Absorption Proprieties of Rhodamine 6G (Rh-6G) Laser Dye doped in Sol-Gel glass

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Abstract:
Nanoporous glass samples are prepared by using sol-gel technology mainly which consist hydrolysis and poly condensation of tetraethyl orthosilicate (TEOS) using HCl as catalyst at low/room temperature. The prepared glass samples are highly nano porous, optically purely transparent, mechanically and thermally stable and therefore organic dye molecules or any other biological materials can be incorporated in this gel network, with no risk of thermal degradation, whereas conventional glass production requiring high temperature which organic molecules cannot withstand. Sol -gel crystal glass also has in numerous applications in various fields of science and technology such as host matrix for various type of organic biological and chemical molecules, protective and porous films, optical sensors, Solar Concentrator, antireflection coatings and Laser technology. In our research laboratory we prepared Rhodamine Laser Dye (Rhodamine-6G) embedded in nano-composite sol-gel glass and studied their absorption properties. From various physical and optical properties these nanostructured glass samples can be useful as silica gel host matrices for solid state dye lasers and many other applications.

Keywords: Sol–gel glass, Nanoporous, Rhodamine 6G (Rh-6G) dye

1 INTRODUCTION:

The dye Rhodamine 6G (Rh 6G) belongs to the xanthene series of the laser dyes [1]. It is the most widely used laser dye. The spectroscopic and lasing properties of this dye in solution as well as in solid matrices have been studied extensively by various workers [2-7]. Like Rhodamine B (Rh B), Rh 6G has a symmetrical molecular structure. Rh 6G is known for very high fluorescence quantum yield (96% in alcoholic solution). The reason for this different behavior lies in the excited-state Π-electron density within the C=N bond which depends upon the number of electron donating alkyl substituents [6-7]. In case of Rh 6G the Π-electron density is high and the thermal energy of the solvent molecules is not sufficient to twist the amino groups out of planarity as in the case of Rh B.

Rh 6G being the first laser dye to be trapped in sol-gel glasses [8] was studied by many workers in combination with different sol-gel matrices to investigate its spectroscopic behaviour, and also to understand the sol-gel process itself. Rh 6G has been doped into silica and silica / titania films [9], in alumimium film [10-11], in aluminosilicate xerogels (monoliths) [12], in Ormosils [13-18, 21-24] and in many other matrices by sol-gel method. This paper deals with the preparation of Rh-6G sol-gel glass samples using three different methods and studied their spectroscopic properties such as absorption .

2. EXPERIMENTAL:

2.1. Purification of the Materials:

Purity of the laser dyes was checked by uv-visible absorption spectroscopy. The values of the extinction coefficient and absorption wavelength maximum of all the dyes were obtained by absorption measurements in methanol and the values were compared with the reported ones [1, 2, 3]. All the chemicals used for the preparation of sol-gel are of analytical grade. The solvents used for comparative study of dyes in liquid state are of GR grade. All the dyes and chemicals were used as received without further purification.

2.2 Methods of preparation of the Sol-gel Materials:

As mentioned in the introduction, the preparation of sol-gel is a two-step process involving hydrolysis and polycondensation of metal alkoxide in presence of a catalyst. The sol-gel materials are prepared in the present work by carrying out hydrolysis and polycondensation of tetraethylorthosilicate (TEOS) using HCl as catalyst.

The materials were prepared by employing three different methods.

Method I: using HCl as catalyst and glycerol as DCCA

A sol was prepared by mixing 11.2- ml TEOS, 6-ml MeOH, 9 ml- H_2O, 1.0 ml HCl (0.1 N) as catalyst and 10 ml glycerol as DCCA to reduce the cracking of monoliths during drying under magnetic stirring at room temperature. After 17 hours of stirring, 3.5 ml sol was poured in the rectangular polystyrene cuvettes of size (4.5 × 1.0 × 1.0) cm^3. The cuvettes were sealed with teflon tape to ensure slow drying of sol, which decreases the probability of cracking in solid. Drying and aging of gel were carried out at room temperature in clean and controlled environment.

After about 2 months from the date of preparation, solid blocks were obtained in the form of parallelopipeds with dimensions (0.8 × 0. 8 × 2.0) cm^3. These glass samples were immersed in MeOH / H_2O (50:50 by volume) for 16 hours and then subsequently in 15 ml methanolic solution of Rh-6G dye of known concentration for one hour. After removing the samples from the solution, they were dried at room temperature. After 05 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^{O}C and drying at room temperature

A sol was prepared by mixing 78- ml TEOS, 102 ml- H_2O, 2.4 ml HCl as catalyst under magnetic stirring at $60^{O}C$ temperature for 1 hour. After 1 hour stirring, 3.5 ml sol was poured in the rectangular polystyrene cuvettes and then sealed with teflon tape. Drying and aging of gel were carried out at room temperature in clean and controlled environment.

After about 20 days from the date of preparation, solid blocks were obtained in the form of parallelopipeds with dimensions (0.8 × 0. 8 × 2.8) cm^3. These glass samples were given dip treatment by immersing them in MeOH / H_2O (50:50 by volume) for different intervals of time such as 1 hour, 4 hours, 8 hours, 12 hours and 16 hours and then subsequently in methanolic solution of Rh-6G dye of known concentration for one hour. After removing the samples from the solution they were dried at room temperature. After 5 days of drying the surface of the samples gets dried so that sample is handable and can be subjected to various measurements.

Method III: using HCl as catalyst at $60^{O}C$ and heated at $600^{O}C$ temperature for 3 hours

A sol was prepared by mixing 78- ml TEOS, 102 ml- H_2O, 2.4 ml HCl as catalyst under magnetic stirring at $60^{O}C$ temperature for 1 hour. After stirring, 3.5 ml sol was poured in the rectangular polystyrene cuvette and then sealed with teflon tape. Drying and aging of gel were carried out at $60^{O}C$ temperature in heating blocks. After about 4 days from the date of preparation, solid blocks were obtained in the form of parallelopipeds with dimensions (0.6 × 0. 6 × 1.7) cm^3. These glass samples were given heat treatment by heating in programmable microwave furnace at 600 ^{O}C for 3 hours and then subsequently they were cooled and kept at room temperature for one day and then the blocks were immersed in 15 ml methanolic solution of Rh-6G dye of known concentration for one hour. After removing the samples from the solution, they were dried at room temperature. After 3 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 dye doped molecules in the solid host was calculated by difference method from the optical density (OD) of absorption of Rh-6G dye solution before and after dipping of the glass sample. The desired number density of dye molecules in solid host can be obtained by dipping of glass samples in varied concentration of methanolic solution of dye. The dried solids obtained by all the above methods were visually of good surface finish with plane parallel side faces. They were used directly for spectroscopic and laser studies without any polishing of the faces.

3. EXPERIMENTAL / INSTRUMENTAL TECHNIQUES:

3.1 Absorption Spectroscopy Study:

Absorption spectroscopy involves relative measurement of the transmitted light as a function of wavelength. The measurements are relative because the intensity of light transmitted by the sample material I_S is related to the intensity of light transmitted by the reference material I_R. According to Beer’s law, a relationship among the transmittance (T), concentration (c) of an absorbing species and the path length of the sample used is given by

$$T = (I_S / I_R) = 10^{-\varepsilon bc}$$

where Is = intensity of transmitted light by the sample,

I_R = intensity of transmitted light by reference,

ε = extinction coefficient or molar absorptivity of dye species,

b = path length the sample used, and

c = concentration of the dye species.

In a spectrophotometer, this relative amount of transmitted light is converted into absorbance (A) which is equal to -log T leading to the relation A = εbc. Absorbance A is also called as optical density (OD). This relation is true for low dye concentration only whose optical density is nearly 0.2. UV- visible absorption spectra of dye/sol-gel glass samples were recorded on a conventional spectrophotometer (PerkinElmer, Lambda 35). Transmission spectra of undoped glasses were recorded with air as reference and absorption spectra of RH-6G dye-doped solids samples prepared by all the three methods were recorded with undoped glass as reference. Absorption wavelength maximum **(λ_a)** and molar absorptivity **(ε)** of the dye in solid were determined and were compared with the respective properties in solution.

4 RESULTS AND DISCUSSION:

4.1 Absorption Properties:

The absorption and fluorescence properties of Rh 6G dye embedded sol-gel glass samples are listed in Table 1.

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

	No. density ($\times10^{15}$ cm^{-3})	**λ_a (nm)**	**$\varepsilon\times10^{-5}$ (l mole^{-1} cm^{-1})**
Rh 6G/MeOH	1.35	528	1.17
Method I	1.68	532	1.32
Method II	4.79	525	1.50
Method III	5.32	528	1.64

Uncertainty 1 nm in (λ_a)

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.

Fig.1 (a, b, and c) show the absorption spectra of Rh 6G/sol-gel glass solids obtained by three methods respectively, after a period of 15 days and after a period of 240 days from the preparation of the samples.

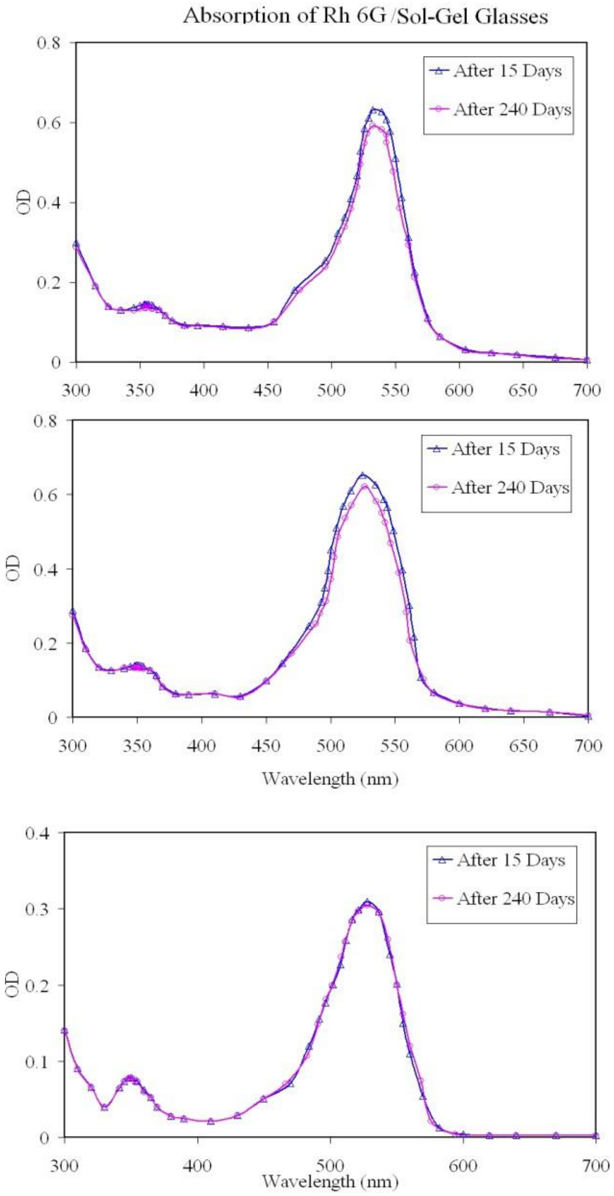

Fig. 1: Absorption spectra of Rh 6G containing sol-gel glass sample a) Method I b) Method II and c) Method III (no. density Method I: 1.12×10^{16} per cm^3 ; Method II: 4.39×10^{15} per cm^3 ; Method III: 6.62×10^{15} per cm^3)

From the absorption spectra it can be seen that the absorption maxima of Rh 6G in all the three types of matrices remain unchanged with time.

The changes in the absorption properties of Rh 6G/sol-gel glass samples after 15 dats and after 240 days are shown in Table 2.

Table 2: Changes in absorption properties of Rh 6G/sol-gel glass solids with time in comparison with Rh 6G/MeOH.

	λ_a (nm)		**$\varepsilon x10^{-5}$ (l mole^{-1} cm^{-1})**	
Rh 6G/MeOH	**528**		**1.16**	
	a	b	a	b
Method I	532	532	1.30	1.19
Method II	525	525	1.48	1.40
Method III	528	528	1.64	1.63

Uncertainty 1 nm in (λ_a)
a: Values after 15 days.
b: Values after 240 days

4.2 Laser Study:

Fig. 2 (a, 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.

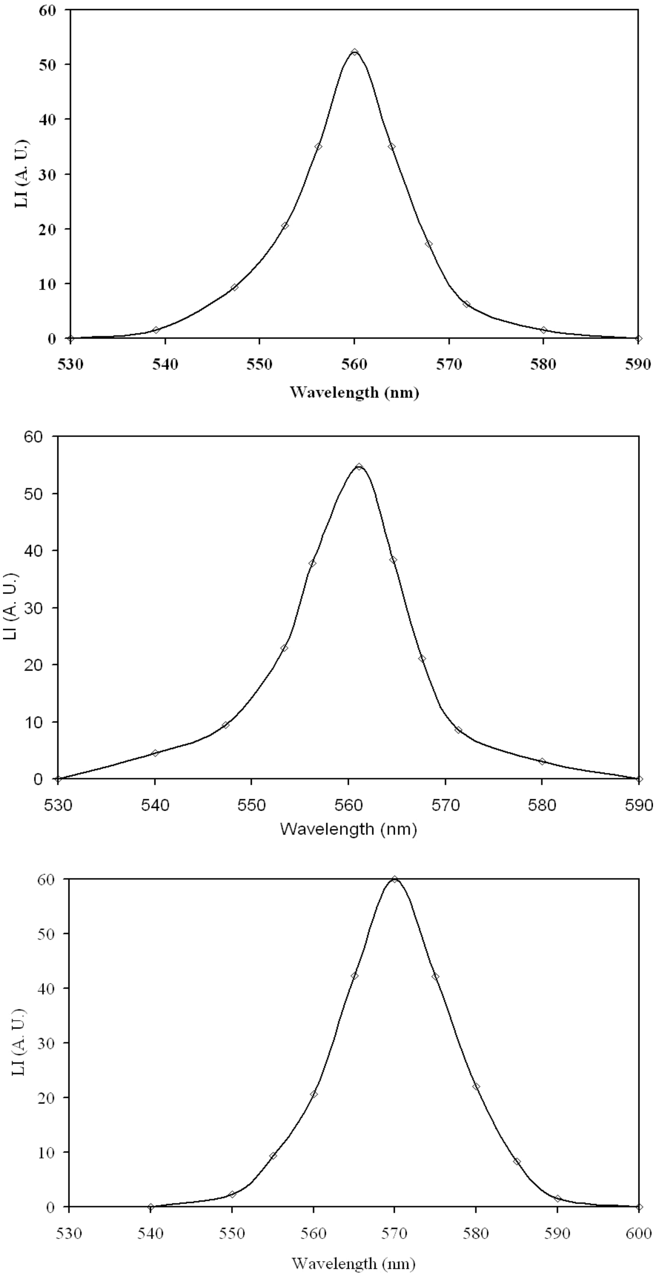

Fig 2: Laser spectra of the Rh 6G/sol-gel glass solids, a) Method I, b) Method II and c) Method III; for optimum concentration

Fig. 2 (a, 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 Fig3 (a, b, and c).

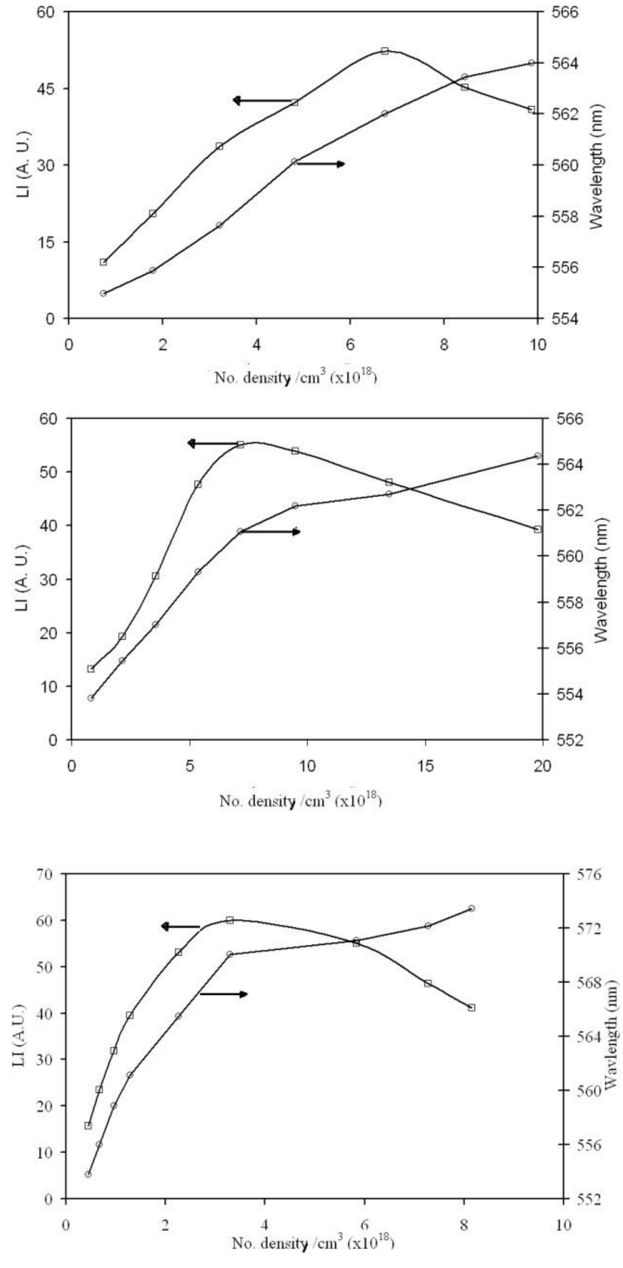

Fig 4: Laser Profile of the Rh 6G/sol-gel glass solids, a) Method I, b) Method II and c) Method III; with concentration

There is a 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 [27]. The laser wavelength maximum shifts to longer wavelength side as concentration increases.

5 CONCLUSIONS:

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 absorption and lasing properties of these materials are studied.

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

- Fast drying and aging (Method III)
- Longevity of the host matrix (Method III)
- Longest photostability under N_2 laser pumping (Method I)

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