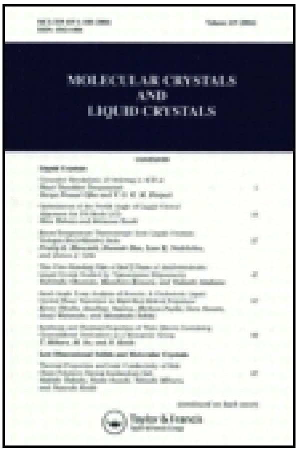

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High-Pressure Entrapment of Rhodamine 6G into a Silica Matrix

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High-Pressure Entrapment of Rhodamine 6G into a Silica Matrix

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The entrapment of organic dyes with interesting optical properties in silica produced by sol-gel method, has been studied over the last years, aiming to obtain a new class of optical materials. The monoliths produced by this method present cracks, large shrinkage during the silica gelation and drying, and a great porosity, which decreases their optical performance. In a previous work, to overcome these difficulties, a high pressure (4.5 GPa) technique at room temperature was used to produce compacts of silica gel doped with rhodamine 6G (R6G). In this work, we extended this study to pressures up to 7.7 GPa to verify the effect of high pressure in the fluorescence spectra of the R6G and in the density and hardness of the compacts. High density (98% of the silica density), transparent and crack-free compacts were produced, being resistent to polishing. The fluorescence spectra were similar to the ones observed in ethanol solutions. These new class of materials are potentially useful for optical applications.

<u>Keywords</u> high-pressure; fluorescent dyes; rhodamine 6G; silica; optical materials.

INTRODUCTION

The entrapment of several organic dyes with interesting optical properties in systems like silica produced by sol-gel method, has been widely studied over the last years, due to its potentiality for production of a new class of optical materials [1]. Usually, the monoliths produced by sol-gel method present crack developments, large shrinkage during the silica gelation and drying, and a great porosity, which decreases the optical performance of the material. In laser applications, for example, a very good polished surface must be attained, which requires that the material should have good mechanical properties, so that it can be machined and polished. In order to improve the mechanical properties of the silica matrix with incorporated organic dyes, we recently proposed a cold sintering process [2,3] using the high-pressure technique up to 4.5 GPa, at room temperature, under nearly hydrostatic conditions, to produce high-density, transparent, crack-free and hard compacts of this material. In this work, we extended this study to silica gel doped with rhodamine 6G (R6G), using pressures between 3.0 and 7.7 GPa, in order to verify the effect of high pressure in the fluorescence spectra of the R6G and also, in the density and hardness of the produced compacts. The best conditions to have compacts with good optical and mechanical properties were determined.

EXPERIMENTAL PROCEDURES

The silica gel matrix was prepared by hydrolyses and polycondensation of tetraethyl orthosilicate (TEOS) in water and ethanol solutions under acidic conditions (HF - 40% by wt.)[4]. R6G was previously dissolved in ethanol and this solution was added to TEOS. The dye concentration was about 0.001% by wt. The sol-gel solution was distributed in three small plastic dishes, that were put in a large Petri dish just covered, without sealing. These solutions were then left to gelify and to evaporate slowly, in air, at room temperature for about 15 days. The gel formed was then comminuted, placed in a lead container that acts as a pressure-transmitting medium [5], which is assembled in a toroidal-type high-pressure chamber [3,6]. The compaction was accomplished at 3.0, 4.0, 5.0, 6.0, 7.0 and 7.7 GPa, at RT. The final compacts had a cylindrical shape with diameter of about 5 mm and thickness of 4 mm. The Vickers microhardness (HV) were performed using a Shimadzu micro-indenter with load of 100 g. Density measurements were made using the picnometer method. Fluorescence spectra were obtained by transmission, in the range of 400 to 700 nm, excited by a high pressure xenon lamp with an UV filter and detected by a CCD system coupled to a monochromator.

RESULTS AND DISCUSSION

High density, transparent and crack-free compacts were produced, which were very stable, being resistent to polishing. Comparing the visual transparency of the samples, it was observed that it increases with pressure, and the most transparent sample was obtained at 7.7 GPa. Non-broken samples were obtained at pressures between 3.0 and 6.0 GPa.

In figure 1, it is shown the density and Vickers microhardness measurements for different pressures. The density at 7.7 GPa is about 98% of the silica theoretical density. However, the hardness did not increase after 6 GPa. These high density and hardness values are remarkable considering that the high-pressure compaction was performed at room temperature.

Figures 2a and 2b show the fluorescence spectra for the R6G in silica for different pressures, corresponding to a broad band in the wavelength range between 520 and 650 nm, approximately the same range of the dye in ethanolic solution, which has a maximum at 560 nm. In figure 2a, for pressures of 3 and 6 GPa, it can be observed other peaks, which can be attributed to dimers formation or other fluorescent species formed during the compaction processing [3]. In figure 2b, it was shown the spectra of a similar sequence of high pressure experiments, using a powder obtained from the same sol-gel synthesis, however prepared in another day. In this case we compared the fluorescent spectra at several pressures with the original doped powder. In this experiment it was not observed the peaks attributed to dimers formation or other species [7,8]. This fact is related to the differences between the original powders due to the lack of reproductibility of the sol-gel method.

The fluorescence band of R6G in ethanolic solution can be deconvoluted in two peaks centered close to 560 and 580 nm. Figure 3 shows the behavior of these two peaks for the compacted samples as a function of the applied pressure, comparing to the position corresponding to the R6G in original powder and the R6G in ethanolic solution. The data considered correspond to the spectra shown in

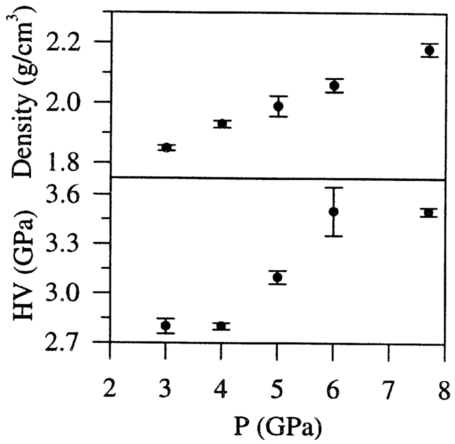

FIGURE 1 Density and Vickers microhardness measurements for different pressures.

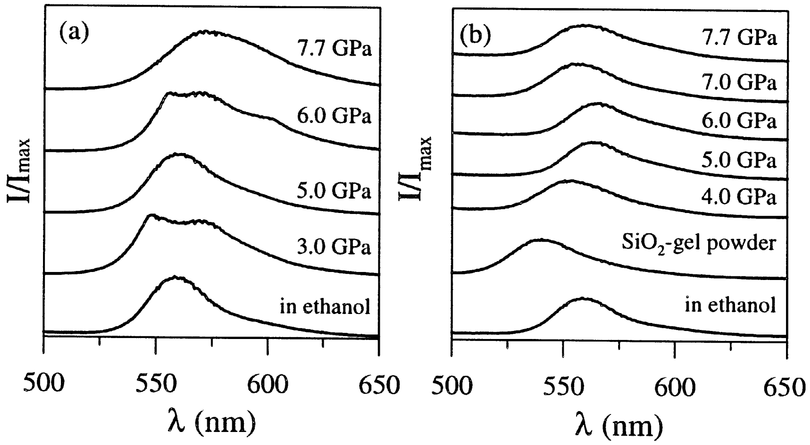

FIGURE 2 Fluorescent spectra for R6G in silica matrix at different pressures and in ethanolic solution.

Figures 2a and 2b. There is a blue shift comparing the peak positions of the ethanol and the powder, however the high pressure treatment shifts the peaks to their original position, similar to that of the dye in ethanol. This blue shift is ascribed to interactions of the dye with the matrix after solvent evaporation. However, 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. It was observed in a previous work [2,3] that after the compaction there is almost no interaction of the dye with the matrix, because the H bridges between silanol groups of the matrix are favored by high-pressure treatment. Therefore it is possible to occur dye aggregation and retaining of ethanol in closed pores formed during the cold sintering process.

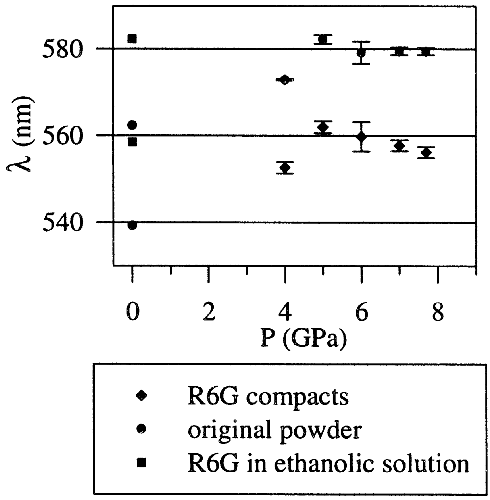

FIGURE 3 Comparison of the fluorescence peaks (near 560 and 580 nm) resulting from the deconvolution of the fluorescence band for the compacts prepared at different pressures, with the fluorescence peaks of the original powder and of the R6G in ethanolic solution.

CONCLUSIONS

The best silica-gel compacts doped with R6G dye, intacts and transparents, were obtained by high-pressure processing using pressures between 4.0 and 7.0 GPa. The maximum density value was obtained at 7.7 GPa (98% of the silica glass theoretical density), however the hardness (3.6 GPa) did not increase after 6.0 GPa. These high density and hardness values are remarkable considering that the high-pressure compaction was performed at room temperature (cold sintering process).

It was observed a blue shift comparing the fluorescence peak positions of the R6G in ethanolic solution and in powder. However, after the high pressure treatment, the fluorescence peak of the R6G in silica is almost at the same position as in the case of the R6G in ethanolic solution. A more detailed study is being done to a better understanding of the small shifts observed in the fluorescence peak positions with high-pressure processing, in order to determined the different species formed.

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