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## High pressure loading of organic dyes into a silica matrix

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### Abstract

High density, transparent and crack-free compacts of silica gel doped with naphthazarin, quinizarin and rhodamine 6G, were produced by sol–gel synthesis with high pressure at room temperature. Compacts are very stable, being resistant to polishing and leaching by ethanol and acetone. They show optical properties, as absorption and fluorescence, similar to those at dilute solutions, indicating that the dyes are dispersed in the silica matrix as individual molecules. Heat treatment to 150°C for 1 h led to almost no degradation. © 1997 Elsevier Science B.V.

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### 1. Introduction

Entrapment of organic substances with interesting optical properties into inorganic systems like silica produced by sol–gel method has been widely studied over the last years, due mainly to its potential for production of a new class of optical materials [1,2]. Introduction of a host molecule is usually done by adding to the polymerizing mixture and, when the polymerization is completed, the dopant molecules are entangled in the inorganic matrix [1]. The nature of these interactions are not fully understood, and the molecules could be trapped, adsorbed on pore surfaces or chemically bound in the inorganic structure.

There are serious difficulties to produce these materials with ideal characteristics. Some limitations

are in the sol–gel process itself, because it depends on specific procedures, mostly in the drying process of the gel that sometimes can take months of preparation. If the goal of the processing is to produce a pore-free silica glass, it is necessary to heat the gel to a temperature high enough to promote sintering, and it is known that the organic compounds rarely survive temperatures above 200°C. In a review by Levy and Esquivias [2] about materials with optical properties obtained by incorporation of organic dyes using the sol–gel method, they described these systems after the first stage of drying, at temperatures below 150°C. They found crack development, large shrinkage during gelation and drying, and high porosity in the monoliths produced [3,4]. Porosity facilitates the leaching of the dyes and decreases optical performance. Canva et al. [5] developed an impregnation treatment using SiO<sub>2</sub> sonogels, which reinforces the matrix mechanical properties by sealing the pores.

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Use of DCCA (drying control chemical additives) that modify surface tension of the interstitial liquid and lead to a small pore size result in a crack-free dried gel after heat treatment to improve mechanical properties [6,7].

High pressure techniques were used [8] to produce high-density, transparent, crack-free and hard compacts of silica gel under conditions to 4.5 GPa, at room temperature. Compacts produced were analyzed by FTIR spectroscopy and thermogravimetry. Results obtained point out that the mechanism for consolidation by high pressure is a cold sintering process, where silanol groups condense to form siloxane bonds between the particles, resulting in a stiff body with closed nanopores. Thus, the high pressure technique seems to be a very efficient alternative method to densify the doped-silica gel, without dye destruction.

In this work, we present a new method to embed organic substances in a silica matrix, applying a high pressure technique, to produce high density and hard materials, which are transparent, homogeneous and highly resistant to leaching. The compacts obtained can be used in optical applications which do not require molecular motions. They are not suitable for chemical sensors and catalysts, which requires reaction of the dopant with external molecules.

## 2. Experimental procedure

1,4-Dihydroxynaphthoquinone-naphthazarin (NAPHT), 1,4-dihydroxyanthraquinone-quinizarin (QUIN) and rhodamine 6G (RHO6G) were entrapped in the silica matrix. The typical structures for these three dyes are shown in Fig. 1. The silica gel

matrix was prepared according to published procedures, by hydrolyses and polycondensation of tetraethyl orthosilicate (TEOS) in water and ethanol solutions under acidic (HF 40 wt%) conditions [3,9]. Separate solutions of hydrofluoric acid (0.1 ml) in distilled water and TEOS (5 ml) in ethanol (5 ml) were prepared. All the organic dyes were previously dissolved in ethanol and this solution is added to TEOS. The dye added is up to 0.02% for NAPHT, 0.05% for QUIN and 0.001% for RHO6G, by wt% of TEOS. The acid solution is dropped in the solution of TEOS plus the organic dyes, in a continuous mixing with a magnetic stirrer for about 5 min. This mixture is then divided among three small plastic dishes, that are put in a large Petri dish and covered without sealing. These sol-gel solutions are then let to gel and evaporate slowly for about 15 d in air, at room temperature. The gel formed is then processed at high pressure. Silica gel powder is initially pre-compacted in a piston-cylinder type die to approximately 0.1 GPa. The weight ratio in the pre-compacted samples was estimated for NAPHT as 0.03%, for QUIN as 0.06% and for RHO6G as 0.001%. These samples are then placed in a lead container that acts as a pressure-transmitting medium, and assembled in a toroidal-type high pressure chamber [10]. The compaction is then accomplished at 4.5 GPa, at room temperature. Detailed description of the high pressure method is given elsewhere [11]. The final compacts have a cylindrical shape with diameter of about 3 mm and maximum thickness of 3.5 mm. They are polished with 1000 and 2400 silicon carbide.

The mechanical properties of the compacts were analyzed by Vickers microhardness measurements, using a Shimadzu microindenter with a load of 50 g.

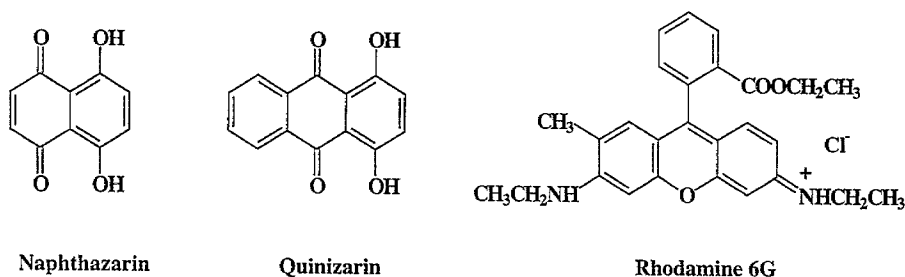


Fig. 1. Typical structures for the dyes used in this work.

Density measurements were performed, using the Archimedes method. Their optical properties were analyzed at room temperature by molecular absorption spectroscopy, in the range of 400–600 nm, with a conventional spectrophotometer using a tungsten lamp. Fluorescence spectra were obtained in the range of 500–700 nm, using an argon laser operating at 488 nm.

Qualitative tests and absorption measurements were made at different times to detect dye leaching. In the qualitative tests, the compacts and the gel monolith that did not suffer the high pressure treatments were immersed separately in two kinds of solvents, acetone and ethanol. In order to examine more closely a possible leaching of the different dyes not detected by naked eyes in the qualitative tests, absorption measurements were made with all compacted samples. They were separately immersed in quartz cuvetts containing solvent. The intensity measurements at the wavelength corresponding to the maximum of the absorption peak for each dye in the respective solvent, were made at different times during an interval of 60 min. Compacts were submitted to heat treatments to 150°C for 1 h, to observe thermal effects.

### 3. Results

Doped silica samples are crack free, dense, optically transparent, homogeneous and hard. The average density for the three samples was  $2.02 \pm 0.03$  g/cm<sup>3</sup> (90% of full density). The Vickers microhardness of all samples, with the three different dyes is  $4.0 \pm 0.2$  GPa, which is the same value obtained for pure silica-gel, compacted at the same pressure [11].

Qualitative tests were made to detect dye leaching. For the gel monolith that did not suffer high pressure treatment, the incorporated dye almost immediately started to leach when it was immersed in both solvents. No color change was observed in both solvents for all three compacts, indicating that the dye was trapped in closed nanopores. Absorption measurements in the solvents were also made to detect leaching, and the values were always near zero for all compacted samples, indicating that the

process of leaching is not occurring for high pressure samples.

In order to test the thermal stability of the compacts they were warmed at 0.5°C/min. and no changes were observed to 150°C, where some micro-cracks appeared.

Fig. 2a, b show the normalized absorption spectra for NAPHT and QUIN in an ethanol solution (dotted

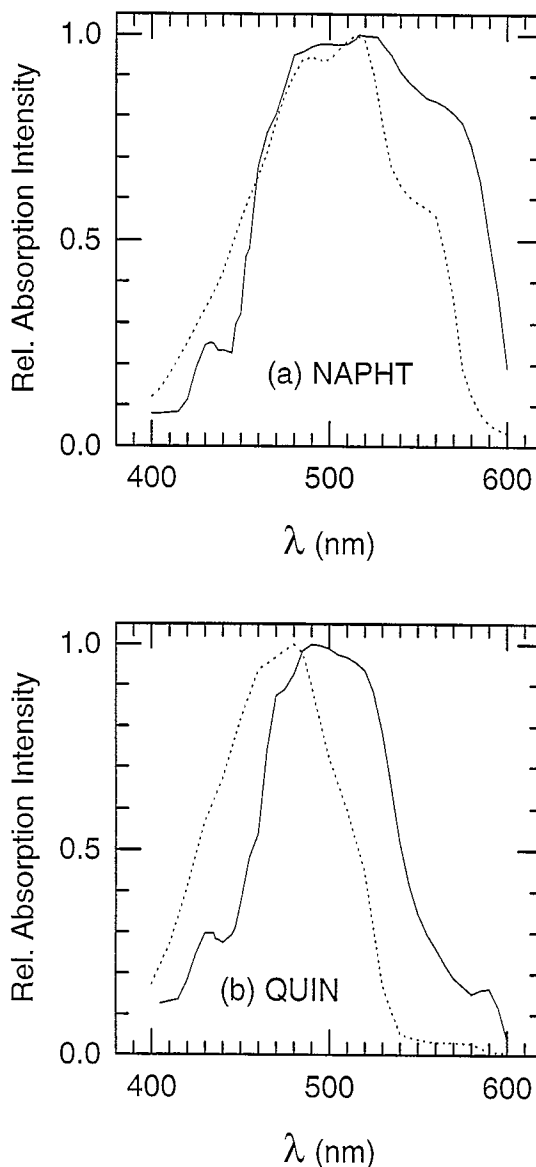


Fig. 2. Normalized absorption spectra in the range of 400–600 nm, in ethanol solution (dotted line) and incorporated in the silica matrix compact (solid line) for (a) NAPHT and (b) QUIN.

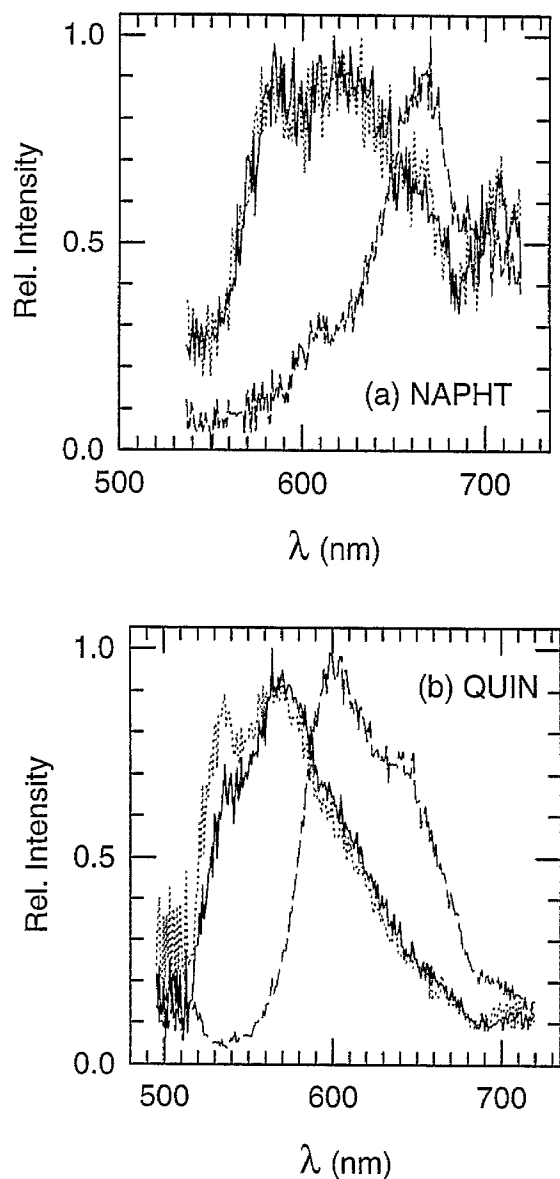


Fig. 3. Normalized fluorescence spectra in the range of 500–700 nm, in ethanol solution (dotted line), incorporated in the silica matrix compact (solid line) and as a solid (dashed line) for (a) NAPHT and (b) QUIN.

line) and incorporated in the silica matrix compact (solid line). The fluorescence spectra for both dyes, NAPHT and QUIN are shown in Fig. 3a, b. The dotted line represents the dye in ethanol solution, the

solid curve is the incorporated dye in the silica matrix and the dashed line represents the dye as a solid. As a general feature, both dyes incorporated in the silica-gel matrix by high pressure, absorb and fluoresce roughly in the same range observed for the dye in the ethanol solution, as can be seen in Figs. 2 and 3. The profiles of the absorption spectra of NAPHT and QUIN in ethanol solution are typical ones, reproducing what is known in literature [12,13]. For QUIN, a large band is observed in the region of 380–540 nm, with a maximum of absorption at 480 nm and for NAPHT this maximum is about 518 nm. For the QUIN incorporated in the silica-gel matrix, there is a very small shift of that maximum to 490 nm and the whole band showed a red shift.

Fluorescence spectra for QUIN (Fig. 3b) showed that the spectrum for the dye in ethanol solution and for the dye trapped in the silica matrix are at the same range of wavelength, and both have a blue shift relative to the fluorescence spectrum of the solid quinizarin, of about 35 nm. The same behavior is observed for the fluorescence spectra for NAPHT.

A widely known dye used as laser probe is RHO6G. Fig. 4 shows the absorption spectra for

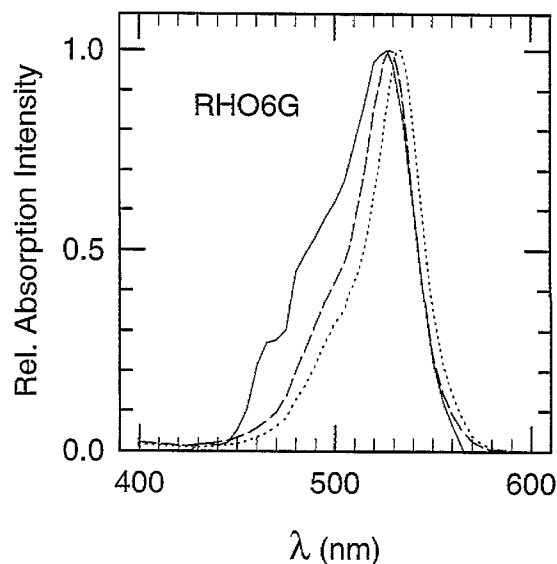


Fig. 4. Normalized absorption spectra in the range of 400–600 nm, in ethanol solution (dotted line), incorporated in the silica matrix compact (solid line) and in water solution for RHO6G.

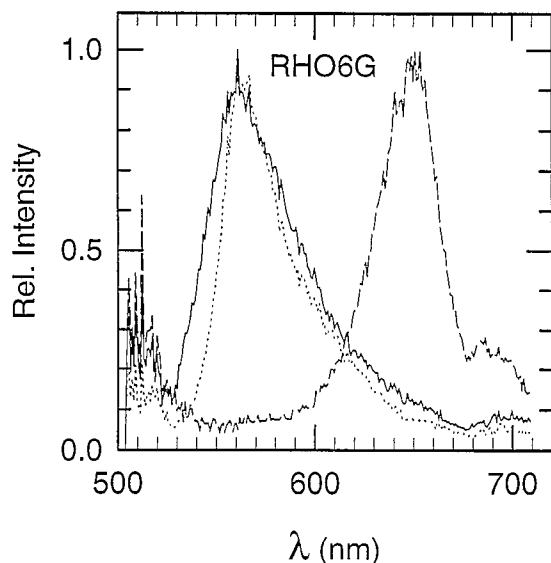


Fig. 5. Normalized fluorescence spectra in the range of 500–700 nm, in ethanol solution (dotted line), incorporated in the silica matrix compact (solid line) and as a solid (dashed line) for RHO6G.

RHO6G in ethanol solution (dotted line), trapped in the silica matrix (solid line) and in water (dashed line). The absorption bands for RHO6G are in the range between 440 and 580 nm, where the maximum of the absorption band is at 534 nm for the RHO6G in ethanol solution, 528 nm in water, and practically the same value in the silica matrix. There is a blue shift in the last two spectra, related to the ethanol solution, as can be observed. Also, there is an increase in the band width, of 33 nm in the ethanol solution, 36 nm in the water and 57 nm for the dye incorporated in the silica matrix.

Fig. 5 shows the fluorescence spectra for the RHO6G in ethanol solution (dotted line), trapped in the silica matrix (solid line) and as a solid (dashed line). In this case, the same behavior is observed as already shown by the other two dyes, QUIN and NAPHT, namely there is a coincidence in the wavelength range of the spectrum for the dye in ethanol solution and for the dye incorporated in the silica matrix, having a blue shift relative to the fluorescence spectrum of the solid RHO6G.

#### 4. Discussion

The 4.0 GPa Vickers microhardness for all samples is high compared to silica quartz (10 GPa). This result, together with density measurements, is very interesting because it indicates that this mechanical property is not affected by dyes embedded in the silica gel matrix and they reinforce the idea of the cold sintering process, stressed in a previous paper of Costa et al. [8]. According to them, there is a strong and closed pore structure formed during the high pressure treatment. The high density, optical homogeneity and transparency of the samples confirmed that porosity is low and average pores size is much smaller than the wavelength of light.

The red shift observed for QUIN in Fig. 2b was already noticed for some dyes incorporated by sol-gel method during densification and heat treatment at 150°C [14]. This effect has been attributed to an increase in the component of dispersion forces with density, as described by Rao [15]. In our case we have a large increase in density due to the high pressure treatment, which could be responsible for this effect. It was observed that the interactions of the dyes with Si–OH and Si–O–Si groups have lower polarity than with ethanol and water [16], which also could cause this red shift. The nature of interaction of dye with the silica matrix is not yet clarified. It could be an interaction with adsorbed water on the pores as well as with the solvent remaining from the synthesis, or with the silanol and siloxane groups of the pores surface. In the case of the absorption spectrum of naphthazarin, there is almost no red shift of the maximum of the absorption peak, however there is an enlargement in the absorption band for the dye trapped in the silica matrix, and this is also in the direction of higher wavelengths. This enlargement was observed [12,17], and attributed to multiple and complex interactions of dyes with the different groups of the internal surface of the pores in the matrix.

The fluorescence spectra showed in Fig. 3 for QUIN and NAPHT indicate that the dye is dispersed at molecular level in the silica matrix as it is in the ethanol solution, without precipitation or dimerization, which is very desirable from the point of view of optical properties. The capability of the matrix to isolate each molecule of the dye efficiently, even at

high concentrations, without any degradation or basic modifications in the structure is very promising in optical applications, such as dyes for laser probes [18].

The behavior of RHO6G in different environments shown in Fig. 4 is qualitatively similar to that observed in absorption spectra of NAPHT. An interesting result that can be observed from the absorption spectrum for the RHO6G incorporated in the silica matrix is that there is no dimer formation, because the peak related to the dimerization, at 496 nm, is not observed. This is an important fact and can give us an estimate of the size of the closed pores in the silica matrix, they should be not very much larger than the size of the molecule (about 1 nm). However, the RHO6G molecule could not be alone in the pore, but trapped also with some water molecules, which could remove the dye from the pores surface, replacing the interactions with silanol and siloxane groups. This could explain the similarities of the absorption spectra of the dye in the silica matrix (Fig. 4a, solid line) with the dye in water (Fig. 4a, dashed line).

## 5. Conclusions

A new method to incorporate organic dyes in silica matrix using sol–gel synthesis and high pressure at room temperature proved to be effective to produce doped compacts with optical functions. Vickers hardness (50% of the value for quartz), high density, high homogeneity, high optical transparency and high stability, allow easy handling and polishing. Entrapment of dyes protect them from chemical degradation by external agents, making samples stable and resistant to leaching. Dyes maintain optical properties observed in ethanol solutions.

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