

# Solid state dye lasers: new materials based on silicon

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**Abstract:** In this paper an overview of the results obtained by our group over the last few years on the development of new silicon based materials for solid-state dye lasers is presented. Organic-inorganic hybrid materials and silicon-modified organic matrices incorporating laser dyes have been developed which exhibit highly photostable laser emission with good laser efficiency.

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The development of tunable solid-state dye lasers (SSDL), in which an organic dye is incorporated into a suitable solid matrix, is an area of active research [1]. SSDL exhibit well-recognized advantages over conventional liquid dye lasers as they avoid the problems of toxicity and flammability posed by the use of organic solvents, present a low-cost gain medium, and are compact and easy to operate and maintain.

Although over the years a number of materials have been tried as solid hosts for lasing dyes, properly modified polymeric formulations and advanced hybrid materials are the main candidates for developing efficient and stable SSDL. Polymers are attractive materials to be used in SSDL because of their high optical homogeneity, good chemical compatibility with organic dyes, and the easiness to modify their structure and chemical composition, which allows introducing controlled changes to optimize their properties. However, pure organic polymeric SSDL suffer from thermal degradation under laser irradiation, which can shorten significantly their useful lifetime. One way to improve the thermal resistance of the host material without losing the benefits provided by polymers is using organic-inorganic hybrid copolymers, composed of inorganic silicon oxidic structures substituted or crosslinked by organic groups.

The above considerations led us to proceed to the synthesis of materials of hybrid character, prepared from organosilane precursors by sol-gel processing in combination with simultaneous organic crosslinking of polymerizable monomers. In the first place, we proceeded to analyze the influence of the composition and proportion of the inorganic component on the SSDL lasing performance. As inorganic components we chose tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) (Fig. 1), and prepared hybrid matrices with 2-hydroxyethyl methacrylate (HEMA) (Fig. 1) in different weight proportions of TEOS and TMOS. Dye Rhodamine 6G (Rh6G) was incorporated into the matrices, and the lasing properties of the dye-doped material were investigated under transversal pumping with nanosecond pulses at 355 nm and 532 nm (third and second harmonics, respectively, of a Q-switched Nd:YAG laser) [2,3]. In

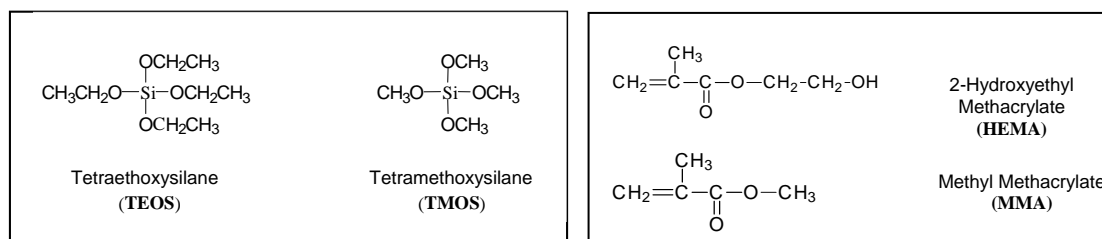


Fig. 1. Molecular structure of inorganic alkoxides (TEOS and TMOS) and organic monomers (HEMA and MMA)

all the studies here reviewed, the laser samples were cylinders (10 mm length, 10 mm diameter) with a cut parallel to the axis of the cylinder defining a lateral flat surface onto which the pump radiation was focused. The oscillation cavity, with a length of about 2 cm, was formed by a flat aluminum mirror and the end face of the cylindrical sample as the output coupler.

As expected, the SSDL lasing performance was much improved with pumping at 532 nm with respect to that achieved with pumping at 355 nm. Particularly relevant was the improvement in the lasing stability. The lower energy difference between pump and laser photons at the 532 nm pump wavelength minimize the photochemical degradation of the dye as well as the energy released to the medium as heat, which results in less thermal degradation of the dye.

In the hybrid matrices based on TEOS, both the lasing efficiency and stability first increase with the proportion of the inorganic component, peaking at compositions with 10-15% wt% proportion of TEOS. When pumping at 532 nm, laser efficiencies of up to 26% and laser emission with no sign of degradation, albeit with some oscillations, after 100 000 pump pulses in the same position of the sample at 10 Hz repetition rate were obtained. In hybrid matrices based on TMOS, the lasing stability was significantly worse than in the TEOS-based hybrid materials, evidencing the influence of the size of the lateral substituent group of the alkoxide on the laser properties of the resulting material.

Higher proportions of the alkoxide in the sample result in a drastic decrease in both efficiency and useful lifetime or stability of the laser emission. It is clear that the presence of the inorganic component in the matrix plays an important role in the photochemical degradation of the dye. The pump radiation leads to a fraction of the dye molecules being converted into active species (radicals, triplets) which, in turn, react with nearby dye molecules, impurities, oxygen, radicals, and groups from the polymer chains or any other active species present in the material. An increase in the proportion of the inorganic alkoxide in the material leads to an increase in the remanent acidity of the medium which could boost these reactive processes. In addition, because the photochemical mechanism is at least bimolecular, the process can be highly dependent on the microstructure and flexibility of the polymeric chains in these materials. Thus, in order to optimize the photostability of the dye/hybrid system, a compromise must be reached between the enhancement of thermal dissipation in the material and the increase in the photochemical destruction of the dye by carefully controlling the inorganic-organic matrix composition.

In purely organic matrices, the best laser performance of dye Rh6G was achieved with copolymers of HEMA and MMA (methyl methacrylate, Fig. 1) in proportion 1:1 v/v [4]. Thus, we prepared hybrid matrices with the 1:1 v/v copolymer of HEMA and MMA as organic component and TEOS as the inorganic part, added in wt.% proportions ranging from 5% to 20%. The presence of MMA resulted in a worsening of the lasing stability properties of the material [2], due to the hydrophobic character of MMA which does favour neither the compatibility with the inorganic network nor the solubility of the Rh6G dye. This result

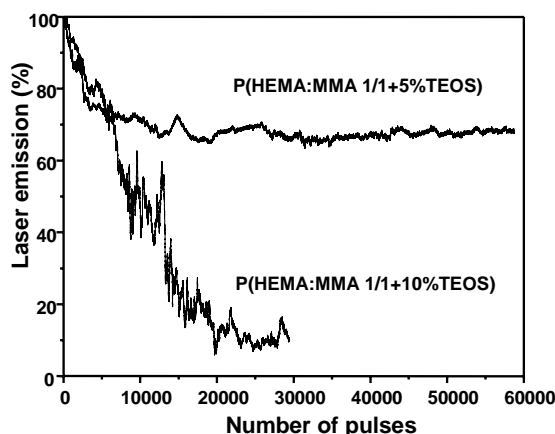


Fig. 2. Normalized laser output as a function of the number of pump pulses for PM567 ( $1.5 \times 10^{-3}$  M). Pump energy and repetition rate: 5.5 mJ and 10 Hz, respectively.

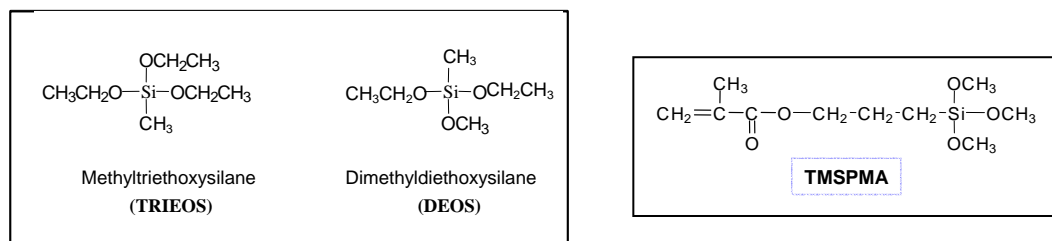


Fig. 3. Molecular structure of inorganic alkoxides (TRIEOS and DEOS) and silicon-containing monomer TMSPMA

indicates that for optimizing the laser properties of the final material the composition of both organic and inorganic parts has to be chosen carefully.

Contrary to Rh6G, pyromethene dyes exhibit good solubility in MMA. Thus, we explored the incorporation of dye pyromethene 567 (PM567) into hybrid matrices composed of 1:1 v/v copolymer of HEMA and MMA with different weight proportions of TEOS as inorganic component [5]. In this case, the laser operation is optimized in matrices with 5% content on TEOS, where, under pumping at 532 nm, the lasing efficiency was 26%. After an initial decrease, the laser output stabilizes, and remains at 70% of its initial value after 60 000 pump pulses in the same position of the sample (Fig. 2). When PM567 was embedded in a P(HEMA:MMA 1:1) copolymer without TEOS and pumped under identical experimental conditions, the lasing efficiency was only 10%, and the laser output decreased to 70% of its initial value after just 3000 pump pulses at 1 Hz repetition rate.

The presence of the inorganic component in the hybrid matrices increases the rigidity and fragility of the resulting materials. To optimize the laser action of a dye in the solid medium a proper adjustment of the host material structure and composition is required in order to obtain adequate optical, thermal, and mecano-dynamic properties. A way to decrease the rigidity of the materials while maintaining, or even increasing, the proportion of the inorganic component could be decreasing the functionality of the inorganic compounds, selecting double and triple functionalized alkoxides instead of the usual tetrafunctionalized ones, TEOS and TMOS. Pursuing this idea, we proceeded to prepare hybrid matrices where the inorganic compounds were trifunctional methyltriethoxysilane (TRIEOS) and difunctional dimethyldiethoxysilane (DEOS) (Fig. 3), and performed a systematic study of the influence on the laser action of Rh6G of the composition and structure of these new hybrid matrices [6-8].

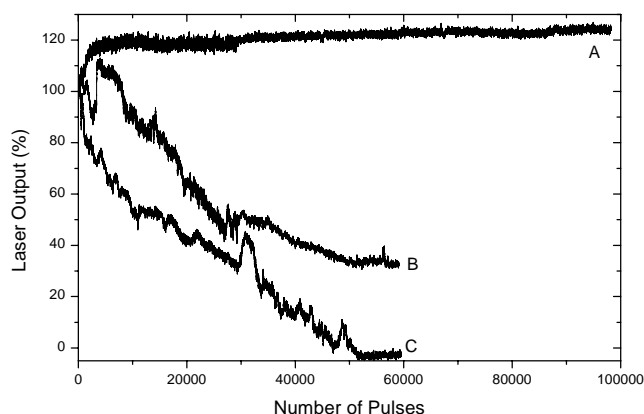


Fig. 4. Normalized laser output as a function of the number of pump pulses for PM597 ( $6 \times 10^{-4}$  M) in matrices of P(HEMA:MMA 1:1) with different wt%. proportions of TRIEOS: (A) = 15% and 10 Hz, (B) = 15% and 30 Hz, and (C) = 5% and 30 Hz. Pumping with 5.5 mJ/pulse at 534 nm ( $2^{\text{nd}}$  harmonic of Nd:KGW) (10 Hz) and at 532 nm ( $2^{\text{nd}}$  harmonic of Nd:YAG) (30 Hz). Initial lasing efficiency: 23%. (From García-Moreno *et al.* [8]).

The laser operation was optimized by using TRIEOS as the inorganic component in wt% proportion of 20%, with no decrease in the laser output after 100000 pump pulses at 10 Hz repetition rate. When the dye incorporated into the matrix was PM597, the optimal amount of TRIEOS was 15% wt%. (Fig. 4).

The above studies showed that the conditions of synthesis and nature of the precursors exercise a great influence on the lasing properties of the different dyes. Thus, our next step was trying to establish a relationship between the lasing behavior and the micro/nanostructure of the matrix material. To this end, we studied the organization of the molecular units in the hybrid materials using structural analysis by solid state NMR [7,8], and analyzed the composition, stability, and thermal properties of the materials by Fourier transform infrared spectroscopy (FT-IR), thermogravimetry (TGA), and differential scanning calorimetry (DSC), respectively. The microscopic morphological features related to both their chemical composition and optical properties were examined by atomic force microscopy (AFM) [8]. It was found that the optimal size of the inorganic cavity (best compromise between enhancement of thermal dissipation in the matrix and photochemical degradation of the dye) regarding the laser properties of the matrix incorporating Rh6G is obtained in hybrid materials where the chemical structure of the inorganic network is dominated by di-/tri-substituted silicates, in a proportion  $\approx 35:65$ , corresponding to samples of HEMA with a 15-20 wt % proportion of TRIEOS. It was confirmed the formation of covalent bondings between the organic and inorganic components. The AFM studies evidenced a material with high homogeneity, with the silica domains uniformly dispersed in the polymer matrix in domains with sizes in the scale of nanometers. The resulting structural and morphological uniformity led to the absence of a clear glass transition temperature. The prepared hybrid materials exhibited a refractive index that is tunable as a function of the silica content in the matrix, opening the way to potential applications in optical devices.

In spite of the good results obtained with the hybrid materials, these compounds present their own problems such as, complex and lengthy synthesis process, fragility which makes mechanization and polishing of the final material difficult, and sometimes optical inhomogeneity caused by refractive index mismatch between organic and inorganic parts. A way to avoid these problems while maintaining the combined advantages of polymer and inorganic materials could be using organic compounds with silicon atoms directly incorporated into their structure. Thus, the matrix would remain organic, which means plasticity and a relatively more simple synthesis procedure, but with improved thermal properties due to the presence of the silicon atoms. Following this approach, we incorporated dyes PM567 and PM597 into copolymers of MMA or HEMA with 3-(trimethoxysilyl)propyl methacrylate

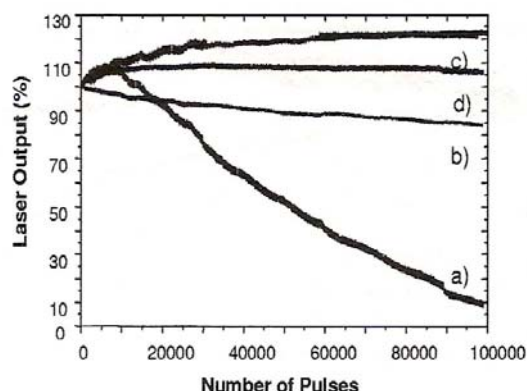


Fig. 5. Normalized laser output as a function of the number of pump pulses for dye PM567 in (a) COP(MMA:TMSPMA 3:7) and (b) COP(HEMA:TMSPMA 7:3), and for dye PM597 in (c) COP(HEMA:TMSPMA 7:3) and (d) TERP(MMA:HEMA:TMSPMA 5:5:10). Dye concentration:  $1.5 \times 10^{-3}$  M (PM567) and  $6 \times 10^{-4}$  M (PM597). Pump energy and repetition rate: 3.5mJ/pulse and 30 Hz, respectively. (From Costela *et al.* [9])

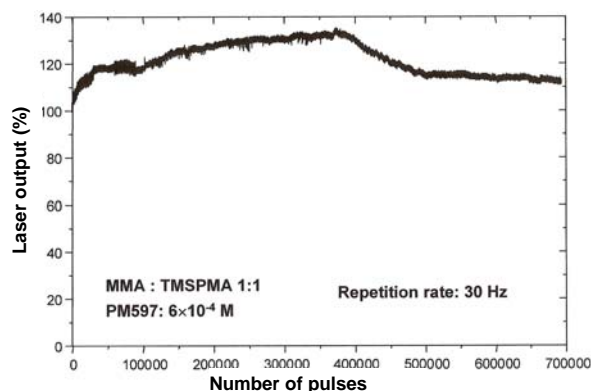


Fig. 6. Normalized laser output as a function of the number of pump pulses in the same position of the sample for dye PM597 in silicon-modified organic matrix

(TMSPMA, Fig. 3) and into terpolymers of MMA, HEMA and TMSPMA, and proceeded to study the photophysical, structural and laser properties of these novel materials [9, 10].

Highly photostable laser operation was obtained with the silicon-modified organic matrices, with lasing efficiencies of up to 34% with PM567 and up to 42% with PM597 under transversal pumping at 532 nm in no optimized laser cavities. At 10 Hz repetition rate, formulations were found with no sign of degradation in the laser output after 100 000 pump pulses in the same position of the sample for both PM567 and PM567 dyes. This corresponds to an accumulated pump energy absorbed by the system per mole of dye molecules of 518 and 1295 GJ/mol for PM567 and PM597, respectively. When the pump repetition rate increased to 30 Hz, the dye PM567 exhibited a steady decrease in the laser output, which is rather drastic in the samples with the highest content of silicon (Fig. 5). Dye PM597 was much more stable, and in all but one of the formulations the laser emission remained stable after 100 000 pump pulses at 30 Hz repetition rate (Fig. 5), corresponding to an accumulated pump energy of 2472 GJ/mol. In two selected matrices, COP(MMA:TMSPMA 1:1) and COP(HEMA:TMSPMA 1:1), the laser emission of the dye PM597 remained stable after 700 000 pump pulses in the same position of the sample at 30 Hz repetition rate (Fig. 6), corresponding to an accumulated pump energy absorbed per mole of dye molecules of 17 300 GJ/mol.

When comparing our results with the efficiency results obtained by other authors, some care should be taken because our studies have been performed under demanding transversal pumping and with the oscillator cavity not optimized, whereas in most of the reported studies pumping was longitudinal and the reflectivity of the output coupler optimized. Under transversal pumping, slope efficiencies of 32% [11] and 43% [12] have been obtained for dyes PM567 and PM597, respectively, incorporated into ORMOSIL glass samples and placed in an optimized laser cavity consisting of a full reflector and a 50% broadband reflector as output coupler. Regarding photostability, the best previous results for PM567 in solid matrix have been reported by Ahmad *et al.* [13], who obtained a normalized photostability (accumulated pump energy absorbed by the system per mole of dye molecules before the output energy falls to one-half its initial value) of only 350 GJ/mol for a mixture of PM567 and Coumarin 540 in polymer samples longitudinally pumped at 532 nm with pulses at a fluence of 1 J/cm<sup>2</sup> and 10 Hz repetition rate. With dye PM597 incorporated into hybrid xerogel matrices and pumped longitudinally at 532 nm with 1.8 mJ pulses at 10 Hz repetition rate, Nung *et al.* [14] reported a drop in the laser emission to 75% of its initial value after 100 000 pump pulses.

Recently, Duarte and James [15,16] followed an approach which involved incorporating a laser dye into polymer-silica nanoparticle media. The new gain medium consisted of Rh6G-doped PMMA including uniformly dispersed silica nanoparticles and exhibited lower  $|\partial n/\partial T|$  values and improved optical homogeneity than in previous composite gain media. With a longitudinal pumping scheme, laser conversion efficiencies of 63% with low-beam divergence were obtained.

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