Study of Optical properties of saffron dye doped silica based material

Monika Chahar[1*] and Anjali Ahlawat[1]

1 Baba Mastnath University, Asthal Bohar, Rohtak- 124 021, India.

Abstract

During the polymerization of silica-gel matrix, saffron dye is trapped . The samples were produced with varied dye concentration . We have recorded diffraction spectra of silica gel doped solid dye laser materials produced from the sol -gel method with various dye concentration . The behavior of FTIR, flourescence spectra and diffraction motif allows exploring the production of doped solid state silica based laser materials .

Keywords: Sol-gel Method , laser dyes, x-ray diffraction.

1. Introduction

Material which shows both lasing & tunable nature are called as laser materials . In field of lasers , many different kind of laser materials are utilised. From all laser materials , dye lasers materials are most frequently selected materials for laser purpose and in these materials organic dye act as the lasing or gain medium . There are many different kinds of dyes available in market which have different pattern & absorbance region and this feautre of these dye allows these lasers to be extremely adjustable or they can easily create very short-duration pulses (on the order of a few femtoseconds). The broad bandwidth makes them ideal for tunning lasers & pulsed laser . Tunable lasers are vary from regular laser to traditional lasers because , in a certain spectral region , they can constantly change their emission wavelength, or color, in a given spectral range. “Dye lasers have been discovered by P. P. Sorokin and F. P. Schafer et al. in 1966 [1]. At first, the radiation came in form of wideband emission from these organic laser”. Broadband emission consist of numerous transverse modes and multitude of longitudinal modes in each transverse mode. “Paterson et al. in 1970 provided a significant advance towards emission control with the invention of continuous wave dye laser in the areas of high power pulsed dye laser a most important contribution was the introduction of the telescope grading oscillator by Hansch in 1972”[2}. The laser cavity introduced by Hansch used most of the wavelength tunings and frequency restriction concepts necessary to practical tunable lasers.

“R. L. Fork, B. I. Greene, and C. V. Shank demonstrated, in 1981, the generation of ultra-short laser pulse using a ring-dye laser (or dye laser exploiting colliding pulse mode-locking). Such kind of laser is capable of generating laser pulses of ~ 0.1 ps duration" [3]. The dyes employed in these lasers compromise organic molecule which are wide and fluorescent. The emission of dye laser is naturally wide . " Dye lasers are used in many applications including: astronomy (as laser guide stars), atomic vapour laser isotope separation manufacturing medicine and spectroscopy etc" [4-6]. We can thus state that dye laser gave importance to those materials which show basic two characterstics and theses two characterstics are continuos & wide range tunability with all families of laser dyes, which show absorbance in UV-VIS region . Feature of broadened electronic levels of organic dyes is the main reason for the tunability of dye laser materials **.** Due to their wide application in various fields ,many research groups have paid more attention for synthesis of these types of materials. Trapping of organic dye molecules in the silica gel matrix can explore new path way for development of advanced dye laser materials.

Although huge works, have been reported in literature based on sol gel process for synthesis of glasses, ceramics and inorganic-organic hybrid materials. "Guilhem Arrachart et al.[8] have been reported synthesis and characterization of carboxylate-terminated silica nanohybrid powders and thin films".

"Resfield et al. [9,10] have manufactured smart optical materials by sol gel method & also investigated their spectroscopic & ultra structural properties. Additionally research work was focused on doping nanometer sized particles of CdS, CdSe, CdTe and PbS", which have been doped by chemical methods in silica glass films. "These films were prepared either of pure silica or silica zirconia or combined zirconia with ormosils. YU. V. Vorobiev et al.[11] have been reported preparation and optical properties of SiO_2 sol-gel made glass colored with carminic acid."

"R. Ken Kuriki et al. [12,13,14,15] have been reported plastic optical fiber lasers and amplifiers containing lanthanide complexes. N.T.M. An et al have been reported spectral evolution of distributed feedback laser of gold nanoparticles doped solid-state dye laser medium" [16]. In this paper, we made a effort by a simple synthetic pathway for the preparation as well as incorporation of saffron dyes molecules in the silica gel based materials. The characterization of prepared samples is under taken with the help of FTIR, XRD and Flourescence study.

2. Experimental Section

2.1 Chemicals

The following chemicals were used in the experimental work for the preparation of silica gel based material; saffron, N,N-dimethylformamide(GC Grade, Spectrochem Pvt.Ltd. Mumbai, India), ethanol(AR Grade, Changshu Yangyuan Chemical China), hydrochloric acid (Qualigens fine chemicals, Glaxo Smith Kline Pharmaceuticals Limited Mumbai, India), ethylene glycol(AR Grade, Spectrochem Pvt.Ltd. Mumbai, India), acetonitrile(Qualigens Fine Chemicals, Glaxo Smith Kline Pharmaceuticals Limited Mumbai, India).

2.2 Methodology and chemical doping

The silica gel was manufactured by using sol-gel method . The reaction mixture is then poured in flat, round bottom glass tubes and then placed in oven for approximately about 42 hours at 40ºC . The temperature varies slowly and slowly to 85ºC for 50 hours to ensure that the produced silica gel materials has a good mechanical strength.. The sample of required requirement with desired shape & size were therefore obtained at low temperature. The prepared samples of silica gel are doped by saffron dye with different concentration such as $3.08x10^{-3}$, $3.26x10^{-3}$, $3.36x10^{-3}$, $3.42x10^{-3}$ and $3.46x10^{-3}$ mol/L

3. Results and discussion

FTIR study

Spectroscopic characterization is key technique for understanding the optical characterstics of the synthesized materials and the connected (interacting group) . Formed silica gel rods were distinguished by IR spectroscopy. The spectra of pure silica gel and dye doped silica based material are shown here with numerous peaks Fig.1. The concentration of dye varies as $3.36x10^{-3}$ and $3.46x10^{-3}$ mol/L. In the area of 4000-3000 cm^{-1} the absorption band is largly due to combination of Si-OH or water vibration. In general, the wide absorption band consist of the stretching modes. The 3000-2800 cm^{-1}range is consistent with the symmetric and asymmetric stretching vibration of alcohol and solvent residue in groups (CH_2 & CH_3 groups) .

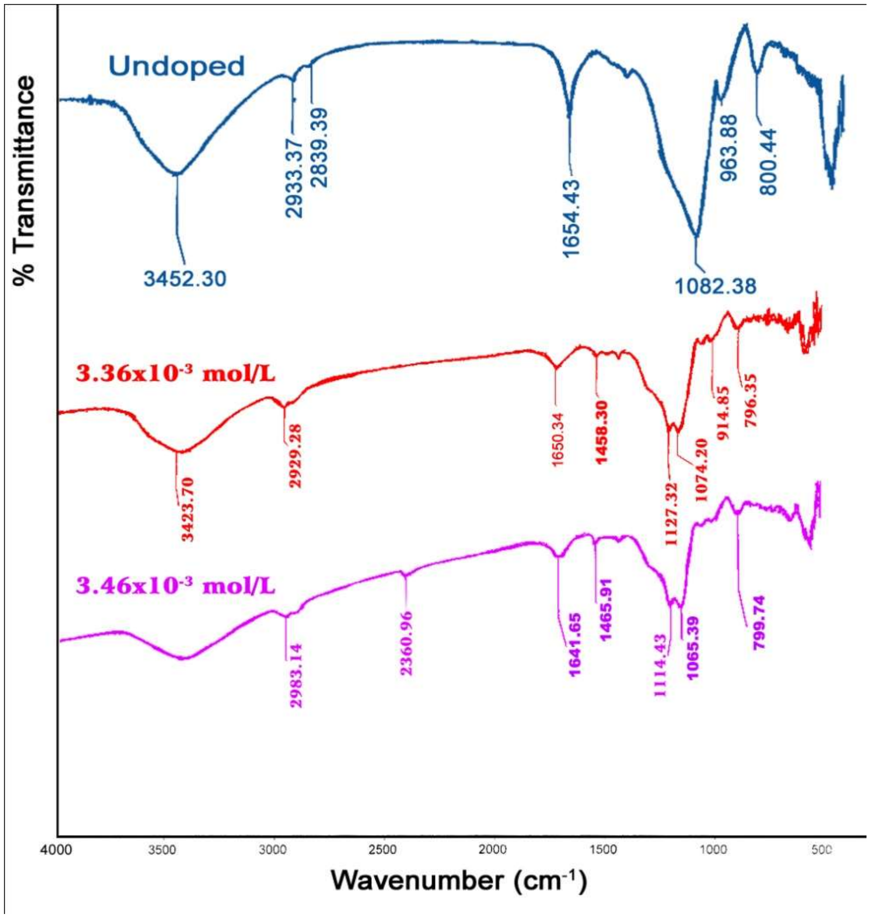

Fig. 1: FTIR spectra of undoped and saffron dye doped silica based material

The core band in the 1300-400 cm^{-1}range is combined with vibration of silica network. Region 1200-1000 cm^{-1} relates to Si-O-Si bonding stretching vibrations . The band area of 950 cm^{-1} associated with Si-OH stretching is typical of the gel structure which reduces intensity and becomes negligible if material suffers from a poly condensation process during drying. It has also been found the gel get dried with rise in temperature. The physical and mechanical characteristics were enhanced and the Si-O-Si bonds with heating were increased . Moreover, with the increased temperature the surface area & pore volume decreases, and resulting in gel shrinkage . It is clear from the dye doped materials that as concentration of dye increases in the silica gel matrix the absorption band region 1200-1000 cm^{-1} becomes widened & less intense owing to the presence of dye molecules in the pores of silica gel network and the formation of aggregates at greater concentration . The current study revealed that the production of formamide-based silica gel rods shows stronger networks and less shrinkage.

Photoluminescence (PL) study

Fluorescence study of dye doped silica based material has been performed with the Fluorescence Spectrophotometer (F-7000 FL Spectrophotometer). Fig.2 exhibits undoped and dye doped silica based material fluorescence emission spectra . from the spectrum of undoped sample that the sharp emission peak appears at wavelength 689 nm. The dye doping varies as $3.08x10^{-3}$, $3.26x10^{-3}$, and $3.36x10^{-3}$ and $3.42x10^{-3}$ mol/L. It seems that as concentration of dye varies from $3.08x10^{-3}$ mol/L to $3.42x10^{-3}$ mol/L in the silica gel matrix the peaks of fluorescence emission wavelength remains at position 659,685; 657,689; 658,682 and 653;683 which lies in the visible range and slightly shifted between 650-690 nm towards blue shift. The photophysical properties are shown in Table 3.1

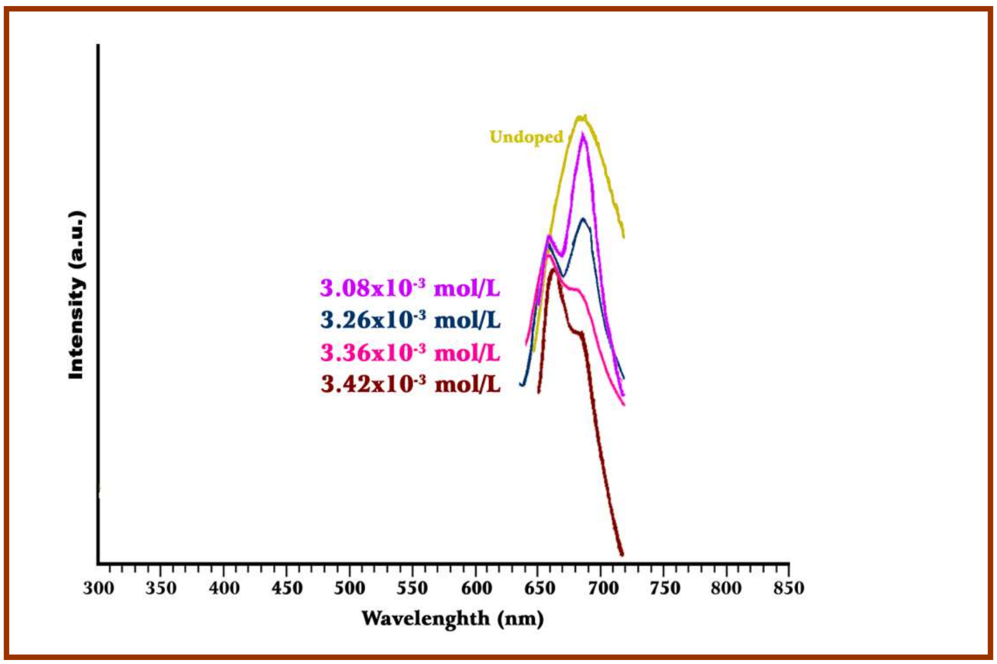

Fig. 2: PL spectra of undoped and saffron dye doped silica based material

Table 3.1: Photophysical properties of saffron dye doped silica based material

Concentration in (mol/L)	**λ_{abs}^{max} (nm)**	**λ_{em}^{max} (nm)**	**Stoke's shift (nm)**

3.08×10^{-3}	316	659	343
3.26×10^{-3}	272	657	385
3.36×10^{-3}	274	658	384
3.42×10^{-3}	335	653	318

XRD Study

The X-ray diffraction patterns of undoped and saffron dye doped silica based material are shown in Fig.1. Samples have been prepared with different concentration of dopant such as 3.08×10^{-3}, 3.26×10^{-3}, 3.36×10^{-3}, 3.42×10^{-3} and 3.46×10^{-3} mol/L. The X-Ray Diffraction pattern of the synthesized samples have been recorded to determine the crystallite size using the Scherrer formula ($D = K\lambda / \beta \cos\theta$). The X-ray pattern tells about the nature & structure of the sample. XRD pattern of silica generally differs & depend on the synthesis route, solvent and ionized state. It has been observed that the diffraction peaks are broad, which is a typical feature of the amorphous nature. In other words the samples are found to be amorphous because no sharp peak has been observed in X-ray diffraction patterns.

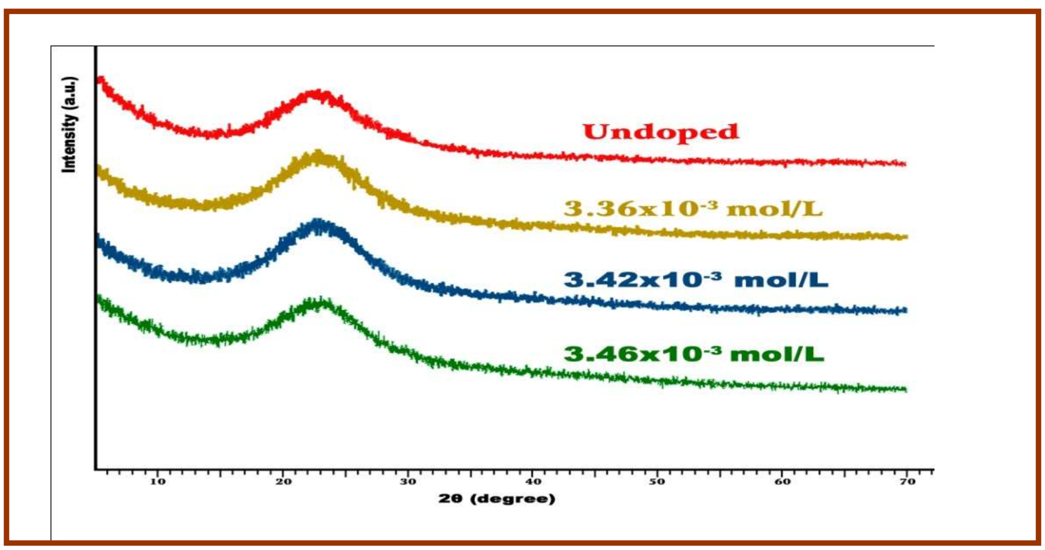

Fig.3: XRD spectra of undoped and saffron dye doped silica based materials

Conclusions

Synthesis of saffron doped silica based material has been carried out by a chemical route, sol–gel process. Doping of saffron is done in the silica gel matrix by making different concentration of dopant such as $3.08x10^{-3}$, $3.26x10^{-3}$, $3.36x10^{-3}$, $3.42x10^{-3}$ and $3.46x10^{-3}$ mol/L. Trapping of saffron dye molecules in the silica gel matrix during polymerization process may open up new possible trends for advanced laser materials. The spectroscopic characterization of synthesized samples has been done by spectroscopic techniques such as FTIR, PL (photoluminescence) and XRD. FTIR study has been performed to see the effect of dopant (saffron dye) in silica gel matrix. It has been observed from the IR spectra of dye doped material that the absorption band appears at 1200-1000cm^{-1} which corresponds to stretching vibrations of Si-O-Si bonding becomes broaden as concentration of dye varied in the silica gel matrix

PL study has been done to observe the emission spectra. It has been find out from emission spectra that as concentration of dye vary as $3.08x10^{-3}$, $3.26x10^{-3}$, and $3.36x10^{-3}$ and $3.42x10^{-3}$ mol/L in silica based material, the emission peaks appears with blue shifting at wavelength 659, 657, 659 and 650 respectively which lie in UV-visible region. X-ray diffraction patterns of the synthesized samples show that the synthesized materials are of amorphous nature.

References:

[1] F. P. Schafer, Dye Lasers, Springer-Verlag, Berlin, 1990.

[2] F. J. Duarte and L. W. Hillman, Dye Laser Principles, Academic, New York, 1990.

[3] R. L. Fork, B. I. Greene, and C. V. Shank, Appl. Phys. Lett., **38** (1981) 671.

[4] F. J. Duarte, Appl. Opt. 33(1994) 3857.

[5] D. A. Gromov, K. M. Dyumaev, A. A. Manenkov, A. P. Maslyukov, G. A. Matyushin, V. S. Nechitalio, Prokhorov, et al., J. Opt. Soc. Am. B. 2(1985) 1028.

[6] N. K. Chaudhury, R. Gupta and S. Gulia, Defence Science Journal, 57, 3, May (2007), 241-253.

[7] H. Podbielska and Ulatowska – Jarza, Sol-gel technology for biomedical engineering, Bulletin of The Polish Academy of Sciences Technical Sciences 53, 3, 2005.

[8] Guilhem Arrachart, Inna Karatchevtseva, David J. Cassidy, Gerry Triani, John R. Bartlett and Michel Wong Chi Man, Journal of Materials Chemistry, 18 (2008) 3643-3649.

[9] Reisfeld R. and Jorgenson, optical properties of colorants or Luminescents Species

in Sol-Gel glasses; Structure and Bonding, Springer Verlag, Reisfeld R. and Jorgensen C. K.; eds. 77 (1992) 207-256.

[10] Reisfeld R.; Harry Minti; Marck Eyal and Valery Chemyan, Journal of Nonlinear Optics, 5 (1993) 339-360.

[11] Dr Vijay Kumar Salvia , World Research Talent Quality, 29, 2013, 45-52

[12] L. L. Diaz - Flores, G. Luna-Barcenas, J. Gonzalez-Hernandez and Yu. V. Vorobiev, Journal of Sol- Gel Science and Technology 33 (2005), 261-267.

[13] Ken Kuriki, Yasuhiro Koike and Yoshi Okamoto, J. Chem. Rev. 102 (2002), 2347-2356.

[14] Orcel, G.; Phalippou, J.; Hench, L. L. Journal of Non-Crystalline Solids, 88 (1986) 114.

[15] Bartholomeu, R. F.; Butler, B. L.; Hoover, H. L. ; Wu, C. K. Journal of the American Ceramic Society, 63, 9-10 (1980), 481.

[16] Almedia, R.M.; Pantano, C. G. Journal of Applied Physics, 68, 8(1990), 4225.

[17] N.T.M. An, N.T.H. Lien, N.D. Hoang, N.T. Nghia and D.Q.Hoa, J. Applied Physics, 2017