学术期刊可以用微信做什么，快来看看！

微信自动应答服务平台
微时代 微革命

微服务
移动互联网时代的营销革命
简单快捷 • 高效互动 • 随时随地 • 广泛传播
Preparation and optical properties of a Rhodamine 6G-doped sol-gel AlPO₄-SiO₂ film

Youyu Fan, Rihong Li, and Long Zhang

Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China

*Corresponding Author: lzhang@siom.ac.cn

Received May 10, 2013; accepted May 20, 2013; posted online August 2, 2013

AlPO₄-SiO₂ films doped with Rhodamine 6G (Rh6G) are prepared using the sol-gel dip-coating method. The surface morphology is characterized by atomic force microscopy. The results indicate that the surface morphology of the films is not significantly affected by the amount of dyes loaded. The absorption and excitation spectra indicate low aggregation even at a Rh6G doping concentration of 1.0×10⁻³ mol/L. Efficient fluorescence with a band centered at 553 nm is observed.

OCIS codes: 310.6860, 240.0310.

doi: 10.3788/COL201311.083101.

Rhodamine 6G (Rh6G) is widely used as a luminescent material because of its high quantum yield and excellent lasing ability. Incorporating dyes into solid matrices can increase thermal and photo-stability, thereby providing more high-quality luminescent materials. Numerous studies show that J dimer or H dimer aggregates readily form when the dye concentration loading reaches 10⁻³ mol/L. Large numbers of aggregates are formed in solid matrices. Numerous studies show that J dimer or H dimer aggregates readily form when the dye concentration is high. Thus, controlling dye aggregation at high concentrations has been challenging. In general, Rh6G aggregates show strong dependence on the chemical environment. Most studies conclude that large numbers of aggregates are formed when the dye concentration loading reaches 10⁻⁵–10⁻¹⁷ mol/L. However, Rh6G dye doped in film has been demonstrated to exhibit efficient emission. Moreover, dye aggregation in films probably decreases because of surface effect. Films are potential hosts for laser dyes at high dye concentrations.

Recently, AlPO₄-SiO₂-based materials have been widely investigated for various applications in optical devices because of their similar structure and isoelectronic relationship with SiO₂. Furthermore, these materials exhibit excellent thermal stability as well as a porous structure with high specific surface area, which may be beneficial for the incorporation of dyes. In this letter, we prepared AlPO₄-SiO₂ films doped with Rh6G via sol-gel processing.

Precursor sols were prepared from Si(OS₂H)₄ (TEOS) (99%, APCR), aluminum lactate (98%, Fluka), and NH₄H₂PO₄ (99%, Merck). For the preparation of the AlPO₄-SiO₂ sol, 2.35-g aluminum lactate and 0.92-g NH₄H₂PO₄ were dissolved in 50-ml deionized water and then stirred for 1 h. Afterward, 1.75-ml TEOS was added after dissolution in 5-ml isopropanol. After stirring for 10 h, the desired Rh6G ethanolic solution was added, and the mixture was then stirred for 2 h. The resulting solution was transferred to a sealed plastic bottle and aged for 3 days at room temperature.

The glass substrates were all K9 glass. Prior to film coating, all substrates were cleaned using the following procedures: (1) all substrates were ultrasonically oscillated for 15 min in ethanol; (2) the substrates were dipped in a basic KOH solution (KOH:H₂O:ethanol = 10 wt%:10 wt%:80 wt%) for 10 h; (3) the substrates were ultrasonically oscillated for 15 min in ethanol and then oscillated for 5 min in deionized water. The final cleaned substrates were dried at 120 °C for 30 min and then preserved in sealed boxes.

Dip-coating was conducted by immersing the clean K9 glass substrates in the sol. The withdrawal speed was controlled at 0.3 cm/min. The loading of the Rh6G dye on the film was adjusted by the dye concentration (1×10⁻⁵–1×10⁻³ mol/L). After deposition, the films were aged and dried at 50 °C for 30 min and then dried at 120 °C for 2 h in an electric furnace. All films coated on the glass substrates were uniform and crack free.

Atomic force microscopy (AFM) was performed using a Nanoscope IIIa microscope from Digital Instruments. The thicknesses of the coated films were measured by a profilometer (Dektak II).

Fluorescence spectroscopy was performed on a HORIBA Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450-W xenon arc lamp, double-grating excitation and emission monochromators (2.1 nm/mm dispersion; 1200 grooves/mm), and a Hamamatsu R928 photomultiplier tube. Each emission was excited at 460 nm. All spectroscopic measurements were performed at room temperature.

Absorption spectroscopy was conducted using an ultraviolet-visible light spectrophotometer (Varian Company, Cary-50 UV-Vis).

The development of the sol-gel dip-coating method for preparing films incorporated with dyes is convenient because the dye concentration can be controlled and optical uniformity can be achieved. Dyes incorporated in films at high concentrations without forming aggregates may be used as efficient gain media for solid-state dye lasers.

The morphologies of the films were characterized by AFM imaging. Figure 1 shows the images of the monolayer films at different dye concentrations (1×10⁻⁵–1×10⁻³ mol/L). The results show that the films consist...
of particle aggregates with grain sizes ranging from 20 to 40 nm. However, the morphology of the whole films is not significantly affected by the dye loading. In addition, the roughness factors (root-mean-square roughness) are fairly small (from 0.29 to 0.52 nm) and are of the same magnitude. Furthermore, the thicknesses of the monolayer films are all approximately 50 nm. Therefore, the films are uniform and dense.

Figure 2 shows the normalized absorption spectra of the films at different dye loadings. For the film with dilute dye loading (10^{-5} mol/L), only one main absorption peak at 527 nm, which is due to the monomeric Rh6G molecule, is observed. Aggregation is significant in silica materials and PMMA when the Rh6G dyes introduced into these materials reach 10^{-5} mol/L.[8-12] A further increase in the dye concentration (from 10^{-5} to 10^{-3} mol/L) results in the formation of H dimer and J dimer aggregates.[10-12,24] This increase also results in the broadening of the main absorption peak and an increase in the absorption at the shoulder around 499 nm. However, the observed degree of aggregation is significantly lower than that in silicate materials[8-10] even at high dye concentrations (1×10^{-3} mol/L).

The excitation spectra show trends similar to those of the absorption spectra (Fig. 3). The increase in the band intensity at 499 nm with the increase in dye concentration mainly results from the formation of a number of J dimer aggregates. This phenomenon can be explained by the exciton theory[24], which is more applicable in excitations than in absorptions. Thus, the increase at 499 nm, which is ascribed to the J dimer, in the excitation spectra and the broadening of the main band at 531 nm are more observable. No shift is observed for the main excitation band at 531 nm. Therefore, the small number of aggregates is dominated by J dimers even though some H dimers also exist based on the exciton theory.

Regarding the normalized fluorescence spectra (Fig. 4), a very slight red shift of the main emission peak from 553 to 556 nm is observed with the increase in the Rh6G concentration. This result is a general observation in solid matrices and is ascribed to the restriction of the solid “cage” as well as to the interaction of the Rh6G molecules as the dye concentration increases. The fluorescence spectra also show that the aggregation is very slight even when the dye concentration reaches 10^{-3} mol/L, which results in the very slight increase in the intensity of the shoulder band at 490 nm as deduced from the exciton theory. In addition, a wide tunability beyond 50 nm can be observed. This result indicates that the film is suitable and may be an excellent host of the Rh6G dye at high concentrations. Therefore, the film is a good candidate for the preparation of solid tunable-laser dyes[25,26].

In conclusion, AlPO_4-SiO_2 crack-free films doped with Rh6G on a glass substrate is fabricated through the sol-gel dip-coating method. The AFM images indicate that the monolayer film is uniform and dense, with a thickness of approximately 50 nm. In addition, the surface morphology is not significantly affected by the varied dye concentrations. The absorption and excitation spectra
indicate that the slight aggregation of Rh6G in this film is predominated by J dimers and is significantly lower than those in silica glass and PMMA at high concentrations ($1 \times 10^{-3}$ mol/L). The efficient fluorescence without an observable shift of the main emission peak at 553 nm indicates that the aggregation is insignificant. Thus, this film is a potentially excellent host for the Rh6G dye and can probably be applied to solid tunable-laser dyes at high concentrations.

This work was supported by the National Natural Science Foundation of China (Nos. 50802103 and 51072207) and the Natural Science Foundation of Shanghai (No. 11ZR1441500). Rihong Li contributed equally to this work.

References