

Pressure-induced changes on the optical properties and microstructure of silica-gel matrices doped with rhodamine 6G

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Abstract

Sol–gel method and high-pressure technique were associated to produce silica compacts with low porosity and doped with rhodamine 6G (R6G). Acid catalyzed solutions of tetraethyl orthosilicate mixed with dye previously dissolved in ethanol were used for the synthesis of doped silica gel. The monolith obtained was comminuted and the powder was compacted between 3.0 and 7.7 GPa, at room temperature, using a toroidal-type high-pressure chamber. Excitation–emission fluorescence spectroscopy was used to investigate the optical properties of R6G embedded in the closed pores of the silica matrix. Measurements of surface areas and pore size distribution for the powders and compacts, using the N₂ isotherms were performed, showing a great reduction in surface area and porosity, after compaction. The dye entrapped in the compacted silica maintains its optical properties similar to that in ethanolic solutions, meaning that the dye is dispersed in a molecular level. Additionally, these samples are optically transparent, hard and resistant to dye leaching and to chemical attacks, being a promising material to be used in optical devices.

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1. Introduction

The entrapment of organic dyes into solid inorganic matrices has attracted a wide interest over the last years due to its useful and potential applications as laser materials and nonlinear optical materials [1–4]. Compared to liquid solutions, the incorporation of dye molecules into solid host increases the photostability and fluorescence yield of the dye. The solid matrices are able to isolate

the dye molecules from each other, which reduces unwanted formation of nonfluorescent aggregates or complexes [5]. It is well-known that the aggregation of laser dye molecules, in dimeric or polymeric form is a source of degraded lasing ability. Generally the dimers are not fluorescent and consequently strong decay of fluorescence quantum efficiency is observed at high concentrations [6]. Therefore, high lasing ability is achievable by preparing materials containing well dispersed dye monomers. Rhodamine 6G has been one of the most frequently used probes in these studies, due to its high quantum yield of fluorescence [3,6–8].

Several works in the literature are concerning to the process of incorporation of organic dyes in coating films of sol–gel derived oxide matrix, in organic polymers, in composite glasses, as well as in bulk solid inorganic

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matrices [2,3,5–10]. One of the most widespread techniques to perform this kind of incorporation is through the sol–gel method [11]. It is based on hydrolysis and polycondensation reactions of metalorganic compounds. A typical starting solution contains tetraethoxysilane (TEOS), water, organic solvents, and the dye, being the hydrolysis performed by acidic, basic or nucleophilic catalyzes, forming at the end a doped silica matrix. The porosity of this doped silica monolith is normally high, which is undesirable for lasers and other applications [2]. This problem can be bypassed, generally adding surfactants in the synthesis or doing heat treatments. However, there is another powerful tool, the high-pressure technique, which can improve the matrix, changing the microstructure and lowering the porosity at room temperature [12,13]. Pressure can also produce large changes in the electronic and vibrational states of the dye entrapped in the organic matrix, inducing modifications on the optical properties of the dye, as for example in their emission–excitation fluorescence spectra [14].

Costa et al. reported that the silica-gel powder undergoes a process called cold sintering when it is used a special configuration, with a quasi-hydrostatic pressure transmitting medium. The porosity is drastically reduced, and it was proposed in that work, the embedding of dye molecules in closed pores of the inorganic matrices [9]. This solves the problem of leaching, and improves the mechanical stability, producing materials that are hard, dense, optical transparent and crack free. However, a more complete study of the morphological properties, mainly porosity and surface area would be interesting to confirm the proposed model.

In the present work, the authors studied the state of R6G dye molecules in the silica sol–gel monolith/powder prepared using two dye/TEOS molar ratios, and in the compacted powders obtained by high-pressure technique. The excitation–emission fluorescence spectra were measured in samples prepared at pressures between 3 and 7.7 GPa, in order to investigate pressure-induced changes in the optical properties of R6G. These measurements were compared to their respective non-compacted samples. Measurements of surface areas and pore size distribution in both kinds of samples, using the N₂ isotherms, were performed, aiming to give a more complete insight of the pore structure of the samples.

2. Experimental

2.1. Sample preparation

The silica powders doped with rhodamine 6G (R6G—Kodak, laser grade) were obtained by the sol–gel technique based on the hydrolyses and polycondensation of the precursor tetraethyl orthosilicate (5 ml—

Table 1
Synthesis conditions for different samples

Sample	Mol dye/mol TEOS
A	Without dye
B	1.0×10^{-4}
C	2.4×10^{-5}
D ^a	2.4×10^{-5}

^a Triton 100-X was added.

TEOS, Merck—Schuchardt, for synthesis) in water (1.6 ml) and ethanol (5 ml—EtOH, Merck, grade for analysis) solutions under acidic conditions (0.1 ml—HF—40% by wt., grade for analysis) [11]. The dye was previously dissolved in ethanol and this solution was added to TEOS. In some dye/ethanol solutions Triton X-100 (1 drop for 5 ml TEOS) was added, as a surfactant agent. All samples were prepared with water-to-TEOS molar ratio 4:1 and the concentration ratio mol dye/mol TEOS is described in Table 1.

The sol–gel solution was distributed in three small plastic dishes that were inside a large Petri dish and just covered, without sealing. Drying and aging were carried out in air, at room temperature for about 15 days. A monolith was formed, which is comminuted in an agate mortar, during 7 min, to obtain the best quality powder to be compacted. This control makes the process quite reproducible.

2.2. High-pressure compaction

The R6G doped silica powder is pre-compacted in a piston-cylinder apparatus at approximately 0.2 GPa and placed in a lead container with internal diameter of 8 mm, that acts as a pressure-transmitting medium [13]. The compaction was then accomplished in a toroidal-type high-pressure chamber, at room temperature [15]. The pressure calibration was performed by the “fixed points” technique, using Bi and Yb, which allowed calibrating the pressure in the following three fixed points: Bi with phase transitions at 2.5 GPa and 7.7 GPa, and Yb with a phase transition at 4.0 GPa. The pressure is considered accurate to ± 0.5 GPa. Detailed description of the high pressure calibration method is given elsewhere [12]. At first, the experiments were performed at pressures of 3.0, 4.0, 6.0 and 7.7 GPa, at room temperature, during 10 min to promote the cold sintering process [9]. Based on the results of this set of experiments, we choose to process several samples at 6 GPa, in order to study more deeply the pressure-induced changes in the optical properties and in the microstructure of these compacts.

2.3. Mechanical and optical measurements

The Vickers microhardness (HV) measurements were performed using a Shimadzu micro-indenter with a load

of 100 gf. Density measurements were made using the picnometer method.

The emission–excitation spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The excitation wavelength for the emission spectra was 500 nm and for the excitation spectra the selected emission wavelength was 580 nm. All the measurements were performed using a standard solid sample holder at room temperature, in front face excitation–emission geometry.

2.4. Porosity measurements

The specific surface areas of the powders and compacts were determined from the BET multipoint method and the pore size distribution was calculate using the BJH method [16,17]. Both methods were based on the nitrogen adsorption–desorption isotherms of the previously degassed solids, at 150°C. These isotherms were determined at liquid nitrogen boiling point in a home-made volumetric apparatus, with a vacuum line system employing a turbo molecular Edwards vacuum pump, and the pressure was measured with a capillary Hg barometer.

3. Results and discussion

The silica compact discs doped with R6G were obtained combining sol–gel method and high-pressure technique. The discs have a diameter of about 5 mm

Table 2
Physical properties of samples type B at different pressures

Pressure (GPa)	Hardness (GPa)	Density (g/cm ³)
3.00	2.80 ± 0.04	1.85 ± 0.01
4.00	2.80 ± 0.02	1.93 ± 0.01
6.00	3.50 ± 0.15	2.06 ± 0.02
7.70	3.50 ± 0.02	2.18 ± 0.02

and thickness of 4 mm. They are remarkably stable, retaining its mechanical and optical properties for years, as far as we could observe. Visually they are crack free and transparent, presenting high density, and can be polished to optical grade.

Table 2 shows the density and Vickers microhardness measurements for compacts obtained from samples type B (dye/TEOS molar ratio of 1.0×10^{-4}) at different pressures. The density at 7.7 GPa is about 98% of the silica theoretical density. The maximum hardness is 3.50 ± 0.05 GPa and it did not increase after 6 GPa. This value is high compared to silica quartz (10 GPa) considering that our samples are amorphous. The same measurements were made for samples type C (dye/TEOS molar ratio of 2.4×10^{-5}) and the values were within the uncertainty obtained for samples type B. These high density and hardness values are remarkable since the high-pressure compaction was performed at room temperature.

Figs. 1 and 2 show the excitation and emission spectra for the R6G dye in silica for compacted samples,

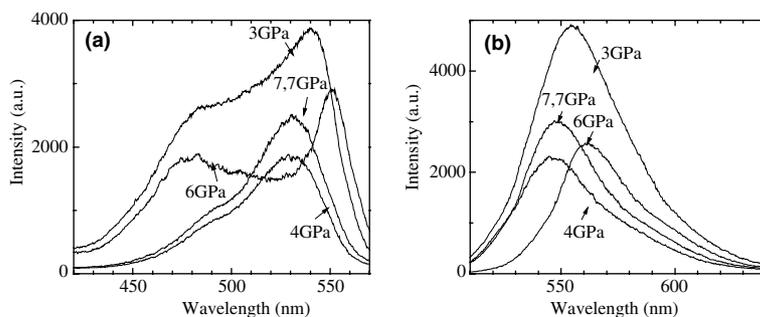


Fig. 1. (a) Excitation and (b) emission spectra for R6G incorporated into silica matrix at different pressures, for samples type B.

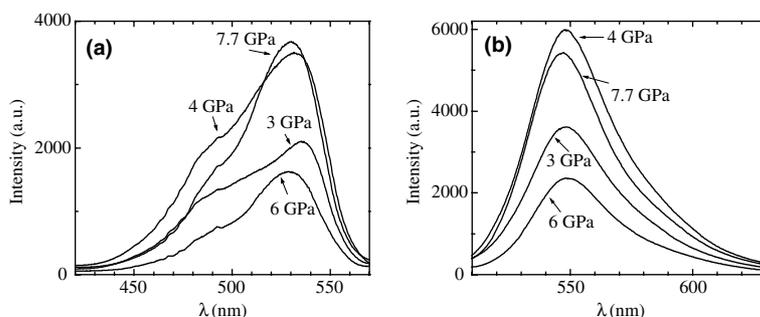


Fig. 2. (a) Excitation and (b) emission spectra for R6G incorporated into silica matrix at different pressures, for samples type C.

type B and C, prepared at different pressures, respectively. In Fig. 1(a), the samples processed at 4.0 and 7.7 GPa, showed a typical excitation spectra of R6G, containing contributions of monomeric forms (near 530 nm), and a lower intensity dimeric forms (near 490 nm). According to the literature [5,6] there is a vibronic shoulder at 500 nm, which is very difficult to separate from the dimeric forms. However, many authors considered that when the intensity ratio between the peak at 530 and 490 nm decreases, the dimers concentration is higher [5,6]. Our results corroborate this; it was observed that with the increase of dye concentration, the contribution of the dimeric forms near 490 nm also increases. These spectra are very similar to the absorbance spectrum of R6G in ethanolic solution. On the other hand, samples compacted at 3.0 and 6.0 GPa, showed the absorption wavelength red-shifted, and a higher intensity in the dimeric contribution as compared to the previous ones. The deconvolution of these excitation spectra showed the presence of a third peak near 550 nm attributed to a fluorescent J-dimer, formed during the compaction processing [3,6]. The differences observed between the excitation spectra for these samples that have higher dye concentration (type B), can be attributed to dye aggregation caused by an increase of local dye concentration, and water retaining in closed pores formed during the cold sintering process [3,9,10].

Fig. 1(b) shows the emission spectra for the same samples of Fig. 1(a). It was not observed any regularity concerning the influence of pressure on the fluorescence peaks in the range between 3.0 and 7.7 GPa. For the samples processed at 3.0 and 6.0 GPa, the spectra are red-shifted related to the other samples. This can be attributed to the dimer formation observed in the excitation spectra in Fig. 1(a).

Fig. 2 shows the excitation–emission spectra at different pressures, obtained for samples type C, where the concentration ratio dye/TEOS is lower. In this case, the excitation spectra (Fig. 2a) for 4.0, 6.0 and 7.7 GPa were similar, showing a maximum intensity around 530 nm, as well as a shoulder around 490 nm. The only spectrum that shows a broader band and a red shift comparing to the others is for 3.0 GPa and this was attributed to some scattering observed for this sample, which was not very well compacted (see Table 2), as the others. In this case, all the excitation spectra could represent a typical excitation spectra of R6G, containing contributions of monomeric forms (near 530 nm) and a lower intensity dimeric form (near 490 nm), for all pressures, without the dimeric contribution (J-dimer) showed in Fig. 1a. In Fig. 2b, the emission spectra for all samples have the maximum intensity around 550 nm. It means that after the high-pressure treatment, the fluorescence of the dye entrapped in the compacts is similar to the fluorescence of the dye in ethanolic solutions, indicating that the dye is completely solvated, as

it was observed in previous works [9,10]. It is interesting to notice that this effect is independent of the pressure in the range from 3.0 to 7.7 GPa, as long as the concentration ratio dye/TEOS is lower, as in sample type C. Though, the pressure is still an important tool to improve the mechanical properties of the doped silica.

Analyzing the results discussed above, we found that the best sample that achieved a good compromise between an intense fluorescence, low dimer formation and good mechanical properties were samples type C, compacted at 6 GPa. We choose than these samples to make a more complete study of the morphology and optical properties, comparing them to the powders before compaction. As it was mentioned before, these compacted samples reproduce the fluorescence (emission) and absorbance (excitation) spectra of the dye in ethanolic solution, regardless of the dye had been incorporated in a solid silica matrix.

Comparisons of excitation–emission spectra for powder and compacted (6 GPa) samples type C are showed in Fig. 3. For the powder (full line), the maxima intensities are at wavelengths of 520 nm and 540 nm for the excitation and emission spectra, respectively. The spectra are slightly blue-shifted if compared to the R6G in ethanolic solution, where the maximum absorbance is at 529 nm and the maximum emission, at 560 nm. This is attributed to interactions of the dye with the matrix after solvent evaporation [18]. For the compacts (dot line), the maxima are red-shifted, compared to the powder, for both, excitation (530 nm) and emission (550 nm) spectra. In this case the spectra are very similar to the dye in ethanolic solution. The observed red-shift can be attributed to several effects as dye solvation, dye aggregation and cage effects [5,6,9,10]. In a previous work, it was presented a cold sintering model to explain the silica compaction at high pressure, where a strong structure with closed pores containing trapped water or ethanol is formed [9]. It was also proposed that after the compaction, the silanol groups of the matrix are

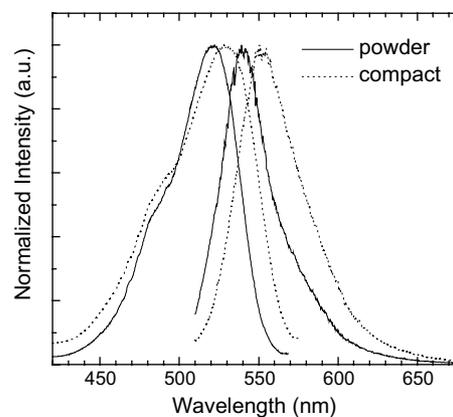


Fig. 3. Comparison of excitation and emission spectra for samples type C, powdered and compacted (6 GPa).

strongly bonded and consequently the H bridges between silanol groups and the R6G dye are prevented. Therefore there is almost no interaction of the dye with the matrix and it could be solvated in closed pores. It is expected that when the local dye concentration increases due to the high pressure compaction, some aggregation and dimer formation can form, causing the red-shift observed [6]. Cage effects are certainly also involved, because the dye is completely confined in the closed pores of the microstructure of silica matrix, which make the doped silica compact nonleachable. It is a much desired property for these materials, hindering the dye oxidation [5].

We tried still to improve these samples, adding a surfactant (Triton X-100) in the syntheses [6], which is largely used in sol-gel technique to decrease the sample porosity. The excitation-emission spectra for these samples, called type D, are shown in Fig. 4. We can observe that there is almost no blue-shift for the powder, compared to the dye in ethanolic solution, and that the spectra for the doped compact reproduces very well the spectra of R6G in ethanolic solution, with the maxima at wavelength of 530 nm and 560 nm, for the excitation and emission spectra, respectively. Also, the linewidths are smaller than the ones observed for the samples type C without Triton (Fig. 3), which could indicate a reduction of dimer formation, as already observed by other authors [6]. Regarding the mechanical properties, the compacted samples are very resistant, allowing also polishing to optical grade. However, these samples are completely opaque and even with satisfactory dye dispersion in the compact, the lack of transparency, makes this sample not useful for optical devices.

Table 3 shows the results of surface area and porosity for the silica powder (samples A, C and D) and their respective compacts (samples AP, CP, DP). Sample A has the highest surface area and porosity, which is expected because this sample is from undoped silica gel. Sample C presents a reduction in surface area and

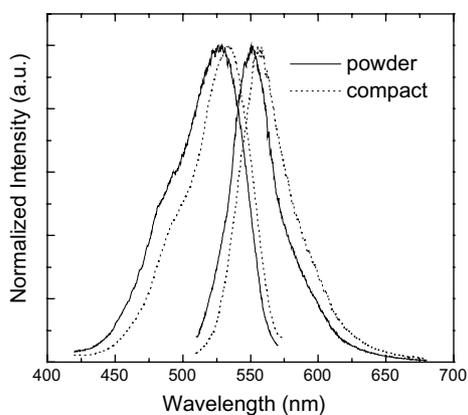


Fig. 4. Comparison of excitation and emission spectra for samples type D, powdered and compacted (6 GPa).

Table 3
Morphological properties of powdered and compacted samples

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)	Porosity ($\text{cm}^3 \text{g}^{-1}$)
A	280 ± 14	0.89 ± 0.04
AP	37 ± 2	0.04 ± 0.01
C	253 ± 13	0.57 ± 0.03
CP	44 ± 2	0.02 ± 0.01
D	138 ± 7	0.37 ± 0.02
DP	31 ± 2	0.04 ± 0.01

porosity. Although it is not so high, this behavior is already observed comparing doped and undoped powders [4]. For sample D, the surface area and porosity are much lower than the other two. This can be explained by the presence of the surfactant agent. According to Table 3, the high pressure processing (samples AP, CP, DP) causes a marked reduction on the surface area and porosity.

Fig. 5 shows the pore size distribution curves, for samples described in Table 3. For samples A and C there is a maximum for pore diameters between 7 and 8 nm. Sample C shows also that there is a pore fraction with diameter lower than 4 nm. For sample D, there is no preferential pore size in the range measured. After the compaction, all samples show a considerable reduction in the porosity for the whole diameter range measured. Below the diameter of 4 nm, the samples present a very low open porosity. These results are important to give a clear vision of the porous structure and the pressure-induced effects on these samples. In order to obtain a similar porosity reduction in a silica xerogel matrix using a conventional method as, for example, heat treatments, the temperature would be near 1500°C , which will destroy completely the dye molecules [19].

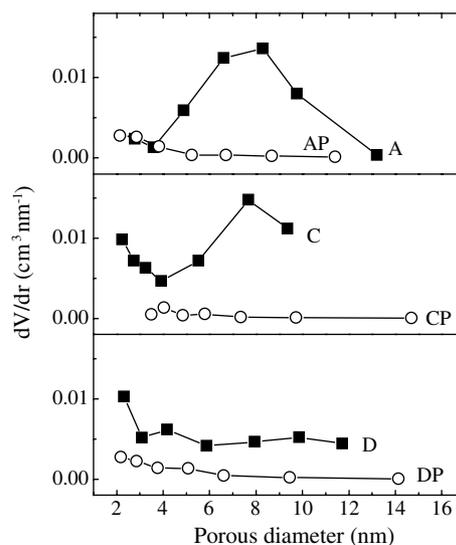


Fig. 5. Pore size distribution for powdered samples (A, C, D) and compacted samples (AP, CP, DP), obtained by BJH method.

4. Conclusions

The set of measurements presented in this work showed that the sol–gel method and the high-pressure technique are effectively useful tools to produce doped silica compacts with a very low porosity, promoting the entrapment of dyes in closed pores. An important characteristic of these compacts is that the dye molecules maintain its optical properties similar to that in ethanolic solutions, which means that they are dispersed in a molecular level. The best samples were obtained with molar ratio of 2.4×10^{-5} mol dye/mol TEOS (type C), without surfactant (Triton). These samples were optical transparent, hard and resistant to dye leaching and to chemical attacks, being a promising material to be used in optical devices.

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