

CHAPTER ONE

INTRODUCTION

1.1 Introduction to dye lasers

Organic dyes absorb strongly in the visible, and the fact that their emission bandwidths are broad makes organic dyes suitable as tunable lasers. With such dye lasers, tuning can be carried out by varying either the concentration of the dyes or the reflectivity of the resonator mirror¹. A wavelength-selective resonator² can also be used for this purpose. More importantly, an extensive choice of organic dyes is commercially available, which enables the tunability of dye lasers to span the near-ultraviolet to far-infrared. Broad emission bandwidths are associated with ultra-short pulses³⁻⁷, a property that enables high temporal diagnostics resolution. In addition, the extremely large absorption and emission cross-sections of dyes find applications in high-gain optical amplification⁹⁻¹⁰ and image intensification¹¹. The tunability characteristics of dye lasers are further exploited in fields as diverse as spectroscopic diagnosis¹², photodynamic therapy¹³⁻¹⁵ and holography¹⁶.

In the normal operation of dye lasers, dye molecules are excited by optical pumping; either a second laser system^{1, 17-20} or by a flash lamp^{16, 21-23} is used to provide the energy for this excitation. In a flash lamp-pumped laser system, the undesirable accumulation of the triplet states of the dye molecules is avoided by the

introduction of triplet-quenching agents²⁴⁻²⁶; triplet states can also be eliminated by rapidly circulating the dye solution^{27, 28} in the case of liquid dye lasers.

Early dye laser experiments²⁹⁻³¹ used dyes dissolved in organic solvents; today, liquid dye lasers remain the most widely used dye laser systems. The early studies were followed up with studies on dyes dissolved in a solid matrix^{2, 18, 32-42} as well as on dyes in the vapour phase^{43, 44}. Vapour-phase dye lasers offer the possibility of more efficient laser systems that can be pumped electrically; unfortunately, they must be operated at extremely high temperatures (330°C⁴⁴), temperatures at which organic dyes would have decomposed.

Compared with the operation of a liquid dye laser, a solid state laser has the advantage of being more compact and manageable; it also lacks the inherent toxicity and flammability associated with volatile organic solvents. More importantly, solid state dye lasers completely eliminate the twin problems of flow fluctuation associated with liquids, as well as changes in the concentration of the dye as a result of solvent evaporation.

1.2 Review of solid-state dye lasers

The lasing of dyes incorporated in solid matrices has been reported for carbon- and silicate-based materials as well as for polymer-silicate composites and osmosils. These matrix materials can be conveniently classified into homopolymers, modified polymethylmethacrylate, co-polymers, sol-gel glasses, sol-gel glass-polymer composites, and ormosil glasses.

Although inorganic sol-gel glasses generally show higher photo-stability than do organic polymers⁴⁵, polymer-based matrices are more compatible with organic dyes. Polymeric matrices are also optically more homogenous⁴⁶. Recently, several modified polymers^{47, 48} have been reported to have a radiation-resistance threshold comparable with those of inorganic glasses and also a laser efficiency as high as those of liquid dye lasers^{48, 2}.

The fabrication and characteristics of several important classes of matrices are summarised below.

Homo-polymeric matrices

Polymers such as polymethylmethacrylate (PMMA), polystyrene, polyethylacrylate, polyvinyl acetate and polybutadiene^{32-35, 49} can be used as the matrix material owing to their high optical transparency. The laser dye is first dissolved in the (liquid) monomeric material, which is then allowed to polymerise, a process that usually takes several days for completion. The solidified material is then removed from the mould and checked for flaws before being polished.

Modified PMMA matrices

Polymethylmethacrylate is a polymer that shows useful optical transparency over the entire visible range. Unfortunately, PMMA is a non-polar material (dielectric constant $\chi \approx 2.9$) and an ionic dye such as Rhodamine 6G will form aggregates when embedded placed in the PMMA matrix. The aggregation of the dye into higher-order entities effectively reduces its lasing efficiency, and additives such as ethanol¹⁸, methacrylic acid³⁶, ethylene glycol dimethylacrylate³⁷ and other low molecular-weight compounds^{38, 50} must be used to prevent their formation. These compounds are usually introduced in the polymerisation process itself.

Co-polymers

A co-polymer of PMMA and poly(2-hydroxyethyl methacrylate)^{2, 39, 40} has been claimed to exhibit improved lasing efficiency and lifetime compared with PMMA. The characteristics are finely controlled by varying the degree of cross-linking between the monomers, and consequently, the resulting microstructure of the polymeric matrix.

Sol-gel glasses

The production of glasses requires temperature in excess several hundred degrees Centigrade, temperatures that will decompose most organic dyes. In

contrast, the sol-gel method allows the preparation of porous glasses at temperatures well below 100°C ³⁵. In the sol-gel process⁵¹, the sol (a solution of the metal precursor) undergoes hydrolysis to form a gel; on removal of the solvent and the volatile hydrolytic by-products by evaporation, a dried gel, called a xerogel, is obtained that is rigid, transparent and porous. The organic dye can be incorporated into the matrix either by pre-doping (in which the dye is introduced into the precursor components) or by post-doping (in which the dye is allowed to diffuse into the porous glass after the glass has formed). Sol-gel glass fabrication takes only a few days; however, the dye diffusion usually takes a much longer time, typically, about two weeks for completion.

Sol-gel glass/polymer composites

Unlike sol-gel glasses that are fragile and not compatible with organic dyes such as the perylene dyes⁴⁵, composites of sol-gel glasses and polymers show better mechanical properties. In their production, porous glasses prepared by the sol-gel method⁴¹ are immersed in a dye-doped solution of the PMMA precursor (i.e., methyl methacrylate). The polymerisation reaction is initiated with a catalyst such as benzoyl peroxide. After being left in the monomer solution for several hours, the glass is taken out of solution and the reaction allowed to proceed in the solid state for several days.

Organically modified silicates

Ormosil glasses³⁵ are organic/inorganic composites whose molecular components are linked to each other by covalent bonds. The strong covalent bonds result in excellent mechanical strength; the non-porous nature of the osmosils also contributes to this. Fabrication is usually carried out by reacting an organic monomeric reagent with an inorganic metal oxide; the dye is introduced at this stage. The reaction⁴⁵ takes two to three weeks, during which the gel will lose about half its initial volume owing to the evaporation of the volatile by-products. The resulting transparent material has to be heated at 55°C for several weeks to remove any remaining volatile components.

1.3 Hot-press moulding of dye-doped PMMA

In the fabrication of dye-doped PMMA by conventional polymerisation^{2, 49, 40, 34} methods, a measured quantity of a selected organic dye dissolved in a monomer; the solution is poured into a mould, which is then sealed. The monomer is allowed to undergo polymerisation through the addition of radical initiators. The liquid mixture is then poured into a polypropylene mould and the contents deaerated by bubbling with either nitrogen or argon. The mould is sealed and placed in a warm oven (set at about 50°C) for the material to set, the solidification typically taking several days. With this method, particularly for PMMA, the dielectric constant falls (from approx. $\chi = 4$ to $\chi = 3$). However, this decrease adversely shifts the equilibrium between the monomeric dye molecules and their higher-order oligomers, which, being unconjugated entities, are less conversion efficient¹⁸. More importantly, laser dyes, being radical scavengers, could be decomposed in radical polymerisation⁵², as exemplified by Rhodamine B in PMMA, which has been reported⁵³ to suffer a 70% degradation.

It is a curious fact that despite the wealth of information published on the decomposition of dyes during polymerisation, a search through the *Inspec* did not reveal any method of fabricating polymeric solid-state dye lasers that does not involve polymerisation. On the other hand, this approach, which will involve doping the dye directly into PMMA, should eliminate the formation of free radicals,

has been reported for thin films⁴². This procedure necessitates the use of a solvent, but the removal of the solvent from the bulk polymer presents enormous difficulties; for example, the evaporation of solvent will also cause bubbles to be formed and the dye concentration to fluctuate.

1.4 The present project

We report in this dissertation the first example of a solid-state PMMA dye laser whose fabrication involves the doping of a dye directly into PMMA polymer, The material is moulded by low pressure compression for use a solid-state dye laser. An extension of this study has also examined the effect of thermal degradation on the absorption, fluorescence and lasing efficiency and the wavelength shifts, laser efficiency and operating lifetime.