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EFFECT OF DCCA ON THE OPTICAL AND LASING PROPERTIES OF DYE DOPED SILICA GELS/ORMOSILS

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ABSTRACT

Dye 597 pyrromethene incorporated silica gel host/organically modified silicates (ORMOSILS) was synthesized by sol-gel process using N, N-dimethylformamide (DMF), γ -glycidoxypropyltrimethoxysilance (GLYMO) and Dimethylsalfoxide (DSMO) as a drying control chemical additive (DCCA). Silica sols were prepared using DMF, and ORMOSILs were made using GLYMO and DMSO. Absorption and emission spectra of two host samples were recorded during the sol-gel transition and effect drying time from the date of preparation. The change in absorption/emission spectra of dye doped Silica gel has been shown during the sol-gel transition in comparison to ORMOSILs. The lasing performance of both dye doped silica and ORMOSILs was shown to be different. The effects of DCCA in Silica/Ormosils on optical and lasing properties of the molecule were discussed.

Keywords: Absorption, emission, laser dye, sol-gel, ormosils

INTRODUCTION

The sol-gel process is a versatile solution process for making ceramic and glass materials. In general, the sol-gel process involves the transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. The sol-gel process allows synthesizing ceramic materials of high purity and homogeneity by means of preparation techniques different from the traditional process of fusion of oxides. This process occurs in liquid solution of organometallic precursors (TMOS, TEOS, Zr(IV)-Propoxide, Ti(IV)-Butoxide, etc.), which, by means of hydrolysis and condensation reactions, lead to the formation of a new phase (SOL) (Brinker and Scherer, 1990).

The sol gel process has widely attracted in materials research in the past decade due to its unique advantages such as low temperature processing, high homogeneity of final products and its capability to generate materials with controlled surface properties and pore structures (Damrau and Marsmann, 1994; Lenza and Vasconcelos, 2000; Mansur *et al.*, 2000). Sol gel glass offers a host in which organic dye can be impregnated into a solid medium which can provide high optical quality using hydrolysis and polycondensation reactions (DeLange *et al.*, 1995; Nair *et al.*, 1997).

Recently many efforts have been made to produce embedded organic dyes in various solid matrices, such as organic polymers, silica gels, xerogels, alumina gels, ORMOSILs, for solid state lasers that may substitute liquid dye lasers (Avnir *et al*., 1984, 1985; Li and King, 1996). The solid state dye lasers have advantages over liquid dye by being non-volatile, non-flammable, non-toxic, compact and mechanically stable (Lintner *et al*., 1988 and Tseng *et al*., 1992).

Although great attempts have been made on the synthesis of highly photostable lasers and host media such as polymers or ormosils Rahn and King, (1998), Ahmad *et al*. (1999), Faloss *et al*. (1997) and Nechitailo *et al*. (1999), transmittance of most polymeric host in the UV region is commonly very low for their application in UV and blue bands and shown to be lacking in mechanical, thermal properties and refractive index Dunn *et al*. (1990). However, the silica gel glasses have been used as the host media in previous research to build solid state dye lasers in the UV and blue region because of their high transmittance (Lo *et al*., 1998; Wu and Zhu, 1999). It was however, made clear that pure silica gel have serious drawbaks i.e. causing cracks and facture formation, migration and aggregation of the dyes and thus decreasing their efficiency (Sakka *et al*., 1986).

For this reason, workers have turn to nanocomposite organic/inorganic matrices such as *sol-gel derived* ORMOSILs which offer several advantages over pure sol-gel silica like crack free; low light scattering, better mechanical properties, flexibility and easy hand polish (Zhang *et al*., 2002). Some dyes such as Rhodomine, Perylimide and other Pyrromethene doped in matrix by sol-gel method (Yariv *et al.* 2001) were found to have high efficiencies. But the heat dissipation, the damage threshold of host materials and photostability i.e. the longetivity of dye doped samples, low laser conversion

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efficiency and degradation (photo bleaching) are, however, still remain to be solved for applications that require high powers at either CW or pulsed high repetition rate laser operation (Valverde, 2006).

It is reported that the photostabilty of solid state dye lasers depends on chemical composition of the host matrices, dye concentration, pump wavelength, pulse rate, pump fluorescence sample, sample thickness and geometry (Suratwala *et al.*, 1997a) which may be reduced either by improving the matrices. The bleaching of the fluorescent output depends on the nature of the solvent or matrix and the presence of the other reactive impurities such as oxygen (Kosar, 1965; Kaminov *et al*., 1972). Additives to the host composition can be used to prevent photooxidation of the dye and to provide a more stable chemical (acid/base) environment, resulting in improved photochemical stability Suratwala *et al.* (1997b).

The use of DMF as a "Drying Control Chemical Additive" (DCCA) in Silica gel was found to give best quality of samples in term of monolithicity, transparency and low density (Rao *et al*., 1999; Zhang and Jiang, 2001). The use of GLYMO could greatly change the structure properties of sol-gel derived xerogels and thus a denser structure and better mechanical properties of ORMOSILs have been obtained (Hu and Ziang, 1998). In addition, the use of DMSO decreases the magnitude of the capillary stress and minimizes the differential capillary stresses to protect the drying gels from crack generation (Lin and Baerner, 2000). The effect of host preparation method on spectroscopic properties of dopant molecules is of great importance for the application of solid state dyes embedded sol-gel glasses. The stability and lasing action of dye molecule depends on its photophysical properties which are greatly influenced by the host matrix.

In this connection, we report here a detailed study of spectroscopic and lasing properties of PM597 dye doped silica gels/ORMOSILs using DMF, GLYMO and DMSO as DCCA.

MATERIAL AND METHODS

Tetraethylorthosilance (TEOS) (Aldrich, 98 %) was used as the inorganic precursor. EtoH (Riedel-de Haen) were used as solvent without further purification. The silica sols was obtained from hydrolysis and polycondensation of TEOS using ethanol as solvent, DMF as DCCA, Nitric acid as catalyst and distilled water. The molar ratio used of TEOS: EtOH: DMF: water: Nitric acid was [1:2:1.5:2:.01] and the initial volume was 100 ml. DMF was added to the TEOS/Ethanol under stirring after 45 minutes in an open glass beaker. Water/nitric acid mixture was added to the solution and after 30 minutes of mixing, the dye was added using a concentration of $1X10^{-4}$ M. The final sol was kept at room temperature for one month; drying and aging were continued at 40^{o}C in an oven.

Similarly, Ormosils was prepared in one step by acid hydr olysis and polycondensation of TEOS with Ethanol, GLY MO, DMSO, water and Nitric acid. The molar ratio used of TEOS: EtOH: GLYMO:DMSO water: Nitric acid was [1:2:1.5:2:4.01] and the initial volume was 100 ml. The Ormosils sol was kept under vigorous stirring at 50^{o}C for 1 hr to yield clear stable sol. After stirring the mixture for 1 hr, laser dye PM597 dissolved in ethanol was added to the solution with a nominal concentration of $1 X 10^{-4}$ mol/l. The final sol was kept at 60^{o}C for several weeks in an oven. In both methods, an ultrasonic bathing was used to obtain homogeneous sols and in order to insure dye distribution. The sol gel solution is poured into the rectangular polystyrene cuvettes during which period, the absorption and emission spectra of the sample were measured to register the evolution of the peaks with time. For lasing properties study, solid cylindrical shape of the samples was made and cut about 2-3 cm lengths. The surfaces were hand polished for laser action.

The absorption and emission spectra were recorded on UV-Visible Spectrophotometer (Perkins Elmer) and LS-45 Luminescence Spectrophotometer (Perkins Elmer) respectively. The fluorescence spectra and laser properties were obtained by a Monochromator/Spectro-graph (Solar Co. model M266) followed by a CCD Camera type synchronized with Ti: Saphire Laser (Solar Laser Co.). Laser Pulse excitation of 532 nm, 4ns and beam diameter of 10 mm was used for the fluorescence spectra and lasing properties. Transverse pump was chosen for such configuration. In this configuration, a cylindrical lens was used to focus the input energy with 10 cm focal distance. The cavity consisted of 75 % reflectivity front mirror and a back mirror with 100 % reflectance at the laser wavelength. Cavity length of 3 cm was chosen.

RESULTS AND DISCUSSION

Figures 1 and 2 show the absorption and emission spectra of PM597 dye doped Silica sol gel during sol-gel transitions at various times of drying silica sol gel. The absorption peaks at 524, 519, and 509 nm were blue shifted on the transition from sol to gel. After solidified of the silica gel, the peak was red shifted at 522 nm is shown in Fig.1. Shifting in the peaks was due to physical influence of host matrix that changes with temperature and times. Similarly, emission spectra of the dye of same silica host show slow red shifting with times. A gradual small red shifting of emission peaks were observed with times. The emission peak of solid sample observed at 574 nm after 60 days is shown in Fig. 2.

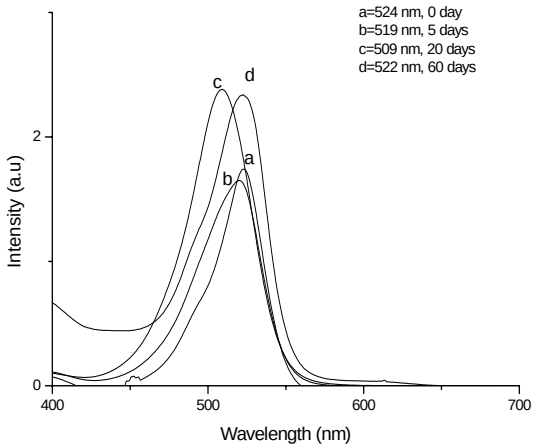

Fig. 1. Absorption spectra of PM597 doped Silica sol-gel.

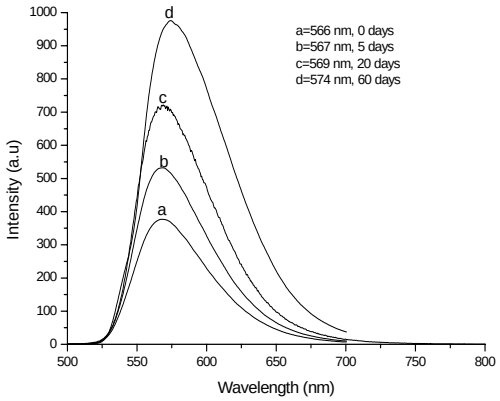

Fig. 2. Emission spectra of PM597 doped Silica sol-gel.

Figures 3 and 4 show the absorption and emission spectra of PM597 dye doped ORMOSILs. All spectra were recorded during sol-gel transition and effect of drying time is listed in Fig. 3. The observed peaks do not shift during sol-gel transition but it was blue shifted after 100 days i.e. solidified the host. Further the peaks position of emission spectra during the transition of sol-gel was constant up to 60 days. After the gel become solid the peak appeared red shifted as few nm as shown in Fig. 4. It can be expressed that the absorption and emission peaks were shifting when the physical state of host changed i.e. during the sol-gel state; the peaks are uniformly observed means the peaks are constant but after solidified of the matrix, peaks are observed stable as shown in Fig. 4. It means ORMOSILs host is influenced by the physical state. It did not show any temperature dependence on shifting the peaks. Moreover, formation of gel from sol in GLYMO–DSMO derived ormosil is very slow as compared with silica sol-gel. It shows that the photophysical stability of the former host is found to be better than the latter host which might be influenced by DCCA properties. No doubt, the intensities of the absorption and emission spectra are shown variation due to the phase transition of the both host. During this phase transition of host, it may change the species concentration and condensation.

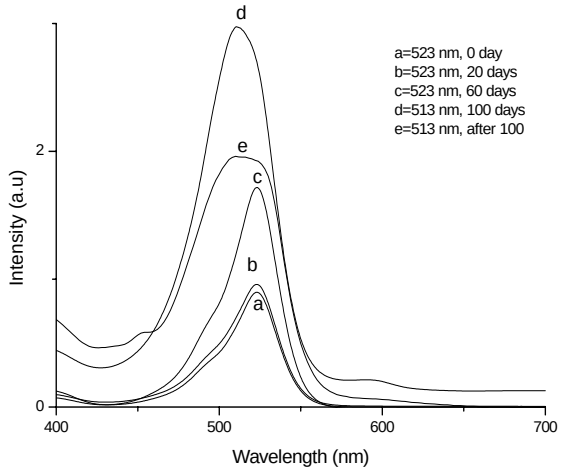

Fig. 3. Absorption spectra of PM 597 doped ormosils.

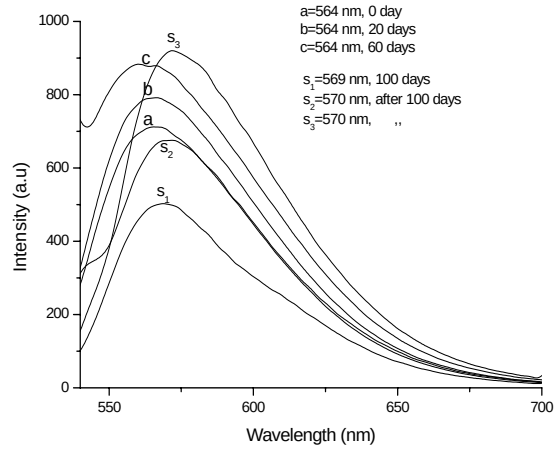

Fig. 4. Emission spectra of PM 597 doped ormosils.

Figure 5 shows the fluorescence spectra of PM597 doped sol-gel silica excited by different energy of laser pulses. When the pump energy increases, the behaviour of fluorescence peaks are gradually shifting toward the higher wavelength region. Further amplified stimulated emission peak was obtained when pump by 14 mJ of laser pulse. Fig. 6 shows the amplified stimulated emission spectra where the wavelength was blue shifted (576 nm) compared with 'f' (581 nm) of Fig. 5. It may state that the physical property of silica host matrix is also influenced by pump energy.

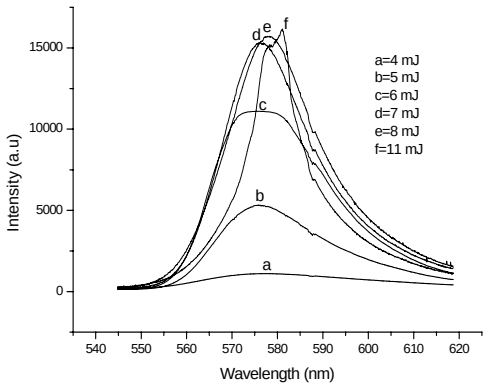

Fig. 5. Fluorescence spectra of PM597 doped silica sol-gel at different pump energies.

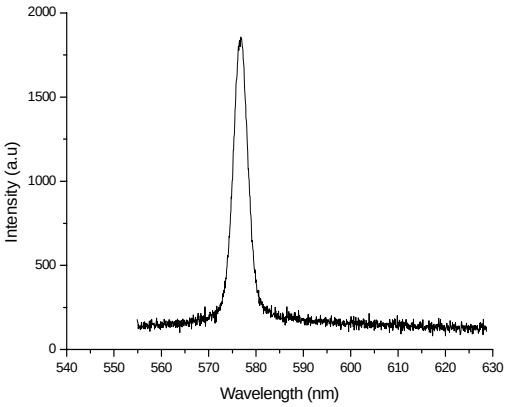

Fig. 6. Amplified Stimulated Emission spectra of PM597 doped silica sol-gel at 14 mJ pump energy.

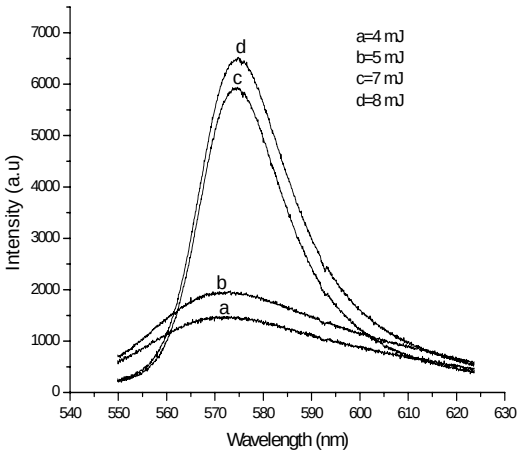

Fig. 7. Fluorescence spectra of PM597 doped ORMOSIL at different pump energies.

Figures 7 and 8 show the fluorescence and amplified stimulated emission spectra of PM597 doped Ormosils obtained at different pumping energies. On the other hand, the observed peaks in the fluorescence and stimulated spectra do not much shift when the pump energy increased. Therefore, shifting the peaks of PM597 dye in the silica host on temperature variation with time is a result of physical instability of the host, not dye. Earlier studies (Zhang and Jiang, 2001) revealed that the stability of PM dye parents was found to be excellent as compare to other parent dyes.

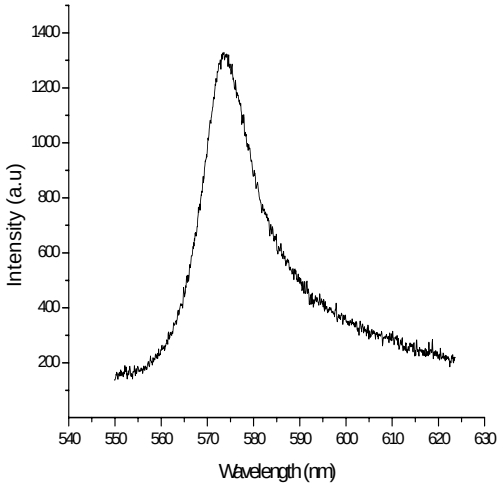

Fig. 8. Amplified Stimulated Emission spectra of PM597 doped ormosil at 7mJ pump energy.

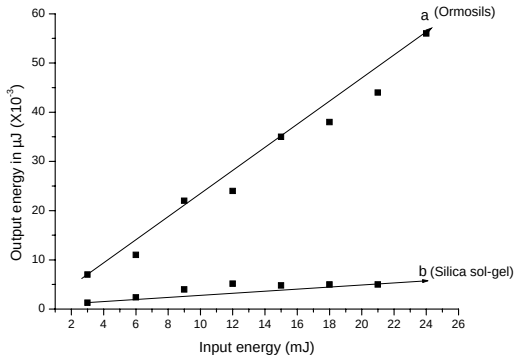

Fig. 9. Comparison of lasing efficiency of PM 597 doped Silica sol-gel and ormosils.

Figures 9 and 10 show the comparison between the Silica and Ormosils host to their efficiency and photostability. Efficiency of dye in Ormosils is shown greater than the silica host. It seems that stability of dye in the Ormosils is much better than the Silica gels. The lasing output energy also from the Ormosils is given larger than silica host. The efficiency of both host matrixes is obtained less than 10 % but Ormosils shows reasonably good.

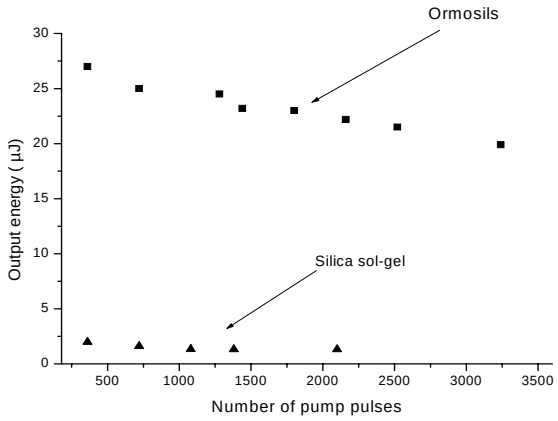

Fig. 10. The output energy of PM 597 doped in silica sol-gel and ormosils as a function of the number of pump pulses.

The ORMOSILs by sol-gel process offer an opportunity to incorporate organic dyes, enhancing their optical properties such as photophysical properties, efficiency and photostability in comparison to other silica gels prepared by the same process.

The photophysical properties of the dye with different DCCA derived ORMOSILs can be studied, under different drying times by spectroscopic and laser techniques. Sol-gel organically modified type host is given more stability for solid state lasers. It depends on the type of DCCA which can provide stability in the matrix. For the future work DCCA can play a role in improving the host matrix. Therefore, it may conclude from the study that the stability of dyes in sol-gel host matrix and photophysical properties, photostability and efficiency are greatly influenced by the type of host matrix. The GLYMO-DMSO derived ORMOSILs is shown good for incorporating the laser dyes in sol-gel process which may enhance longetivity and efficiency.

CONCLUSIONS

Laser dye doped Silica gel and Ormosils using different DCCA are prepared by sol gel process. The lasing performance such as lasing efficiency and photostability of the dye doped of both sol gels is studied. DCCA influences on the optical and lasing properties of the sample are observed. It may conclude that DCCA can be improved the stability of sol gels and desired molecule inside the host as well, efficiency and photostability.

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