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Spectroscopic study of sulforhodamine 640-doped sol–gel silica

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Abstract

The sol–gel process is a technique which provides a low-temperature route for the preparation of organic dye-doped porous silica glass. Extended UV transmission was observed for HCl-catalysed sol–gel silica. Properties of a solute may differ greatly between a free solution and that solution confined in pores of a sol–gel glass. Absorption and fluorescence properties of sulforhodamine 640-doped silica samples prepared by sol–gel process were investigated. In the TEOS-derived gel, the emission of the dye does not shift during aging but exhibits a large change during drying. The emission maximum of sulforhodamine 640 blue shifts was discussed as a function of increasing rigidity of the surrounding matrix.

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Keywords: Tunable solid state dye laser; Laser dye; Dye/matrix interaction

1. Introduction

During the past decades, the sol–gel process has been extensively studied in many laboratories. In 1984, Avnir et al. [1–3] have reported the preparation and optical properties of alkoxide-derived silica gels doped with rhodamine 6G and pyrene [1–3]. They have also demonstrated that other organic molecules can be successfully incorporated into sol–gel matrices [1,4]. The advantages of the sol–gel process are lower temperature processing, excellent homogeneity at a molecular level, high compositional purity and the possibility of incorporating organic molecules at low temperature that will otherwise be destroyed in conventional glass-forming process. The most useful feature of dye lasers is their tunability, i.e., the lasing wavelength for a given dye may be varied over a wide range. Taking advantage of the broad fluorescent line widths available in organic dyes,

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one can use a wavelength-selective resonator to perform selective tuning [5]. Organic dye molecules as laser gain media enjoy the advantage of broad tunability ranging from 300–900 nm with high efficiency, high photostability and superior thermal–optical properties. Reports on the spectroscopic behaviours [6,7], lasing properties [6,8–16] and optical non-linearities [17] of a large number of dyes trapped in sol–gel-derived silica glasses have already appeared in the literature. The applications of tunable solid-state laser in visible are in remote sensing, isotope separation, high sensitivity analytical spectroscopy and underwater communications. Development of the above-mentioned applications requires a good understanding of the structure of the doped sol–gel matrices, the properties of the matrices on the molecular level and the conditions that the oxide network imposes on the optical properties of the dopant.

2. Experimental

Two types of sol–gel silica samples, one using HCl and another using HNO_3 as catalyst were fabricated following the sol–gel procedures outlined in [12,14]. The initial solution is typically composed of 15 ml of TEOS, 12.5 ml of ethyl alcohol, 18 ml of water, 12.5 ml of formamide and 2 ml of acid serving as catalyst. Sulforhodamine 640 was added to the initial solution under magnetic stirring until the desired molar concentration was reached. The organic dye and chemical used in these experiments were procured from commercial vendors (Exciton, Merk and Sigma Aldrich, respectively). The concentration of sulforhodamine 640 as suggested by the vendor (Exciton) is 1×10^{-4} molar in the initial solution. Kept at a temperature of 60 °C, gelling occurs in hours. After aging and drying for about 1 week, the containers were opened and the pore liquid expelled during shrinkage was evacuated. Drying and aging were continued for 3 weeks at 60 °C. The bulk density of the samples prepared using HCl as a catalyst is 1.42 g/cm^3 and that of using HNO_3 is 1.39 g/cm^3. For all data presented here. Cylindrical-shaped samples with a diameter of 14 mm and a thickness of 10 mm were used for the measurement. All samples were visually of good surface finish with end faces appearing to be plane parallel. Experiments were carried out at room temperature immediately after hydrolysis through the gelation stage until the sol–gel material dried. The absorption spectra were measured with a Jasco V-570 spectrophotometer and the fluorescence spectra were recorded on Hitachi fluorescence spectrophotometer model F- 4500.

3. Results and discussion

When HCl was used as a catalyst during the sol–gel process, improved UV cutoffs can be achieved [12,13]. The improved UV transmission is a result of smaller size concentrated pore distribution is effected by the HCl-catalysed hydrolysis, so we choose HCl-catalysed sol–gel silica for our further experiments. To understand the effects of dye/matrix interaction on the fluorescent properties, one needs to explore how a dye behaves in different molecular environment. A continuous red shift in absorption spectra was observed as the polarity of the solvent increases because of the polar nature of dye (Fig. 1). The lowest energy transition is the (π,π*) transition due to dipole–dipole interaction with the solvent molecules. The (π,π*) excited state is more polar and more polarizable than the ground state, resulting in greater lowering of the excited state and reducing the transition energy, and therefore it experiences a red shift upon increase in solvent

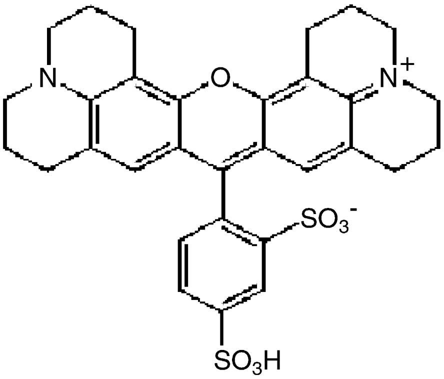

Fig. 1. Molecular structure of sulforhodamine 640.