3.1 SYNTHESIS OF β-DIKETOBORONATE DERIVATIVES

The β-diketoboronates $(RCOCHCOR')(O_2CCO_2)B$ were synthesized by melting equimolar quantities of the diketone, oxalic acid dihydrate and boric acid according to the following equation; sufficient 1,2-dichloroethane was added to the melt to ensure complete solution.

$$RCOCH_2COR' + B(OH)_3 + (COOH)_2.2H_2O \longrightarrow (RCOCHCOR')(O_2CCO_2)B + 5H_2O$$
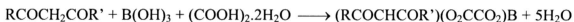
Removal of solvent yielded the required products for R = R' = phenyl, R = CH_3, R' = C_6H_5, R = R '= t-$C(CH_3)$ and R = R' = C_5H_4N derivatives; toluene was used as solvent for recrystallization. Theoretical study of molecular structures for the above products can be referred to Appendix A.

Another two flavonone derivatives were synthesized based on the reactions below:
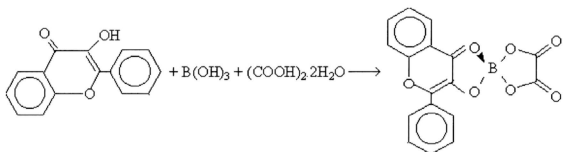
Flavonolato(oxalato)boron **(5)**
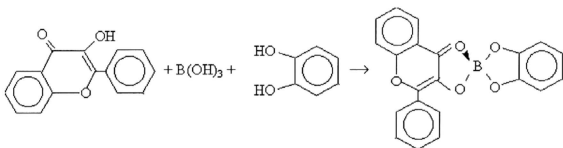
Flavonolato(catecholato)boron **(6)**

3.2 DYE SAMPLE PREPARATION

3.2.1 Preparation of dye solution

A weighed quantity of the β-diketoboronate was dissolved in chloroform and the dilution method was used to obtain the required concentration. The solution was kept in a dark room.

3.2.2 Preparation of thin film solid dye

The PMMA solution was prepared by dissolving granular poly(methyl methacrylate) in chloroform. Various combinations of PMMA and chloroform were prepared to achieve the ultimate viscosity. The optimum combination for achieving the best film thickness was 40 ml chloroform and 10 g PMMA. Weighed quantities of the β-diketoboronate were added into the PMMA solution and the mixture was stirred until a homogenous clear solution obtained. A glass slide (AS cut, 76 x 26 x 1 mm) was slowly dipped into the solution and then pulled out to obtain a transparent dye/PMMA film. A consistent dipping rate and viscosity were maintained in order to achieve a minimum variation on the dye/PMMA film thickness. The slide was kept into a container and the container covered to slow down the evaporation of solvent during the process of drying. Excessive drying was found to cause the cloudy films. The concentration was calculated based on the weight of solid laser dye to the weight of granular solid PMMA with assumption that all the solvent would be lost.

The dye/PMMA films with thickness ranging from 20 - 30μm were prepared on each side of the slide. The thickness was measured by using a dry film thickness gauge (model elcometer 345 FB Mark II) that had an accuracy of ±1% and calibrated with a SIRIM approved thickness foil.

Only three of β-diketoboronate dyes were prepared as thin film slide samples because the other dyes did not laze in solution.
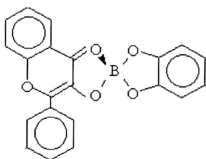
Below are the dyes were prepared to test the lasing characteristics:
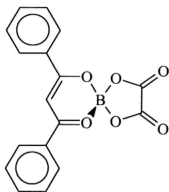
(Diphenylpropen-1, 3-dialato)(oxalato)boron **(1)**
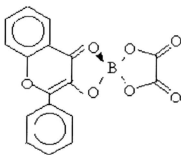
(Flavonolato)(oxalato)boron **(5)**

(Flavorfolato)(catecholato)boron **(6)**

Figure 3.1 Molecular structures of β-diketoboronates

3.2.3 <u>Preparation of dye doped PMMA slab by low-pressure compression</u>

After the PMMA and dye had completely dissolved, the mixture was poured into a flat Teflon plate and the assembly was placed in a vacuum oven (< 1 mbar) maintained at 175°C for a half an hour. The amount of chloroform used was just enough to dilute PMMA for the purpose of achieving no solvent entrapment during the heating process. The dye-doped PMMA pre-form product was ground into powder for the preparation of the slab.

The laboratory compression mold was adapted from a compression mold used industrially for PMMA. Two springs provided the necessary 35N cm^{-1} pressure. The top (plug) and lower parts were made of brass, and the smooth glass window formed the front and backsides of the mold.

The pre-form (approximately 10 g) was packed in the mold cavity and covered with plug. Pressure was applied through the screws. The entire assembly was placed into a heated (175°C) vacuum oven. The pressure was maintained below 1 mbar. After approximately half an hour, the assembly was taken out and the skews re-tightened again in order to achieve a maximum density slab. About another half an hour, the assembly was removed from the vacuum oven and the pressure of the spring was released. The assembly was placed into a regular oven and left to anneal for another 7 hours before the slab was taken out from the molds. The surface of the slab was polished and the slab was kept in the dark room. Approximately 1 cm x 1 cm thickness slabs were prepared by using this method.

3.3 <u>ABSORPTION SPECTRA</u>

The absorption spectra were recorded at room temperature on a UV-VIS NIR scanning spectrophotometer (Shimadzu Model UV-3101 PC). The acquisition mode was preset to a fast scanning mode (1600 nm min^{-1}) for the measurements. Absorption by the quartz cuvette or the substrate (glass slide) was eliminated by baseline subtraction. The horizontal axis (wavelength) was set at 300 – 450 nm.

3.4 <u>PULSED ND: YAG LASER EXCITATION</u>

The samples were tested for lasing action in a dye laser cavity transversely excited by using a commercial EKSPLA Nd: YAG Laser (Model Laser NL301 Laser head and STH Unit). The 648 μJ pulse^{-1} laser beam was line-focused onto the sample by using a Beam Expander and Cylindrical lens. Pulse duration of the laser beam was 3 – 6 ns with the pulse energy stability of ± 2% were used.

The laser operated in the regime of resonator quality modulation. The laser geometry was a cavity comprising a concave back mirror of 99% reflection and a convex front mirror of variable with radius reflection coefficient.
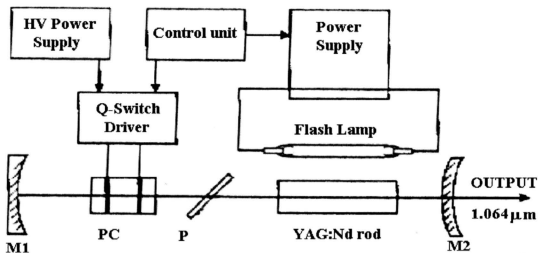
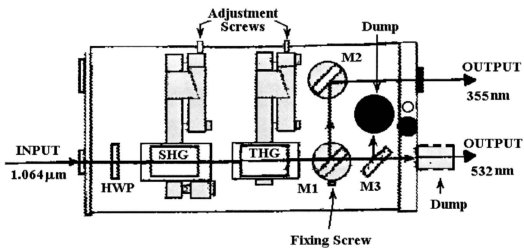Figure 3.1. Optical/electrical scheme pf NL301 laser head

Figure 3.2. Optical/mechanical scheme of STH units

The fundamental radiation of 1064 nm from the laser head enters the STH unit where the second and third harmonics are generated in nonlinear DKDP crystals mounted on the adjustable supports (SHG and THG in Figure 3.2). Radiations of 355 nm and 532 nm output are generated from the STH unit.
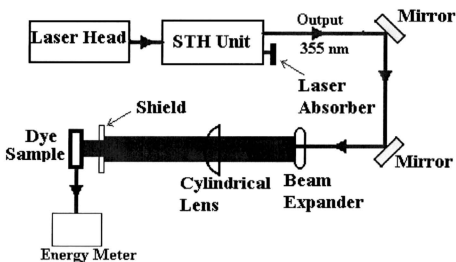

Figure 3.3. The setup of the pulsed Nd:YAG laser excitation

3.5 ENERGY MEASUREMENT

The laser output energy was measured by using a calibrated joule meter equipped with a pyroelectric metallic detector head (PE-10, NOVA, Ophir Opronics). The sensitivity, as specified by manufacturer, was of the order of μJ. The corresponding error was ±8% in the 190 – 350nm wavelength range and ±4% in the 400 – 800 nm wavelength range. The wavelength for (diphenylpropen-1,3-dialato)(oxalato)boron **(1)** was set at 428 nm and for (flavonolato)(oxalato)boron **(5)** or (flavonolato)(catecholato)boron **(6),** thus was set at 538nm. The measurement of the laser output energy was taken at 10 mm from the edge of the sample and a shield was used to obtain a consistent density of laser beam focus to the sample.

3.6 LASER SPECTRA

The laser spectra were obtained on a calibrated optical multi-channel analyzer (OMA III, EG&G, Princeton Applied Research), which consisted of a diode array detector, a detector interface unit and a host computer. The emission was captured and guided by a UV-VIS optical fibre to the detector unit. Strong and intense emissions required attenuation by a neutral density filter to avoid saturation and also to avoid damage to the photodiode array.

The detector exposure time was set to 1 s for most measurements whereas some weaker emissions required an exposure time of 3 s. The detector was configured for a slow mode pixel time scanning (28 μs) at a lower noise level and a default temperature of $5^{\circ}C$; the background attenuation was taken into account by subtracting the background noise.