

Solid-state polymeric dye lasers

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Abstract

This paper presents a review of the organic solid-state polymer materials, which have become established as a new laser media. The photostability of these materials is discussed. Different types of solid-state lasers built around these materials are also reviewed.

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1. Introduction

Liquid dye lasers are a coherent source of radiation with a wide tuning range and find many applications in various fields. However, these lasers cannot be used in certain applications due to the need for large volumes of organic solvents. The use of solid matrices containing laser dyes is an attractive alternative to the conventional liquid dye solutions. The first solid-state dye lasers were reported in the late 1960s by Soffer and McFarland [1] and Peterson and Snavely [2]. They demonstrated stimulated emission from polymeric matrices doped with organic dyes. However work on solid-state dye lasers was not pursued for over a decade due to low lasing efficiencies and fast photodegradation of the dye. In recent years, significant breakthroughs have been achieved in the development of practical tunable solid-state dye lasers [3–13]. The solid-state dye lasers [14,15]

have several advantages over the conventional liquid dye lasers. Along with the ease of handling, these lasers possess commercial advantage because of low cost of production and the safety of operation. Other technical advantages are compactness, manageability, versatility, lack of flammability and lack of toxicity. The flow fluctuation and solvent evaporation is considerably reduced in the case of solid-state dye lasers.

2. Types of host materials

There are a number of materials which have been used as solid hosts for laser dyes such as polymers, porous glasses, organically modified silicates or silicate nano-composites, polycom glass (combination of polymer and sol-gel). However in this review we will discuss polymeric host materials. Solid-state dye lasers based on polymeric and sol-gel glass have been reported extensively in literature [16–22]. In general, the solid host materials suitable for use in solid-state dye lasers

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should have the following requirements. They should be highly transparent to the pump laser and dye laser wavelengths. They should be hard enough to undergo mechanical treatment such as diamond cutting, grinding and polishing as required by any optical material and the materials should possess good thermal stability over a wide range of temperatures. Polymeric matrices have some important advantages over other host materials because they are simple to prepare and cheap to produce. In general, the polymers used are polyacrylics, polyurethanes (PUA), polycarbonates, etc. In polyacrylic class, the commonly used polymeric hosts are polymethylmethacrylate (PMMA). They possess high optical homogeneity, their chemical composition can be controlled at the formation stage and they can be treated mechanically. These polymers are highly transparent in the visible region of the electromagnetic spectrum. Polymer based systems have limitations such as a low damage threshold of the host material and limited lifetimes. Polymers are poor thermal conductors and have large time of heat dissipation ' τ ' [25] from the focused pump laser spot to low heat boundary (for PMMA, $\tau = 0.5$ s). A large number of laser dyes are insoluble in PMMA therefore low molecular weight additives such as ethyl alcohol, ethylene glycol, ether, polyether are added to PMMA to form modified PMMA known as MPMMA. Low molecular weight additives together with monomer purification can also lead to increased laser damage threshold [15]. P(MMA: HEMA) is a copolymer of heterogenous mixtures of monomers such as methylmethacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA). When this mixture is polymerised it provides enhanced crosslinking and compatibility of dye with macromolecule. HEMA provides enhanced solvation for the dye molecule. Costella et al. have reported improved laser operation [8,19] with P(MMA:HEMA) in some specific cases. More recently solid copolymers of methyl methacrylate (MMA) and trifluoromethyl methacrylate (TFMA) along with crosslinking monomer ethylene glycol dimethacrylate (EGDMA) have been reported [26]. This matrix was found suitable for the highly efficient and photo-stable pyrromethene 567 dye as a

dopant. Copolymers of methyl methacrylate (MMA) with TFMA lead to materials, which have mechanical and optical properties, suited to efficient laser systems [26]. These new solid materials show lasing efficiencies up to 18% when transversely pumped at 534 nm using Nd:KGW laser with good photostabilities. Co-polymers of MMA (methylmethacrylate) and pentacrythritol triacrylate (PETA) when pumped with the green line of copper vapour laser produced 290 mW of average power at 1 KHz repetition rate after which the laser power decreased [27]. Polymer filled porous glass impregnated with dye molecules has also been used as an active medium [31]. The thermo-optical and mechanical parameters are determined by a matrix of silica whose thermo-optical constants are better by two orders of magnitude than the polymers. However these materials have optical inhomogeneities, which can affect laser performance. Rhodamine 6G dye doped in polymer and porous glass composition can withstand pump pulses of 50 ns with energies of 7–10 J/cm². Such systems are used on-board, in vacuum under low temperature where the dye flow system operation becomes a problem.

Recently, a narrowband laser with dye doped polymer as the gain medium with a linewidth of ~ 0.011 cm⁻¹ (350 MHz) at FWHM has been reported by Duarte [23]. Tunable lasing from a dye laser in the near infrared region 1.1 μ m using polymethine dye in a polyurethane matrix pumped by 1.06 μ m was reported [24]. The conversion efficiency was 43% and tuning range ~ 520.6 cm⁻¹ (63 nm).

3. Method of preparation

3.1. Polymerisation process

Polymers can be made from monomers using bulk polymerisation techniques with proper polymerisation initiator. The dye is dissolved in ethanol or DMSO (dimethyl sulfoxide) in the case of homopolymerisation and in the case of copolymerisation it is dissolved in HEMA or TFMA. The dye used should be highly pure (>99%) as the impurities lead to a decrease in lasing efficiency.

The dye concentration can be varied between 10^{-6} and 10^{-3} M. Larger dye concentration leads to aggregation of dye molecules to form dimers thereby reducing the photostability of the host. The monomer used should also be pure, hence it is exhaustively treated with aqueous sodium hydroxide solution, dried, filtered and distilled. The dye dissolution is carried out in a sonicator.

Polymerisation process is carried out in polypropylene or glass moulds of the desired shape. Polymerisation is brought about by using initiators like benzoylperoxide or 2,2'-azo bis isobutyronitrile (AIBN). The initiator concentration is varied between 0.015 and 3 g/l. The dissolution of the initiator is again done with sonicator. In the case of copolymerisation use of either benzoylperoxide or AIBN does not show any significant difference [15], in the lasing efficiency. But in the case of homopolymerisation such as MPMMA, AIBN is preferred. Deaeration is done by bubbling dry argon before sealing the mould. Thermal polymerisation is carried out under controlled temperature conditions for several days (around 10 days) and cooled gradually to avoid thermal stress/strain.

4. Photostability and quantum efficiency of SSDL materials

The photostability of the dye doped solid materials depends on the inter-molecular and intra-molecular interactions [25] of the dye molecule with surrounding chemically active molecules such as the polymer macromolecule end groups, unreacted monomers, absorbed atmospheric oxygen molecules and another dye molecule. In general there are three accepted reasons for degradation of the dye molecule:

- (1) Photodeactivation from the excited state caused by chemical oxidation reaction.
- (2) Formation of dimers that absorbs irradiation without any fluorescence [6].
- (3) Thermal destruction.

Dye doped solid-state laser materials have low quantum efficiency and a limited useful operation

time. The low quantum efficiency is mainly due to photo-destruction of dye molecules as mentioned above. The mobility and the concentration of the dye molecules are the important factors that decide the probability of the photodeactivation reaction. Different methods are used to decrease the mobility of the dye molecules and to reduce the rate of destructive collisions and diffusion out of the active area. The mobility of the dye molecule is minimized by the following methods. The dye can be doped in copolymer host e.g.: P (MMA: HEMA). Due to crosslinking in the copolymer the mobility of the dye molecule is reduced. Another method is filling free volumes in the polymer host with low molecular weight additives. It is important that additives do not form any chemical bond with dye or macromolecules so that the optical properties of the material do not get affected. These additives also improve the thermal conductivity of the material and help cool the lasing material. The additives are smaller in size than the dye molecules and polymer macromolecules. Hence the additives fill the polymer free volumes more easily and also prevent the dye from diffusing into the thermal region. Working with polymer matrices that contain low molecular weight additives one can achieve considerably longer operational lifetimes than has been reported using similar matrices without additives [3]. One such additive is diphenyl thiourea. It has been reported that addition of diphenyl thiourea in copolymers of PMMA increased the photostability of the copolymer samples containing laser dyes like rhodamine and coumarin. By doping dye in a polymer host with controlled crosslinking [26] the photostability and the efficiency were improved for the pyromethene 567 (PM 567) in poly trifluoromethyl methacrylate (TFMA) with crosslinking monomer ethylene glycol dimethacrylate (EGDMA).

Another reason for the degradation of dye molecules is thermal destruction of the dye because of the low thermal conductivity of the polymer host. Since the polymer host is transparent to the pump radiation, the excited dye molecule heats up the host through non-radiative thermal relaxation. The polymers have poor thermal conductivity. Also a large time of heat dissipation from the

focused pump laser spot to low heat boundary, limits the repetition rate of the dye laser to few hertz. This accumulated heat increases the mobility of the dye and increases the probability of photodeactivation reaction with the surrounding chemically active molecules. Hence the direct thermal destruction of the material has insignificant role. To overcome this problem, the dye molecules are covalently linked to the polymeric chains so that the additional channels for the dissipation of the excess heat energy are provided.

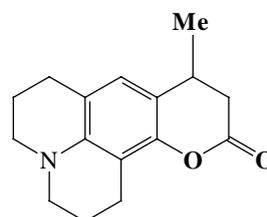
Polymers have been developed with higher laser damage resistance, comparable with inorganic glasses and crystals [28]. The single shot damage resistance of MPMMA was higher than 13 j/cm^2 for pump spot of 1 mm diameter. Single shot damage is caused either by inclusions or microstructures and the multiple shot damage is intimately related to the visco-elastic properties of the host. By controlling the inter and intramolecular interactions of dye with polymer host the conversion efficiency and the critical number of pump pulses before the photobleaching sets can be improved. The conversion efficiency can also be improved by choosing dye with large volume anion substitutes. This shifts the equilibrium of monomer to dimer reversible reaction towards the monomer side and improves the quantum yield and conversion efficiency. The experiments with rhodamine 6G chloride and rhodamine 6G perchlorate show that the latter has large quantum yield and hence large conversion efficiency. The conversion efficiency can be further improved by adding Low Molecular Additives (LMA) to the polymer, which enhances the dielectric constant of the polymer and facilitate the formation of expanded ionic pairs. The efficiency of the PMMA based rhodamine 6G chloride dye was improved from 14% to 28% by the addition of ethyl alcohol-carbonic acid ether mixture into PMMA [28].

5. Dyes used in solid-state dye lasers

The dyes to be doped in the polymeric host are chosen depending upon the desired wavelength of operation, efficiency and photostability of

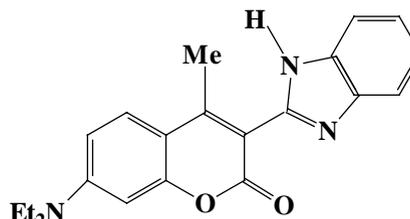
the dye molecule. Coumarin and rhodamine dyes are frequently used in solid-state dye lasers. Coumarins are laser dyes, which show laser emission in the blue–green region of the spectrum. The presence of a hydroxy or amino group at the 7-position has been found to be necessary for the merocyanine chromophore to exhibit lasing action. Replacement of the two amino hydrogens by various alkyl groups has been reported to increase their lasing efficiency. Introduction of a phenyl group at the 3-position has also been found to increase the lasing efficiency and a number of 7-*N,N*-diallylamino-3-phenyl coumarins have been synthesized and their lasing action reported [8–10].

Coumarin 10



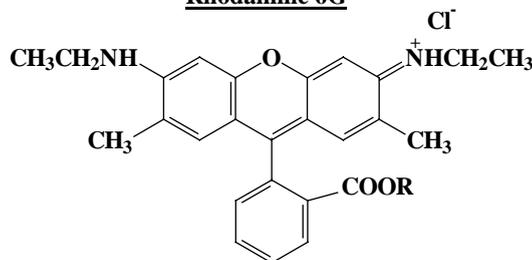
Absorption Max 389 nm Lasing Max 480 nm

Coumarin 7



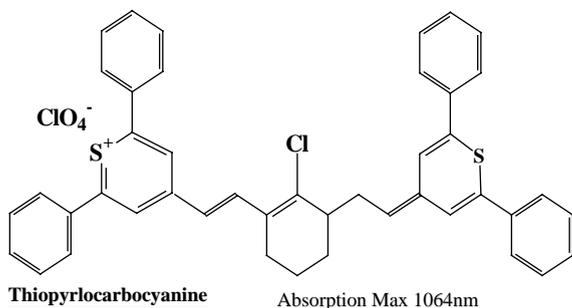
Absorption Max 436 nm Lasing max 573 nm

Rhodamine 6G

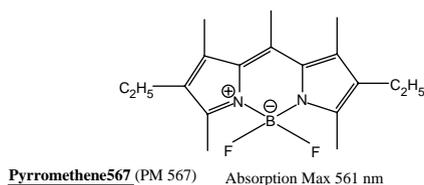


Absorption Max 526 nm

The structure of rhodamine 6G, which is more often used as a laser dye is shown above. Several other derivatives of rhodamines are also frequently used depending on the requirements for lasing.



The above dye thiopyrlocarbocyanine is used more commonly in polyurethane host. The maximum in its main absorption band in polyurethane lies at 1.079 μm . The thiopyrlyotricarbocyanine dye has a relatively large excited state relaxation time in liquid solutions of the order of 50 ps [11].



Pyrromethene dyes of the above structure are also used for many related applications. Pyrromethene BF_2 complexes are a class of laser dyes, which have been synthesized during late 1980s and early 1990s. In certain cases the pyrromethene and the polymethine laser dyes have been found to give better results than the rhodamines and the coumarin dyes [4,5]. The pyrromethene dyes show reduced triplet–triplet absorption over the fluorescence and lasing spectral region but at the same time exhibit a high fluorescence yield. These dyes show laser emission over the spectral region from the green–yellow to red. These dyes have demonstrated lasing with good performance when incorporated into solid hosts. Oxazine dyes such as cresyl violet, Nile blue, etc. are also used as laser dyes. These oxazine dyes are cationic dyes.

Aggregation is well known to take place for many cationic dyes in water. Dye aggregates are an integral component of many imaging and light conversion application. The aggregates of the oxazine laser dye have been a focus of research owing to the potential industrial applications of the aggregates strong absorption bands in the visible oxazine dyes are used as laser dyes because of their long term stability and high quantum yield [12]. The structure of oxazine dye is given below.

6. Different types of solid-state dye lasers

The pump lasers employed in the solid-state dye lasers depend upon the laser dye doped in the host. For the dyes such as rhodamine 6G, rhodamine B, pyrromethene, perylene orange dyes operating in the visible range 550–650 nm, the most widely used pump source is second harmonic (532 nm) of Nd:YAG laser. For coumarin class of dyes the pump lasers used are Excimer, third harmonics of Nd:YAG and Nitrogen laser.

In a recent communication [24] polymethine dye doped in a polyurethane matrix was pumped by Nd:YAG laser operating at 1.06 μm . Operational lifetimes of 10^6 shots at a pump energy of 270 mJ/pulse with output energies > 100 mJ have been achieved [29]. Using dye doped polyurethane acrylate (PUA) prepared by radical photo polymerization, laser efficiency of 30% was obtained in a hemi-spherical resonator. Dual wavelength operation has been achieved from a single rod doped with two dyes. A mixture of pyrromethene 580 (PM580) and pyrromethene 650 (PM650) doped in high temperature plastic or Excilite™ (HTP) in the ratio 10:1 gave dual wavelength emission centered at 552 and 616 nm. High repetition rate solid-state laser operating at a repetition rate of 25 KHz with a broad band output has been reported. Lasing was obtained at 4.0 W output for 2 h [30].

Single mode operation at linewidths of $\sim 0.001 \text{ cm}^{-1}$ has been obtained in solid-state dye lasers [23]. A short multiple prism near grazing incidence cavity with Rh6G dye doped in modified PMMA was used as the gain medium. Solid-state dye lasers with an active medium of polymer filled

porous glass impregnated with dye molecules have been reported [31]. The thermo optical and mechanical parameters are determined by a matrix of silica whose thermo optic constants are better by two orders of magnitude than that of polymers. The conversion efficiencies using Rh6G dye were 50%. The polymers have also been used in the integrated compact distributed feedback laser (DFB) [32] pumped by nanosecond Nd:YAG laser, using PMMA waveguide and the mixture of laser dye Rh6G and the saturable absorber 3,3'-Diethyloxadicarbocyanine Iodide (DODCI), generating a series of spikes of 20–30 ps and later compressed to 9 ps. Recently high repetition rate polymeric solid-state dye lasers pumped by copper vapour laser with the operation time of 8 h ($\sim 10^8$ pulses) have been reported [35]. The phenamine 512 dye doped with 2.5 mmol/l was tried out in a transverse pumping geometry. This resonator geometry improves the useful lifetime of the host material.

7. Conclusion

Solid-state dye laser technology has progressed and matured to a stage where these lasers can be used for commercial applications such as atmospheric and underwater sensing, local area communications network, medicine, isotope separation and spectroscopy [5,34]. Currently the main challenge in the development of solid-state dye lasers is to increase the operational lifetime of the gain medium. Due to recent development of new and improved host materials with higher laser damage threshold and longer lifetimes, there is a renaissance in the field of solid-state dye lasers [33–35]. In addition, the synthesis of new high performance dyes and the implementation of new ways of incorporating the organic molecules into the solid host matrices has produced a great deal of activity in the field of solid-state dye lasers.

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