Synthesis and spectral investigations of kiton red-620 doped silica based materials

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Kiton red-620 impregnated transparent glasses in rod shape (length ~40mm, dia ~10mm) have been prepared by sol-gel route. The trapping of Kiton red-620 laser dye with different concentrations has taken place during the polymerization of silica-gel matrix. The prepared samples have been characterized by spectroscopic techniques such as FTIR, UV-visible, photoluminescence spectroscopy and scanning electron microscopy. The analysis of FTIR spectra shows that the dye molecules are embedded in the pores of silica gel. UV-visible study reveals that an absorption peak has been observed at about 570 nm. It has been observed that the laser dye doped silica gel rods showed sharp fluorescence peak in the visible region having red shift with concentrations. SEM micrographs exhibited that the particles of dye are embedded in the pores of silica based rods. Kiton red-620 dye doped silica based materials explore the possibility of new tunable dye lasers.

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1. Introduction

Laser dye doped materials are used in many potential applications such as optics, electronics, photodynamic therapy, spectroscopy, isotopes separation, non-linear optics, dye chemistry, materials processing, birthmark removal, atmospheric and underwater sensing, local area communications network, sensors and biomedical applications etc.[1-4] The incorporation of organic dye molecules in the silica gel matrix can explore new possibilities in the development of solid state dye laser materials. Dye lasers have drawn attention to the materials having valuable properties like continuous and wide range tunability with different laser dyes, ranging from near-UV to near-IR regions. The tunability of a dye laser is a result of broadened electronic levels which is the characteristic of organic dyes**.** Ferrer et al. [5] have reported absorption process of sulforhodamine B dye in sol-gel silica glasses through fluorescence study. He observed that there is the formation of fluorescent J-dimers with different dye concentrations in porous sol-gel silica matrix. Although various methods have been used to develop this type of materials, but sol gel method received great attention in the area of materials science as it has some specific advantages like low temperature processing conditions, sintering capability, high quality coatings, high purity, high homogeneity, thin bond-coating to provide excellent adhesion, controlled surface property, shape and pore structures etc.

A lot of work has been reported in literature based on sol gel process for the manufacturing of silica gel glasses, ceramics and inorganic-organic hybrid materials. G. Arrachart et al. [6] have reported synthesis and characterization of carboxylate-terminated silica nanohybrid powders and thin films. Reisfeld et al. [7] have synthesized smart optical materials by sol gel method and also studied their spectroscopic and ultra structural properties. Further, research work was focused on doping nanometer sized particles of CdS, CdSe, CdTe and PbS, which have been doped by chemical methods in silica gel films. Y. V. Vorobiev et al. [8] have reported the preparation and optical properties of SiO_2 sol-gel made colored silica gel rods with carminic acid. In this research work, we made an effort towards simple synthetic pathway for the fabrication of silica based rod shaped materials by doping of organic dye molecules with different concentrations. This novel material synthesis is carried out by taking tetraethylorthosilicate (TEOS) as precursor, additives such as polar solvents dimethylformamide, water, ethyl alcohol and ethylene glycol. It is also found that the size of silica gel rods depends on the aging and drying processes. These synthesized laser rods have been characterized using spectroscopic techniques such as FTIR, UV-visible, photoluminescence spectroscopy and scanning electron microscopy.

2. Experimental details

2.1 Chemicals used and dye doping

The following chemicals were used for the preparation of silica gel rods; tetraethylorthosilicate(TEOS) (Hi Media Lab. Pvt. Ltd. Mumbai, India), Kiton red-620 (M.W. 580.66, $C_{27}H_{29}N_2O_7S_2Na$) (Exciton Inc. Dayton, USA), N,N-dimethylformamide (DMF) (GC Grade, Spectrochem Pvt. Ltd. Mumbai, India), ethanol (AR Grade, Changshu

Yangyuan Chemicals China), hydrochloric acid (Qualigens Fine Chemicals, Glaxo Smith Kline Pharma. Ltd. Mumbai, India), ethylene glycol (AR Grade, Spectrochem Pvt. Ltd. Mumbai, India), acetonitrile (Qualigens Fine Chemicals, Glaxo Smith Kline Pharma. Ltd. Mumbai, India).

The silica gel cylindrical rods (length ~40mm and dia ~10mm) have been prepared using the following formulation of synthesis: tetraethylorthosilicate (TEOS) and dimethylformamide (DMF) in the molar ratio of (0.072 **:** 0.45), H_2O (5 ml (v/v)), ethanol (20 ml), ethylene glycol (10 ml), acetonitrile (10 ml(v/v)) and three drops of catalyst HCl (2N) were taken and mixed thoroughly for about 40 min by magnetic stirrer. This chemical formulation of silica gel synthesis is an original formulation developed by us using organic solvents and an additive ethylene glycol to reduce intermolecular forces (cracking) of silica gel matrix. The stock solution of Kiton red dye was 5.0×10^{-4} mol L^{-1} which was further diluted with ethanol for different concentrations such as 0.31×10^{-4}, 0.62×10^{-4}, 1.25×10^{-4} and 2.5×10^{-4} mol L^{-1} to obtain the dye doped silica gel rods. The reaction mixture was then casted into flat bottom glass tubes and kept in an oven at 60ºC for about 30 h. After that, the glass tubes containing reaction mixtures were kept at 40 ºC for about 15 days in order to complete polymerization and to strengthen the silica gel rods. Further, the temperature was raised upto 90ºC for 48h for final curing to achieve good mechanical strength of prepared silica gel rods. In this way, the kiton red-620 dye doped silica gel samples with desired shape and size have been prepared at low temperature conditions.

Kiton red-620

2.2 Characterization

Spectroscopic characterization is an essential tool employable to understand the optical properties and the behavior of interacting groups after doping of the synthesized materials. Kiton red-620 laser dye doped silica based materials, prepared on the basis of above reaction mechanisms, have been characterized using FTIR spectrophotometer (Nicolet 360) and UV-visible spectrophotometer (Perkin Elmer Lambda**)**. Fluorescence study of samples have been performed using Fluorescence spectrophotometer **(**F-7000 FL). SEM images of samples were taken by scanning electron microscope (JEOL-JSM 6380).

3. Results and discussion

3.1 FTIR study

The FTIR spectra of pure silica gel rod are shown in Fig.1 which has several absorption peaks. To see the effect of dopant on absorption peaks of pure silica gels, we have recorded FTIR spectra of undoped and 0.31×10^{-4}, $0.62x10^{-4}$, 1.25×10^{-4}, 2.5×10^{-4} and 5.0×10^{-4} mol L^{-1} doping concentrations of Kiton red-620 dye in silica gels as shown in Fig. 1. The absorption band in the region 4000–3000 cm^{-1} is due to the overtones or combinations of vibrations of Si-OH or H_2O.[9-11] The broad absorption band is generally composed of stretching modes. The region of 3000-2800 cm^{-1} corresponds to symmetric and asymmetric stretching vibrations of CH_2 and CH_3 groups of alkoxide and solvent residue. The main band in the region 1300-400 cm^{-1}, is associated with the combination of vibrations of silica network. Region 1200-1000 cm^{-1} corresponds to stretching vibrations of Si-O-Si bonding.[12, 13] The band around 950 cm^{-1} is associated with Si-OH stretching, a typical of gel structure that decreases in intensity and becomes insignificant when the material undergoes polycondensation mechanism during drying. The physical and mechanical properties of samples are improved which may be due to increase in the Si-O-Si bonds on heating moderately. In general, as the temperature increases the surface area and pore volume decreases, resulting in the shrinkage of gel. It is clear that as concentration of dye in silica gel matrix increases the absorption band region 1200-1000 cm^{-1} broadens, which may be due to the interaction of dye molecules with the Si-O-Si bridge structure of silica gel matrix. It has been found that formamide based silica gel rod formation show stronger networks, low shrinkage and dye embedded in the pores of silica gel matrix.

3.2 UV-visible study

The absorption spectra of undoped silica gel and Kiton red-620 dye doped silica gels are shown in Fig. 2. The concentration of dye in silica gel rods varies as 0.31×10^{-4}, 0.62×10^{-4}, 1.25×10^{-4}, 2.5×10^{-4} and 5.0×10^{-4} mol L^{-1}. It has been observed from the absorption spectra of undoped sample that there is no peak at about 570 nm, while all the doped silica gel based samples show peak at wavelength about 570 nm. It has been observed that as concentration of dye varies the sharpness of absorption peak changes which may be due to some loss in concentration of dye during aging and drying process of silica gel rods [14].

3.3 Photoluminescence study

Fig. 3 shows photoluminescence spectra of Kiton red-620 dye doped silica gel rods with different concentrations of Kiton red-620 as 0.31×10^{-4}, $0.62x10^{-4}$, 1.25×10^{-4}, $2.5x10^{-4}$ and 5.0×10^{-4} mol L^{-1}. It has been seen that sharp emission peaks are appeared in the visible region at wavelength between 580 to 590 nm as concentration of dopant varies from 0.31×10^{-4} to 5.0×10^{-4} mol L^{-1}.

It is also observed that stokes shift increases as concentration of dopant in the base material increases. Fluorescence decay time (τ) decreases as the concentration of dye increases in the silica based rods. The changes in Stokes shift and decay time both with dye concentration may be attributed to the formation of loosely bound dimmers and higher order aggregates on the surface of nanopores. Some of the aggregates may be non-flourescent and act as quenchers: the others may retain the ability to fluoresce but their emission spectra are shifted to the red. [14, 15] The photophysical properties of Kiton red-620 doped silica gel at different concentrations are depicted in Table 1.

3.4 SEM study

SEM micrographs of undoped silica and kiton red-620 dye doped silica based samples, with doping concentrations 0.31×10^{-4}, 0.62×10^{-4}, 1.25×10^{-4}, 2.5×10^{-4} and 5.0×10^{-4} mol/L, are shown in Fig. 4(a-f). It has been clearly observed that the nano/micro particles of kiton red-620 dye are embedded in the amorphous silica matrix.

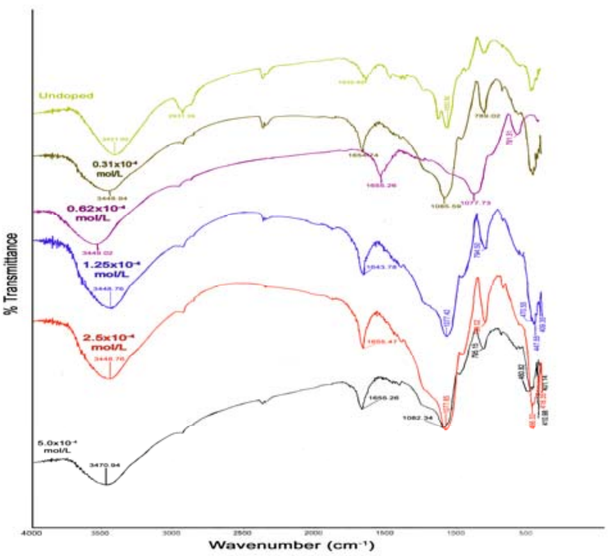


Fig. 1. FTIR spectra of undoped and kiton red-620 doped silica based material

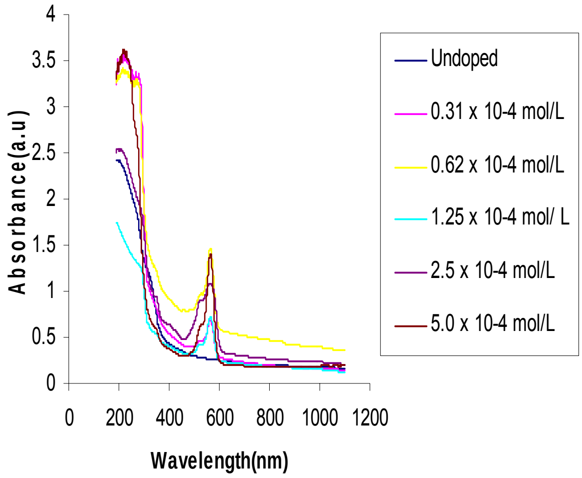


Fig. 2. Absorption spectra of undoped and kiton red-620 doped silica based material

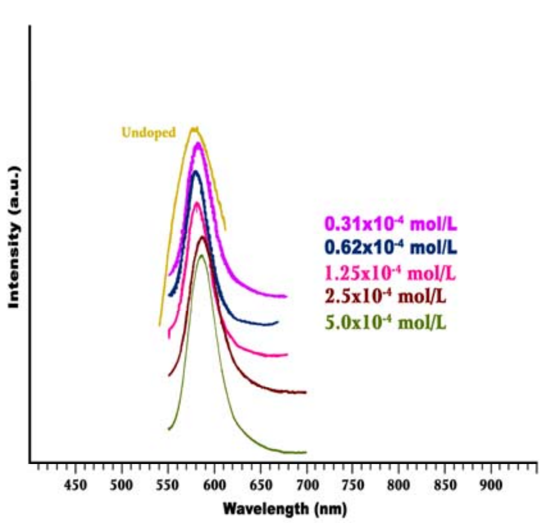
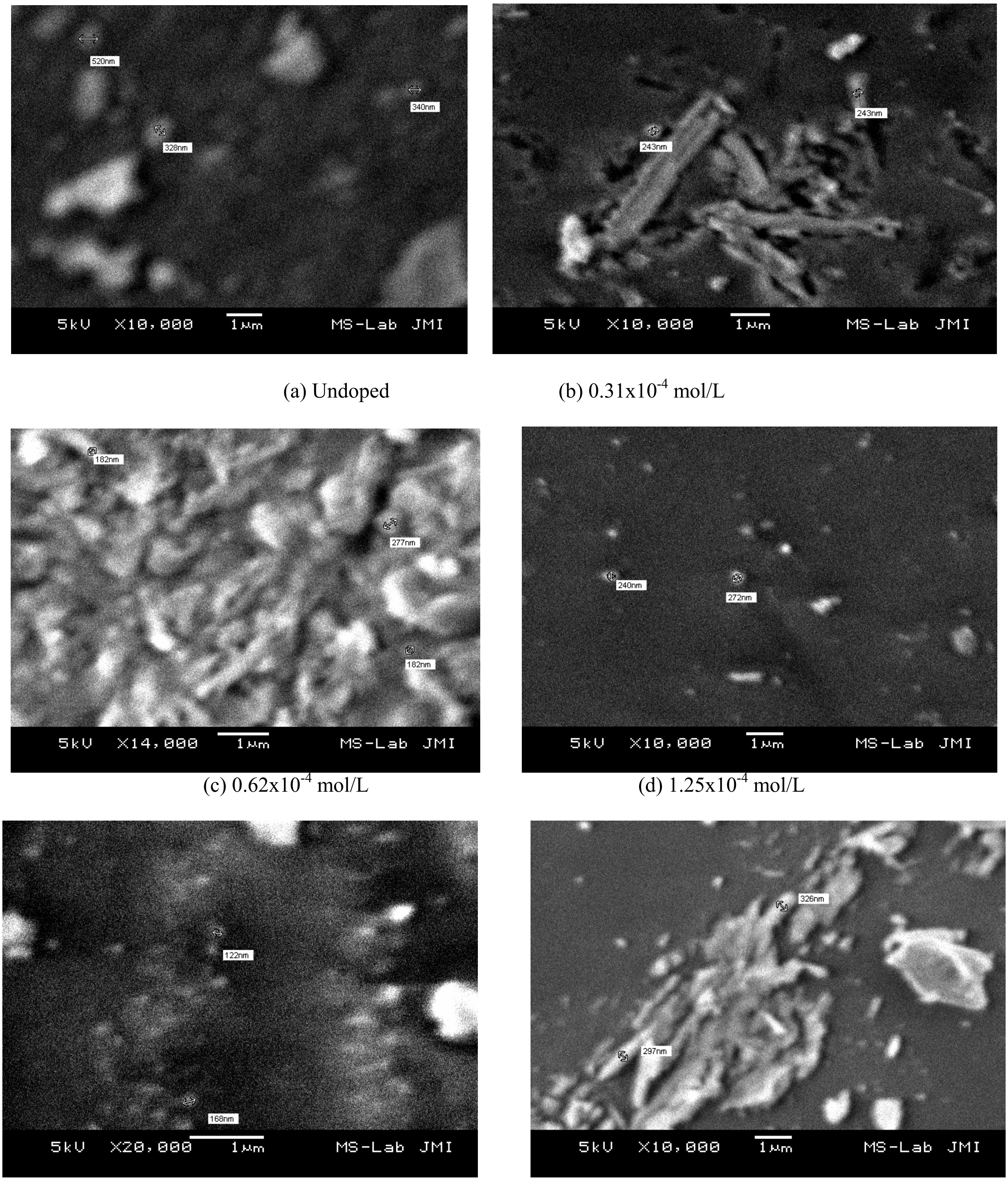


Fig. 3. PL spectra of undoped and kiton red-620 doped silica based material

Table 1. Photophysical properties of kiton red-620 doped silica based material

Concentration of dye in (mol/L)	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Stoke's shift (nm)	Decay time (τ) ns
0.31×10^{-4}	573	580	7	11.6
0.62×10^{-4}	571	587	16	7.8
1.25×10^{-4}	570	588	17	1.2
2.5×10^{-4}	570	589	19	0.6
5.0×10^{-4}	569	590	21	0.1



(a) Undoped (b) $0.31x10^{-4}$ mol/L

(c) $0.62x10^{-4}$ mol/L (d) $1.25x10^{-4}$ mol/L

(e) 2.5×10^{-4} mol/L (f) 5.0×10^{-4} mol/L

Fig. 4 (a-f): SEM micrographs of undoped and kiton red -620 doped silica based materials.

4. Conclusions

In summary, the technological interest is focused on the investigation of low temperature sol-gel processed and suitably doped silica gel derived transparent materials of desired shape and size. The silica based materials (length ~40mm and dia ~10mm) doped with different concentrations of Kiton red-620 dye have been prepared by sol-gel method. FTIR transmission spectra exhibit the interaction of kiton red-620 dye molecules with Si-O-Si bridge structure of silica gel matrix. The doped silica gel samples have stronger networks, low shrinkage and dye molecules embedded in the pores of silica gel matrix. UV-visible absorption spectra of doped samples exhibit an absorption peak at about 570 nm, not found in undoped samples, which may be due to the presence of kiton red-620 dye. The prepared material shows sharp fluorescence peak in visible region having red shift with concentration. Therefore, the doping of kiton red-620 dye in silica gel matrix modifies photoluminescence properties which may be useful for continuous wave and wide range tunability in dye lasers. SEM micrographs exhibit that the particles of dye are embedded in the pores of silica gel based materials**.** It may be concluded that the doping concentration (5.0×10^{-4} mol L^{-1}) is more significant than other concentrations because strong absorption at excitation wavelength occur and the value of stoke's shift is maximum.

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