

Comparison of Spectroscopic and Lasing Properties of Different Types of Sol-Gel Glass Matrices Containing Rh-6G

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Abstract Rhodamine-6G (Rh-6G) is embedded in sol-gel glass samples which have been prepared by three different methods namely: 1) using HCl as catalyst and glycerol as Drying Control Chemical Additive (DCCA), 2) using HCl as catalyst at 60 °C and drying at room temperature and 3) using HCl as catalyst at 60 °C and heated at 600 °C for 3 h. Comparative studies of spectroscopic and lasing properties of the three types of Rh-6G containing samples were carried out with the lapse of time upto 8 months. Photostability of Rh-6G containing sol-gel samples is measured in terms of half life under Nitrogen laser pumping as number of pulses of N₂ laser necessary to reduce the dye laser intensity to 50% of the original value and value is 7500 pulses at 1.67 Hz rate. The best performance of Rh-6G, as far as its spectroscopic and lasing properties are concerned was found in third type of host matrices using HCl as catalyst at 60 °C and heated at 600 °C for 3 h.

Keywords Sol-Gel Glass · Rhodamine-6G · Absorption · Fluorescence · Quantum yield · Photostability

Introduction

Organic dye molecules in solutions have been widely used as an amplifying media in tunable dye laser [1]. But, there are various drawbacks to using liquid dye lasers, such as the volatile solvents, cumbersome system design, poor thermal stability of the dye solutions etc [2–5]. The possibility of incorporating these molecules in solid host leads to a new field of applications of these lasers. A solid matrix for laser dyes has technical advantages such as compactness, better manageability and suitability for field measurements [2–11]. A number of solid polymeric matrices have been used in the past [5–17]. However, these host materials have been shown to be inherently lacking in mechanical and thermal properties and photostability [6, 7]. Glasses can be other alternative as host. In contrast to the conventional method of glass preparation, which involves very high temperatures which laser dyes can not withstand, the sol-gel method is a low temperature method. Hence, laser dyes can be introduced into the glass by sol-gel process without the fear of thermal degradation of dye.

Dye/host compatibility is most important while embedding the laser dye into the matrix. An ideal host matrix should possess good optical transparency in the region of absorption and emission of dopant dye. It should not have chemical and photophysical interaction with the dye. It should possess thermal and mechanical stability and time durability. Sol-gel glasses have shown a promising performance as host matrices for laser dyes by taking into consideration all the above properties [2–5, 17–33].

There are number of reports describing the methods of preparation of the sol-gel materials and effect of various parameters on their performance [17–23]. The behaviour of the dyes incorporated into polymers and sol-gel materials have also been reported [2–31]. The photophysical properties

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of the dye embedded materials are very much dependent on the matrix and method of matrix preparation. Hence it is interesting and very useful to understand the photophysical and lasing behaviour of the material in relation with its preparation method. With this objective laser dye Rh-6G containing sol-gel materials are prepared by dipping the sol-gel glass matrix in varied concentration of solution of Rh-6G. The sol-gel matrices are prepared by three methods. The spectroscopic properties of these materials are studied with the lapse of time from the preparation. The photostability of Rh-6G embedded matrices of three types when pumped by a nitrogen laser has been also studied and is found to be better/comparable to the reported values of Rh-6G in sol-gel materials by other authors.

Experimental

The preparation of sol-gel materials involved the hydrolysis of metal alkoxide followed by polycondensation. The sol-gel matrix is first prepared by following methods and then dye is incorporated into the matrix by dipping the matrix in the solution of Rh-6G.

Method I: using HCl as catalyst and glycerol as DCCA

This method involves the use of glycerol as DCCA to reduce the cracking of monoliths during drying. Using Tetraethylorthosilicate (TEOS) (Merck-Schuchardt, for synthesis) 11.2 ml, Methanol (MeOH) (Merck, GR for analysis) 6 ml, Distilled water (H₂O) 9 ml, HCl (Merck, about 35% pure, Sp. gr. 1.18) 1 ml (0.1N) and 8 ml Glycerol (Merck, IP for analysis) as DCCA, sol is prepared followed by 14.5 h of ultrasonic stirring. Approximately 3.5 ml sol was poured into rectangular polystyrene cuvette and then sealed with teflon tape. Drying and aging were carried out in controlled clean environment at room temperature.

After 2 months from the date of preparation the samples were given dip treatment [32], by first immersing the samples in MeOH solvent for 4 h and subsequently the samples were immersed in 15 ml of Rh-6G/MeOH of known concentration for 1 h. After removing the samples from the solution they were dried at room temperature. After 10 days of drying the surface of the samples gets dried so that it is handable and can be subjected to various measurements.

Method II: using HCl as catalyst at 60 °C and drying at room temperature

A sol was prepared by mixing TEOS (Merck-Schuchardt, for synthesis) 78 ml with H₂O 102 ml and HCl 2.4 ml

(Merck, about 35% pure, Sp. gr. 1.18) as catalyst at 60 °C and stirred for 1 h. The sol (approximately 3.5 ml) was poured into rectangular polystyrene cuvette and then sealed with teflon tape. Drying and aging were carried out in controlled clean environment at room temperature.

After 20 days from the date of preparation the samples were given dip treatment [33] by first immersing in MeOH solvent for 1 h and subsequently the samples were immersed in 15 ml of Rh-6G/MeOH solution of known concentration for 1 h. After removing the samples from the solution they were dried at room temperature. After four days of drying the surface of the samples gets dried so that it is handable and can be subjected to various measurements.

Method III: using HCl as catalyst at 60 °C and heated at 600 °C for 3 hours

A sol was prepared by mixing TEOS (Merck-Schuchardt, for synthesis) 78 ml with H₂O 102 ml and HCl 2.4 ml (Merck, about 35% pure, Sp. gr. 1.18) as catalyst at 60 °C and stirred for 1 h. The sol (approximately 3.5 ml) was poured into rectangular polystyrene cuvette and then sealed with teflon tape. Drying and aging were carried out in controlled clean environment at 60 °C.

After 4 days from the date of preparation the samples were almost dried on the surface and can be removed from the cuvette. The samples were then heated in programmable microwave furnace at 600 °C for 3 h, subsequently the samples were cooled at room temperature for one day and then given dip treatment. In this treatment it is immersed in 15 ml of Rh-6G/MeOH solution of known concentration for 1 h. After removing the samples from the solution they were dried at room temperature. After three days of drying the surface of the samples gets dried so that it is handable and can be subjected to various measurements.

The number density of Rh-6G molecules in the solid host was calculated by difference method from the knowledge of absorption spectrum of the Rh-6G solution before and after the dipping of glass samples. The concentration of the dye in the solids was varied by varying concentration of dye in the dipping solutions.

Absorption and transmission spectra of the prepared samples were recorded on the UV-Vis spectrophotometer (PerkinElmer, Lambda 35). The transmission spectra of the undoped glasses were recorded with air as the reference and the absorption spectra of the dye embedded solids were recorded with the undoped glass as the reference. The fluorescence spectra were recorded on assembled fluorimeter in front surface excitation-emission geometry. The excitation wavelength was kept constant at 528 nm for all the fluorescence measurements. Rh-6G/MeOH solution in quartz cuvette (1 × 1 × 4.5 cm³) with a quantum yield (Φ_f) of 0.96 [10] was used as a reference to determine the quantum

Table 1 Absorption properties of Rh-6G/sol-gel glasses in comparison with Rh-6G/MeOH

	No. density ($\times 10^{15} \text{ cm}^{-3}$)	λ_{ab} (nm)	$\epsilon \times 10^{-5}$ ($1 \text{ mole}^{-1} \text{ cm}^{-1}$)
Rh-6G/MeOH	1.53	528	1.16
Method I	3.62	530	1.27
Method II	4.38	524	1.46
Method III	5.35	528	1.66

yield (Φ_f) of the dye containing solids. The emission spectra were corrected for the monochromator and photomultiplier response at different wavelengths. The fluorescence intensity of the dye embedded solid was normalized with the fluorescence intensity of the methanolic solution of the dye to obtain the relative fluorescence intensity I_n . Fluorescence lifetime (τ_f) of Rh-6G/sol-gel glass samples were measured on the model SP-80 nanosecond fluorescence spectrometer by using single photon counting technique. The experimental set-up consists of flashlamp excitation source, excitation/emission monochromators, start and stop photomultipliers, time to amplitude converter, multichannel analyzer and a computer. The deconvolution technique has been used to find lifetime value. They are single exponential decay with chi square value between 0.9 and 1.1. From the obtained fluorescence lifetime (τ_f) and the fluorescence quantum yield (Φ_f), the nonradiative deactivation rate constant (K_{nr}) can be determined by $K_{nr} = (1 - \Phi_f) / \tau_f$ [12]. To examine the degradation of the dye/matrix with respect to time, the respective properties were measured with time after the dip treatment of the samples.

The Rh-6G/sol-gel glass samples prepared by all the three methods were subjected to laser study pumped by N_2 laser (Laser science, Inc., 400 μJ energy/pulse and 4 ns pulse duration, variable repetition rate) at 337.1 nm at the rate of 1.67 Hz in transverse dye laser cavity. The detection system consists of a 0.35 m McPherson monochromator, a UDT energy meter and a plotter. Laser spectra for each sample are scanned several times and the average values of lasing wavelength maximum and laser output intensity are obtained.

Results and discussion

The absorption and fluorescence properties of dye embedded solids after drying for a required period of time (mentioned as above after dipping treatment 10 days: Method I, 4 days: Method II, 3 days: Method III) are listed in Tables 1 and 2 respectively.

Table 1 lists the absorption properties of the dried dye embedded solids containing low concentration of dye molecules (no. densities of dye molecules are of the order of 10^{15} cm^{-3} in solids) prepared by the three methods. The absorption wavelength has slight variation namely little bit

red shifted for Method I and little bit blue shifted for Method II as compared to the Rh-6G/MeOH solution. The extinction coefficient of Rh-6G in the solid prepared by Method I, II, and III are about 10%, 25% and 43% more respectively than that in the methanol solution.

Fluorescence properties of solids containing various dye concentrations (no. densities of dye molecules in the order of 10^{15} – 10^{18} cm^{-3} of the solid) are reported in Table 2. Fluorescence wavelength of the dye embedded solids shows some variation (about 2 to 4 nm) between 559–563 and 552–554 nm, with varied concentration in the samples prepared by Method I and Method II respectively. The fluorescence wavelength is almost constant and comparable with methanol in the samples prepared by Method III. FWHM and fluorescence intensity are increased initially as

Table 2 Fluorescence properties of Rh-6G/sol-gel glasses with different concentrations

No. density (cm^{-3})	λ_n (nm)	FWHM (cm^{-1})	I_n (A.U.)
Method I			
5.05×10^{15}	559	912	0.33
4.24×10^{16}	559	989	0.45
6.30×10^{16}	561	1241	0.73
4.90×10^{17}	560	1342	0.86
7.56×10^{17}	561	1210	0.79
2.16×10^{18}	562	1160	0.58
5.30×10^{18}	563	955	0.45
Method II			
5.87×10^{15}	552	921	0.40
4.45×10^{16}	552	995	0.56
8.20×10^{16}	552	1180	0.78
4.94×10^{17}	553	1290	0.93
8.60×10^{17}	553	1120	0.82
2.70×10^{18}	554	1024	0.65
4.79×10^{18}	554	955	0.53
Method III			
5.35×10^{15}	556	786	0.54
4.56×10^{16}	556	914	0.79
9.15×10^{16}	555	1050	0.91
4.98×10^{17}	556	1283	0.98
9.86×10^{17}	556	1012	0.86
3.19×10^{18}	557	922	0.72
4.98×10^{18}	557	845	0.63

Fig. 1 Transmission and absorption spectra of the undoped sol-gel glass solids and Rh-6G/sol-gel glass solids **a** Method I **b** Method II and **c** Method III; after a period of 1 month and after a period of 8 months from the preparation of the samples. (No. density Method I: 3.78×10^{15} per cm^3 ; Method II: 4.38×10^{15} per cm^3 ; Method III: 3.25×10^{15} per cm^3)

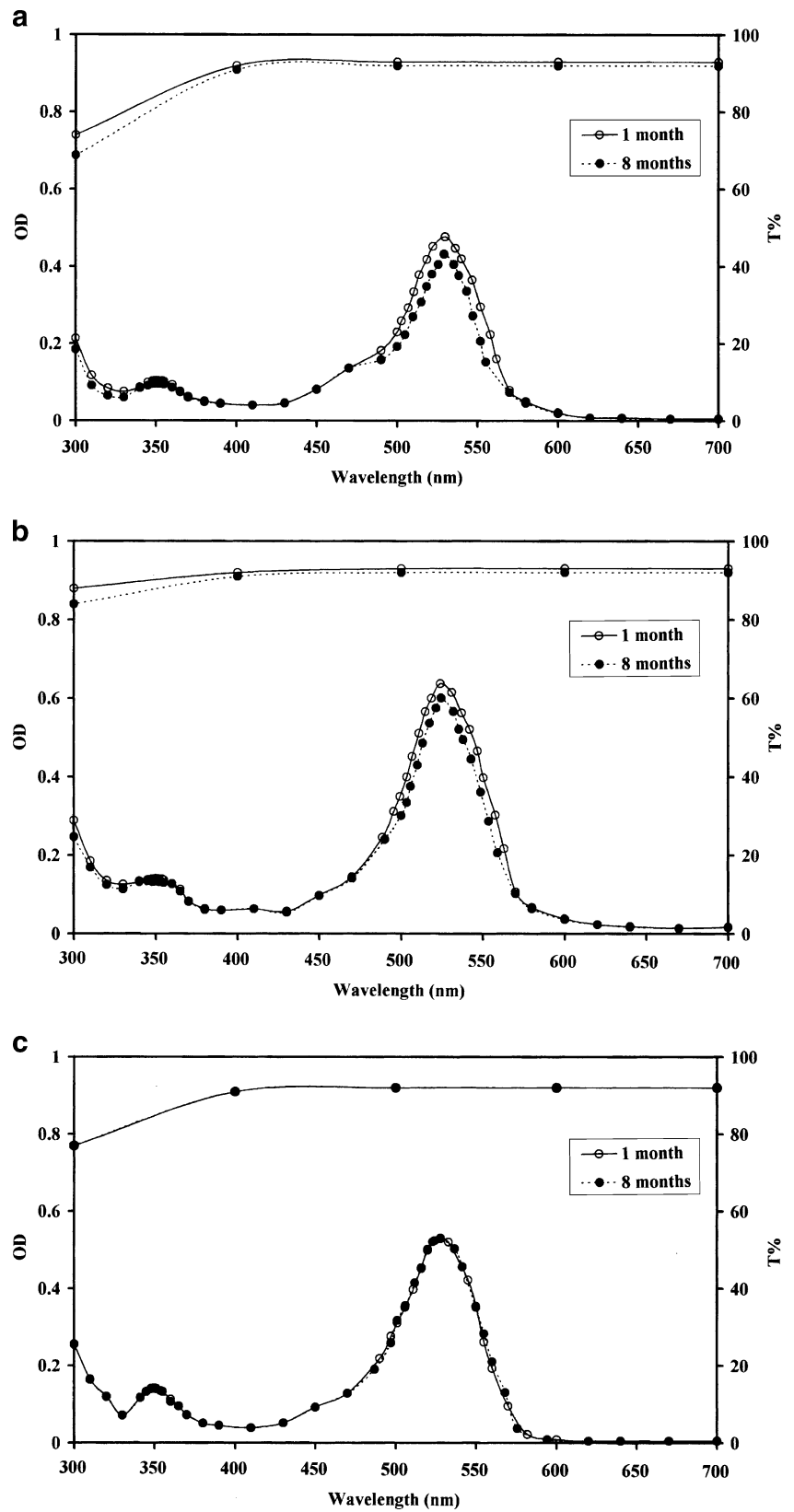


Fig. 2 Fluorescence spectra of the Rh-6G/sol-gel glass solids, **a** Method I, **b** Method II and **c** Method III; after 1 month and after 8 months from preparation of the samples. (No. density Method I: 4.96×10^{15} per cm^3 ; Method II: 4.63×10^{15} per cm^3 ; Method III: 4.78×10^{15} per cm^3)

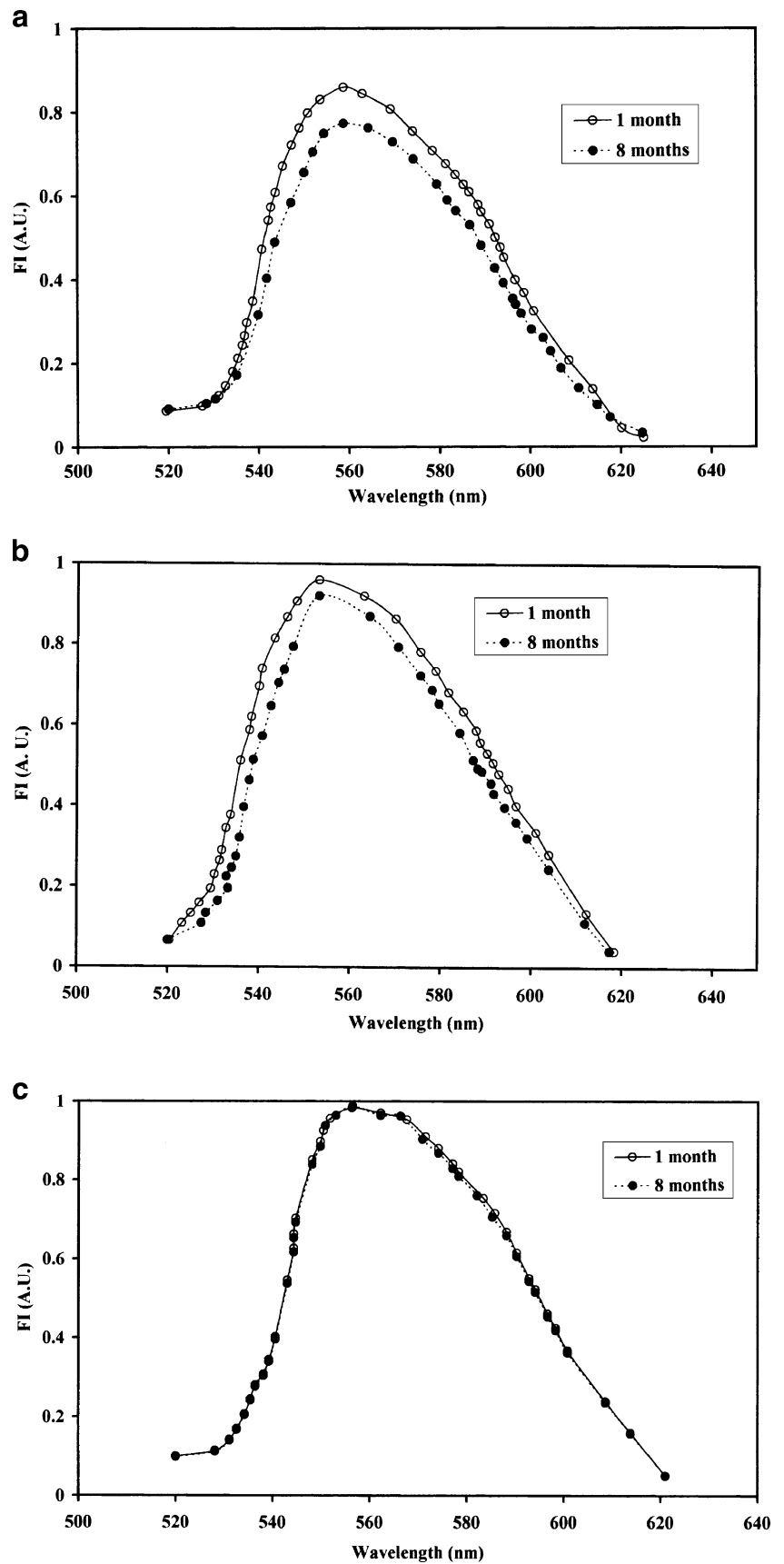


Table 3 Changes in absorption properties of Rh-6G/sol-gel glass solids in comparison with (Rh-6G/MeOH) with time

Rh-6G/MeOH	λ_{ab} (nm)		$\varepsilon \times 10^{-5}$ (l mole ⁻¹ cm ⁻¹)	
	a	b	a	b
	528		1.16	
Method I	530	530	1.27	1.15
Method II	524	524	1.46	1.38
Method III	528	528	1.66	1.66

^a Values after 1 month^b Values after 8 months

the concentration of the dye increases but further decreased for the higher concentrated samples for all the three methods. The fluorescence intensity (I_f) is decreased as the concentration of the dye in solid increases beyond the peak which is due to concentration quenching. Samples prepared by Method I show that the fluorescence intensity (I_f) values are lower than those prepared by other two methods.

Figure 1a, b and c show the transmission spectra of the undoped sol-gel glass solids and absorption spectra of Rh-6G/sol-gel glass solids obtained by the three methods respectively, after a period of 1 month and after a period of 8 months from the preparation of the samples. All undoped solids show good transmission in the visible region as can be seen from the transmission spectra. The undoped solids prepared by Method I and Method II showed little bit decreased in transmission with time. After a period of 1 month of the dip treatment, the samples prepared by Method II showed a good transmission from 300 to 800 nm compared to those prepared by Methods I and III. Also, after a period of 8 months of the preparation, the transmission was decreased by 5% to 6% for the samples prepared by Method I and Method II, where as no change of transmission observed in the sample prepared by Method III. This may be due to the loss of water/alcohol from the pores of the solids prepared by Method I and II with time of drying. But in samples prepared by Method III, the residual solvent/chemicals are already removed during heating the sample at high temperature and therefore no

change of transmission observed in these samples with time. This also suggests that, the pore size of the solids prepared by Method III is smaller than those prepared by Method I and II. In Method I and Method II samples the pore size is getting reduced with drying time which is one of reasons for observing changes in transmission with time.

Figure 2a, b and c show the fluorescence spectra of the Rh-6G/sol-gel glass solids prepared by three methods respectively, after 1 month and after 8 months from the preparation of the samples. From the absorption and fluorescence spectra it can be seen that the absorption and fluorescence maxima of Rh-6G in all the three types of matrices remain unchanged with time. The changes in the absorption and fluorescence properties of Rh-6G/sol-gel glass samples are shown in Tables 3 and 4 respectively. The quantum yield (Φ_f) and fluorescence lifetime (τ_f) of Rh-6G/sol-gel glass solids prepared by Method I and Method II were having slightly low values compared to Method III and showed slight reduction after eight months, where as nonradiative deactivation rate constant (K_{nr}) showed slight increase in value after eight months for Method I and Method II samples. Also Method I samples show highest value of nonradiative constant but it is not very large compared to the value for the Method III samples. The quantum yield, fluorescence lifetime and nonradiative deactivation rate constant of Rh-6G/sol-gel glass solids prepared by Method III were found to remain almost unchanged upto a period of 8 months. The reason for high and constant quantum yield value of Rh-6G in Method III samples compared to Method I, II is that in Method III samples all the chemical residues get destroyed at the high (600 °C) temperature and matrix is only SiO₂ matrix holding Rh-6G molecules. This reduces the possibility of interaction of Rh-6G molecules with other chemicals/solvents to nearly zero so that there is no degradation of Rh-6G with time in samples prepared by Method III. Where as in Method I and Method II samples still there are ingredients like glycerol/water/HCl etc with which Rh-6G molecules can interact and form some other product with time of drying degrading the sample which shows reduction in absorption/fluorescence intensity with time. But one can observe that such reduction in photophysical properties in Method I and Method II samples with time is not very large

Table 4 Changes in fluorescence properties of Rh-6G/sol-gel glass solids in comparison with (Rh-6G/MeOH) with time

Rh-6G/MeOH	λ_{fl} (nm)		Φ_f		τ_f (ns)		$K_{nr} \times 10^9$	
	a	b	a	b	a	b	a	b
	556		0.96		3.79		0.011	
Method I	559	559	0.90	0.88	4.10	4.00	0.024	0.030
Method II	553	553	0.92	0.91	4.13	4.11	0.019	0.022
Method III	556	556	0.95	0.95	4.26	4.26	0.012	0.012

^a Values after 1 month^b Values after 8 months

Fig. 3 Laser spectra of the Rh-6G/sol-gel glass solids, **a** Method I, **b** Method II and **c** Method III; for optimum concentration

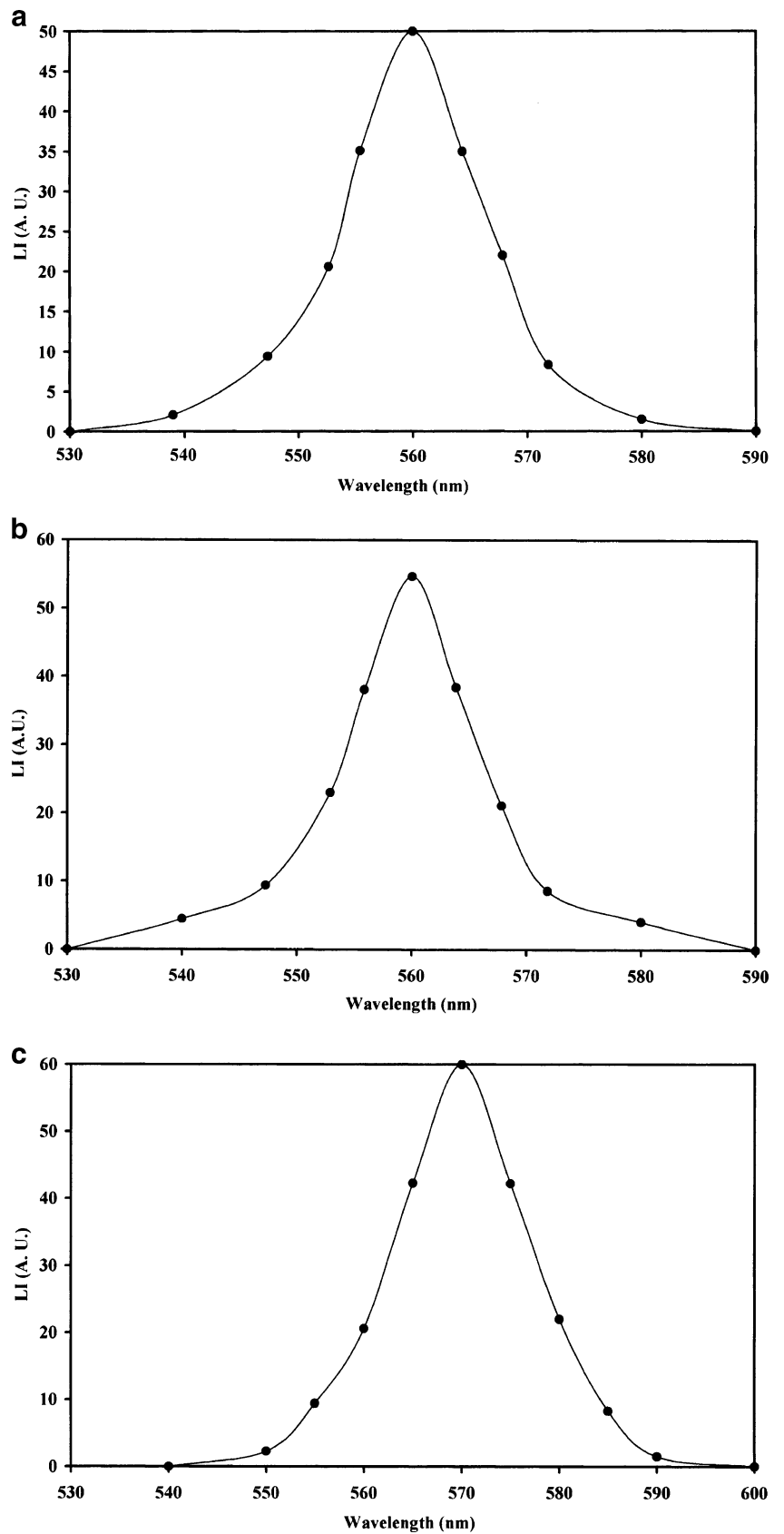


Fig. 4 Laser profile of the Rh-6G/sol-gel glass solids, **a** Method I, **b** Method II and **c** Method III; with concentration

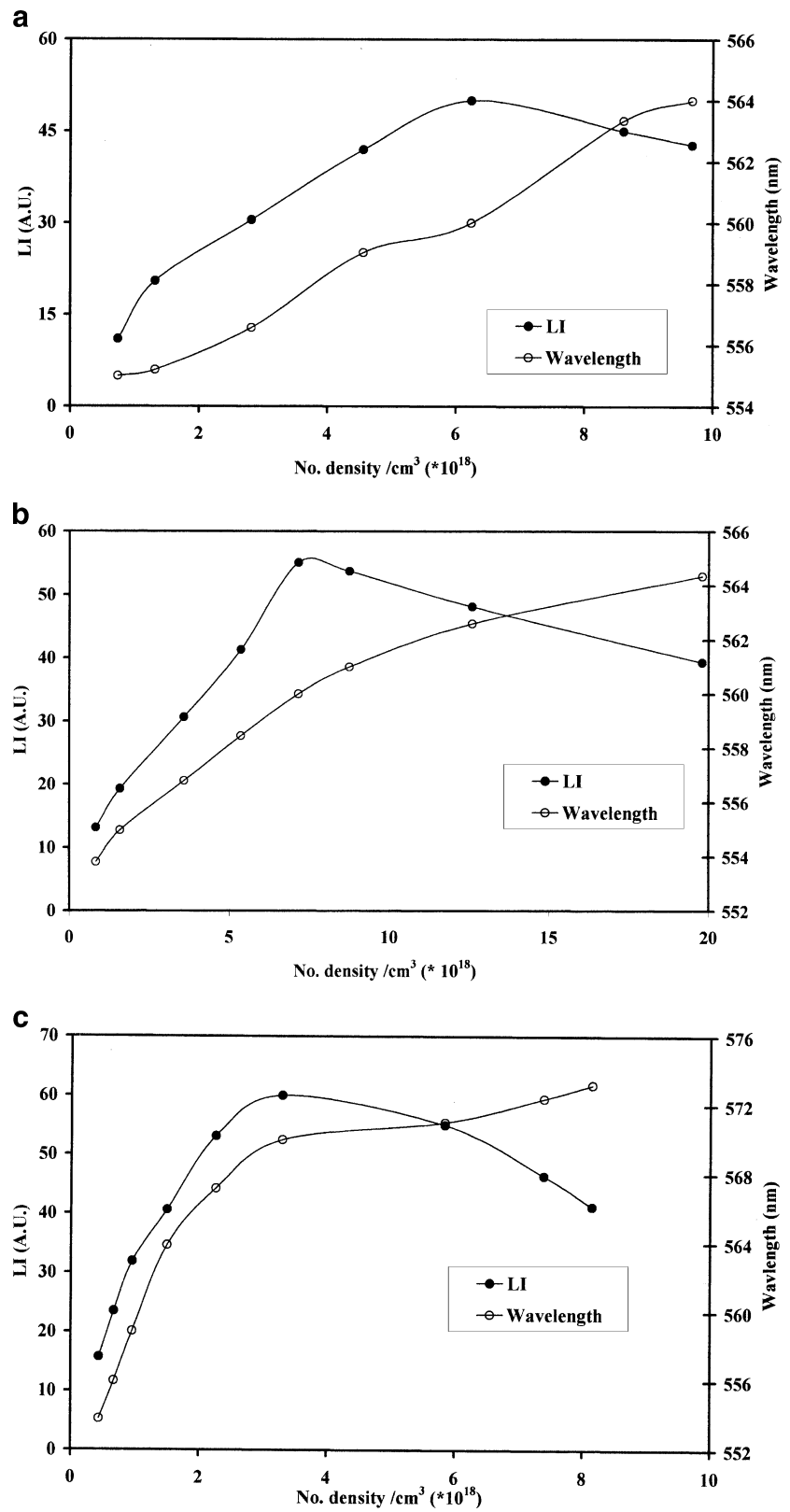


Table 5 Comparative study of lasing properties of Rh-6G in sol-gel glasses

Method	λ_L (nm)	LI (A.U.)	FWHM (nm) (Tunability)	Half-life (no. of pulses)
Method I	560	50	9	7500
Method II	560	54	8	4600
Method III	570	60	10	850

compared to value of Φ_f and τ_f in methanolic solution (Table 4). The single lifetime values of Rh-6G in the range of 4.00 – 4.26 ns in these samples are an indication of the existence of a single fluorescent species.

Figure 3a, b and c show the typical laser spectra of the Rh-6G/sol-gel glass solids prepared by three methods respectively for optimum concentration. The laser spectrum is much narrower than the fluorescence spectrum as expected. Figure 4a, b and c show the plot of the dye-laser output intensity (LI) of the Rh-6G/sol-gel glass solids prepared by three methods respectively vs the concentration of Rh-6G. Variation of the wavelength maximum of the laser spectra with concentration is also plotted in Fig. 4a, b and c. There is common observation that the output laser intensity (LI) initially increases with the concentration to reach a maximum value and then decreases in all Rh-6G/sol-gel glass samples prepared by three methods. This is attributed to the concentration quenching effect and aggregation of the dye molecules [8]. The laser wavelength maximum shifts to longer wavelength side as concentration increases. Table 5 lists the lasing characteristics of Rh-6G in sol-gel glass samples prepared by three methods which include the laser intensity (LI), laser wavelength maximum, FWHM and half life.

An important factor in solid state dye lasers is photostability. The photostability of dye/sol-gel glass samples is expressed in terms of half-life of lasing materials defined as the number of pulses needed to reduce the laser output intensity to half of its initial value. Figure 5 shows the

photostability of Rh-6G/sol-gel glass samples prepared by all the three methods. This was studied by monitoring the output laser intensity with number of nitrogen laser pump pulses. The half-life of Rh-6G/sol-gel glass samples for Method I, Method II and Method III samples are 7500, 4600, 850 pulses respectively. The photodegradation of Rhodamine dye molecules depends on the micro-viscosity environment about the molecule in the solid matrix [1, 8]. The glass samples prepared by Method I contain glycerol even after long drying. This may be helping the mobility of the embedded dye molecules which are available for lasing. This helps in taking place of degraded (because of photo-destruction) molecules by the fresh molecules during lasing. This happens very efficiently in liquid state as the self repair in liquid is natural because of brownian motion. In solid state as well the resultant intensity depends on the number of dye molecules getting excited by pump radiation in the front surface. If the degraded molecules get replaced by fresh molecules quickly the net photodegradation is slow. This is also supported by the fact that a dark line is seen on the sample if sample is irradiated by pump radiation for very long time. This line disappears after some time. This confirms that the rearrangement of the dye molecules take place in solid matrix as well. Hence in Method I samples the photodegradation is observed to be minimum with longest half life values. In Method II samples the microviscosity helps in supplying fresh dye molecules but with lesser rate and in samples prepared by Method III the photodestruction is comparatively at fastest

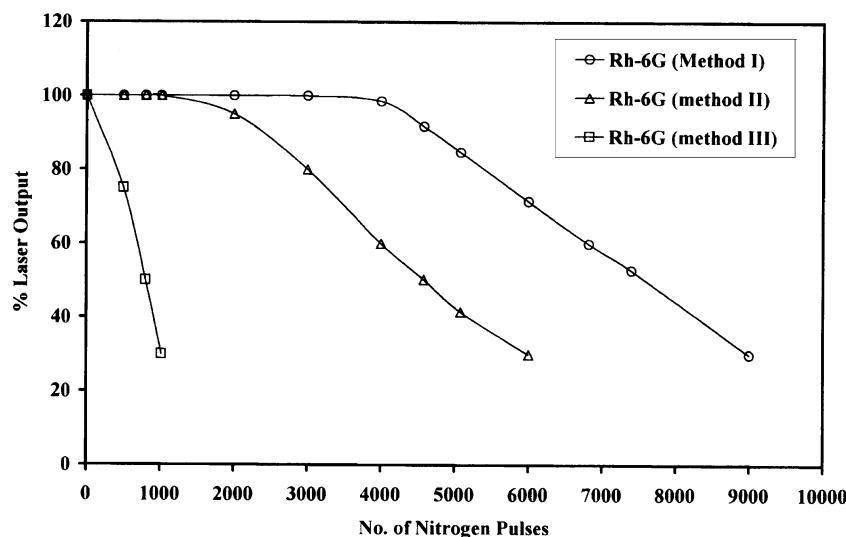
Fig. 5 Photodegradation of the Rh-6G/sol-gel glass solids prepared by the three methods

Table 6 Photostability comparison of Rh-6G in various hosts with the data in the present work for Rh-6G/sol-gel glasses

Matrix	Pumping source and parameters	No. of pulses for 50% reduction	Ref.
Modified PMMA	530 nm (Nd: glass-SHG) 0.5–1.4J/cm ² (50 ns)	≈ 200	[13]
Poly (2 hydroxy ethyl methacrylate) with crosslinking	337 nm, 1.8 mJ (5 ns), 0.14 Hz	≈ 300	[14]
Copolymer of HEMA and MMA	337 nm, 1.2 mJ (5 ns), 2 Hz	≈ 5500	[15]
Alumina film	337 nm, 500 μJ (5 ns), 1 Hz	600	[27]
Silica	532 nm, (2nd Harmonic Nd:YAG laser) 3mJ, (8 ns), 10 Hz	6000	[28]
Zirconia	532 nm, (2nd Harmonic Nd:YAG laser) 3mJ, (8 ns), 10 Hz	6500	[28]
Aluminosilicate xerogel	511 nm (dye laser), 2 mJ, 1 Hz	1500	[29]
ORMOSIL	532 nm (dye laser) 2 mJ, (15 ns), 1 Hz	2700	[30]
HEMA/TEOS	534 nm, 5.5 mJ/pulse, 2 Hz	2300	[31]
Sol-Gel Glass			
(Method I)	337.1 nm, 400 μJ,	7500	Present Report
(Method II)	(4 ns), 1.67 Hz	4600	
(Method III)		850	

rate. This is because if the dye molecules are photo-destructed that place may not be taken by any fresh molecules. This is because in Method III samples the Rh-6G molecules are surrounded by only SiO₂ matrix with negligibly small solvent around it in the pores. The photostability of Rh-6G in sol-gel glasses in present work can be compared with the earlier reported values of Rh-6G in various host matrices which are listed in Table 6.

Table 6 lists the matrix for Rh-6G, the pumping source and parameters for the pumping source, and the number of pumping pulses giving a 50% reduction in the intensity of the material. It can be seen from Table 6 that the pumping laser parameters in our present work (N₂ laser, 337.1 nm, 400 μJ energy/pulse, 4 ns pulse duration and 1.67Hz) and that reported by Muto et al. [27] are comparable. They have reported a 50% reduction in intensity with 600 pulses for Rh-6G doped in (Alumina film) host. This value is comparable with Rh-6G /sol-gel glass matrix prepared by third method and an order of magnitude greater value than this reported value has been observed in other two methods in present work. Costela et al. [15] have reported 5500 pulses for a 50% reduction with a copolymer host matrix. The value of half life in present work is greater than that value. Photostability of Rh-6G doped in silica and zirconia host are 6000, 6500 pulses respectively when they are pumped by Nd:YAG laser at 532 nm reported by Reifeld et al. [28]. There are other reports [29–31] in which a pulsed dye laser (λ=511/532 nm) is used as a pumping source for exciting the Rh-6G dye molecules. They have reported 1500/2700 pulses as half life which are less than the value in the present work.

It may be pointed that the comparison of results for two pumping wavelengths 337 nm and 532 nm indicates that the life of the materials is increased by a factor of 8 if pumped by 532 nm as reported by Costela et al. [15]. This is due to less thermal degradation with pumping at 532 nm.

Conclusion

Laser dye Rh-6G could be introduced successfully in blocks prepared by sol-gel technique using three methods. From the above studies, it is evident that optically transparent glass matrices prepared by three methods are excellent host matrices. This has been shown by spectroscopic and lasing properties of Rh-6G as compared to its respective properties in MeOH solution. The samples have been also studied for the possibility of use of the samples as solid state dye laser materials. The lasing properties and photostability of these materials are studied and compared with the reported values by other authors.

The performance of the three matrices as host matrices for laser dye Rh-6G are listed as follows:

- > Fast drying and aging (Method III)
- > Good optical transmission in the UV-near UV region (Method II and III)
- > High quantum yield of the dye embedded solid (Method III)
- > Longevity of the host matrix (Method III)
- > Longest photostability under N₂ laser pumping (Method I)

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