Photostability of luminescent dyes in solid-state dye lasers

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Abstract

Fluorescence photobleaching was measured in dye-impregnated sol–gel/polymer composite glasses. These fluorescent glasses were used as the gain medium in a transverse-pumped solid-state dye laser. In this configuration, the fluorescent glass was excited by a pulsed Nd:YAG laser (about 6 mJ/pulse) either while placed in an optical cavity (i.e., functioning as a pulsed laser) or with the optical cavity blocked, so that lasing did not occur. The decay of the fluorescence signal versus cumulative excitation energy was recorded. We found that the rate of photobleaching decreased when the glass was lasing, as compared to the case where the optical cavity was blocked. This paper presents these results, and suggests a simple kinetic model that may explain this phenomenon.

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1. Introduction

Solid-state tunable dye lasers based on laser dyes embedded in a sol–gel matrix were first prepared in 1989 [1,2]. The first such lasers were based on the orange perylene derivative BASF-241 dissolved in methyl methacrylate (MMA), which was allowed to diffuse into the porous glass and then undergo polymerization. Thus, the resulting laser host was a composite of a porous sol–gel glass with PMMA/dye filling the pores [3]. Since then, many variations of these lasers have been demonstrated. These include the use of different dyes (e.g., rhodamines, polymethenes), and different solid-state matrices (e.g., various organically modified silicates (ORMOSIL)) [4,5].

The photostability of the dye determines the longevity of the solid-state dye laser in which it is used. This parameter is often determined by measuring the photodecay time of the dye with a conventional fluorescence spectrometer. Alternatively, one can use a laser scanning fluorescence microscope to characterize the dye inside the sol–gel matrix [6]. However, one might ask whether the rate of photobleaching inside the laser cavity is predicted by these experiments which take place outside of the laser, and often with continuous (as opposed to pulsed) excitation. In this report, we present preliminary data which suggest that for pulsed excitation, the rate of photobleaching decreases when the sample is in a laser cavity as compared to the identical sample under identical excitation, but not in a laser cavity. This has
implications as to the use of dyes which have high slope efficiency, but higher rates of photobleaching when measured in conventional spectrofluorometers.

2. Methods

2.1. Preparation of sol–gel dye lasers

The lasers presented in this study used either pyromethene 597 (PM597) or rhodamine 6G (Rh6G) as the gain medium in a sol–gel matrix based on a composite glass host. The synthesis of these lasers is described in [7,8]. Briefly, composite glass lasers were made using a two step process in which first a porous sol–gel glass was synthesized, followed by diffusion of an MMA/dye solution into the porous glass, and polymerization for at least 1 week at 65 °C. The sol–gel glass was made from tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) which first underwent hydrolysis and then polymerization/crosslinking. More details of the sol–gel procedure can be found in [9–11]. The dye concentrations in the MMA solution were 10^{-3} M (PM597) and 3 \times 10^{-4} M (Rh6G).

2.2. Fluorescence measurements

All of the measurements were carried out in a transverse-pumped laser configuration, which is described in [8]. The laser configuration is repeated in Fig. 1. In order to measure fluorescence of the sample, the rear mirror (100% reflector) was blocked, thus destroying the laser cavity. The laser was then run under conditions that were identical to those obtained during lasing (i.e., with the optical cavity intact), and the fluorescence obtained from the sample was detected. The sample was excited with the pulsed Nd:YAG pump laser (Lumonics HY600, 6 mJ/pulse), and the fluorescence output was measured with a fast silicon photodetector (Det-110, Thorlabs Inc., Newton, NJ). The pump energy per pulse was measured with a LaserStar power meter equipped with a PE-25 head (Ophir Optronics Inc., Jerusalem, Israel). Pulse energy was measured at the start of each experiment, and also checked periodically during the experiment to check laser stability. Accumulated excitation energy was calculated as pulse rate times energy/pulse.

In order to compare the fluorescence decay obtained by the above procedure with the photobleaching that occurs within a laser cavity, the experiment was repeated with the laser cavity intact (rear reflector not blocked). The sample was then excited as before, except that periodically (every 3–5 J of accumulated excitation energy), the laser cavity was blocked and the fluorescence was measured, as above. The results were normalized to the initial fluorescence emission.

Relative fluorescence output versus cumulative excitation energy was fit to one or two exponentials using the Levenberg–Marquardt method [12] as implemented in the KPL program (V2.3.0, under SuSE Linux V8.0).

3. Results and discussion

The results obtained with a composite-glass/Rh6G sample are shown in Fig. 2. The best fit exponentials are also given. The best fit equations which describe these data are

\begin{align*}
I_{\text{lasing}} &= 0.007 + 1.078 \cdot e^{-E/20.2} \\
I_{\text{nolasing}} &= 0.503 \cdot e^{-E/5.48} + 0.540 \cdot e^{-E/17.3}
\end{align*}

where \( E \) is the cumulative excitation energy in Joules and \( I_{\text{lasing}} \) and \( I_{\text{nolasing}} \) are the normalized fluorescence intensities of in the presence of an intact laser cavity or with the laser cavity blocked, respectively.
A similar phenomenon is observed in a composite-glass/PM597 sample (Fig. 3). Here, the best fit equations for the fluorescence decay are

\[
I_{\text{lasing}} = \frac{1}{C_0} e^{-E/15.8}
\]

and

\[
I_{\text{no-lasing}} = 0.466 \times e^{-E/2.59} + 0.533 \times e^{-E/11.6}
\]

The fluorescence decay for the sample in a working laser cavity was best fit by one exponential, and some offset, as expected. The decay rate was less than for the sample which was excited under identical circumstances, but with the rear mirror blocked, so that there was no (or very little) lasing. In this case, the fit obtained using two exponentials was much more accurate than the fit obtained with one exponential and an offset. A similar phenomenon was observed when photobleaching rates were measured using a laser scanning confocal microscope (data not shown). For both PM597 and Rh6G, the two exponentials have almost equal contributions. This might suggest that there are two subpopulations of the dye, which have different photostabilities. We have no explanation for why the fluorescence observed under conditions of lasing shows only one exponential component, but we note that the decay rate observed with lasing is similar (but still a bit slower) than the longer of the two components observed when there is no lasing. This may suggest that one of the two populations participates in the lasing, and the other does not, and the population that serves as the gain medium does not decay much over the energy range that we measured. Indeed, in lasers in which these samples were used in the past, the laser output declined to 50% of its original output only after 150–300 J of cumulative pulse energy (25000–50000 pulses) [8].

These experiments, though preliminary, motivated us to consider why the rate of photobleaching might decrease inside a laser cavity. We propose the following kinetic model that might explain this phenomenon. The excitation pulse supplied by the Nd:YAG laser is a few ns wide, which is on the order of or even a bit less than the emission lifetime of the dye. Photobleaching is one process that competes with other processes (notably radiative emission) when a molecule is photoexcited. The probability of photobleaching \( P_{\text{pb}} \) following a particular excitation pulse can be written as:

\[
P_{\text{pb}} = \frac{K_{\text{pb}}}{K_{\text{em}} + K_{\text{pb}} + K_{\text{nr}}}
\]

where \( K_{\text{pb}}, K_{\text{em}} \) and \( K_{\text{nr}} \) are the kinetic rate constants for photobleaching, radiative emission, and nondestructive nonradiative transitions, respectively. \( K_{\text{em}} \) is normally the inverse of the spontaneous emission lifetime of the dye. However, in a laser cavity, the stimulated emission rate constant becomes significant, so that

\[
K_{\text{em}} = K_{\text{stimulated}} + K_{\text{spontaneous}}
\]

where \( K_{\text{stimulated}} \) and \( K_{\text{spontaneous}} \) are the stimulated emission and spontaneous emission rate constants, respectively. Thus, we can write
\[ P_{pb} = \frac{K_{pb}}{K_{\text{spontaneous}} + K_{\text{stimulated}} + K_{\text{pb}} + K_{\text{nr}}} \] (7)

Under conditions of population inversion and lasing, the stimulated emission rate constant must be higher than the spontaneous emission rate constant. When this occurs, Eq. (7) shows that the probability per pulse of photobleaching will decrease. Therefore, it is possible that a dye which appears to be easily photobleached under CW excitation may in fact work well in a pulsed laser.

4. Conclusions

The results presented here motivate further study of the stability of dyes in solid-state dye lasers under actual operating conditions. We are now planning to modify the laser configuration in order to be able to measure fluorescence emission simultaneously with laser operation. In addition, the use of multiphoton excitation with an IR pump source will allow localization of the fluorescence excitation to the optical axis of the cavity, and make detection of fluorescence from this cavity during lasing simpler and more accurate.

References