Preparation and properties of laser dye–ORMOSIL composites

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Various organic laser dyes have been incorporated into organically modified silicates (ORMOSILs), derived from polydimethylsiloxane and tetraethoxysilane. These sol–gel derived PT-ORMOSILs proved to be good hosts for the laser dyes in terms of stability and optical gain. Some of the dyes, for example, Rhodamine 610, Rhodamine 620, and Rhodamine 640, have shown higher stability in PT-ORMOSILs than in methyl alcohol. The stability of Rh6G in a PT-ORMOSIL is 76% higher in dry nitrogen than in air, because of the contribution of oxygen and/or moisture to the dye degradation processes. The fluorescence intensity for Rh610 was enhanced by a factor of 3.9 as the temperature was cooled from room temperature to 77 K.

1. Introduction

Organic dyes with high fluorescent quantum yields have been extensively used as laser materials. The main feature of a dye laser is its tunability over most of its fluorescence spectrum. Indeed, laser dyes can be used as tunable laser sources within the visible spectrum range. These organic dyes are mostly used in the form of solutes in solvent, such as methyl alcohol, ethyl alcohol, or water, at 10^{-5}–10^{-2} mol l^{-1} concentration. However, it is desirable to host these dyes in a solid-state matrix for such applications as fluorescent solid-state chemical transducers, tunable fibre optic lasers, slab wave-guide lasers, integrated non-linear optical wave guides, etc.

In addition, solid matrices for organic dyes have the following advantages in comparison with fluid media.

1. Intermolecular interaction such as the formation of dimers, which degrades the quantum yield, can be avoided because translational freedom is eliminated.

2. The isolation of the dye molecules from each other allows high dye concentrations. Therefore, optical properties are immune from high-concentration interferences [1].

3. Rotational relaxation of the excited state of laser dyes, which is the main source of non-radiative energy loss, can be reduced [2, 3].

4. Desired geometries are achievable.

5. Environmental considerations can be addressed.

Much research on the incorporation of these dyes into solid host media has been published. Organic polymeric matrices [4–9], such as polymethyl methacrylate, polycarbonate, polystyrene and polyvinyl alcohol, have been used. These organic polymeric materials are generally undesirable because of their lack of thermal stability, their permeability to gases and water, poor optical stability and mechanical properties. However, if transparent inorganic oxides such as silicate glasses or crystalline ceramics are preferable, conventional processing techniques involve high temperatures which preclude their use as a host for organic dyes.

In 1984, Avnir et al. [1] embedded an organic dye, Rhodamine 6G, into silica matrix via a low-temperature chemical process known as the sol–gel technique. Since then, many dyes have been placed in oxide matrices via the sol–gel method [10–16]. The advantages of the sol–gel process are (a) lower processing temperatures than conventional glasses, (b) excellent homogeneity at a molecular level, (c) high compositional purity, and (d) the possibility of incorporating organic dyes at low temperatures during the sol stage, or through impregnation of the interconnected pores after gelation.

Prior to heat treatment, the sol–gel derived oxide matrices, however, exhibit an inherent brittleness which hampers polishing and the obtention of optical quality surfaces. Their porosity can also cause large optical scattering losses. Heat treatment to densify the oxide matrices is necessary in order to obtain better mechanical properties and lower optical scattering losses. Nevertheless, it is far beyond the decomposition temperature of organic dyes and is apparently not applicable.

These organically modified silicates (ORMOSILs) usually exhibit lower porosity and enhanced mechanical properties which allow cutting, grinding and polishing prior to heat treatment. A typical ORMOSIL gel network contains a significant amount of organic functionalities, which offers great flexibility with respect to the chemical compatibility of the gels with the dye to be incorporated. The incorporation of Rh6G and C540A into TMOS/MMA/TMSPM ORMOSILs was demonstrated by Dunn et al. [17] and Knobbe et al. [18]. The photostability of Rh6G in

ORMOSILs showed a useful lifetime improvement by a factor of more than 15 with respect to that in modified polymethyl methacrylate (MPMMA) matrix. In the case of C540A doped ORMOSILs, an improvement of at least one to two orders of magnitude in photostability compared with that of PMMA was revealed.

The present paper reviews our recent results involving the utilization of the sol–gel process to prepare the PT-ORMOSIL rigid host for organic dyes such as Rhodamine 6G, Rhodamine 610, Rhodamine 620, Rhodamine 640, and Coumarin 540A. The optical transmission of solid matrices and the optical gain, as well as the stability of the dyes in both solid and liquid media, are reported. Also, the effects of ambient atmosphere and temperature effects are studied. In order to compare with previous studies on organic polymeric matrices [4–9], PMMA–dye composites are studied using the same apparatus for transmission, fluorescence and optical gain.

2. Synthesis

Sol–gel processes usually utilize metal alkoxides of network-forming cations as glass precursors. The alkoxides are hydrolysed and condensed at low temperatures in alcoholic solutions to form glassy networks. For instance, the sol–gel process of a silica from tetraethoxysilane (TEOS) can be sequenced as follows:
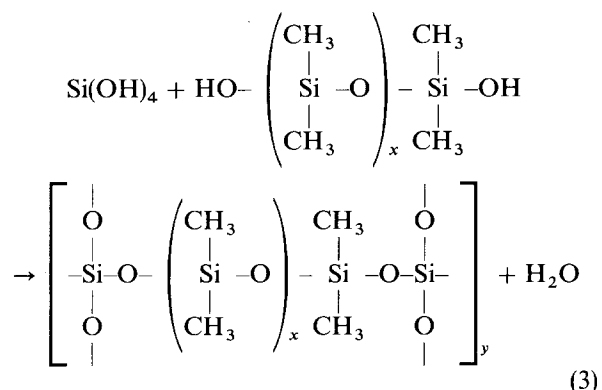hydrolysis

$$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH \quad (1)$$
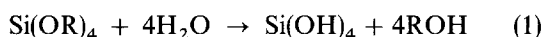
R: ethyl group
condensation

$$2Si(OH)_4 \rightarrow (OH)_3Si-O-Si(OH)_3 \quad (2)$$
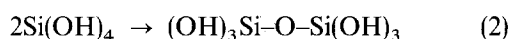
Under acidic conditions, hydrolysis is nearly completed in the early stage of synthesis [19]. Therefore, TEOS is hydrolysed in Reaction 1 to form a soluble polymerizable species. Self-condensation would take place among these polymerizable species as shown in Reaction 2. Polymerization will continue to form an even larger scale SiO_2 network as long as the OH groups are retained.

In the case of PT-ORMOSILs, an organic polymeric species such as polydimethylsiloxane (PDMS) is introduced into the SiO_2 network. The reactions following the hydrolysis of TEOS in Reaction 1 would consist of the self-condensation of hydrolysed TEOS species, i.e. Reaction 2, and the inter-condensation between hydrolysed TEOS and PDMS, i.e. Reaction 3.

$$Si(OH)_4 + HO-\left(\begin{array}{c} CH_3 \\ | \\ Si -O \\ | \\ CH_3 \end{array}\right)_x \begin{array}{c} CH_3 \\ | \\ - Si -OH \\ | \\ CH_3 \end{array}$$

$$\rightarrow \left[\begin{array}{c} | \\ O \\ | \\ -Si-O- \\ | \\ O \\ | \end{array} \left(\begin{array}{c} CH_3 \\ | \\ Si -O \\ | \\ CH_3 \end{array}\right)_x \begin{array}{c} CH_3 \\ | \\ - Si -O- \\ | \\ CH_3 \end{array} \begin{array}{c} | \\ O \\ | \\ Si- \\ | \\ O \\ | \end{array}\right]_y + H_2O$$

$$(3)$$

The co-polymerization of TEOS and PDMS forms an organically modified silica network. The incorporation of chains such as PDMS is responsible for the improved strength of PT-ORMOSILs compared to silica gel, which is brittle and tends to crack. Moreover, the mechanical properties of PT-ORMOSILs can be modified by changing the TEOS/PDMS ratio. With a larger amount of PDMS, a rubbery behaviour can be achieved. Hence, a figure of merit of an organic–inorganic medium such as PT-ORMOSILs is the flexibility and controllability of its mechanical properties.

The synthesis flow chart of PT-ORMOSILs–organic laser dye composites is shown in Fig. 1. High-purity TEOS and PDMS, MW = 1700, were used as precursors. The appropriate amounts of TEOS (90 wt %) and PDMS (10 wt %) were mixed with organic solvents (isopropanol and tetrahydrofuran), distilled water and acid catalyst (HCl), and then refluxed at 80 °C for 30 min. The organic dye was added to the sol after reflux, before casting. The dye concentrations are shown in Table I. The gels were dried for 2 weeks at room temperature. PT-ORMOSILs slabs (3 mm × 3 mm × 10 mm) and discs (25 mm diameter × 3 mm thick) with good optical and mechanical quality could be obtained.

3. Measurements

Optical gain measurements were performed using the experimental apparatus shown in Fig. 2. A nitrogen laser, PTI model PL 202, with a pump pulse width of approximately 600 ps (FWHM) and a pulse repetition rate of 1 Hz at the fundamental 337 nm wavelength, served as the pumping source for both amplifier dye cell and oscillator dye cell. The oscillator dye cell held
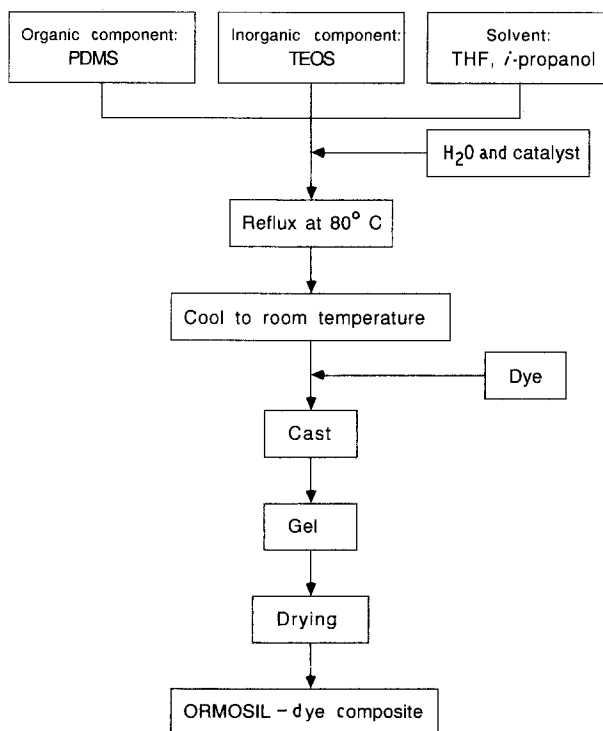

Figure 1 Processing of PT-ORMOSIL–laser dye composites.

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TABLE I Optical gain of organic laser dyes in PT-ORMOSILs, PMMA, and methanol

Wavelength (nm)		Dye[a]				
		C540A 540	Rh6G 590	Rh610 610	Rh620 620	Rh640 640
PT-ORMOSIL	conc. $(mol\,l^{-1})$	1.0×10^{-3}	1.0×10^{-3}	3.2×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
	gain (cm^{-1})	1.2	10.5	10.9	7.8	3.9
PMMA	conc. $(mol\,l^{-1})$	5.0×10^{-4}		5.0×10^{-4}	5.0×10^{-4}	5.0×10^{-4}
	gain (cm^{-1})	0.7		1.7	2.1	1.9
Methanol	conc. $(mol\,l^{-1})$	3.2×10^{-3}	3.2×10^{-3}	3.2×10^{-3}	3.2×10^{-3}	3.2×10^{-3}
	gain (cm^{-1})	7.0	10.0	9.2	8.7	8.0

[a] Rh, rhodamine; C, coumarin.
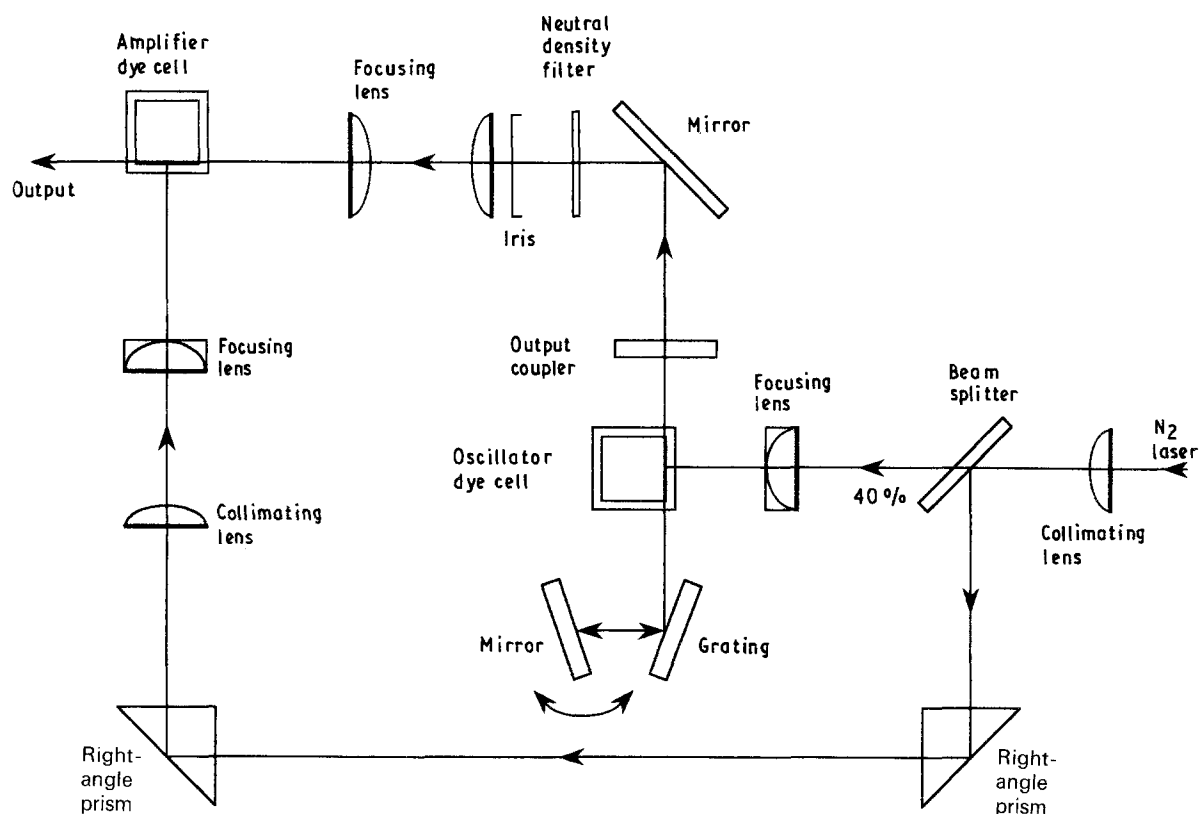

Figure 2 Gain measurement apparatus: PTI model PL 202.

a methanol solution of the studied dye at a concentration of $3.2 \times 10^{-3}\,mol\,l^{-1}$. The laser beam generated by the oscillator dye cell served as the probe signal for gain measurements. The tuned wavelengths for various laser dyes are shown in Table I. A reverse-biased pin diode was used to measure the amplitudes of each of the following:

1. probe signal, I_s, generated by the oscillator dye cell;

2. fluorescent emission, I_f, from the amplifier dye cell where the measured sample was held;

3. total output, I_t, due to the fluorescence emission and the amplified probe signal through the sample.

When measuring the probe signal, the pumping source of the amplifier dye cell was blocked; when measuring fluorescent emission, the probe signal out of the oscil-

lator was blocked. The probe signal needed to be attenuated by utilizing the neutral density filters, so that the small signal gain could be measured. However, the probe signal had to be sufficiently large so that the signal/noise ratio satisfied the minimum requirements for gain measurement.

In order to study the effects of atmosphere, the sample was held inside a sealed quartz cuvette in which dry nitrogen or air was circulated.

Fluorescent emission spectra at different temperatures were measured using a Spex model F112A Fluorolog spectrofluorometer. All fluorescence spectra were recorded in the "front face" configuration. Entrapped laser dyes were excited at 337 nm, corresponding to the wavelength at which they were pumped for optical gain measurements.

Absorption and transmission spectra were measured on a HP8452 spectrophotometer. Absorbance was recorded for Rh6G in PT-ORMOSILs at concentrations of 3.2×10^{-5} and 1.0×10^{-3} mol 1^{-1}. The absorbance of 3.2×10^{-5} mol 1^{-1} composition was measured and multiplied by 31.25 in order to compare with that of 1.0×10^{-3} mol 1^{-1}. Transmission spectra were recorded and normalized to a 3 mm thickness for both pure PT-ORMOSIL and PMMA media.

4. Results and discussion

The transmission spectra of PT-ORMOSILs and PMMA are shown in Fig. 3. Apparently, the optical transmission of PT-ORMOSILs is as good as that of PMMA. The transmittance of PT-ORMOSILs is 85%–95% in the visible range (400–700 nm) for a 3 mm thick material. The scattering and/or absorption of visible light is as low in PT-ORMOSILs as it is in PMMA; the inorganic silica clusters and the organic chain-like PDMS molecules form composites with high accommodation of each other.

Organic dyes exhibit highly conjugated bonding, thus making the displacement of delocalizable π-electrons easier upon the absorption of resonant energy photons. The π-electron network of organic molecules is intimately associated with the immediately surrounding environment, due to structural and electronic factors. Hence, organic dyes are very sensitive to their immediate surroundings. The effect of the host material has to be characterized in terms of optical gain, stability and fluorescence intensity.

According to the small signal gain relationship

$$I_t = I_f + I_s \exp(\gamma x) \tag{4}$$

where x is the path length of the signal (sample thickness), and γ the optical gain, the optical gain can be calculated as follows:

$$\gamma = (1/x) \ln [(I_t - I_f)/I_s] \tag{5}$$

The optical gain of various dyes, Rh6G, Rh610, Rh620, Rh640, and C540A, in different host media, PT-ORMOSILs, PMMA and methyl alcohol, are listed in Table I. Considering optical gain, PT-ORMOSILs are a better host for organic dyes than
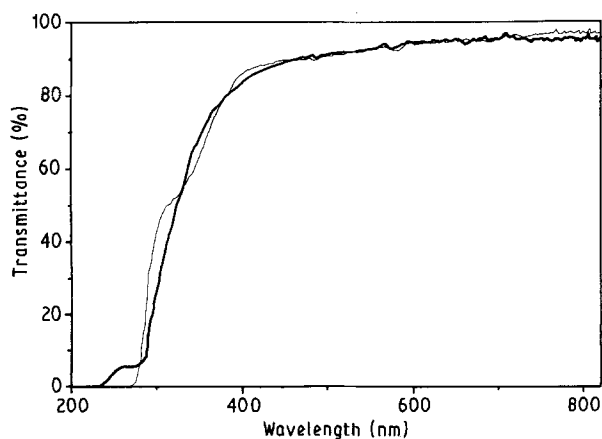
PMMA, and are comparable with liquid methyl alcohol solvent. Such dyes as Rh610 even exhibit higher optical gain in PT-ORMOSILs ($\gamma = 10.9$) than in methyl alcohol ($\gamma = 9.2$). A possible mechanism for the gain improvement in this solid matrix is the reduced possibility of movement of a dye molecule, the degradation in optical gain due to intermolecular interaction such as vibrational, rotational, and/or translational movement is avoided.

In a liquid, as well as in a solid matrix, dyes will degrade with time as they are pumped by the laser pulses. The usual measurement of stability of the dye is the energy required to decrease the gain to half its original value, per volume of dye excited. Experimentally, the volume, V, of excited dye is the volume of the pumped region, or $V = 0.75$ mm^3. This volume was noticeable as the colour of the dye turned black, due to chemical decomposition. The energy delivered to the sample is 0.35×10^{-3} J/pulse. Stability is defined as the amount of the absorbed energy when the gain is reduced by half of its original value

$$\text{Stability} = 0.35 \times 10^{-3} \times n/0.75 \text{ mm}^{-3} (\text{J mm}^{-3}) \tag{6}$$

where n is the number of laser pulses causing 50% degradation of optical gain. Fig. 4 shows the optical gain versus the number of pumping laser pulses for Rhodamine 610 in PMMA and PT-ORMOSILs. PMMA-dye composites exhibited low initial gain and rapid dye degradation, as no signal gain could be obtained after 100 pumped pulses. PT-ORMOSILs exhibited the lowest gain decrease, hence enhanced dye stability.

Polymerization of methyl methacrylate, MMA, is initiated by ultraviolet radiation. If polymerization is not complete prior to testing, it takes place during gain measurement. Therefore, a PMMA matrix, part of which still contains MMA, absorbs part of the pumping ultraviolet light during the measurement, and only the rest of the ultraviolet contributes to electron excitation of the laser dye. As a result, organic laser dyes show relatively poor optical gain and stability in the case of a PMMA medium.

Table II shows a comparison for stability of several dyes in different matrices and methyl alcohol. PT-ORMOSILs is a better environment for organic dyes
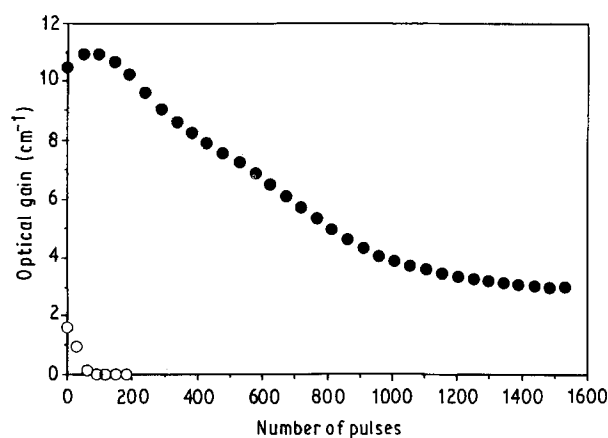

Figure 3 Transmission spectra of (———) PT-ORMOSIL and (———) PMMA.

Figure 4 Comparison of the optical gain of Rh610 hosted in (●) PT-ORMOSIL and (○) PMMA as a function of the number of laser pulses.

	Rh6G	C540A	Rh610	Rh620	Rh640
PT-ORMOSIL	0.11	≪ 0.1	0.34	0.19	0.35
PMMA	0.05	≪ 0.1	0.04	0.09	0.08
Methanol [20]	0.32	0.40	0.27	0.17	0.17

than PMMA. However, Rhodamine 6G and Coumarin, which are the most stable dyes in solvents such as methyl alcohol, ethyl alcohol, etc. [20], exhibit poor stability in both PMMA and PT-ORMOSILs. Dimerization [21] of these dyes is a possible cause for such low stability values. The absorption spectra due to photonically active monomers and dimers which possess quantum yields approaching zero, are shown in Fig. 5 for Rh6G in PT-ORMOSILs for dye concentrations of 3.16×10^{-5} and $1.0 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$, respectively. Obviously, dimers become more important species at higher concentrations; $1.0 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$, at which the stability is measured and calculated. It is worth noting that because of their characteristics of dimerization, Rh6G and C540A exhibit greater degradation in the solid matrices.

Environmental changes can cause peak emission wavelength shifts by modifying excited state–ground state transition energies or altering excited species equilibria. Organic dyes are extremely sensitive not only to the surrounding host but also to the ambient atmosphere. The enhancement of stability of Rh6G by the flux of 99.99% dry nitrogen is 76% as shown in Fig. 6:

$$\text{stability (dry nitrogen)} = 0.35 \times 10^{-3} \times 405/0.75$$

$$\simeq 0.19\,\mathrm{J\,mm^{-3}}$$

$$\text{stability (air)} = 0.35 \times 10^{-3} \times 230/0.75$$

$$\simeq 0.11\,\mathrm{J\,mm^{-3}}$$

This means that oxygen and/or moisture are promoting the degradation processes, and that their removal from the surroundings of the sample can improve laser properties.

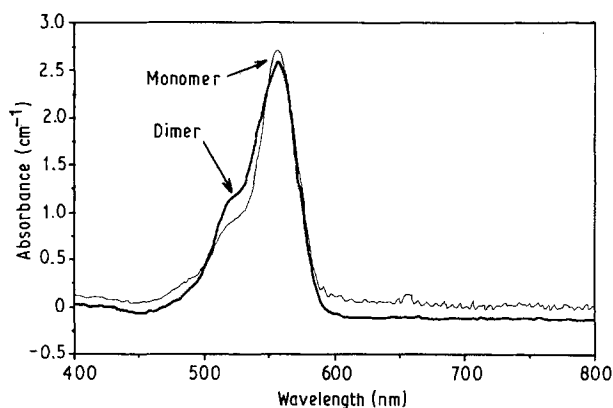In addition to the atmosphere effect, the temperature effect was also studied. The intensity of fluores-
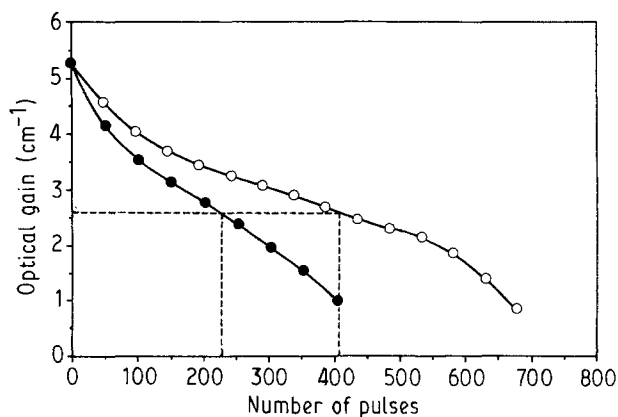
Figure 6 Optical gain of Rh6G in PT-ORMOSILs versus the number of laser pulses under the flux of (○) dry nitrogen and (●) air. Stabilities were 0.19 and 0.11 $\mathrm{J\,mm^{-3}}$ for dry nitrogen and air, respectively.

cence for Rhodamine 610 in PT-ORMOSILs was measured at room temperature and 77 K (liquid nitrogen), respectively. The fluorescence intensity shown in Fig. 7 is obviously enhanced by the factor of $320\,000/82\,000 \simeq 3.9$ as the temperature is cooled to 77 K. Dye lasers are a three-level system, as shown in Fig. 8. The combined vibronic levels of the ground state serve as the lower lasing level, E_1, of the three-level laser. An electron is pumped from the ground state to one of the vibronic levels in the first excited state, E_3. The electron then spontaneously undergoes a transition, of which the relaxation time, $\tau_1 \to 0$, to the upper lasing level, E_2. The emission of a photon upon relaxation from E_2 to E_1 takes place, i.e. fluorescent emission. The relaxation time corresponding to
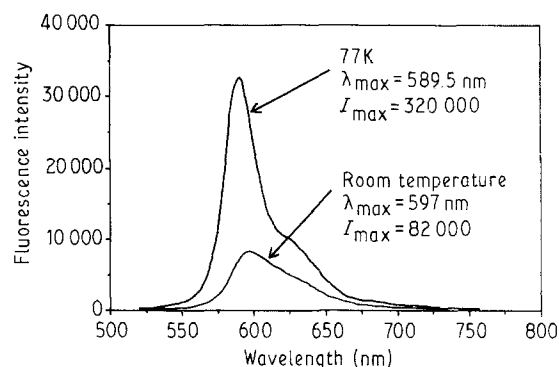
Figure 7 Fluorescence intensity of Rh610 ($3.2 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$) hosted in PT-ORMOSIL at room temperature and 77 K.

Figure 5 Absorption spectra of Rh6G hosted in PT-ORMOSILs at concentrations of (——) 3.2×10^{-5} and (——) $1.0 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$. The absorbance of $3.2 \times 10^{-5}\,\mathrm{mol\,l^{-1}}$ was multiplied by 31.25 in order to compare it with that of $1.0 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$.
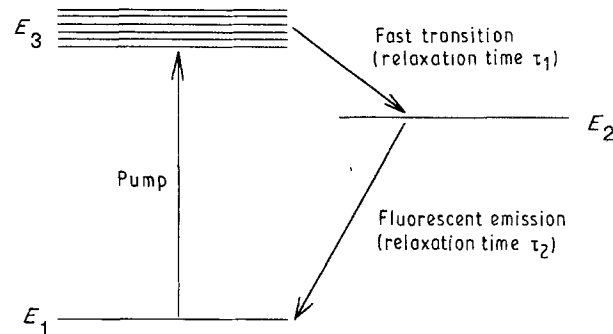
Figure 8 The three energy levels of dye lasers.

fluorescence is of the order of a few nanoseconds. The transition relaxation time, τ_1, is a strong function of temperature, and increases when temperature is lowered. So that τ_1, which is much smaller than τ_2 at room temperature, is enhanced to the order of magnitude of τ_2 at 77 K. Some excited electrons might undergo an emission directly from E_3 to E_1. Hence, the fluorescence peak is expected to shift to shorter wavelength. Such a shift is observed in our work, as shown in Fig. 7. The thermal contraction of PT-ORMOSILs, due to cooling causes the conformational changes of organic laser dyes, which might impose the increase of fluorescent emission energy. This effect is also expected to contribute to the shift.

The PT-ORMOSILs are very thermally stable at 77 K, while none of the frequently used liquid solvents, such as methyl alcohol (freezing point, $f_p = -97.7\,°C$), ethanol alcohol ($f_p = -114.1\,°C$), toluene ($f_p = -95\,°C$), n-hexane ($f_p = -95.4\,°C$) are liquid at 77 K (1 atm). Therefore, the circulation system used for liquid laser dye solution is no longer usable. The advantage of PT-ORMOSILs at lower temperatures is then obvious.

A free-running cavity was set up to evaluate the laser oscillation behaviour of Rh610 incorporated PT-ORMOSILs. A Lambda Physik dye laser, which was pumped by an Excimer laser and tuned at the wavelength of 540 nm, was used as a transversely pumping source for the laser oscillator in which a slab-shaped sample was placed and positioned parallel to a highly reflective rear mirror. The outer surface of the sample served as the output coupler. A lasing spot was observed out of the free-running cavity, confirming that PT-ORMOSIL is an appropriate host material for organic laser dyes.

5. Conclusion

PT-ORMOSILs were synthesized via the sol–gel technique at room temperature and up to 80 °C during refluxing. They exhibited high optical transmission and were shown to be better hosts than PMMA matrices for organic dyes. The degradation of optical gain with time was reduced. Therefore, some organic dyes, such as Rh610, Rh620, and Rh640, exhibited higher stability in PT-ORMOSILs than in methyl alcohol. A flux of dry nitrogen replacing air reduced the effects of oxygen and/or moisture and, therefore, enhanced the stability. Rh6G showed a 76% increase in stability under a dry nitrogen atmosphere. Reducing the temperature led to a blue shift of the fluorescence intensity peak due to the longer relaxation time of the $E_3 \rightarrow E_2$ transition. The fluorescence intensity peak was enhanced by a factor of 3.9 when the temperature was cooled to 77 K, because the non-radiative processing was reduced.

Based on the results, PT-ORMOSILs are promising materials in optics and photoprocesses.

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