Comparative study of oscillator strengths in dye and metal doped silica glasses

S Dihingia1*, D Bora 1, R Singha1, P Saikia2

1Department of Physics, Assam University (Diphu Campus), Karbi Anglong, Assam, India
2Department of Physics, Dibrugarh University, Dibrugarh, Assam, India

*Email: sangitadihingia@rediffmail.com

Abstract: In the present study sol gel silica glasses doped with rhodamine dye (Rh6G) and transition metals like silver, copper and iron were prepared at room temperature through sol gel route. The molar concentrations of dye and metal are varied and synthesized to get a uniform dye and metal doped clusters in silica matrices. Structural characterization is performed by SEM and XRD on doped silica glasses. SEM micrographs reveal the size of particles to be 10-50µm. The amorphous structures of the glasses are confirmed by XRD. The absorption spectra are monitored and analyzed. The absorption spectra of fluorescent dye doped sol gel silica glasses are found within the limit of 400-600 nm and the absorption spectra of different metal doped glasses are in the range of 250-350nm. Oscillator strengths of dye doped and metal doped glasses are calculated and compared. Oscillator strength of rhodamine dye doped silica glasses is comparatively higher than the other doped glasses. Silver is seen to have high oscillator strength among the metal doped silica glasses.

1. Introduction

In recent years, sol gel technology has become one of the most magnificent method for the production of glasses, films etc. with varied applications in different fields. The process involves formation of sol by hydrolysis and polymerization reaction of alkoxide precursors (TMOS/TEOS) and gelation of the sol accompanied by ageing and drying. The process enables to control the particle size, porosity, separation of particles with varying composition etc. Several initial parameters such as time of reaction, nature and concentration of catalyst, time of gel formation etc. if controlled can be helpful in exploring new properties of the sol gel derived glasses [1-3]. According to S. Sakka diverse applications have been achieved in electronics, optics, photonics, chemical technologies etc by using the sol-gel method [2]. The sol gel process still needs intense research to understand and explore the newer properties in developing new materials. Synthesis of metal nanoclusters or nanoparticles in sol-gel method is also an area of extensive research because of their potential applications in different field [5-7]. The development in the field of photonics, optics or optoelectronics needs exploration of new materials in which amorphous materials are of great significance [6] R. Reisfeld and her group have worked tremendously on different fluorescent dye doped glasses studied their properties and have worked on various applications [11-15]. Incorporating dyes and transition metals in the porous silica matrix can
open new ways in the field of photonics. The purpose of our work is to study the comparison between the Rhodamine 6G dye doped glass and metal doped silica glasses and find their oscillator strengths.

2. Experimental Techniques

For the preparation of dye and metal doped silica glasses, the sol–gel process was carried out. Tetraethylorthosilicate (TEOS), rhodamine 6G dye from Merck and methanol, doubly distilled water, nitric acid, silver nitrate from Rankem, iron filings from Fisher Scientific and cupric nitrate from Sigma Aldrich was used in the preparation of the glasses. The sols were prepared by dissolving specified amount of Rh6G dye or Ag/Fe/Cu in 10.5ml mixture of methanol (8.75ml), distilled water (1.25ml), dilute nitric acid (0.5ml) taken in proportion of 70(methanol):10(H2O):4(HNO3) by stirring continuously in a magnetic stirrer for 15 minutes. 2ml of TEOS i.e the 16 parts of the total mixture of 12.5ml solvent was added and further stirred for an hour. When the formation of gel began, it was transferred to plastic shells and left to dry and solidify at room temperature. The gel solidifies to form coloured stiff hard mass pellet in 48-72 hours accompanied by ageing and drying for 22 days. Eight sets of samples were prepared varying the concentrations of the dopants. Composition of the prepared samples is shown in table 1.

| Samples | Conc. (M)x10^-4 | Methanol(ml) | H2O(ml) | HNO3(ml) | TEOS(ml) |
|---------|----------------|--------------|---------|----------|----------|
| Rh6G/01 | 1              | 8.75         | 1.25    | 0.5      | 2        |
| Rh6G/02 | 0.1            | 8.75         | 1.25    | 0.5      | 2        |
| Ag/01   | 1              | 8.75         | 1.25    | 0.5      | 2        |
| Ag/02   | 0.1            | 8.75         | 1.25    | 0.5      | 2        |
| Cu/01   | 10             | 8.75         | 1.25    | 0.5      | 2        |
| Cu/02   | 1              | 8.75         | 1.25    | 0.5      | 2        |
| Fe/01   | 10             | 8.75         | 1.25    | 0.5      | 2        |
| Fe/02   | 1              | 8.75         | 1.25    | 0.5      | 2        |

The SEM micrographs are recorded in High Resolution Scanning Electron Microscope of model JSM-IT 300 (JEOL). The X- ray diffraction patterns of dye/metal doped glasses are recorded in Ultima –IV (Rigaku) to study the structure of the glasses. The UV-VIS absorption spectra of the prepared glasses are recorded by using UV-2600 (SHIMADZU) UV- Vis spectrometer in the wavelength range of 250-700nm.

3. Result and Discussion

3.1. Structural Analysis

The SEM micrographs along with EDAX of Rh6G doped (Rh6G/02) and metal doped (Fe/01) sol gel derived silica glasses are shown in figure 1(a,b). The micrographs present inhomogeneous surface morphology of the solid silica matrices with particle size ranging from 10-50µm. The EDAX spectra shows the presence of Si and O in the matrix which forms Si-O-Si and Si-O groups along with other elements of the dopants.
Figure 1(a). SEM-EDAX of Rh6G/02 glasses.

Figure 1(b). SEM-EDAX of Fe/02 glasses.

The XRD patterns of the dye (Rh6G/02) and metal (Fe/02) doped glasses are shown in the figure 2: below. The XRD spectra reveal the amorphous nature of solid silica matrices and do not reveal any trait of crystalline nature.
Figure 2. XRD spectra of Rh6G/02 glasses and Fe/01 glasses, respectively.

3.2. Absorption Spectra Analysis
The absorption spectra of dye (Rh6G) and Metal (Ag/Fe/Cu) doped sol gel silica glasses are shown in figure 3 below. The spectra of the doped glasses are found to be within the range of (250-700) nm.

Oscillator strength of the doped glasses is calculated using the formula

\[ f = 4.32 \times 10^{-9} \int \varepsilon (\nu) d\nu \]  

(1)
where $\int (u) \, du \approx (u) \times \Delta u$ and $(u)$ is the molar absorption coefficient at frequency $u$ (cm$^{-1}$) and $\Delta u$ is the band width at $1/2(u)$ measured directly from absorption spectra (FWHM) using “Origin Pro 8” software [11].

### Table 2. Oscillator strength of doped silica glasses.

| Sample glass | Abs. Max (nm) | Oscillator strength (f) | FWHM ($\Delta \nu$) nm | Abs. Coefficient M$^{-1}$ cm$^{-1}$ |
|--------------|---------------|-------------------------|------------------------|-----------------------------------|
| Rh6G/01      | 516           | 0.0106                  | 68.69                  | 36000                             |
| Rh6G/02      | 517           | 0.0875                  | 61.39                  | 330000                            |
| Ag/01        | 297           | 0.0061                  | 48.03                  | 29500                             |
| Ag/02        | 297           | 0.0769                  | 53.12                  | 335000                            |
| Cu/01        | 296           | 0.0008                  | 48.78                  | 3850                              |
| Cu/02        | 296           | 0.0041                  | 40.77                  | 23500                             |
| Fe/01        | 246           | 0.0004                  | 36.54                  | 2800                              |
| Fe/02        | 246           | 0.0063                  | 36.57                  | 40000                             |

### 4. Conclusion

In the present work, the oscillator strengths of dye (Rh6G) and metal (Ag/Fe/Cu) doped sol-gel silica glasses are calculated where the dye doped glass with molar concentration $0.1 \times 10^{-4}$ (Rh6G/02) exhibits highest oscillator strength. The inhomogeneous broadening of the absorption band is due to the static local environment of the disordered glass. This higher oscillator strength may be attributed to the contribution of the delocalized $\pi$-electrons of the conjugated bonds in dye molecules to the transition ($\pi-\pi^*$). These $\pi$-electrons are less strongly bound electrons in dye molecules than its $\sigma$-electrons and can be excited with photons with low energy which does not occur in metal doped glasses [17]. Amongst the metals, silver exhibits highest oscillator strength.

### Acknowledgement

The authors would like to acknowledge CSIC, Dibrugarh University for sample analysis and the senior research scholars of Dibrugarh University for their encouragement and support in carrying out the research activities.

### References

[1] Dimitriev Y, Ivanova Y and Iordanova R 2008 *J. Univ. Chem. Technol. Metallurgy* 43 181
[2] Reisfeld R 2005 *Handbook of Sol-Gel Science and Technology, Processing, Characteristics And Applications* vol 3, ed S Sakka (London: Kluwer Academic Publishers) chapter 12 p 239-261
[3] Chattopadhyay K K and Banerjee N A 2012 *Introduction to Nanoscience and Nanotechnology* (New Delhi: PHI) chapter 6 p 142
[4] Kalkman J, Gersen H, Kuipers L and Polman A 2006 *Phys. Rev. B* 73 075317
[5] Reisfeld R, Saraidarov T and Levchenko V 2008 *Opt. Appl.* 38 83
[6] Popov O, Ziberstein A and Davidov D 2006 *Appl. Phys. Lett.* 89, 191116
[7] Saraidarov T, Levenchenko V, Grabowska A, Borowicz P and Reisfeld R 2010 *Chem. Phys. Lett.* 492 60
[8] Costela A, Garcia-Moreno I and Sastre R 2009 *Tunable Laser Applications* ed F J Duarte (NewYork: CRC) Chapter 3 pp 97-120
[9] Mallick P and Mishra C N 2012 *Am. J. Mater.* 2 66
[10] Armellini C, Ferrari M, Montagna M, Pucker G, Bernard C and Monteil A 1999 *J. Non-Cryst. Solids* 245 115
[11] Bora D and Hazarika S 2013 *Int. J. Cur. Eng. Technol.* **3** 1977
[12] Reisfeld R 1990 *Proc. SPIE Sol-Gel Optics* vol 1328 p 29
[13] Reisfeld R, Levchenko V, Saradarov T, Behrendt M, Kuklinski B and Grinberg M 2012 *Opt. Mater.* **34** 2021
[14] Reisfeld R 1987 *J. Phys. Colloq.* **48** A23-
[15] Reisfeld R, Saraidarov T and Levchenko V 2009 *J. Sol-Gel Sci. Technol.* **50** 194
[16] Righini C G and Pelli S 1997 *J. of Sol-Gel Sci. Technol.* **8** 991
[17] Hofkens J, Sauer M and Enderlein J 2011 *Handbook of Fluorescence Spectroscopy and Imaging* ed M Sauer and J Enderlein (Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA) ch.2 p1