

# Effect of Matrix Treatment on Spectroscopic Properties of HCl Catalysed Sol-Gel Glasses Containing Coumarin Laser Dyes

Aparna V. Deshpande · Laxman V. Jathar · Jayraj R. Rane

Received: 12 September 2008 / Accepted: 24 November 2008 / Published online: 7 December 2008  
© Springer Science + Business Media, LLC 2008

**Abstract** Coumarin 1, Coumarin 2 and Coumarin 120 are embedded in transparent sol-gel glass samples prepared by sol-gel process using dip method. The sol-gel matrix is given dip treatment with Methanol /Distilled Water (50/50vol) for 1 to 16h before dipping into dye solution. The effect of dipping time of matrix in Methanol/ Distilled Water on spectroscopic properties of coumarin dye doped glass samples has been studied. The Optical Density (OD) at absorption maximum wavelength and Fluorescence Intensity (FI) at fluorescence maximum wavelength of all coumarin dyes increase with the time of dipping of the sol-gel sample. These absorption/fluorescence properties of coumarin dyes in sol-gel glass matrices are compared with its respective properties in methanolic solution in acidic environment. The cause of these changes in OD/FI with dipping time is discussed by taking into account the absorption / fluorescence of dye in acidified methanol.

**Keywords** Laser dye · Coumarin dye · Sol-gel glasses · Absorption · Fluorescence

## Introduction

Since last four decades liquid solutions of organic laser dye molecules have been widely used as efficient laser gain media from the near UV-to the near IR region of the spectrum [1]. But using liquid solutions of organic laser dye molecules have various limitations like cumbersome system design, requirement of large volume of solutions, need of significant maintenance, poor thermal stability of the dye solutions etc. [2–5]. These difficulties can be overcome by developing solid-state tunable dye laser materials by incorporation of stable laser dye molecules into solid host matrices like polymers, silica gels, xerogels, organically modified silicates (ORMOSILS) and sol-gel glasses [4–25]. These solid-state dye laser materials using polymers and sol-gel glasses as solid host matrices have technical advantages such as compactness, better manageability, high laser damage threshold and suitability for field measurement. A number of solid polymeric matrices have been used in the past [6–12]. However polymeric host materials have been shown to be inherently lacking in mechanical and thermal properties and photostability [7–8]. In 1984 Avnir and coworkers first demonstrated the possibility and applications of doping a gel with an organic dye [2]. The recent research work with sol-gel glass used as solid host for solid-state dye laser materials has attracted a great deal of attention because of its high potential utility than polymers.[4–5, 13–25]. The sol-gel reaction occurs at low/room temperature and therefore organic dye molecules can be incorporated in the gel network, with no risk of thermal degradation, whereas conventional glass production requiring high temperature which laser dyes cannot withstand. Also the host matrices prepared by sol-gel method are highly porous, transparent in the UV-near UV region and can be prepared in the form of rectangular blocks, films or

---

A. V. Deshpande (✉) · L. V. Jathar · J. R. Rane  
Department of Physics,  
Mumbai University Institute of Chemical Technology,  
Matunga,  
Mumbai 400019, India  
e-mail: daparna@udct.org

L. V. Jathar  
e-mail: laxmanjathar@rediffmail.com

J. R. Rane  
e-mail: jayrajrrane@yahoo.co.in

cylinders. Therefore the sol-gel method is a novel method for incorporation of organic dye molecules into an inorganic silica host. Various procedures are utilized to incorporate the laser dyes into sol-gel matrices [2, 4–5, 13–14] such as dope or dip methods. In dope method dye is mixed at the sol stage, drying is carried out afterward; while in dip method matrix is first prepared and the matrix is dipped in desire dye solution and subsequently sol-gel sample is dried. Sometimes the matrix is given some treatment such as heating at higher temperature before doping the dye into the matrices [14, 15]. To achieve the appropriate desired quality of dye doped material in sol-gel matrices for a particular application such treatments are utilised. It is necessary to know and understand the effect of various treatments of host matrix on the various properties, in particular photophysical properties when the material is to be used as laser active material. This is because the photophysical properties provide basic information about the lasing behaviour of the material [1]. With this objective sol-gel host samples are prepared by HCl acid catalysed hydrolysis of Tetraethylorthosilicate (TEOS). These samples are treated by Methanol (MeOH) / Distilled Water (H<sub>2</sub>O) (50/50 by volume) by dipping into it for various times from 1 to 16h and then dipped into desired coumarin laser dye solution in MeOH for 1h. Coumarin laser dyes with an amino group at 7-position (as shown in Fig. 1) known as very efficient laser dyes for the spectral response in the blue-green region of the electromagnetic spectrum have been used for doping [1, 4, 13, 16, 26–37].

In the present paper in continuation to our study of laser dyes [4–5, 11–13], changes in absorption/fluorescence properties of laser dye Coumarin 1, Coumarin 2 and Coumarin 120 (C 1, C 2, and C 120 respectively) doped into silica sol-gel glass are reported. C 1, C 2 and C 120 in sol-gel glass materials are found to show increase in absorbance and fluorescence intensity with increasing dipping time in MeOH / H<sub>2</sub>O (50/50vol). To understand this behaviour of the dye doped sol-gel glass samples, the absorption/fluorescence properties of the coumarin dye are studied in methanol solution containing varied quantity of HCl acid.

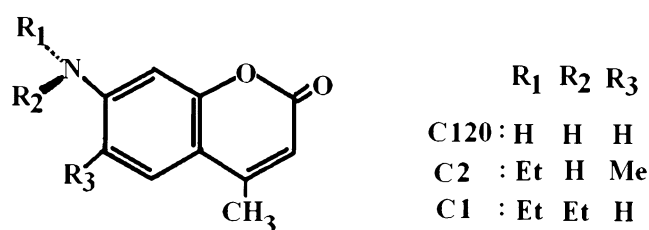


Fig. 1 Molecular structure of the 7-Aminocoumarin derivatives

## Experimental

Purity of laser grade C 1, C 2 and C 120 dye (Lambda Physik) was checked by UV–Visible absorption spectroscopy and then it was used as it was received. TEOS, MeOH (GR grade), HCl all from Merck were used without further purification. Sol was prepared by mixing 26- ml TEOS, 37ml- H<sub>2</sub>O, and 0.8ml HCl (as catalyst) under magnetic stirring at 60°C. After 1h of stirring, 3.5ml sol was poured in the rectangular polystyrene cuvettes of size (4.5 × 1.0 × 1.0) cm<sup>3</sup>. The cuvettes were sealed with teflon tape to ensure slow drying of sol, which decreases the probability of cracking in solid. Drying and aging of gel were carried out at room temperature in clean and controlled environment. After about 3 to 4weeks, solid blocks were obtained in the form of parallelepipeds with dimensions (0.8 × 0.8 × 2.8) cm<sup>3</sup>. These glass samples were used to immerse in MeOH / H<sub>2</sub>O (50:50 by volume) for different intervals of time such as 1h, 4h, 8h, 12h and 16h and then subsequently in methanolic solution of coumarin dye of known concentration for one hour. The number density of coumarin dye doped molecules in the solid host was calculated by difference method from the OD of absorption of dye solution before and after dipping of the glass sample. The desired number density of dye molecules in solid host can be obtained by dipping of glass samples in varied concentration of methanolic solution of respective coumarin dye. The concentrations of dye solution used were in the range of 1.15 × 10<sup>-5</sup> to 1.87 × 10<sup>-3</sup> mol l<sup>-1</sup> to obtain number densities of the order 1.52 × 10<sup>16</sup> to 7.23 × 10<sup>18</sup> cm<sup>-3</sup> in the dried samples respectively. After 5 to 7days from the dipping the dried glass samples show good surface finish with plane parallel side faces, and they were then used directly for absorption/fluorescence studies without any polishing. Optical absorption spectra of all the prepared samples were recorded on UV-Vis spectrophotometer (PerkinElmer, Lambda 35), where as the fluorescence spectra were scanned using an assembled fluorimeter with front surface excitation emission geometry. The absorption spectra of dye doped samples were recorded by taking atleast three scans with undoped glass as reference. The absorption spectra of methanolic solution of dye with and without acid were recorded with methanol as reference. Fluorescence spectra of all samples were scanned with 350nm excitation wavelength. Atleast three scans (scan speed 50nm per minute) are used to determine fluorescence spectrum. All the recorded spectra were corrected for the photomultiplier and monochromator sensitivities.

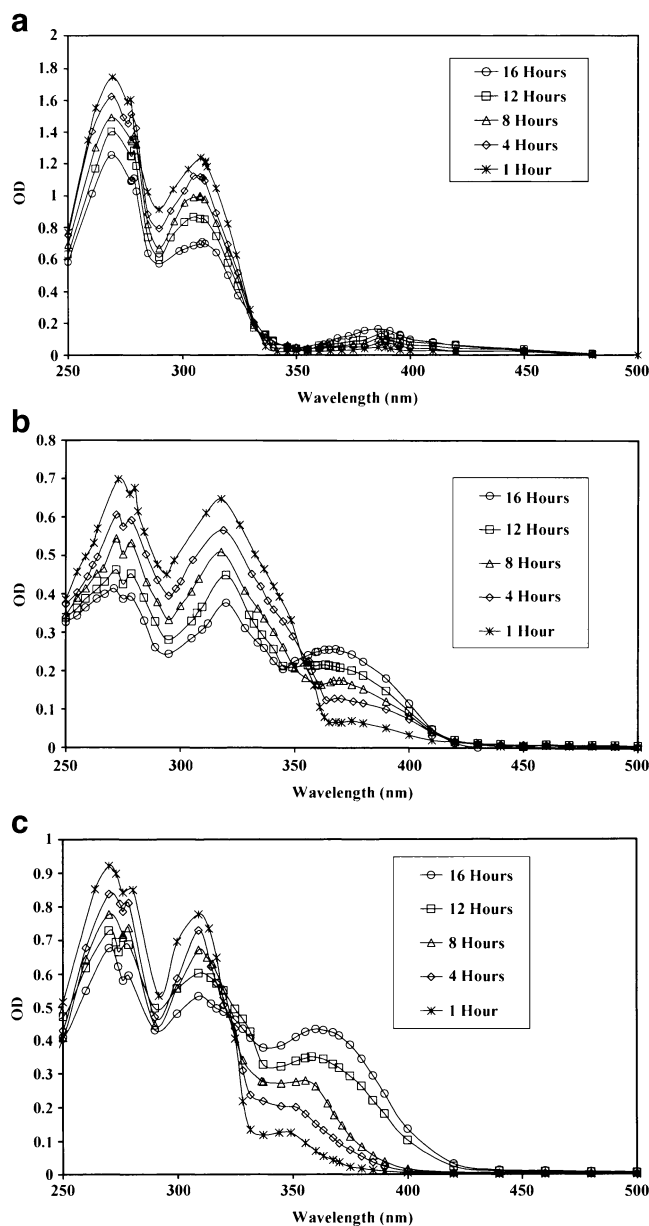
## Results and discussion

The sol-gel glass samples dipped in MeOH/H<sub>2</sub>O for various times show about 92% transparency from 700nm to 400nm

which gradually decreases to 88 % at 300nm. Due to good transparency down to 300nm, the glass samples can be used as host material for embedding C 1, C 2, and C 120 dyes which absorb in near-UV region of the spectrum. The undoped dipped glass block shows the same transparency through all the four faces when held vertical (0.8cm path length) and it did not change even if the position of the block with respect to the incident beam was changed across the width of the block confirming the plane parallel faces of the sample. The absorption spectra of all coumarin dye doped solid samples were recorded in the similar manner as above and also found to show same constant OD value when sample was held vertical. This confirms the uniform distribution of dye molecules throughout the sample. Though the variation in absorption spectra is observed with the varied dipping time of sol-gel sample in MeOH/H<sub>2</sub>O, the number density of the dye molecules in the samples for a particular concentration of dye solution (after 1h dipping) is nearly constant for all the dipped samples.

Figure 2 (a, b, and c) and Fig. 3 (a, b, and c) show the absorption and fluorescence spectra of C 1, C 2 and C 120 dye doped sol-gel glass samples respectively with increasing dipping time of the matrix in MeOH/ H<sub>2</sub>O. It represents the typical behavior of these solids which is observed with all the concentrations of coumarin dye molecules studied in the present work as shown in Table 1 and Table 2. All coumarin doped solids having number densities of the order of  $10^{16}/\text{cm}^3$  to  $10^{18}/\text{cm}^3$  show two near by UV absorption peaks peaking at 269nm, 278nm, where as other two peaks are observed at 308nm and 385nm in C 1, 320nm and 375nm in C 2 and 308nm and 350nm in C 120 dye doped glass samples. As the dipping time increases there is an increase in the OD value of main absorption peak at longest wavelength (385nm for C 1, 375nm for C 2 and 350nm for C 120) as can be seen from Fig 2 (a, b, c). Also slight red shift (8nm) in C 120/sol-gel glass samples and slight blue shift (5nm) in C 2 /sol-gel glass samples are observed with increasing time of dipping. On the other hand, the fluorescence spectra of all the coumarin dyes doped sol-gel glass samples have single emission peak peaking at 473nm, 448nm and 428nm for C 1, C 2 and C 120 containing sol-gel glass samples respectively. The fluorescence intensity also increases with time of dipping accompanied by red shift (8nm) for C 120/sol-gel glass, blue shift (6nm) for C 1 and C 2/sol-gel glass samples respectively as shown in Fig. 3 (a, b, c).

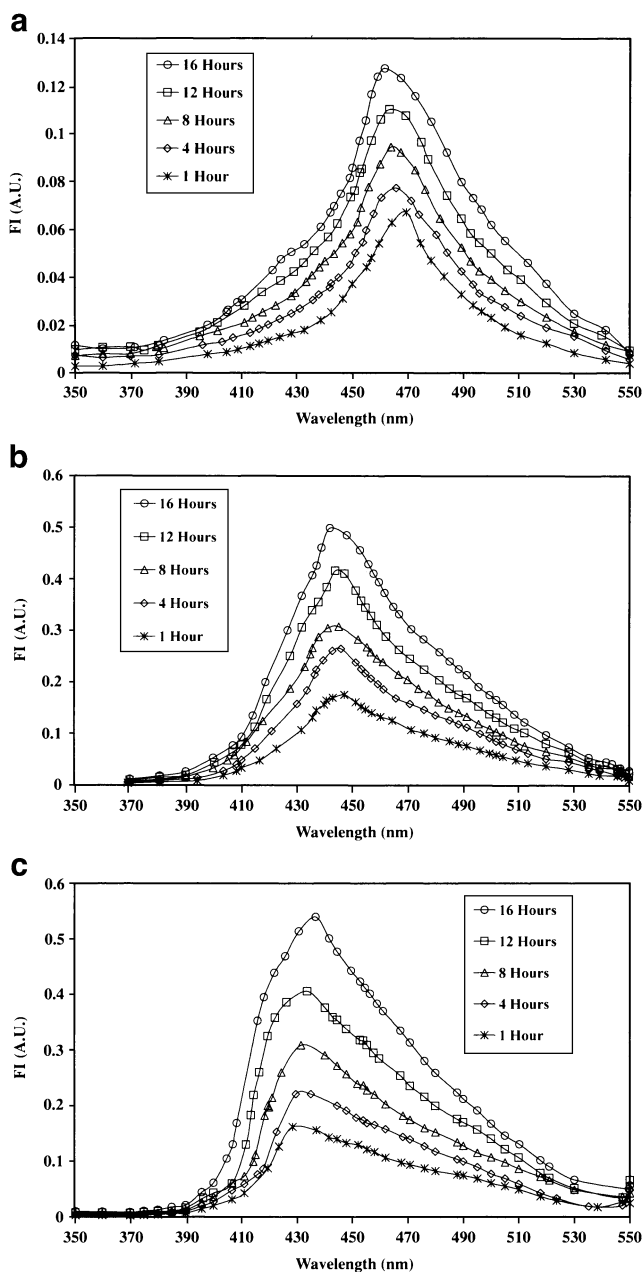
These changes show that the species (neutral monomer species) absorbing around 350–385nm are increasing for all coumarin samples in sol-gel glasses with increasing time of dipping the sample. These are fluorescent species having fluorescence peaking at 430 – 470nm. Such increase in the concentration of these monomer species with increasing dipping time increases the possibility of the samples to be laser active in the dye laser cavity, which is very favourable



**Fig. 2** Absorption spectra of a) C 1, b) C 2 and c) C 120 containing sol-gel glass sample with dipping time of sample in MeOH/H<sub>2</sub>O for no. density  $5.20 \times 10^{16}$  per  $\text{cm}^3$

from point of applicability of the samples as laser active media. There is also an isobestic point clearly seen in the absorption spectra of C 1/sol-gel glass samples (Fig. 2(a)).

To understand this behavior of coumarin doped sol-gel glass samples, absorption/fluorescence spectra of all coumarin dyes were recorded in MeOH solution with the addition of HCl acid. When HCl is added to the methanolic solution of coumarin dyes, it shows similar absorption as those of dye containing dried solid samples. Pure methanolic solution of C 1, C 2, C 120 shows only one absorption peak at 374nm, 365nm, 352nm and fluorescence



**Fig. 3** Fluorescence spectra of a) C 1, b) C 2 and c) C 120 containing sol-gel glass sample with dipping time of sample in MeOH/H<sub>2</sub>O for no. density  $5.20 \times 10^{16}$  per cm<sup>3</sup>

peak 450nm, 436nm, 429nm respectively, as shown in Fig. 4 (a, b, c) and Fig. 5 (a, b, c). OD at main peak of all coumarin dyes (C 1, C 2 and C 120) decreases as the concentration of acid in solution increases. This is accompanied by three more peaks appearing at shorter wavelengths viz one at 308 nm for C 1, C 120 and 320 nm for C 2 and other two at 278 nm and 269 nm for all coumarin dyes. Their shapes are similar to their respective counterparts in solid sol-gel glass samples.

These peaks are not due to absorption of HCl at lower wavelengths because they are absent in case of undoped

samples though all the solids contain equal concentration of acid. The fluorescence maximum in solution is initially constant near 450 nm for C 1, 436 nm for C 2 and 429 nm for C 120, only the fluorescence intensity decreases as the amount of acid in solution increases. Fluorescence at longer wavelength, namely 468 nm for C 1, 485 nm for C 2 and 478 nm for C 120 starts appearing at moderate acid concentrations. At intermediate concentration of acid both peaks appear in the emission spectrum of C 2 and C 120, and finally for high concentration of acid only a single peak at 466 nm for C 1, 489 nm for C 2 and 478 nm for C 120 with diminished intensity as can be observed from Fig. 5 (a, b, c). As the dipping time of sol-gel samples dipped in MeOH/H<sub>2</sub>O increases the absorption spectra of dried sol-gel glass samples resemble to the spectra of methanolic solution of coumarin dye containing dilute HCl acid. From the Fig. 4 (a, b, c) it can also be seen that there exists an isobestic point indicating that the increase in one peak is at the loss of OD at the other peak. This confirms the conversion of monomer species into some other species, probably protonated species. For all coumarin dye doped glass samples, the extinction coefficient at the longest absorption peak is less for C 1, moderate for C 2 and highest for C 120, while the opposite behaviour has been observed for the same dyes in MeOH with maximum extinction coefficient in C 1, moderate in C 2 and minimum in C 120. This photophysical behaviour of 7-aminocoumarin derivatives in acid catalysed sol-gel glass samples is very different from those in alcoholic solutions. This is due to hydrogen bonds interaction between dye molecules and

**Table 1** Absorption properties of C 1, C 2 and C 120 containing sol-gel glass samples with concentration of dye

Dipping Time (1 hour)	$\lambda_a$ (nm)	OD		
C 1	No. Density per cm <sup>3</sup>	$7.12 \times 10^{16}$	$5.10 \times 10^{17}$	$1.94 \times 10^{18}$
	385	0.07	0.15	0.24
	308	1.67	2.54	3.00
	278	2.19	3.00	3.00
C 2	No. Density per cm <sup>3</sup>	$7.38 \times 10^{16}$	$3.86 \times 10^{17}$	$2.21 \times 10^{18}$
	375	0.10	0.29	1.06
	320	0.73	2.36	3.00
	278	0.86	2.78	3.00
C 120	No. Density per cm <sup>3</sup>	$7.45 \times 10^{16}$	$4.36 \times 10^{17}$	$2.54 \times 10^{18}$
	350	0.18	0.26	0.45
	308	1.08	1.71	3.00
	278	1.09	1.75	3.00
	269	1.21	1.99	3.00

**Table 2** Fluorescence properties of C 1, C 2 and C 120 containing sol-gel glass samples with concentration of dye

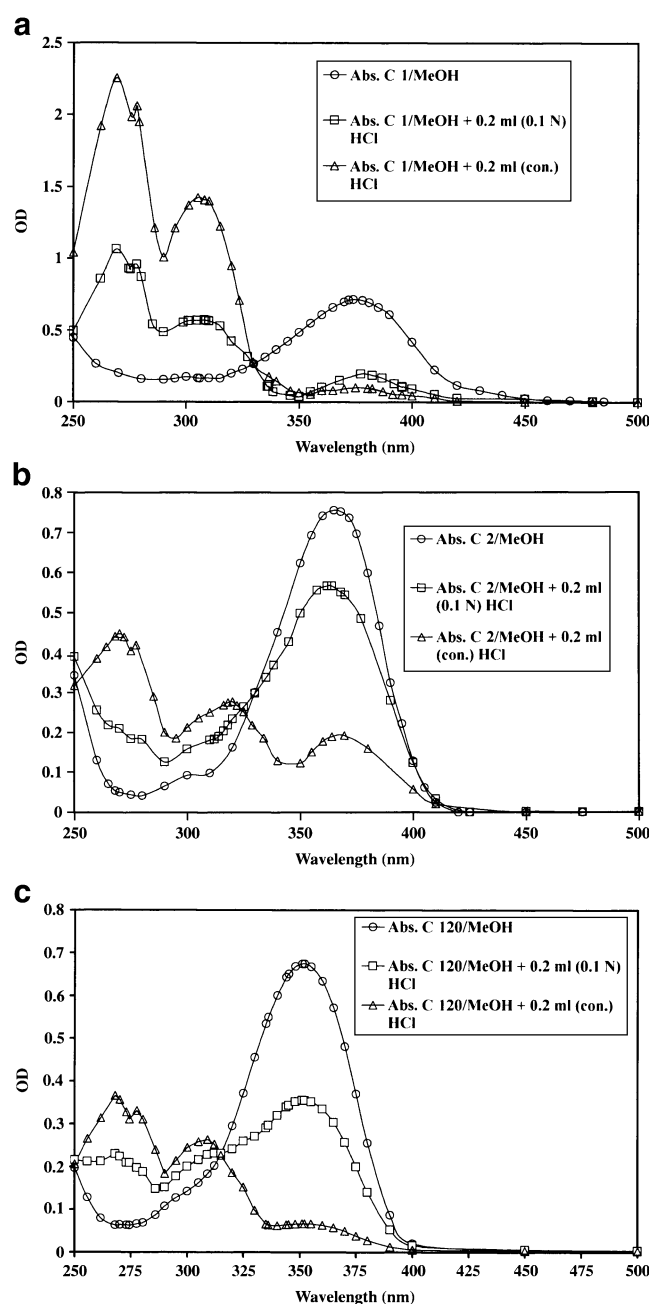
Dipping Time (1 hour)	$\lambda_f$ (nm)	FI(A.U.)		
<b>No. Density per <math>\text{cm}^3</math></b>		<b><math>7.12 \times 10^{16}</math></b>	<b><math>5.10 \times 10^{17}</math></b>	<b><math>1.94 \times 10^{18}</math></b>
C 1	473	0.09	0.13	0.10
<b>No. Density per <math>\text{cm}^3</math></b>		<b><math>7.38 \times 10^{16}</math></b>	<b><math>3.86 \times 10^{17}</math></b>	<b><math>2.21 \times 10^{18}</math></b>
C 2	447	0.21	0.40	0.26
<b>No. Density per <math>\text{cm}^3</math></b>		<b><math>7.45 \times 10^{16}</math></b>	<b><math>4.36 \times 10^{17}</math></b>	<b><math>2.54 \times 10^{18}</math></b>
C 120	428	0.23	0.32	0.18

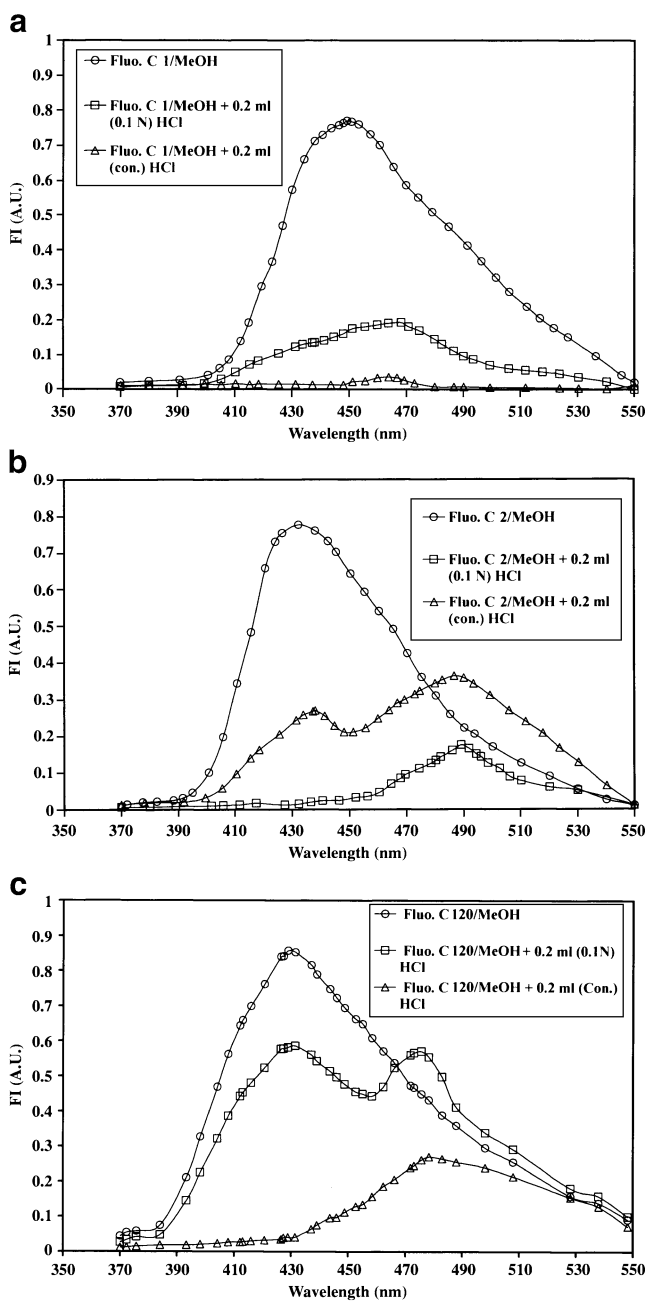
residual solvent in the matrix, which depend on alkylation degree of amino group of dye and this alkylation degree of amino group is increased from C 120 to C 1 ( $C 120 < C 2 < C 1$ ) [32]. The ratio of conversion of neutral species into protonated and higher protonated form is high for C 1, moderate for C 2 and low for C 120 as can be seen from Fig. 4 (a, b, c).

This behaviour of coumarin dyes can be explained by considering the ground state and excited state equilibria of the dye in the presence of acid as reported earlier by Drexhage [33]. Generally in the electronic ground state of 7-aminocoumarins, neutral or non-polar form is predominant, whereas in the excited state polar form predominates [33]. Therefore on optical excitation the (static) electric dipole moment increases, and a major rearrangement of the surrounding solvent molecules takes place immediately after excitation. As a consequence the energy of the excited state decreases giving rise to a large Stokes shift in coumarins [33]. The similar trend is observed for all studied coumarin dyes in MeOH with absorption/fluorescence peaks 374 nm / 450 nm for C 1, 365 nm / 436 nm for C 2 and 352 nm / 428 nm for C 120 respectively giving rise to Stokes shift of about 70 nm. Also effect of substitution at 7 position on absorption/fluorescence properties is seen having red shift of absorption with ethyl substitution. Hence maximum absorption wavelength is observed for C 1 with two ethyl groups among the studied dyes.

In 7-aminocoumarins, two types of protonation have been reported, one at amino group and other at carbonyl group [33]. In the ground state of coumarin slight basicity is associated with amino group rather than with the carbonyl group. On addition of a strong acid like HCl, the amino group gets protonated and the protonation increases with increase in the acid concentration and the OD at main peak continuously decreases as protonated form does not absorb at this wavelength as shown in Fig. 4 (a, b, c). This decrease in OD has been observed for all the concentrations of studied coumarin dyes in liquid phase. The formation of

higher protonated forms with addition of acid appearing at shorter wavelength has been identified in the case of other coumarins also [13, 36]. When acidified MeOH solution of coumarin dye was excited at shorter wavelengths (308 nm, 279 nm and 270 nm) there was no fluorescence observed. Hence protonated and higher protonated species of coumarin dyes which absorb at 308 nm, 278 nm and 269 nm respectively in acidic MeOH can be concluded to be nonemitting. The same behaviour (non-emitting and exists at shorter wavelength side of the main band) of the species

**Fig. 4** Absorption spectra of a) C 1, b) C 2 and c) C 120 in MeOH with addition of HCl for concentration of dye; C 1 ( $2.81 \times 10^{-5} \text{ mol l}^{-1}$ ) C 2 ( $3.78 \times 10^{-5} \text{ mol l}^{-1}$ ) C 120 ( $3.94 \times 10^{-5} \text{ mol l}^{-1}$ )



**Fig. 5** Fluorescence spectra of a) C 1, b) C 2 and c) C 120 in MeOH with addition of HCl for concentration of dye; C 1 ( $2.81 \times 10^{-5} \text{ mol l}^{-1}$ ) C 2 ( $3.78 \times 10^{-5} \text{ mol l}^{-1}$ ) C 120 ( $3.94 \times 10^{-5} \text{ mol l}^{-1}$ )

appearing at 308 nm, 278 nm and 269 nm absorption peak has been observed in dried coumarin dye doped sol-gel solids as can be seen from Fig. 2 (a, b, c). The protonation at carbonyl group occurs in excited state of dye molecule and is diffusion controlled. Due to proton transfer from surrounding molecules to the carbonyl group, these excited molecules come back to the ground state in non-polar form (by deprotonation process) by emitting radiation at longer

wavelength. The emission shifts to longer wavelength has been observed in case of the other coumarins if the pH of the solution is decreased [4, 15–16, 26, 37].

The studied dried dye doped sol-gel solid samples show only single emission peak at 462 nm, 442 nm and 436 nm for C 1, C 2 and C 120 respectively. As the fluorescence spectra of the all coumarin dye doped sol-gel glass samples do not have any emission in longer wavelength region, one can say that the corresponding carbonyl protonated species is not formed in solid sol-gel glass samples. Thus appearance of carbonyl protonated form cannot be seen in absorbance and fluorescence spectrum of the solid sol-gel samples of all the three coumarins. Therefore the absorption peaks at 308 nm, 278 nm and 269 nm of coumarins in dried sol-gel glass sample can be due to amino-protonated and higher protonated form and cannot be due to carbonyl protonated form. In case of samples in present work, as the dipping time of sol-gel glass samples in MeOH/H<sub>2</sub>O increases, the removal of unreacted residual solvent from the sample also increases. Thus local environment of coumarin molecules in glass may be having more HCl containing water and MeOH for less dipping time samples as compared to high dipping time samples. Hence in addition to neutral coumarin form which exists in ground state absorbing at main peak, there may be protonated, higher protonated and even some higher protonated species present in the sol-gel matrix for less dipped samples, which show absorption in UV region of the spectrum. But as the dipping time of the sol-gel host samples increases the maximum residual solvent containing HCl is coming out from sol-gel glass matrix and therefore existence of neutral form of coumarin dyes is high as compared to low dipping glass samples. This automatically reduces the possibility of formation of protonated form with longer dipped matrix samples. This is supported by decrease in OD value of absorption peaks at 308 nm, 269 nm and 278 nm and increasing in FI at main peak as seen from Fig. 2 and 3 (a, b, c). Hence an increase in OD/FI occurs only because of conversion of protonated species into the fluorescent neutral monomer species with increasing dipping time of the sample. The shift in absorption/fluorescence peak of coumarin containing sol-gel glass samples with respect to its methanolic solution may be the combined effect of increased refractive index of sol-gel compared to methanol, residual chemicals or precursors, the local environment of the dye molecules in the sol-gel and polar nature of the host [4–5, 13, 15].

## Conclusion

C 1, C 2 and C 120 dyes were embedded in HCl catalysed sol-gel glass samples which have been given

dip solvent treatment for various times from 1 h to 16 h using MeOH/ H<sub>2</sub>O and subsequently dipped in the dye solution using dip method during preparation. The samples show changes in absorption/Fluorescence spectra with time of dipping of solid host. In addition to usual neutral molecular form of C 1 ( $\lambda_a=374$  nm,  $\lambda_f=450$ ), C 2 ( $\lambda_a=365$  nm,  $\lambda_f=436$  nm) and C 120 ( $\lambda_a=352$  nm,  $\lambda_f=428$  nm) that exists in MeOH; the dye has been found to co-exist in new distinct molecular form identified as amino-protonated or higher protonated form ( $\lambda_a=308$  nm, 278 nm, 269 nm and non fluorescent) in the sol-gel glass sample. It has been investigated that the neutral form species increase at the cost of protonated form with time of dipping of the host sample in MeOH/ H<sub>2</sub>O. This is a useful change with increasing neutral species concentration in the sample which increases the application potential of these materials as solid state dye laser materials emitting in the blue-green region of the spectrum.

## References

- Schafer FP (1989) Topics in applied physics vol 1, in: Dye lasers. Springer, New York
- Avnir D, Levy D, Reisfeld R (1984) The nature of silica cage as reflected by spectral changes and enhanced photostability of trapped rhodamine 6G. *J. Phys. Chem.* 88:5956–5959 doi:10.1021/j150668a042
- Avnir D, Kaufman VR, Reisfeld R (1985) Organic fluorescent dyes trapped in silica and silica-titania thin films by the sol-gel method. Photophysical, film and cage properties. *Jn. Non-Cryst. Solids.* 74:395–406
- Deshpande AV, Panhalkar RR (2002) Spectroscopic properties of coumarin 2 in HCl and HNO<sub>3</sub> catalysed sol-gel glasses. *J. Lumin.* 96:185–193 doi:10.1016/S0022-2313(01)00218-6
- Deshpande AV, Kumar U (2002) Effect of method of preparation on photophysical properties of Rh-B impregnated sol-gel hosts. *Jn. Non-Cryst. Solids.* 306:149–159
- Sastre R, Costela A (1995) Polymeric solid-state dye lasers. *Adv. Mater.* 7:198–202 doi:10.1002/adma.19950070222
- Rahn MD, King TA (1995) Comparison of laser performance of dye molecules in sol-gel, polycom, ormosil, and poly (methyl methacrylate) host media. *Appl. Opt.* 34:8260–8271
- Popov S (1998) Dye photodestruction in a solid-state dye laser with a polymeric gain medium. *Appl. Opt.* 37(27):6449–6455 doi:10.1364/AO.37.006449
- Bakr NA, Mansour AF, Hammam M (1999) Optical and thermal spectroscopic studies of luminescent dye doped poly(methyl methacrylate) as solar concentrator. *J. Appl. Polym. Sci.* 74 (14):3316–3323 doi:10.1002/(SICI)1097-4628(19991227)74:14<3316::AID-APP4>3.0.CO;2-U
- Huang J, Bekiari V, Lianos P (1999) Study of poly(methyl methacrylate) thin films doped with laser dyes. *J. Lumin.* 81 (4):285–291 doi:10.1016/S0022-2313(99)00010-1
- Deshpande AV, Namdas EB (1996) Efficient lasing action of rhodamine 6G in Nafion membranes. *Chem. Phys. Lett.* 263:449–455 doi:10.1016/S0009-2614(96)01247-X
- Deshpande AV, Namdas EB (1997) Lasing action of rhodamine B in polyacrylic acid films. *Appl. Phys. B* 64:419–422 doi:10.1007/s003400050193
- Deshpande AV, Kumar U (2006) Molecular forms of coumarin-307 in sol-gel glasses. *J. Fluoresc.* 16:679–687 doi:10.1007/s10895-006-0109-5
- Lo D, Lam SK (1998) Lasing behaviour of sol-gel silica doped with uv laser dyes. *Appl. Phys. B* 66:427–430 doi:10.1007/s003400050413
- Li D, Zhao W, Sun X, Zhang J, Anpo M, Zhao J (2006) Photophysical properties of coumarin derivatives incorporated in MCM-41. *Dyes Pigments* 68:33–37 doi:10.1016/j.dyepig.2004.12.015
- Suratwala T, Garadlund Z, Davidson K, Uhlmann DR (1998) Silylated coumarin dyes in sol-gel hosts. 2. photostability and sol-gel processing. *Chem. Mater.* 10:199–209 doi:10.1021/cm97 0340s
- Kopylova TN, Mayer GV, Renzichenko AV, Samsonova LG, Sevetlichnyi VA, Dolotov MS, Tavrizova MT (2004) Active media for tunable blue-green lasers based on aminocoumarins in polymethylmethacrylate. *Appl. Phys. B* 78:183–187 doi:10.1007/s00340-003-1352-y
- Whang CM, Oh EO, Gupta RK (2003) Effect of pH and dye concentration on the optical and structural properties of coumarin-4 dye-doped SiO<sub>2</sub>-PDMS xerogels. *Jn. Sol-Gel Sci. Techno.* 28:279–288
- Qian G, Yang Y, Su D, Wang Z, Wang M (2005) Luminiscence and laser performance of coumarin dyes doped in ORMOSILs. *Mater. Sci. Eng. B* 119:192–195 doi:10.1016/j.mseb.2005.02.059
- Unger B, Rurack K, Muller R, Jancke H, Genger U (2005) Microscopic vs. macroscopic structural evolution of SiO<sub>2</sub> sols and gels employing a tailor-made fluorescent reporter dye. *J. Mater. Chem.* 15:3069–3083 doi:10.1039/b501622c
- Lo D, Parris JE, Lawless JL (1993) Laser and fluorescence properties of dye-doped sol-gel silica from 400 nm to 800 nm. *Appl. Phys. B* 56:385–390 doi:10.1007/BF00324537
- Kim G, Lee D, Kim J, Moon J, Lee H (1997) Effect of microstructural change on the optical property of ormosil embedded with organic molecules. *Jn. Sol-Gel Sci. Techno.* 10:283–289
- Choi D, Lim C, Sohn S (2003) Optical properties of coumarin 314 doped sol-gel silica rods. *Optik – International. Jn. for Light and Electron Optics* 114:347–350
- Hou L, Hoffmann B, Schmidt H, Menning M (1997) Effect of heat treatment and additives on the Photochromic and mechanical properties of sol-gel derived photochromic coatings containing spirooxazine. *Jn. Sol-Gel Sci. Techno.* 8:923–926
- Grandi S, Tomasi C, Mustarelli P, Clemente F, Carbonaro CM (2007) Characterisation of a new sol-gel precursor for a SiO<sub>2</sub>-rhodamine 6G hybrid class II material. *Jn. Sol-Gel Sci. Techno.* 41:57–63
- Campillo AJ, Clark JH, Shapiro SL, Winn KR, Woodbridge PK (1979) Excited-state protonation kinetics of coumarin 102. *Chem. Phys. Lett.* 67(2–3):218–222 doi:10.1016/0009-2614(79)85150-7
- Kunjappu JT (1993) Photophysical properties of five laser dyes (C120, C1, C102, C1F and C153) in homogeneous, surfactant and membrane media. *Jn. Photochem. Photobiol. Chem. (Kyoto)* 71 (3):269–273
- Jones G II, Rahman MA (1994) Fluorescence properties of coumarin laser dyes in aqueous polymer media. Chromophore isolation in poly(methacrylic acid) hypercoils. *J. Phys. Chem.* 98:13028–13037 doi:10.1021/j100100a035
- Samanta A, Fessenden RW (2000) Excited-state dipole moment of 7-aminocoumarins as determined from time-resolved microwave dielectric absorption measurements. *J. Phys. Chem. A* 104 (37):8577–8582 doi:10.1021/jp001676j
- Fisher A, Cremer C, Sterlzer EHK (1995) Fluorescence of coumarins and xanthenes after two-photon absorption with a pulsed titanium—sapphire laser. *Appl. Opt.* 34(12):1989–2003
- Haidekker MA, Brady TP, Lichlyter D, Theodorakis EA (2005) Effect of solvent polarity and solvent viscosity on the fluorescent

- properties of molecular rotors and related probes. *Bioorg. Chem.* 33:415–425 doi:[10.1016/j.bioorg.2005.07.005](https://doi.org/10.1016/j.bioorg.2005.07.005)
32. Arbeloa TL, Arbeloa FL, Tapia MJ, Arbelo IL (1993) Hydrogen-bonding effect on the photophysical properties of 7-aminocoumarin derivatives. *J. Phys. Chem.* 97:4704–4707 doi:[10.1021/j100120a024](https://doi.org/10.1021/j100120a024)
33. Drexhage KH (1989) In F. P. Schafer (Ed.), *Dye Lasers*, Springer, New York, pp. 172–175
34. Costela A, Moreno I, Figuera J, Guerri F, Sastre R (1998) Polymeric matrices for lasing dyes: recent development. *Laser Chem.* 18:63–84 doi:[10.1155/1998/71976](https://doi.org/10.1155/1998/71976)
35. Jones G II, Jackson WR, Choi C, Bergmark WR (1985) Solvent effects on emission yield and lifetime for coumarin laser dyes. Requirments for a rotatory decay mechanism. *J. Phys. Chem.* 89:294–300 doi:[10.1021/j100248a024](https://doi.org/10.1021/j100248a024)
36. Trozzolo AM, Dienes A, Shank CV (1974) Excited-state reactions of laser dye. Evidence for a two- step phototautomerism in 7-hydroxy-4 methyl coumarin. *J. Am. Chem. Soc.* 96(14):4699–4700 doi:[10.1021/ja00821a070](https://doi.org/10.1021/ja00821a070)
37. Moriya T (1983) Excited-state reactions of coumarins in aqueous solutions. I. The photoautomerization of 7-hydroxycoumarin and its derivative. *Bull. Chem. Soc. Jpn.* 56:6–14 doi:[10.1246/bcsj.56.6](https://doi.org/10.1246/bcsj.56.6)