CONCENTRATION DEPENDENT PHOTOLUMINESCENCE BEHAVIOR OF RHODAMINE B IN $AL(NO_3)_3$-SIO_2 SOL-GEL GLASSES

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ABSTRACT

In the search for design of new luminescent host-guest materials, fluorescent xanthenes dye Rhodamine B doped $Al(NO_3)_3$-SiO_2 glass are fabricated and the spectroscopic behavior was investigated. The glass samples were fabricated by the sol-gel method. For comparison, the dye doped samples in methanol were also prepared and the absorption and photoluminescence efficiencies were compared with the dye doped glass samples. Radiative parameters viz. peak emission wavelength, intensity and quantum yields etc. were evaluated for the studied glass samples as a function of concentration which suggests 10^{-4}M as the optimum dye concentration for Rhodamine B in $Al(NO_3)_3$-SiO_2 sol-gel glasses.

Keywords: *absorption spectra, organic dyes, photoluminescence, quantum yield, sol-gel glass*

1. INTRODUCTION

The preparation and the study of photophysical and photochemical properties of organic dyes doped in inorganic and organic -inorganic hybrid hosts, now-a-days are gaining importance among the researchers particularly for technological applications [1]. These dyes form a very interesting class of quantum systems and capable of lasing in a very broad spectral range covering near infrared, visible, and ultraviolet and also having wide applications as non-linear optical materials, optical memories etc [2-4]. Dyes can be used in both solid and liquid phases and their concentration and hence absorption as well as gain can be readily controlled. This active medium for laser can also be obtained in very high optical quality. Because of their low production cost, dye sensitized solar cells are showing promise as an attractive alternative to silicon solar cells recently [5].

In the present scenario, dye lasers based on liquid hosts are much developed and used in many laboratories and for technical applications in spite of the fact that the liquid hosts possess certain inherent disadvantages like flow fluctuations, evaporation of solvents, need of large volumes of organic solvents, etc. [6]. Substitution of liquid hosts by solid hosts will help to overcome these inherent drawbacks of liquid media and also will reduce the problems such as immunization of optical properties from high concentration interfaces, elimination of translational freedom by avoiding intermolecular interaction, reduction of rotational relaxation of the excited states of laser dyes, exclusion of inherent problems with physical pumping [7, 8] etc. Moreover, the solid state dye lasers are compact, safe, easy to handle and reliable. The ability to fabricate in the desired shape and low production cost makes the solid state lasers potential candidates in the field of optoelectronics. Thus the study of materials based on laser dye incorporated in solid hosts bears significant technological potential. Keeping that in mind, we have been working on the spectroscopic study of fluorescent dyes in Al $(NO_3)_3$-SiO_2 sol-gel glasses. In the present work, we have fabricated the popular dye Rhodamine B (Rh-B) doped $Al(NO_3)_3$-SiO_2 sol gel glasses and investigated their spectroscopic behavior. The efficiencies of the glasses were evaluated in comparison to the dyes doped samples in methanol. The changes occurred due to their incorporation in the studied glass host in comparison to methanol medium are explained. As the concentration of these active dyes plays a critical role in the device applications of these dye doped matrices, so due emphasis is given on finding the optimum concentration of the dye in the studied host. Modifications that arose due to the change in concentration of the dyes are also explained with the help of single exciton theory [9]

2. EXPERIMENTAL

For the present study, five sets of $Al(NO_3)_3$-SiO_2 sol-gel glass samples were fabricated for five different concentrations of Rh-B (Exciton, USA). The preparation technique details and the volumetric ratio of tetra ethyl ortho silicate (TEOS), $Al(NO_3)_3 9H_2O$, methanol, distilled water and dilute HNO_3 used in the preparation method were used as explained in earlier papers [10, 11]. Following dye concentrations were chosen for the fabrication of the dye doped glass samples.

(1) Sample A: Rh-B ($5x10^{-5}$ M)

(2) Sample B: Rh-B ($1x10^{-4}$ M)

(3) Sample C: Rh-B ($5x10^{-4}$ M)

(4) Sample D: Rh-B ($1x10^{-3}$ M)

(5) Sample E: Rh-B ($5x10^{-3}$ M)

For the Rh-B doped in methanol medium, the dye concentrations were varied from 5×10^{-5} M to 1×10^{-4} M. The glass samples doped with dyes were obtained with high optical quality, without any cracks and striations. Absorption spectra of the samples were recorded by using Shimadzu UV-2600 UV-Visible spectrophotometer (spectral resolution of 1 nm). For the dye doped methanolic solutions, un-doped methanol and for the glass samples, plain glass were used as references for recording the absorption spectra. PL spectra for the samples were recorded by Horiba Jobin Yvon Fluoromax 4P spectrofluorometer (spectral resolution of 1 nm) using 150W CW Xenon lamp as excitation source and photomultiplier tube as detector. The PL spectra were recorded in front face configuration. To minimize the specular relection of the excitation beam on the photomultiplier tube and also to minimize the reabsorption effects, the sample holder was oriented at 60^o with respect to the initial excitation beam direction. All the recordings were done at room temperature.

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3. RESULTS AND DISCUSSIONS

3.1 Absorption Spectra

Fig. 1 shows the absorption spectra for varying concentrations of Rh-B doped in methanol.

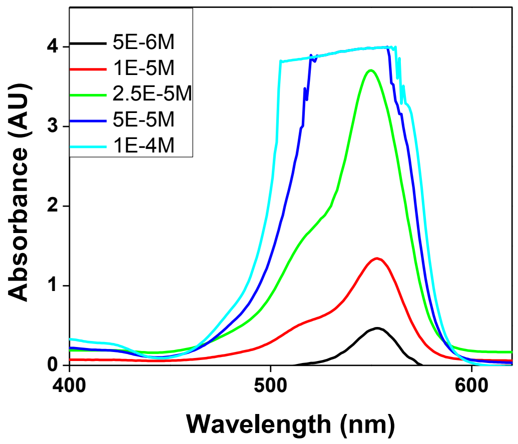

Fig. 1: Absorption spectra for varying concentrations of Rh-B doped in methanol

Strong absorption peaks around the wavelength range of 550-553 nm with a hump around 515nm for Rh-B were observed, that corresponds to $S_0 \rightarrow S_1$ transitions. The absorption intensities show monotonic increase with concentrations due to the increase in the number of dye molecules. For higher concentrations ($\geq 5 \times 10^{-4}$ M), the signal amplitude exceeded the instrument limit. Almost similar peak positions of the absorption spectra for the studied concentrations indicate that there are no or very few dimers formed as the concentration increases.

Fig. 2 represents the absorption spectra for Rh-B doped $Al(NO_3)_3$-SiO_2 sol-gel glass samples by varying the dye concentrations. Absorption maxima for Rh-B doped glasses were observed in the wavelength range 532-586 nm, also arises because of $S_0 \rightarrow S_1$ transitions.

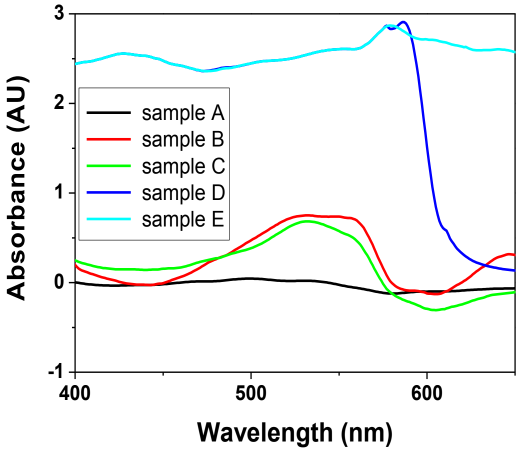

Fig. 2: Absorption spectra for varying concentrations of Rh-B in $Al(NO_3)_3$-SiO_2 sol-gel glasses

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It is observed that the absorption intensities of the glass samples are less in comparison to the dye doped methanolic samples. This decrease in absorption intensity can be attributed to the decrease in vibrations of the amino group attached to the Rh-B molecules in the solid glass matrix in comparison to the methanol medium. Moreover, both red and blue shifted absorption bands in comparison to the methanol medium are observed in the absorption spectra for glass samples. According to single exciton theory [9], these shifting of absorption bands signify the formation of oblique J-dimers when the dyes were incorporated into the glass matrix [12] since in an amorphous solid, monomers and both type of dimers viz. J-dimers and oblique J-dimers are expected. [1]. Similar to the dye doped samples in methanol, the absorption intensities increased on increasing the concentration of dye molecules in glasses as well signifying the enhancement of dimer concentration with the concentration of dye.

3.2. Photoluminescence and Excitation Spectra

Fig. 3(a) and (b) represent the emission intensity variation with the simultaneous variation of excitation and emission wavelengths for the Rh-B: $Al(NO_3)_3$- SiO_2 sol-gel glass. Maximum emission intensities in the range 600 to620 nm with the excitation wavelengths lying in two regions, one around 450 nm and the other between 565 to 580 nm were observed. PLE spectra (shown in Fig. 4) recorded for the peak emission wavelength at 613 nm showed two sharp intensity maxima around 469 and 571 nm excitation wavelengths.

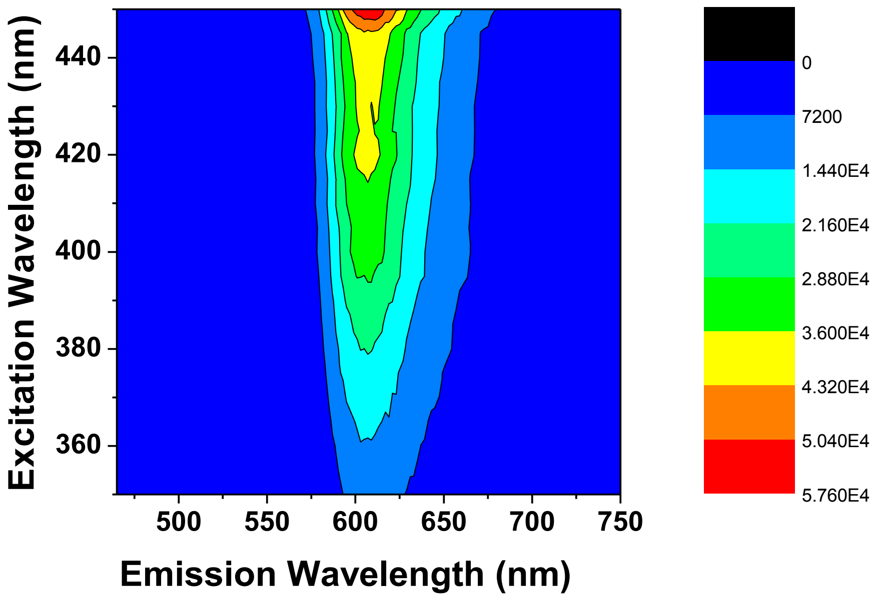

Fig. 3 (a): 3D plot depicting the emission intensity variation with simultaneous variation of emission (465 to 750 nm) and excitation wavelengths (350 to 450 nm) for Rh-B in $Al(NO_3)_3$-SiO_2 sol-gel glass

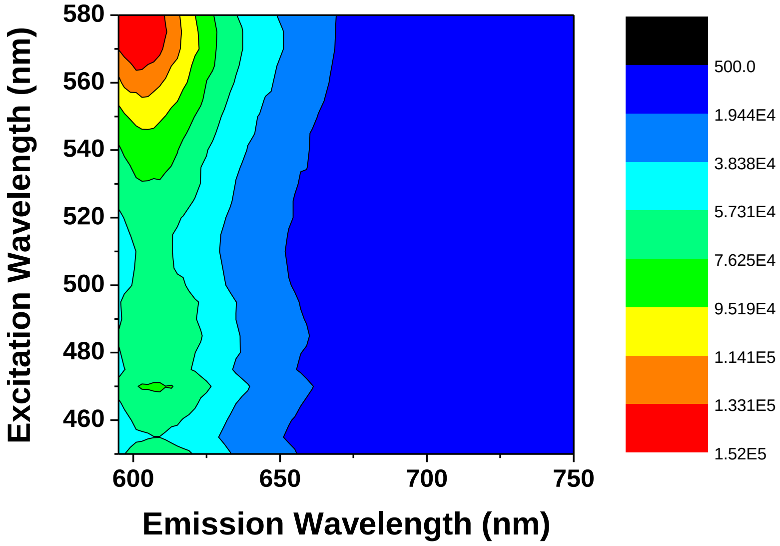

Fig. 3 (b): 3D plot depicting the emission intensity variation with simultaneous variation of emission (595 to 750) and excitation wavelengths (450 to 580 nm) for Rh-B in $Al(NO_3)_3$-SiO_2 sol-gel glass

Based on the 3D plot and PLE spectrum, PL spectra for Rh-B doped glasses were recorded for 469 and 571 nm excitation wavelengths. The respective PL spectra are shown in Fig. 5.

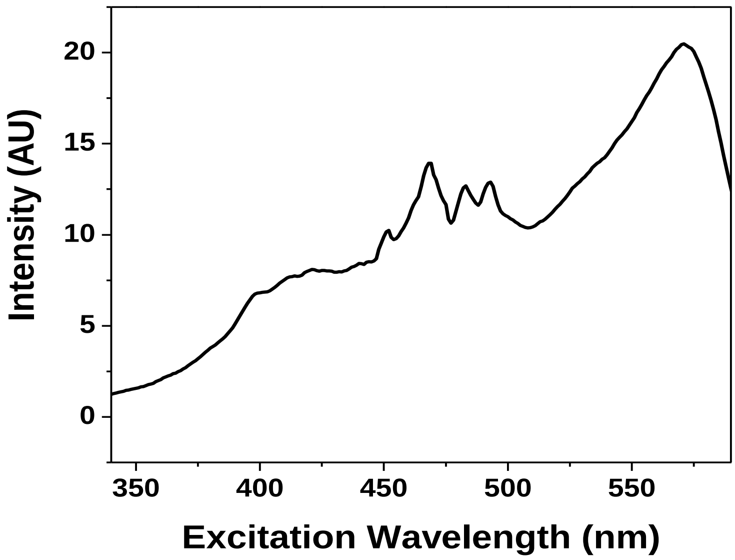

Fig. 4: PL excitation spectra for Rh-B doped $Al(NO_3)_3$-SiO_2 sol-gel glass

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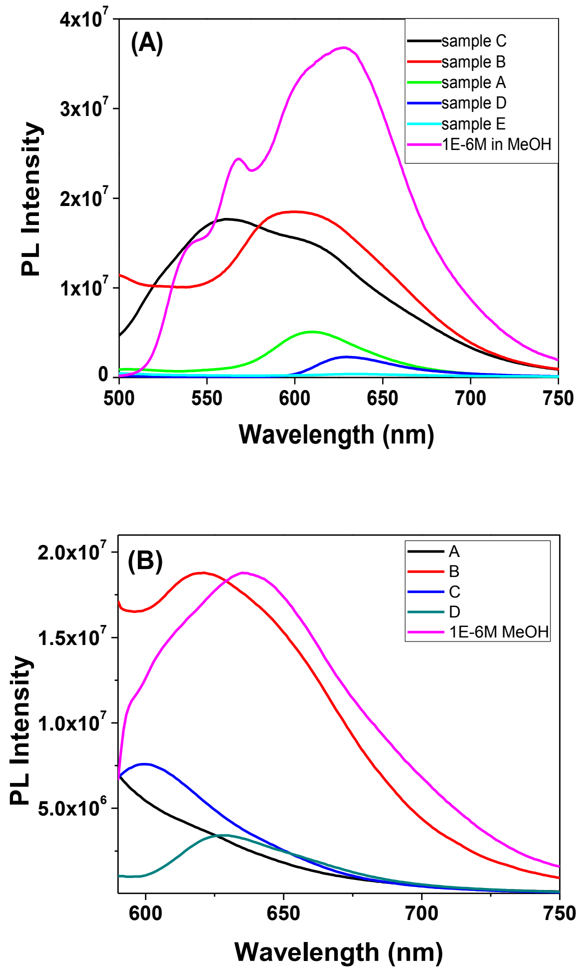

Fig. 5: PL spectra for varying concentrations of Rh-B doped $Al(NO_3)_3$-SiO_2 glasses respectively under (A)469 nm and (B)571 nm excitation wavelengths (PL spectra for Rh-B (10^{-6} M) doped in methanol is also shown for comparison. In 5(B) the PL spectra for Rh-6G (10^{-6} M) doped in methanol is plotted with one fourth the intensity of the original for better comparison)

Study of the observed PL spectra revealed the presence of emission peaks in the wavelength range between 562 and 629 nm depending on the dye concentrations and excitation wavelengths. An initial enhancement of the PL intensity accompanied with a red shift was observed as the concentration of the dye enhanced to 10^{-4}M from $5x10^{-5}$M. The maximum intensity was observed for 10^{-4} M Rh-B concentration which decreases on further increase in concentration to 10^{-3} M. The initial increase in PL intensity and the red shift with increase in dye Rh-B concentration can be attributed to the increase in the polarizability around dye-surrounding environment [13]. This increase in polarisability arises due to the close packing of the dye monomers in dimers and aggregates. The concentration dependent red shift can be correlated to the formation of fluorescent aggregate of the dyes, because fluorescent aggregate of dyes generally show red shift of about 30-50 nm [14, 15]. The result suggests that there was neither the formation of non-fluorescent aggregate nor the concentration quenching up to that concentration [16]. The sharp decrement in PL intensities when the dye concentration was further increased to 10^{-3} M indicates that on increase in the dye concentration no further change in the Rh-B environment had taken place other than just the formation of aggregates that are non fluorescent [17]. This behavior of Rh-B intensity provides direct experimental evidence that both radiation trapping (self absorption and re-emission) and self quenching (migration of excitation energy from excited state molecules to ground state molecules) are equally probable [18] in the studied glasses.

To calculate the relative radiative efficiency of the Rh-B doped glasses, their PL spectra were compared with the PL spectrum of Rh-B doped in methanol and relative quantum yield was calculated. Among the Rh-B doped samples in methanol, highest quantum yield was observed for the dye concentration of 10^{-6} M, hence that sample was used as reference for the determination of quantum yield of the Rh-B doped glass samples.

The observed PL peak wavelengths, their FWHM, PL peak intensities and the quantum yields for the Rh-B doped glasses were determined and are summarized in Table I.

Table I: PL characteristic parameters of Rh-B doped $Al(NO_3)_3$-SiO_2 sol-gel glasses for 469 and 571 nm excitation wavelengths

Conc. of Rh-B (M)	**Peak Wavelength (□$_{PL}$) (nm)**		**FWHM (nm)**		**Peak Intensity (I_{PL}) ($x10^6$) (AU)**		**Quantum Yield**	
	Exc 469nm	**Exc 571nm**	**Exc 469nm**	**Exc 571nm**	**Exc 469nm**	**Exc 571nm**	**Exc 469nm**	**Exc 571nm**
$5x10^{-5}$	609		63		5.09		0.085	
$1x10^{-4}$	598	621	127	79	18.49	18.78	0.501	0.223
$5x10^{-4}$	562	600	137	45	17.65	7.59	0.572	0.057
$1x10^{-3}$	629	628	53	58	2.29	3.42	0.031	0.031
$5x10^{-3}$	…..	…..	…..	…..	…..	…..	…..	…..

It is evident from Table I that the PL peaks show maximum intensities at the Rh-B concentration of 10^{-4} M for both 469 nm and 571 nm excitation wavelengths. The highest quantum yield for 469 nm and 571 nm excitation wavelengths were observed for the Rh-B concentrations of $5x10^{-4}$M and 10^{-4}M respectively. Moreover, equivalent PL peak intensities as well as yields were observed at the Rh-B concentration of 10^{-4} M for both the excitation wavelengths. Thus, the dye concentration of 10^{-4} M shows maximum quantum efficiency for the Rh-B for the $Al(NO_3)_3$-SiO_2 sol-gel glasses. No PL emission peak was observed for the sample with Rh-B concentration of $5x10^{-3}$ M.

4. CONCLUSIONS

In this communication, the spectroscopic behavior of Rh-B doped $Al(NO_3)_3$-SiO_2 sol-gel glasses have been investigated in comparison to the dyes doped in methanol medium. The investigation confirms that 10^{-4} M is the optimum concentration for the dye in $Al(NO_3)_3$-SiO_2 sol-gel glasses for maximum efficiencies in terms of quantum yields and emission intensities. The experimental quantum yield and other radiative parameters clearly suggest that $Al(NO_3)_3$-SiO_2 sol-gel glasses can be a prospective alternative in the search for solid state host for dye lasers and other optical devices.

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