

## CHAPTER ONE

---

### **INTRODUCTION**

---

#### **1.1 INTRODUCTION TO DYE LASERS**

Organic colorants that are used in dye lasers [1] have been widely used in solutions as amplifying materials in tunable lasers [2]. Organic dyes absorb strongly in the visible, and the fact that their emission bandwidths are broad makes organic dyes suitable for use as tunable lasers. The tuning of such dye lasers is carried out by varying either the concentration of the dyes or the reflectivity of the resonator mirror [3].

Dye lasers emit intense and coherent radiation on being pumped by a laser when they are either dissolved in a solvent or are incorporated into a solid matrix material [4]. The use of a solid matrix for dye lasers potentially offers most of the useful characteristics of liquid dye lasers and eliminates many of the common problems associated with liquid systems such as compactness, toxicity of the solutions and solvent evaporation. Unfortunately, problems arise because the dye molecules in the solid matrix will photodegrade in the absence of dye flow in a solid matrix system. Recent interest has focused on the search for photostable dyes but these should be incorporated into a solid matrix of high optical quality, high thermal conductivity and high damage threshold in order to maintain the required properties.

## **1.2 POLYMERIC HOST SOLID DYE LASER**

Solid dye lasers are based on polymers and sol-gel glasses [5-9]. Polymeric matrices have several advantages over sol-gel glasses in terms of lower optical scattering [7] and higher optical homogeneity; they enhance chemical compatibility with organic dyes and are inexpensive to fabricate [10]. However, the main drawbacks of polymeric systems are thermal dissipation, low host-matrix laser threshold and photodegradation of the dye molecules. Accumulated studies on the properties of the host material have shown that polymeric hosts give better monitoring over medium polarity and viscosity compared with solvent-based systems [11]. Moreover, free volume, molecular weight and viscoelasticity can also be modified in a controlled manner to achieve the maximum desirable flexibility.

Homo-polymeric matrices such as poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(vinyl alcohol) (PVA), and polycarbonate (PC) have been effectively used as host materials for dye lasers [12-14]. The most widely used polymeric material to date has been PMMA because of its excellent optical transparency and resistance to laser damage. Thus, the low solubility of some dyes in PMMA has led to a limitation of their use, which can, however be overcome by introducing modifying additives. Ethanol can be added to increase the solubility and to enhance the host laser damage resistance [8].

### 1.3 $\beta$ -DIKETOBORONATES DERIVATIVES

The reaction of boric acid with  $\beta$ -diketones to yield  $\beta$ -diketoboronates was first reported in 1905. Since then, many boronate compounds have been reported in the literature [15]. Four-coordinate boron compounds bearing two chelates such that the two  $\pi$ -systems are oriented orthogonal to each other display a type of electron delocalization over the spiro boron atom termed *spirointeraction* that gives rise to the color in these compounds. Such dyes show extensive delocalization of electrons in their molecular structures, a feature that permits the absorption of near-ultraviolet to visible radiation.

An example of a bis(chelated)boron compound is provided by (diphenylpropen-1,3-diolato)(oxalato)boron, which displays fluorescence [16] as well as a luminescence [17]. The strong fluorescence should ensure application of the compound as a laser dye [18]. Single small crystals of this compound have proved elusive, as attempts to grow crystals have yielded only powders; the difficulty is complicated by the relative insolubility of the compound, melting point, 296-301°C [19], in organic solvents.

Structural details of the  $\beta$ -keto-oxalatoboronates are limited to the 2,4-hexanedionato derivative [20], although the six-membered  $\pi$ -bonded [R-C(=O)-CH-C(O)-R]B entity has been crystallographically documented in a number of acetylacetonato-type of bis-chelated compounds. These include, for example, three catecholato (RCOCHCOR')(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)B derivatives for which R, R' = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub> [21,22] and two other diorganylboron compounds [22, 23]. The (RCOCHCOR')(O<sub>2</sub>CCO<sub>2</sub>)B compounds are yellow whereas other four-coordinate (CH<sub>3</sub>COCHCOCH<sub>3</sub>)BX<sub>2</sub> compounds such as the X = CH<sub>3</sub>CO<sub>2</sub> [24] and X = C<sub>6</sub>H<sub>5</sub> [25] compounds are colorless.

#### 1.4 THE PRESENT PROJECT

We report in this dissertation the lasing properties of selected compounds from the family of  $\beta$ -diketoboronates when the compounds are pumped by a pulsed Nd:YAG laser. The solid-state form was fabricated by doping of the dye directly into the PMMA polymer. The material is either molded by low-pressure compression for use a block type dye laser or dipping into the material to produce a thin-film slide sample. The laser performances of the solution, thin film solid dye and block form solid dye are evaluated on the basis of the spectral features, efficiencies and dye photostability.

The molecular structure of the diphenylpropen-1,3-diolato derivative is obtained through *ab initio* calculations, and the molecular structure is compared with the molecular structures of the three other analogs.