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Efficient lasing action from Rhodamine-110 (Rh-110) impregnated sol–gel silica samples prepared by dip method

Aparna V. Deshpande, Uday Kumar *[1]

Department of Physics, Institute of Chemical Technology, Matunga, Nathalal Parikh Marg, Mumbai – 400 019 (India)

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Rhodamine-110/sol–gel samples are prepared by sol–gel technique using dip method. Concentration dependent photophysical studies of these samples have indicated about the least possibility of aggregate formation. The lasing action of Rh-110 in silica samples is studied as a function of dye concentration. An efficient laser emission is observed when the samples are transversely pumped at 337.1 nm and 1.5 Hz repetition rate using a nitrogen laser (400 μJ energy/pulse and 4 ns pulse duration). The maximum of 166% laser efficiency of dye doped sol–gel samples compared to Rhodamine-6G (Rh-6G) in methanol is achieved. The photostability is also measured by using N_2 laser at 1 Hz and it is found nearly 165 pulses. The possible reasons for the photodegradation of the dye molecules are discussed in detail.

1. Introduction

The beauty of dye laser is its tunability. Solid-state dye lasers have been a subject of renewed research interest since the past three decades. In addition to commercial advantages, these lasers have technical advantages over liquid dye lasers. Several types of materials have been used as host matrices for dye encapsulation [1–8]. Recently, researchers have shown intense interest in the use of low temperature sol–gel technique to prepare solid-state laser materials [4–13]. Also improved photostability of dye in sol–gel materials has been reported [4–15]. Various laser dyes, belonging to Xanthene and Coumarin classes, have been used as dopant in the past for the preparation of dye doped sol–gel solid-state active material [4–13]. Rhodamine-110 (Rh-110) is an important laser dye of Rhodamine family with molecular structure as shown in the Fig. 1.

Monte and Levy have reported the photophysical properties of Rh-110 in sol–gel glasses and dimers of Rh-110 have been observed over all studied range of concentrations except for a few lower concentrations [16]. The authors have identified the dimers as J-type (fluorescent) and H-type (non-fluorescent). Similar types of dimers formation have also been reported with Rhodamine-6G and Rhodamine-B doped in sol–gel glasses [17–19]. Therefore, high dopant concentration is avoided because formation of non-fluorescent H-type dimer reduces the fluorescence efficiency [20–23]. In most of the above mentioned reports, the dyes were added to the starting sol of sol–gel precursor.

In the present paper, as a continuation of our study on dye laser [24–31], we report the enhanced photophysical properties i.e. least possibility of aggregation (dimer formation) of Rh-110, efficient lasing action (166% laser efficiency) and photostability of Rh-110 impregnated sol–gel silica when pumped by nitrogen laser transversely. More importantly, such a high lasing efficiency and characteristics of Rh-110 laser dye in sol–gel matrix is rarely reported in the literature to the best of our knowledge and belief. Originally the aim of the work was to develop such a dye impregnated sol–gel solids, which were free from dimers formation and consequently, could be used as laser active material in solid-state dye laser. To achieve this goal, the dye molecules were incorporated into sol–gel matrices by postdoping (dip) method (in contrast to the conventional dye encapsulation method), where the dye was allowed to diffuse into the pores of the glass structure after synthesis [5]. The following points should be noticed from the present study – (i) the least aggregate formation of Rh-110 in sol–gel samples compared to earlier reports of the same dye in sol–gel [16,17]; (ii) the remarkably high relative laser efficiency of Rh-110/sol–gel compared to Rh-6G in methanol (166%); and (iii) the proposed pin point reasons for the poor photostability of Rh-110 in sol–gel and way to improve it for future study. These results may be significantly

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* Corresponding author.
E-mail address: udayphy@yahoo.co.in (U. Kumar).

[1] Present address: Indian Institute of Science Education and Research Kolkata, Department of Physical Sciences, Mohanpur Campus, P.O. – BCKV Campus Main Office, Mohanpur – 741 252, Nadia, West Bengal, India.

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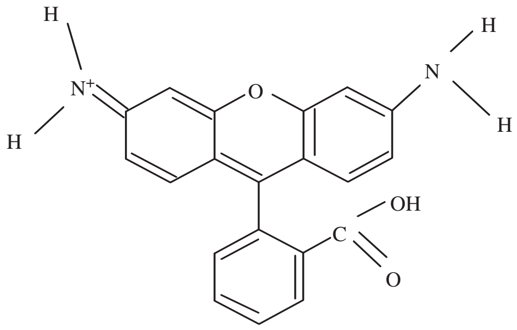

Fig. 1. Molecular structure of Rhodamine-110.

important for the future application of Rh-110/sol–gel materials for various applications in basic and applied research.

2. Experimental

Laser grade Rhodamine-110 was obtained from Lambda Physik. Its purity was checked (by UV visible and IR spectroscopy) and then it was used as it was received. Tetraethylorthosilicate (Merck–Schuchardt), methanol (Merck, GR grade), nitric acid (Merck) and formamide (Merck) were used without further purification.

The molar ratios of TEOS: water: nitric acid: methanol: formamide were 1:10:0.45:3:3. Formamide was added after 6 h of stirring and the sol was used for the sample preparation. Twenty days after preparation, samples were used to immerse in methanolic solution of Rh-110 of known concentration for different intervals of time. The no. density of dye molecules in the solid host was calculated by difference method from the knowledge of absorption spectrum of the Rh-110 solution before and after the dipping of glass sample (with an error of ±6%). Drying of samples was carried out at room temperature. The concentrations of dye in methanol and time interval of dipping were adjusted to obtain desired no. density in solid host. All the samples prepared by this method were in the form of block $0.5\times0.5\times1.5\ \mathrm{cm}^3$ approximately.

Optical absorption spectra of all the prepared samples were recorded by a conventional Spectrophotometer (with scan speed 100 nm per minute) with respect to undoped (without dye) glass sample. The fluorescence spectra were scanned using an assembled fluorimeter with front surface excitation emission geometry [24–31]. Rh-110 in ethanol (basic) was used as the reference (in the order of 10^{-4} M/L) with fluorescence quantum yield (Q_f) equal to 0.90 [32] for the determination of the quantum yield. Fluorescence spectra of samples and reference were scanned at the same excitation wavelength (495 nm) with excitation and emission bandwidths of 5 nm. The scan speed of fluorescence spectra was kept 50 nm per minute. Recorded spectra were corrected for the photomultiplier and monochromator sensitivities. The area under curve of the emission spectra was used for the quantum yield measurement. Fluorescence lifetimes of Rh-110/sol–gel samples were measued at RSIC, IIT, Mumbai by using single photon counting technique. The experimental set-up consists of a flashlamp (hydrogen filled) with 100 kHz frequency (FWHM < 2 ns, rise time < 1 ns) as an excitation source, excitation/emission monochromators, start and stop photomultipliers, time to amplitude converter, multichannel analyzer and a computer. The deconvolution technique has been used to find lifetime value. They are single exponential decay with chi square value in between 0.95 and 1.05.

The Rh-110 impregnated sol–gel samples were transversely pumped at 337.1 nm using a nitrogen laser (Laser Science Inc., 400 μJ energy/pulse and 4 ns pulse duration, variable repetition rate). Rh-6G/PMMA film (90% efficiency compared to Rh-6G in methanol) was used as standard for the comparison of laser intensity [24,27]. There was no external resonator used in the present study. The parallel sides of the sample themselves might be functioning as resonator (sample shape geometry was in the form of parralellopiped type with size $1.5\times0.5\times0.5\ \mathrm{cm}^3$ approximately). The detection system consists of a 0.35 m Mc Pherson monochromator (plane holographic grating with 1200 G/mm) with resolution 0.05 nm and wavelength accuracy 0.2 nm, a UDT energy meter, and a plotter [24–31].

3. Results and discussion:

Unlike to other Rhodamine dyes (e.g. Rh-6G, Rh-B etc.), Rhodamine-110 is an unsubstituted member of the same family. Table 1 lists the photophysical properties of the dye in methanol and sol–gel silica host.

The absorption/fluorescence properties including fluorescence quantum yield and lifetime of the dye in dried sol–gel solid are similar to that of the dye in methanol except for a slight difference in fluorescence lifetime. The increase in the lifetime value of Rh-110 in sol–gel (τ=4.19 ns) compared to that in methanol (τ=3.9 ns) is correlated with the high rigidity of the sol–gel matrix [16], which prevents the free intramolecular rotation of dye molecules that can result in the subsequent reduction of the nonradiative deactivation processes or quenching ($S_1\rightarrow S_0$ internal conversion processes) [16,23,33–36]. In the present study, the concentration of the dye molecules was in the range of 10^{15}–10^{18} molecules/cm^3. A typical absorption/fluorescence spectrum of the Rh-110 impregnated sol–gel host is shown in Fig. 2. The aggregation of dye molecules in Rhodamine dyes is well known.

Drexhage has reported the least tendency of dimers formation of Rh-110 [37]. However, few recent publications have reported the dimerization characteristics of Rh-110 in sol–gel matrix [16,17]. These dimmers may be fluorescent (J-dimmer) or non-fluorescent (H-dimmer) in characteristics depending on its structure. The chemical environment in the surrounding of the dye molecules and or high dye concentration is the main reason for the formation of these dimmers. A concentration dependent spectroscopic property is shown in the Table 2 and Fig. 3. The absorption (497–500 nm)/fluorescence (525–530 nm) peaks of Rh-110 impregnated sol–gel samples in the present study almost remain constant with increasing dye concentration (~range 5.6×10^{15}–6.5×10^{16} molecules/cm^3). No remarkable deviation in spectral profile of Rh-110 in sol–gel, absorption/fluorescence, could be observed. These results do not support the formation of any aggregate in the above mentioned concentration range of dye. Further more, the absorption spectra become broader beyond above mentioned dye concentration range of 6.5×10^{16} molecules/cm^3. However, fluorescence peak position remains constant in the entire studied range of dye concentration

Table 1
Photophysical properties of Rh-110.

Sample/solvent	λ_a (±1)nm	λ_f (±1)nm	ϕ_f (±0.1)	Lifetime (ι in ns)
Methanol[a]	498	520	0.88	3.90
Sol–gel[b]	498	522	0.85	4.19

[a] The dye concentration used was in the range of $(0.1–7)\times10^{-6}$ M/L.

[b] The dye concentration used was in the range of $(2.5–7.8)\times10^{15}$ molecules/cm^3.