J.; Hillman, L. W. *Dye Laser Principles, with Applications*; Academic Press: Boston, 1990.

(7) For an overview of the emergence of new solid state dye laser technologies, see: Caligaris, C. *Photonics Spectra* **1995**, *29* (Jan), 87−88. Caligaris, C. *Laser Focus World* **1994**, *30* (Oct), 34−36; Duarte, F. J. *Laser Focus World* **1995**, *31* (May), 187−189.

(8) For pyranine in sol−gels, see: Kobayashi, Y.; Imai, Y.; Kurokawa, Y. *J. Mater. Sci. Lett.* **1988**, *7*, 1148−1150. Pouxviel, J. C.; Dunn, B.; Zink, J. I. *J. Phys. Chem.* **1989**, *93*, 2134−2139.

(9) Miller indices refer to ratios determined by classical goniometry where $b > c > a$.

(10) Dyes **2a,d** were purchased from Eastman. The following dyes were prepared as described previously. **2c**: Kondo, H.; Miwa, I.; Sunamoto, J. *J. Phys. Chem.* **1982**, *86*, 4826−4831. **2g**: Whitaker, J. E.; Haugland, R. P.; Moore, P. L.; Hewitt, P. C.; Reese, M.; *Anal. Biochem.* **1991**, *198*, 119−130. The syntheses of **2e,f,h−j** were modeled after the general sulfonation procedure reported in the following. Huntress, E. H.; Carten, F. H. *J. Am. Chem. Soc.* **1940**, *62*, 511−514. Huntress, E. H.; Carten, F. H. *J. Am. Chem. Soc.* **1940**, *62*, 603−604. Gilbert, E. E. *Sulfonation and Related Reactions*; Interscience Publishers: New York, 1965; p 84. Gilbert, E. E. *Synthesis* **1969**, *1*, 3−10. For example (**2f**): A solution of finely powdered 1-aminopyrene (869 mg, 4 mmol) in 10 mL of chlorosulfonic acid was stirred under argon atmosphere for 10 h at room temperature. The solution was poured on 30 g of crushed ice, and the crude product was collected by filtration, washed with 20 mL of cold water, and dried under argon to give 1.4 g of 8-amino-1,3,6-pyrenetrisulfonyl chloride (68%). Hydrolysis of 8-amino-1,3,6-pyrenetrisulfonyl chloride in basic water (NaOH, pH = 8) gave a solution of **2f** (8-amino-1,3,6-pyrenetrisulfonate). For the first synthesis of **2f** from **2d** and NH_3, see: Tietze, E.; Bayer, O. *Liebigs Ann. Chem.* **1939**, *540*, 189−210. Spectral data for the intermediate pyrenetrisulfonyl chlorides follow. 8-Amino-1,3,6-pyrenetrisulfonyl chloride: ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 5.55$ (s, 2H), 8.32 (s, 1H), 8.56 (d, 1H, $J = 12$ Hz), 9.15 (d, 1H, $J = 18$ Hz), 9.21 (d, 1H, $J = 18$ Hz), 9.46 (s, 1H), 9.47 (d, 1H, $J = 12$ Hz). 8-Bromo-1,3,6-pyrenetrisulfonyl chloride: ^{1}H NMR ($CDCl_3$) δ 9.14 (d, 1H, $J = 10$ Hz), 9.26 (s, 1H), 9.50 (d, 1H, $J = 11$ Hz), 9.52 (d, 1H, $J = 11$ Hz), 9.62 (s, 1H), 9.70 (d, 1H, $J = 10$ Hz). 8-Formyl-1,3,6-pyrenetrisulfonyl chloride: ^{1}H NMR ($CDCl_3$) δ 9.47 (s, 1H), 9.64 (d, 1H, $J = 9$ Hz), 9.68 (d, 1H, $J = 10$ Hz), 9.70 (d, 1H, $J = 10$ Hz), 9.76 (d, 1H, $J = 10$ Hz), 10.08 (d, 1H, $J = 11$ Hz), 10.89 (s, 1H). 8-Carboxy-1,3,6-pyrenetrisulfonyl chloride: ^{1}H NMR (DMSO) δ 8.29 (s, 1H), 9.05 (d, 1H, $J = 2$ Hz), 9.09 (d, 1H, $J = 2$ Hz), 9.15 (m, 2H), 9.20 (d, ^{1}H, $J =$ 2 Hz), 9.24 (s, 1H), 9.29 (s, 1H). 8-Acetyl-1,3,6-pyrenetrisulfonyl chloride: ^{1}H NMR ($CDCl_3$) δ 2.98 (d, 3H, $J = 4$ Hz), 8.56 (d, 1H, $J = 10$ Hz), 8.64 (s, 1H), 9.22 (d, 1H, $J = 11$ Hz), 9.32 (d, 1H, $J = 11$ Hz), 9.43 (d, 1H, $J = 10$ Hz), 9.51 (s, 1H).

(11) Kaufman, V. R.; Avnir, D.; Pines-Rojanski, D.; Huppert, D. *J. Non-Cryst. Solids* **1988**, *99*, 379−386. Chakraborty, R.; Berglund, K. A. *J. Cryst. Growth* **1992**, *125*, 81−96. The crystals containing **2a** are blue-green (λ_{max} = 400 nm), while the crystals of **2b** are yellow-green (λ_{max} = 440 nm). Despite the fact that the acid and base forms have different excitation spectra, both compounds fluoresce mainly from the excited state of **2b**, because the first excited state of **2a** is quite acidic (pK_a ~ 1); the rate of deprotonation in the crystal is greater than the first excited state lifetime. However, crystals prepared from **2a,b** have distinctly different emissions (516 and 533 nm, respectively), presumably because of local electrostatic differences attributable to the presence of the expelled proton or to differences in the crystallized cavities which formed around the chromophores in the protonated and deprotonated states.

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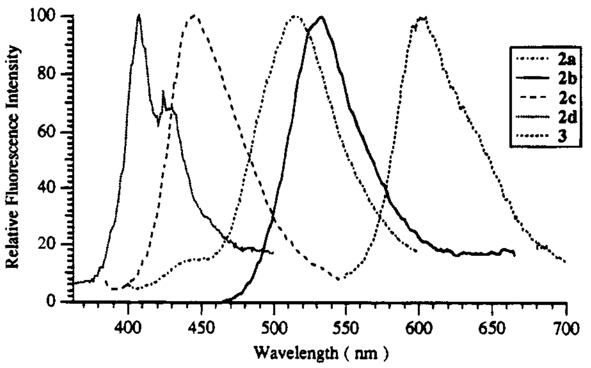

Figure 2. Fluorescence spectra for **2a**–**d** and **3** included in K_2SO_4 crystals.

Table 1. Photophysical Characteristics of Pyrene (**2**) and Rhodamine Dyes (**3**) in Water and K_2SO_4

	in aqueous solution[a]			in K_2SO_4 crystal		
dye	λ_{ex} (nm)	λ_{em} (nm)	τ (ns)	λ_{ex} (nm)	λ_{em} (nm)	τ (ns)
2a	404[b]	511, 443	5.0	400	516, 440	4.6
2b	454	513	4.6	440	533	6.9
2c	409	427	12.0	400	446	11.1
2d	376	402	3.4	370	408	3.3
2e	379	396	*c*	378	410	*e*
2f	430	504	4.4	440	515	4.1
2g	409	430	3.1	410	438	3.0
2h	376	384	7.8	420	409	6.1
2i	373	402	1.3	413	436	2.8
2j	378	386	1.8	373	413	3.8
3	573	584	2.1[d]	580	602	3.5

[a] Adding K_2SO_4 *to the solution* did not appreciably affect the excitation or emission maxima. [b] Molar extinction values for **2a**–**j** in H_2O were between 10 000 and 40 000 L M^{-1} cm^{-1}; that for **3** was 1.6 × 10^5 L M^{-1} cm^{-1}. [c] Indeterminate due to especially low solubility. [d] 1.6 s measured by Tong et al.: Tong, B. Y.; John, P. K.; Zhu, Y.-T.; Liu, Y. S.; Wong, S. K.; Ware, W. R. *J. Opt. Soc. Am. B* **1993**, *10*, 356–359. [e] Biexponential behavior.

recognition process.[10] Synthetic modifications of the common chromophore thereby serve to tune the optical properties of the mixed crystals. The basic form of pyranine (**2b**)[11] may be replaced for the acid form (**2a**) by controlling the pH of the crystallizing solution.[12] The hydroxyl group may be alkylated as in **2c** without precluding incorporation into the growing crystals. The tetrasulfonate **2d** may also be included in K_2SO_4. The emission from dyes **2b**,**d** (533 and 408 nm, respectively; see Figure 2) represent the high- and low-wavelength limits from variously functionalized 1,3,6-trisulfonated pyrenes, **2a**–**j**, all of which recognize the *b* faces of K_2SO_4. Calculated (INDO/S) transition electric dipole moments[13] for the pyrene derivatives were essentially along the long pyrene axis, thereby producing emissions that were highly polarized along [001] in each case. Table 1 lists the excitation maxima, emission maxima, and fluorescence lifetimes for the dyes **2a**–**j** in both aqueous solutions and K_2SO_4 crystals.[14] Emissions from dyes in K_2SO_4 were systematically lower in energy than those from dyes in aqueous solution.

In selecting a second structural type of K_2SO_4–guest dye in order to extend the emission energy range of the crystals, we questioned whether all three sulfonates appended to the pyrene nucleus as in **2** are required for recognition and inclusion in the lattice. Perhaps one of the three pairwise relationships dominates the recognition process. We realized that the nearest pair of $-SO_3^-$ groups represents a stereochemical relationship that is satisfied by any meta-disulfonated arene, such as the laser dye sulforhodamine B (**3**, 3,6-bis(diethylamino)-9-(2,4-disulfophenyl)xanthylium).[15] Remarkably, **3** formed well-defined inclusions in the {110} growth sectors of K_2SO_4 (Figure 1), with an emission centered at 612 nm. Corresponding photophysical data may be found in Table 1. Structural studies of **3** and some of its congeners in K_2SO_4 are currently in progress.

We have constructed pulsed lasers using **2b**-, **2c**-, and **3**-doped K_2SO_4 crystals (Figure 2) that were placed in a Fabry–Perot configuration. We used the harmonics of a Q-switched Nd: YAG laser as the pump source (**2b**,**c**, third harmonic, 355 nm; **3**, second harmonic, 532 nm).[16] The excitation beam was typically at an oblique angle to the {010} faces. The green **2b** laser emission was centered at 541 nm, with a 6 nm full width at half-maximum, whereas the **2c** laser output was blue, with maximum power at 441 nm. In each case, the laser light was linearly polarized along the [001] direction. Without any surface preparation of the salt crystal hosts, the scattering losses endured at the laser wavelengths were typically 40%. In the absence of any cooling mechanism, the lasers exhibited 3 dB optical power degradation after ~10^3 laser pulses (10 ns pulse duration, 500 μJ pump pulse energy). Dye lasers comparable to those using **2b**,**c** were prepared with **3**/K_2SO_4 inclusions. The resulting laser emission covered the spectral range from 595 to 620 nm, with the maximum efficiency at 600 nm.

In each case, laser action was confirmed in several ways. First, the light was coherent, as evidenced by speckle patterns formed by interference of scattered light. Second, the beams were highly directional, with divergences of a few milliradians. Finally, the dependence of the output power on the pump laser power displayed the standard laser threshhold behavior, with a small output until the onset of laser action, followed by a rapidly linear increase for greater pumping levels.

Previous solid state dye laser gain media have employed plastic or glassy matrices.[17] Single crystal K_2SO_4 dye lasers possess several attractive features: (1) they produce linearly polarized light; (2) they show great photostability and (3) optical homogeneity; and (4) single crystal dye-doped K_2SO_4 lasers provide a wealth of structural information about host–guest interactions that cannot be obtained from amorphous materials.

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(12) **2a** is included exclusively in K_2SO_4 grown from acidic solutions (10^{-2} M H_2SO_4), while **2b** is included exclusively from basic solutions (10^{-2} M KOH). Neutral solutions precipitate crystals with absorptions characteristic of both **2a** and **2b**.

(13) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111–134; **1976**, *42*, 223–236.

(14) Fluorescence measurements were made with a Photon Technologies LS-100 fluorometer. Excitation and emission slits were at 90°. Crystals were suspended in sample cuvettes with the {010} faces at about 45° to both the excitation and emission slits. A xenon arc lamp was used as the light source for steady state measurements. For lifetime studies, the light source was the 358 nm line from a N_2 arc lamp. Two single monochrometers were used, one for excitation and the other for emission. The spectra were recorded by a fast PMT interfaced to an IBM-compatible computer.

(15) For a sulforhodamine in a sol–gel, see: Salin, F.; Le Saux, G.; Georges, P.; Brun, A.; Bagnall, C.; Zarzycki, J. *Optics Lett.* **1989**, *14*, 785–787.

(16) To date, each of our three attempts to construct lasers from crystals containing dyes has been successful. From this experience, it is likely that our future efforts to construct lasers using other organic dyes in inorganic salt crystals will produce additional successes.

(17) Lee, I.; Kovino-Hrbacek, J. Silicate Gel Dye Laser. U.S. Patent 5,329,540, 1994. Kuder, J. E.; McGinnis, J. L.; Goldberg, H. A.; Hart, T. R.; Che, T. M. Dye Lasers. U.S. Patent 4,878,224, 1989. Hermes, R. E. Composition and Method of Preparation of Solid State Dye Laser Rods. U.S. Patent 5,136,005, 1992.