Luminiscent dye Rhodamine 6G doped monolithic and transparent TEOS silica xerogels and spectral properties

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Abstract
Sol–gel process was used for the preparation of Rhodamine 6G (R6G) doped silica xerogels, using tetraethylorthosilicate [TEOS, Si(OC2H5)4] as the precursor for the silica network. Silica alcosol was prepared by hydrolysis and polycondensation of ethanol (EtOH) diluted TEOS in the presence of citric acid (CTA) catalyst. The ethanolic R6G was added to the alcosol to trap R6G molecules inside the SiO2 gel network during the gelation of the TEOS alcosol. The effect of CTA/TEOS molar ratio on the gelation time of the R6G doped TEOS alcosol, transparency and monolithicity of the R6G doped silica xerogel was studied by varying the CTA/TEOS molar ratio from $1.2 \times 10^{-4}$ to $180 \times 10^{-4}$ by keeping the molar ratios of TEOS:EtOH:H₂O:R6G constant at $1:5:7:9.2 \times 10^{-2}$, respectively. It was found that the minimum ($\approx 70$ h) gelation time was observed at higher and lower CTA/TEOS molar ratios of $72 \times 10^{-4}$ whereas maximum ($\approx 180$ h) gelation time was observed for CTA/TEOS molar ratios of $1.2 \times 10^{-4}$. While opaque and monolithic R6G doped SiO2 xerogels were obtained for $4.8 \times 10^{-4}$ CTA/TEOS molar ratios, whereas cracked and transparent xerogels were obtained for $120 \times 10^{-4}$ molar ratios of CTA/TEOS. Transparent, homogeneous and monolithic samples were obtained between $4.8 \times 10^{-4}$ and $120 \times 10^{-4}$ of CTA/TEOS molar ratios. Leaching out property was studied by using water, methanol and ethanol solvents for the R6G doped SiO2 xerogels of $9.2 \times 10^{-2}$ and $12 \times 10^{-4}$ of R6G/TEOS and CTA/TEOS molar ratios, respectively, and found that R6G molecules were trapped in the pores of the SiO2 network.

Bleaching out phenomena of the R6G doped SiO2 xerogels was studied by focusing the high intensity light on some part of the samples for a period of 1 h and found that the pores were continuous in SiO2 network. Visible spectra of R6G in water, ethanol, SiO2 alcosol and xerogel were taken for $1.6 \times 10^{-2}$ M R6G and observed that there were two absorption peaks at 499 and 525 nm in the spectrum of R6G in water due to dimerization of R6G molecules and only one absorption peak at 530 nm in the spectra of ethanol, SiO2 alcosol and xerogel because of monomerization of R6G molecules. Visible spectra of the R6G doped silica xerogels for varying R6G/TEOS molar ratios from $9.2 \times 10^{-8}$ to $9.2 \times 10^{-5}$ were taken and found the red shift (5–10 nm) with increasing the R6G/TEOS molar ratio from $9.2 \times 10^{-8}$ to $9.2 \times 10^{-5}$. The effect of temperature on these sample was studied by varying the temperature from 50 to 300 °C and found that the R6G doped silica samples were stable up to 200 °C. IR spectra were taken for pure R6G powder and R6G doped silica xerogels of $9.2 \times 10^{-8}$ and $9.2 \times 10^{-5}$ R6G/TEOS molar ratios and found that most of the peaks present in pure R6G powder spectrum were absent in the spectra of trapped R6G SiO2 xerogels. This shows that, the SiO2 network hinders the rotational and vibrational transitions of R6G when it is caged in the SiO2 network. The peaks related to bending motion in R6G molecules were not disturbed by the SiO2 network.

Keywords: Xerogel; Monolithic; Rhodamine

1. Introduction
The new field of non-linear optics and photonics offers tremendous opportunities for material scientists. The chemical processing of sol–gel methods provides new multifunctional ceramic materials of photonics. The sol–gel process is used to incorporate the optically active organic molecules in the inorganic matrices. The chemical synthesis of sol–gel process is performed around room temperature, so that the organic dye molecules can easily be incorporated into the oxide gel matrix without dissociation. In this process, the components are mixed...
at a molecular level and hence the synthesis of metastable phases can be obtained. Inside the amorphous matrices a large amount of luminiscent probe can be incorporated without fluorescence quenching. Doping of organic laser dye in a solid matrix which has pore size in the range of <20 nm is a key process in controlling a variety of material characteristics especially optical properties. Organic dyes are superior to inorganic dyes from the point of view of intensity of light absorption which is usually much higher and from the point of view of the very wide diversity (tens of thousands) of available organic dyes. The organic dye doped solid matrices have a number of important applications such as light guide lasers [1], luminiscent solar concentrators [2–4], glasses with reduced solar heat transmission [5–7] and imaging detectors [8–10]. Rhodamine 6G (R6G) has been one of the most frequently used in probes in these studies due to its high quantum yield in fluorescence (absorption and emission) in the visible (500–600 nm) range. One of the major problems in the research studies and application of organic laser dyes is the network, which hosts the dye because the nature of network affects all the characteristics of the dye, e.g. it causes the spectral shifts both absorption and emission, affects the photo stability and alters the distribution between processes of the excited state, may undergo, such as inter-system crossing colloidal energy loss and consequently fluorescence life time. The solid matrices containing R6G and other fluorescent organic dye may be grouped into four categories: (1) high surface area powdered materials in slurries or as colloids such as R6G adsorbed on clays [11,12], (2) high surface area porous glass such as fluorescent organometallic compounds adsorbed on Vycor porous glass and on disks of compressed fumed silica [13–15], (3) thin films in which the dye is homogeneously distributed [4,16], (4) monolayers and sub monolayers of low surface area supports [17–19].

In our present study, we described systematically the preparation of R6G doped TEOS silica xerogels by using the low temperature sol–gel process for SiO2 matrix using tetraethylorthosilicate [TEOS, Si(OC2H5)4] as a precursor. In the presence of ethanolic medium and citric acid (CTA) catalyst, TEOS formed SiO2 network in which the R6G laser dye was doped uniformly. The experiments were carried out to get the monolithic, transparent, homogeneous R6G caged SiO2 xerogels by varying the CTA/TEOS, R6G/TEOS molar ratios. Effect of temperature on these samples was studied by varying the heating temperature from 50 to 300 °C. Bleaching out property was examined by focusing the high intensity sun light on the samples. Leaching properties were tested with water, methanol and ethanol solvents for these R6G doped TEOS silica xerogels. Finally the UV–visible and infra red spectral studies were carried out for these samples with the variation of R6G/TEOS molar ratios.

2. Experimental procedures

2.1. Preparation of R6G caged TEOS silica xerogels

In the first step of the preparation of the samples, the TEOS precursor hydrolyzed completely in the presence of ethanolic medium using CTA catalyst. All the chemicals, i.e. TEOS, EtOH, CTA from Fluka of Pursis, Switzerland, R6G from Lobo Company, India, and triple glass distilled water were used in the experiments. In the beginning of the process the TEOS silica alclosol was prepared by keeping the molar ratios of TEOS/EtOH/H2O at 1:5:7 and molar ratio of CTA/EtOH was varied from 1.2 × 10−6 to 180 × 10−6. The mixture was stirred thoroughly until the entire mixture became clear and transparent. In the second step, the ethanolic solution of R6G was added to the mixture with molar ratio of R6G/TEOS of 9.2 × 10−6 and again stirred thoroughly until to get homogeneous mixture. The alclosol was transferred to polyethylene (PE) tubes or boxes and hermetically closed to prevent the evaporation of ethanol. After the gelation, the silica gels were kept for 5 days to strengthen and to reduce the cracks in the alcogel. Slow drying was carried out by making pin holes in the lid of the PE containers and left at room temperature. When the volume of R6G doped silica alcogels became 1/3 of its original volume, these dried gels were removed from the PE containers and heated at the temperature of 100 °C by using PID controller and kept at 100 °C for 2 h for complete removal of residual solvents from the R6G doped silica xerogels.

2.2. Characterization

The optical properties of the R6G doped silica xerogels were studied using ultraviolet visible (UV–visible) spectrophotometer in the range of 200–3200 nm of U-3200 Hitachi and IR spectral studies with infra red spectrophotometer of Perkin–Elmer ranging from 200 to 4000 cm−1. Effect of temperature on the stability of the R6G doped silica xerogels was studied in the temperature range of 50–300 °C by using the Eurotherm temperature controller, England. Sun light was focused on the samples to study the bleaching effect.

3. Results and discussion

In the process of synthesis of R6G laser dye doped silica xerogels, TEOS was used because it gets easily hydrolyzed and condensed in the presence of an acid catalyst giving rise to transparent and homogeneous alcogel within 3 days. The transparency and monolithicity of the silica xerogels were not affected much by doping R6G molecules but the color change was observed. The effect of CTA/TEOS, R6G/TEOS molar ratios and temperature on the absorbance,
transparency, monolithicity and on the other physical properties have been studied.

3.1. Effect of CTA/TEOS and R6G/TEOS molar ratios

It appeared that at a given temperature, the gelation process strongly depended on the respective molar ratio of alkoxide, H₂O, catalyst, ethanol and R6G. We thus tried to check the influence of each parameter separately by modifying the molar ratio of single reagent with respect to TEOS while keeping the other parameters constant. To find out the effect of CTA/TEOS molar ratio on the gelation time of the alcogel, monolithicity and transparency of R6G doped xerogels, the CTA/TEOS molar ratio was varied from 1.2 \times 10^{-4} to 180 \times 10^{-4} (2 \times 10^{-4} to 2.5 \times 10^{-2} M) by keeping the molar ratio of TEOS/EtOH/H₂O/R6G constant at 1:5:7:9.2 \times 10^{-6}, respectively. In our previous studies [20], it was explained that transparent TEOS alcogels were obtained with the molar ratio of TEOS/EtOH/H₂O at 1:5:7 in the acidic medium. The same conditions were used in our present study also. Fig. 1 shows the dependence of gelation time of R6G doped silica alcogel with variation of CTA/TEOS molar ratios from 1.2 \times 10^{-4} to 180 \times 10^{-4}. It was observed from the figure that the gelation time was minimum (<70 h) for the higher and lower molar ratios of CTA/TEOS of 72 \times 10^{-4} where as it was maximum (>180 h) for CTA/TEOS molar ratio of 72 \times 10^{-4}. This is because at lower molar ratios of CTA/TEOS 72 \times 10^{-4}, the rate of condensation over compensates the increased surface charge of all ions in the sol and provides for faster gelation [21]. On the other hand at higher molar ratios >72 \times 10^{-4} of CTA/TEOS, hydrolysis and condensation rates are high which leads to decrease in the surface charge of all ions in the sol and hence faster gelation [22–24]. Where as in the case of CTA/TEOS molar ratio of 72 \times 10^{-4}, the gelation time was maximum (>180 h) because in the CTA/TEOS molar ratio the condensation and polymerization would occur with very slow rates leading in longer gelation times. The sol–gel process of Si(OCH₃)₄ is usually performed via hydrolysis and polycondensation of Si(OCH₃)₄ in the presence of an acid catalyst. Acids are supposed to increase the lability of protonated OR groups and favored the electrophilic substitutes [25–27]. In the presence of strong acids such as HCl, HNO₃ and H₂SO₄, the R6G molecules are dimerized which leads to hindrance of luminescent nature of R6G where as in the case of citric acid even though the CTA/TEOS molar ratio is maximum (>180 \times 10^{-4}) dimerization of R6G was not found in the R6G doped TEOS alcogels. So to retain the luminescent property of R6G, CTA catalyst was used for the synthesis of laser dye R6G doped TEOS silica xerogels.

With respect to transparency and monolithicity of R6G doped silica alcogels and xerogels, turbid alcogels and opaque and monolithic xerogels were obtained for CTA/TEOS molar ratios of <4.8 \times 10^{-4} where as transparent and cracked alcogels and xerogels were obtained for CTA/TEOS molar ratios of >120 \times 10^{-4}. This is because at lower CTA/TEOS molar ratios due to presence of insufficient catalyst, the hydrolysis and condensation process did not occur completely, which leads to formation of silica precipitates, producing the turbid alcogels and opaque R6G doped xerogels, where as in case of high CTA/TEOS molar ratio >120 \times 10^{-4} fast hydrolysis, condensation and polymerization leads to highly cross linked, branched structure forming more compact network resistive to shrinkage causes cracks [28–30]. Even though the gelation was less for lowest (<4.8 \times 10^{-4}) and highest (>120 \times 10^{-4}) CTA/TEOS molar ratios, the obtained R6G doped silica alcogels, and xerogels were either opaque or cracked. Monolithic and transparent R6G doped silica alcogels and xerogels were obtained for the molar ratio CTA/TEOS between 4.8 \times 10^{-4} and 120 \times 10^{-4}. So further studies were carried out with 12 \times 10^{-4} molar ratio of CTA/TEOS.

It was found from the effect of R6G/TEOS molar ratio on gelation time that the variation of R6G/TEOS molar ratio from 9.2 \times 10^{-5} to 9.2 \times 10^{-5}, had no effect on the gelation time of the R6G doped silica alcogels. This is because very dilute R6G solutions (<10^{-4} M) were used in the process which had no effect on the change in the viscosity of alcogel during gelation. Almost similar gelation times were obtained for the entire range of R6G/TEOS molar ratios from 9.2 \times 10^{-5} to 9.2 \times 10^{-5}.

![Fig. 1. Change in the gelation time of TEOS alcogels with the variation of the CTA/TEOS molar ratios.](image-url)
3.2. Effect of drying

Effect of drying on the volume change of R6G doped silica alcogels was studied by keeping the R6G/TEOS and CTA/TEOS molar ratios constant at $9.2 \times 10^{-6}$ and $12 \times 10^{-4}$, respectively, and the results were shown in Fig. 2. From the figure it was found that the rate of volume decrease was fast in the beginning, because of fast evaporation of ethanol present in the R6G doped silica alcogel as if that in the beginning, the alcogel contains bigger holes so that the ethanol comes out easily. The polycondensation reaction leads to contraction of the R6G doped SiO$_2$ matrix which occurs with the vaporization of the alcohol until the gel was dry and solid. As the gel shrinks the polymerization or particles pack together more closely and their mobility consequently decreased. In addition shrinkage may bring reactive alkoxy and hydroxy groups together allowing new chemical bonds to form the stiffen structure. Kinetics of shrinkage of R6G doped xerogels depends on the important processes of evaporation of pore liquid, flow of pore liquid and contraction of the solid phase. Drying is the main problem in the sol–gel technology. To produce large monolithic bodies it is necessary to apply very slow drying rates. So from Fig. 2, it was found that the rate of decrease in volume of the R6G doped silica alcogels was very low after 15 days of drying and there was no change from 20 days onwards. At this stage, it was found that the volume of R6G doped xerogels was almost 1/3 of its original volume and there was no alcohol evaporation because the dried gel contains very small pores, so the residual alcohol finds it difficult to come out of the pores easily. It was observed that there was not any further decrease in the volume of R6G silica dried gels even when they were kept at room temperature for 2 or 3 months. Interesting result was that there was an accountable volume change, i.e. there was a decrease in volume of the R6G doped silica dried gels from 1/3 to 1/4 of its original volume when they were heated at 100 °C for 2 h. Due to heating at high temperature the remaining alcohol acquired sufficient energy to come out of the pores even though the pore size is small in the R6G doped silica dried gels. The resulted R6G silica xerogels were optically clear and glassy in nature and did not require prior polishing for detailed optical measurements.

3.3. Bleaching out effect

The average pore sizes (2–6 nm) in the TEOS silica network is slightly greater than the steric volume of R6G molecules. Hence we assume that the porosity of sample is open with respect to the doping of R6G laser dye molecule. The pores in the silica xerogel network are interconnected, so R6G molecules can migrate from one pore to the other easily. This was confirmed by doing the following experiment that by focusing high energy sun light on a small area of R6G doped silica xerogel of $9.2 \times 10^{-6}$ and $12 \times 10^{-4}$ of R6G/TEOS and CTA/TEOS molar ratios, respectively, for a period of 1 h. It was found that the focused part of the sample was bleached due to the high energy of light and it remained colorless as shown in the Fig. 3a. The sample regained homogeneous coloration by 2 days in the absence of sunlight. This observation shows that R6G doped silica xerogel has continuous porosity and this makes the R6G molecules move from the pores of the focused part to the pores of the normal state causing empty pores in the focused part and in a few days in the absence of sun light the R6G molecules migrate to the emptied pores.

![Fig. 2](image2.png)  
Fig. 2. Change in the volume of the TEOS alcogel with the drying period.

![Fig. 3](image3.png)  
Fig. 3. Change in the R6G color distribution in the R6G doped xerogel by focusing the high energy radiation and regeneration of the sample homogeneity.
so homogeneous coloration is obtained in the samples as shown in Fig. 3b. Thus in this type of R6G doped silica xerogel it can be presumed that the movement of the organic molecule is more or less impeded. This experiment explained that the porosity in the R6G doped silica xerogels was continuous throughout the xerogel network therefore R6G molecules can move in the silica matrix.

3.4. Property of leachability

To find out whether the R6G doped silica xerogels were leachable with any solvent, the samples were immersed in leaching solvents such as water, methanol and ethanol for a period of 1 month. It was observed that even after a month there was no coloration to any of the solvents because equilibrium between the solvent and R6G doped silica xerogel did not occur. It is thus confirmed that the R6G molecules were completely trapped in a surrounding rigid cage of the pore [31] with rigid pore entrances of diameter smaller than the effective diameter of ethanol or H2O of 4 Å [32]. From these results and observations, it was established that the R6G dye molecules are indeed incorporated within pores of the bulk network of SiO2 and not adsorbed on the exposed walls of the pores. If they were adsorbed on the exposed walls of the pores, the equilibrium would be obtained quickly by immersing them in solvents and the solvent becomes colored. The colorization of solvents did not occur when R6G doped silica xerogels were immersed in solvents. So finally it was concluded that the R6G molecules are able to trap in the pores of the three dimensional SiO2 network uniformly, homogeneously, which is very important because many photo physical properties depended on the fact that R6G molecule should be caged in the pores of the solid matrix, and should not be adsorbed on the surface of the pores of the silica matrix. This property was confirmed only by performing dye leaching test.

3.5. UV–visible spectral properties

For retaining the luminiscent properties of fluorescent R6G organic dye, it is necessary to observe the UV–visible spectra of the R6G dye in the free state and trapped form in the silica network. Fig. 4 shows the UV–visible spectra of the pure silica, R6G in water, ethanol, silica alcogel and xerogel at the concentration of R6G at 1.6 \times 10^{-4} M. It was observed that there were two peaks in the spectrum of R6G in water, one was a high intense peak at 499 nm and another low intensity peak at 525 nm, which were related to dimerization and monomerization of R6G molecules, respectively. The reason is that due to the high polar nature of the water, it causes aggregation [33–35] in R6G molecules, so intense peak at 499 nm was obtained in the spectrum of the R6G in water. Only one peak was observed at 530 nm and absence of peak at 499 nm in the spectra of R6G in ethanol, silica alcogel and xerogel. This explains that due to less polar nature of ethanol, silica alcogel and xerogel than water, they reduce or hinder the dimerization or aggregation of R6G molecules. And also solvent dielectric constants as a stabilizing force, reducing columbic repulsion [36] causes the monomerization of R6G molecule in SiO2 network. Drexhage and Reynolds [37] argued that higher the hydrophobicity of the dye greater the tendency to form aggregates. Consequently a polycation organic species such as R6G dimer, dication is more easily water-soluble than monocation organic dye species. It was found that there is no spectral interference to SiO2 network by doping R6G as shown in the Fig. 4. R6G is a laser dye which belongs to the Xanthene family. Their optical properties (absorption–luminiscence) result in \( \text{P}^2 \rightarrow \text{P}^0 \) transition arising from delocalized II electrons. Conjugated polymers with extensive II electron delocalization have emerged as our important class of third order non-linear optical materials because II electrons make a large contribution to optical non-linearity. UV–visible spectra of individual and compounds indicates, that there is quantitative conversion of R6G to conjugated structure with SiO2 matrix. It leads to a strong absorption peak located at 530 nm. The aggregation and dimerization reduces significantly the fluorescence quantum yield and laser properties of the dyes [38–40]. It is therefore important to notice that dimerization is greatly reduced by trapping R6G molecules in the solid matrix even though the concentration of R6G are quite high >10^{-3} M (R6G/TEOS = 9.2 \times 10^{-6}). This deaggregation trend confirm that the polarity of oxide cage is lower than water [1] and the isolation of trapped R6G molecules [41].
Deaggregation of R6G molecules in SiO2 matrix is superior in many aspects when compared to organic carriers. The inorganic oxides are photochemically and thermally stable. This is an important factor when the photoactive molecules are incorporated since the excited states of R6G are unable to react with surroundings. The polymer network should be more rigid, so this restricts great extent of rotational and even transitional (diffusional) freedom of organic dye. In the silica network there are two types of silica groups that form the wall of the silica glass cage. Silanols Si–OH and siloxane Si–O–Si [31], both these groups have indeed lower polarity and higher hydrophobicity than water. The silica cage may be regarded as hydroxyl relative polar environment less polar than water. In these surroundings the R6G laser dye is prone to monomerization than dimerization which makes the R6G doped silica xerogels luminiscent.

The visible spectra of R6G doped silica xerogels with the variation of R6G/TEOS molar ratios from $9.2 \times 10^{-8}$ to $9.2 \times 10^{-5}$ were taken and shown in Fig. 5. It was found from the spectra of the samples that the absorbance increased with increase of the R6G/TEOS molar ratio from $9.2 \times 10^{-8}$ to $9.2 \times 10^{-5}$ and the peak related to dimerization of R6G molecules was not observed even for molar ratio of R6G/TEOS of $9.2 \times 10^{-5}$. It was observed the red shift of 5–10 nm in the wavelength of absorption maxima with the increase of R6G/TEOS molar ratio from $9.2 \times 10^{-8}$ to $9.2 \times 10^{-5}$. This desirable increase in wavelength of absorption maxima shed more light on the silica cage. This red shift may be attributed to a specific absorption of excited state of dye molecules on the polymeric oxide network. Such a phenomena leads to stabilization of excited state arising from restricted freedom of rotational moments of the dye. These red shifts may be interpreted as reflecting, decrease in the dipole moment of the excited molecule [42]. Apparently restricted motion of silica walls and of the dye are suffered for the desired stabilization of mutual reorientation. As the dye concentration increases with increase of R6G/TEOS molar ratio, the pores of the gel become more and more crowded with R6G molecules and as a different conjugation thus adopted by the dyes. Transparent, monolithic and homogeneous R6G doped silica xerogels were obtained throughout the variation of R6G/TEOS molar ratio from $9.2 \times 10^{-8}$ to $9.2 \times 10^{-5}$.

### 3.6. Effect of temperature

To find out the thermal stability of the R6G doped silica xerogels, the sample of molar ratios of CTA/TEOS and R6G/TEOS of $12 \times 10^{-4}$ and $9.2 \times 10^{-6}$, respectively, was heated at various temperatures ranging from 50 to 300 °C by PID controller with temperature raise of 30 °C/h. The absorption spectra of the R6G doped silica xerogel was taken with varying temperatures from 50 to 300 °C and shown in Fig. 6. From figure it was found that there was no change in the absorbance of the sample for temperature $<200$ °C and the absorbance started to decrease with temperature increase $>200$ °C and negligible absorbance.
was found at the temperature of 275 °C. This explains that there was no change in the R6G concentration in the silica xerogel up to 200 °C and R6G molecules started to dissociate and evaporate from the silica network with raise of temperature > 200 °C and completely came out of the SiO₂ network for the temperature of 275 °C leaving the pure SiO₂ xerogels resulting in colorless samples. So it was concluded that R6G doped silica xerogels are thermally stable up to the temperature of 200 °C.

3.7. Infrared spectral studies

To find the structural changes of R6G molecules when they were trapped in the SiO₂ three dimensional solid network, the infrared spectra of pure R6G powder sample and R6G doped silica xerogels of R6G/TEOS molar ratios of 9.2 × 10⁻⁸ and 9.2 × 10⁻⁵ were taken in the spectral range from 200 to 4000 cm⁻¹ and as shown in Fig. 7 (excluding the SiO₂ spectrum). It was observed that there were many peaks in the IR spectrum of pure R6G powder. In the literature the complete IR spectral studies has not been reported, only a few data on vibrational frequencies are available [43,44]. The spectrum contains the peaks at 246, 272, 371, 388, 405, 459, 522, 569 cm⁻¹ related to torsional bending of ring, 614, 630, 662 cm⁻¹ to C–C–C ring in plane bending, 776, 980, 1096 cm⁻¹ to C–H out plane bending, 1131, 1187, 1204 cm⁻¹ to C–H in plane bending and C–C stretching, 1271 cm⁻¹ to C–O–C stretching, 1312, 1365, 1446 cm⁻¹ to aromatic C–C stretching and C–N stretching, 1509, 1575 and 1652 cm⁻¹ to aromatic C–C stretching. These were in good agreement with the literature of Baranov and Babavich. The assignment of bands was based on the proposals in the literature [43,44]. It was found from the spectra of R6G doped silica xerogel that the absence of peaks in the entire region except in the 600–800 cm⁻¹ are due to bending modes of carbon skeleton. The intensity of these peaks increased slightly with the increase of R6G/TEOS molar ratio from 9.2 × 10⁻⁸ to 9.2 × 10⁻⁵. The disappearance of most of peaks in the R6G doped xerogel is due to that by trapping of R6G in three dimensional SiO₂ network, most of the stretching and vibrational modes were hindered. The aromatic stretching vibrations at 1365, 1509, 1575 and 1652 cm⁻¹ decreased to almost zero. The bands related to torsional bending of the ring, C–H out plane bending, C–H in plane bending, C–O–C stretching, C–C aromatic stretching almost disappeared. The stretching vibration band of carbonyl which was at 1700–1750 cm⁻¹ could not be observed in the R6G doped xerogel infrared spectrum. It is interesting to note that the C–H stretching vibration which are active in pure R6G, could be found inactive in R6G doped silica xerogels. All these observations explains that the bonds which were active in the free R6G molecule, were inactive because of confinement of R6G molecule in the holes of SiO₂ network which diminishes the vibrational and stretching modes of transitions of R6G molecule. On the other hand, the bands at

![Fig. 7. IR spectra of pure R6G powder and R6G doped silica xerogels for various R6G/TEOS molar ratios.](image-url)
The effect of CTA catalyst was studied by varying the sol and trapped when the alcosol turned to alcogel. TEOS underwent hydrolysis and polycondensation at room temperature in the presence of CTA catalyst and ethanol R6G was added to the TEOS silica alcosol so that it could be homogeneously distributed throughout the sol and trapped when the alcosol turned to alcogel. The effect of CTA catalyst was studied by varying the CTA/TEOS molar ratio from $1.2 \times 10^{-4}$ to $180 \times 10^{-4}$ by keeping the molar ratio of TEOS/EtOH/H$_2$O/R6G constant at $1.5:7:9.2 \times 10^{-6}$, respectively. It was found from the gelation times of R6G doped TEOS silica alcosol that low gelation times (<70 h) were obtained for higher and lower CTA/TEOS molar ratios of $72 \times 10^{-4}$. Where as maximum gelation time (>180 h) obtained for CTA/TEOS molar ratio of $72 \times 10^{-4}$. Turbid R6G doped silica alcogels and opaque xerogels were obtained for $<4.8 \times 10^{-4}$ of CTA/TEOS molar ratio where as transparent and cracked R6G doped TEOS alcogels and xerogels obtained for the $>120 \times 10^{-4}$ of CTA/TEOS molar ratios. Monolithic, transparent and homogeneously R6G distributed silica alcogels and xerogels were obtained for the CTA/TEOS molar ratios between $4.8 \times 10^{-4}$ and $120 \times 10^{-4}$. Bleaching out property was carried out to find whether the porosity in silica network was continuous or closed by focusing the high intensity sun light in the particular point on the R6G doped silica xerogel of $9.2 \times 10^{-6}$ and $12 \times 10^{-4}$ of R6G/TEOS and CTA/TEOS molar ratios, respectively, for a period of 1 h. It was observed that a colorless dot appeared at the place of focusing sun light, due to the movement of R6G molecules from focused pores to non-focused pores. The samples regained the homogeneous coloration with in 2 days due to returning of the R6G molecules to emptied pores because of continuous porosity of the SiO$_2$ network.

Leaching property of the sample of $9.2 \times 10^{-6}$ and $12 \times 10^{-4}$ molar ratios of R6G/TEOS and CTA/TEOS, respectively, was studied by immersing the sample in leaching out solvents, i.e. water, methanol and ethanol and found that the equilibrium between the R6G doped silica xerogel and solvent was not obtained even for a period of one month, i.e. coloration in the solvent did not occur. This shows that the R6G molecules were trapped or caged in the pores of three dimensional silica network and they were not adsorbed over the surfaces of silica xerogel.

UV–visible spectra of R6G in water, ethanol silica alcogel and xerogel were taken and found that there were two peaks, one was intensive peak at 499 nm another was weak peak at 525 nm in the R6G water spectrum and only one peak at 530 nm in the spectra of R6G in ethanol, alcogel and xerogel spectra. This explained that there is a strong aggregation of R6G molecules in water leading to strong absorbance at 499 nm. Where as in case of R6G molecules in ethanol, alcogel and xerogel, monomerization of R6G molecules occurs therefore the strong absorption band at 530 nm obtained and these samples were fluorescent. Visible spectra of samples with increasing R6G/TEOS molar ratio from $9.2 \times 10^{-8}$ to $9.2 \times 10^{-5}$ were taken and found that there was red shift of 5–10 nm in wavelength of absorbance maxima of the R6G doped silica xerogels with increasing the R6G/TEOS molar ratio from $9.2 \times 10^{-8}$ to $9.2 \times 10^{-5}$. Temperature effect on the thermal stability of R6G doped silica xerogels were studied by heating the sample with the molar ratios of $9.2 \times 10^{-6}$ and $12 \times 10^{-4}$ of R6G/TEOS and CTA/TEOS, respectively, with variation of temperature from 50 to 300 °C with the heating rate of 30 °C/h. It was found that the R6G doped silica xerogels were thermally stable up to the temperature <200 °C and with increase in temperature >200 °C, decoloration started and became colorless by the temperature of 275 °C. Absorption spectra of the sample of different temperatures were taken and found that there was no change in absorbance of the sample up to 200 °C and then decreased the absorbance to negligible for 275 °C.

IR spectra of the pure R6G powder and R6G doped silica xerogels of $9.2 \times 10^{-8}$ and $9.2 \times 10^{-5}$ R6G/TEOS molar ratios were taken and found from the spectra that most of the peaks related to stretching vibrational modes of the bands of R6G molecules that were present in the IR spectra of pure R6G powder were absent in the IR spectra of R6G doped silica xerogels. Because by trapping the R6G molecule in the condensed and closely packed three dimensional network of SiO$_2$ matrix almost all the vibrational, stretching modes were diminished, i.e. the SiO$_2$ network hindered the stretching movements of the bonds of the R6G molecule. The peaks related to bending of the molecule (600–800 cm$^{-1}$ range) remained unchanged. The intensity of these peaks increased with increase of R6G/TEOS molar ratio as observed in the IR spectra.

4. Conclusions

Because of the importance of the optical properties of the organic laser dye doped silica solid materials, sol–gel method was used for the synthesis of R6G laser doped SiO$_2$ matrix using TEOS as a precursor. The elastic TEOS underwent hydrolysis and polycondensation at room temperature in the presence of CTA catalyst and ethanol R6G was added to the TEOS silica alcosol so that it could be homogeneously distributed throughout the sol and trapped when the alcosol turned to alcogel. The effect of CTA catalyst was studied by varying the CTA/TEOS molar ratio from $1.2 \times 10^{-4}$ to $180 \times 10^{-4}$ by keeping the molar ratio of TEOS/EtOH/H$_2$O/R6G constant at $1.5:7:9.2 \times 10^{-6}$, respectively. It was found from the gelation times of R6G doped TEOS silica alcosol that low gelation times (<70 h) were obtained for higher and lower CTA/TEOS molar ratios of $72 \times 10^{-4}$. Where as maximum gelation time (>180 h) obtained for CTA/TEOS molar ratio of $72 \times 10^{-4}$. Turbid R6G doped silica alcogels and opaque xerogels were obtained for $<4.8 \times 10^{-4}$ of CTA/TEOS molar ratio where as transparent and cracked R6G doped TEOS alcogels and xerogels obtained for the $>120 \times 10^{-4}$ of CTA/TEOS molar ratios. Monolithic, transparent and homogeneously R6G distributed silica alcogels and xerogels were obtained for the CTA/TEOS molar ratios between $4.8 \times 10^{-4}$ and $120 \times 10^{-4}$. Bleaching out property was carried out to find whether the porosity in silica network was continuous or closed by focusing the high intensity sun light in the particular point on the R6G doped silica xerogel of $9.2 \times 10^{-6}$ and $12 \times 10^{-4}$ of R6G/TEOS and CTA/TEOS molar ratios, respectively, for a period of 1 h. It was observed that a colorless dot appeared at the place of focusing sun light, due to the movement of R6G molecules from focused pores to non-focused pores. The samples regained the homogeneous coloration with in 2 days due to returning of the R6G molecules to emptied pores because of continuous porosity of the SiO$_2$ network.

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