# CHAPTER FOUR

## RESULTS AND DISCUSSION: LASING CHARACTERISTICS OF β-DIKETOBORONATE DERIVATIVES

### 4.1 UV ABSORPTION SPECTRA ANALYSIS

The ability of the β-diketoboronates to absorb UV radiation is dependent on its electronic and molecular structures. The primary characteristics of an absorption band are its position and intensity [36]. In this work, the β-diketoboronates strongly absorbed within the range of laser excitation wavelength.

The absorption spectra of the β-diketoboronates that were synthesized in this study are shown in Figures 4.1 – 4.6. Compound (diphenylpropen-1,3-dioalato)(oxalato)boron **(1)** in chloroform absorbed strongly in the 350 – 400 nm region. Compound (flavonolato)(oxalato)boron **(5)** and (flavonolato)(catecholato)boron **(6)** in chloroform only absorbed strongly in the region 320 – 360 nm. The region of intense absorption has widened at lower wavelengths for the three compounds if the concentrations are increased. The liquid absorption spectra at a concentration of 11.6 X $10^{-4}$ M, compound **(1)** showed an intense flat band in the 300 – 400 nm region. At a concentration of 5.6 X$10^{-4}$ M and 5.3 X $10^{-4}$ M, compounds **(5)** and **(6)** showed higher absorption as a flat band in the region 300 – 360nm as compared with that of compound **(1)**. The absorption values are listed in Table 4.1.

Table 4.1. Absorbance value of compound **(1)**, **(5)** and **(6)** in chloroform at wavelength 355 nm

| Compound | Concentration | Absorbance |
|---|---|---|
| **(1)** | 1.9x10$^{-4}$M | 3.4966 |
| | 5.8x10$^{-4}$M | 3.6141 |
| | 11.6x10$^{-4}$M | 3.6775 |
| | 46.5x10$^{-4}$M | 4.4369 |
| **(5)** | 1.9x10$^{-4}$M | 2.3286 |
| | 5.6x10$^{-4}$M | 5.0000 |
| | 11.2x10$^{-4}$M | 5.0000 |
| | 44.8x10$^{-4}$M | 5.0000 |
| **(6)** | 1.8x10$^{-4}$M | 2.2150 |
| | 5.3x10$^{-4}$M | 5.0000 |
| | 10.6x10$^{-4}$M | 5.0000 |
| | 42.3x10$^{-4}$M | 5.0000 |

The absorption spectra of the β-diketoboronates in the PMMA host matrix showed a sharp characteristic band. Two maximum absorption wavelengths $\lambda_{max}$ 374 nm and 391 nm were identified for compound **(1)** in PMMA as a thin film matrix. In the PMMA thin-film matrix, the maximum absorption was 342 nm for compound **(5)** and 344 nm for compound **(6)**. Any environment effect of PMMA matrix appeared to decrease the absorbance (optical density) and absorption intensity as compared with a liquid environment [36]. The Beer-Lambert Law states that the proportion of light absorbed by a solute in a transparent solvent is independent of the intensity of incident light and is proportional to the number of absorbing molecules in the light path. Beer-Lambert law is a limiting law and strictly valid only at low concentrations [26]. Moreover, that PMMA was not sufficiently transparent in the ultraviolet region during the determination of spectra contributed to loss in the intensity of the incident light.

The laser with the 355 nm output was selected for this work such that $\lambda_{max}$ for compound **(1)**, **(5)** and **(6)** were near to this excitation wavelength. Obviously, a laser excitation wavelength equal to $\lambda_{max}$ would be more suitable to ensure high dye laser efficiency. At a laser excitation wavelength of 355 nm, compound **(1)** in PMMA matrix displayed higher absorption as compared to the other compounds, and followed by compound **(6)**. Compound **(5)** in PMMA matrix showed lower absorption at the laser excitation wavelength of 355 nm.

Table 4.2. Absorbance ($\epsilon$) of compound **(1)**, **(5)** and **(6)** in thin film PMMA matrix

| Compound | Concentration (C) | $C/M_w$ | $\lambda_{max}$ | $\epsilon_{max}$ | $\epsilon_{355nm}$ |
|---|---|---|---|---|---|
| **(1)** | 3000.6ppm | 9.316 | 374nm | 0.6387 | 0.3527 |
| **(5)** | 3008.1ppm | 8.951 | 342nm | 0.2961 | 0.2436 |
| **(6)** | 3010.8ppm | 8.454 | 344nm | 0.4079 | 0.3328 |

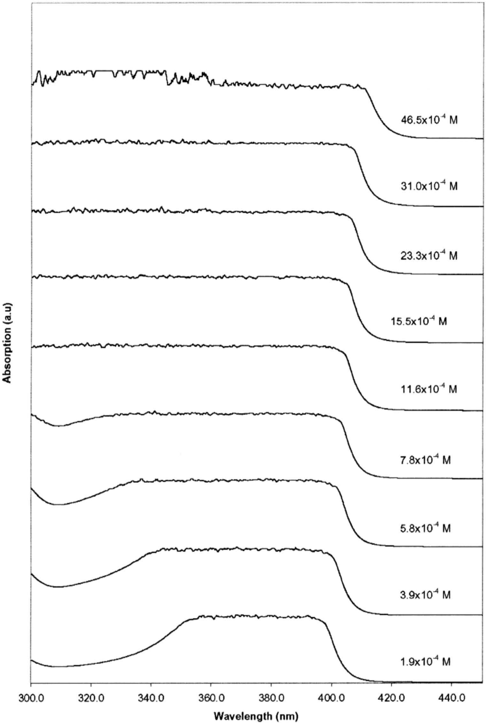

Figure 4.1. Absorption spectra of a solution of compound **(1)** in chloroform at different concentrations

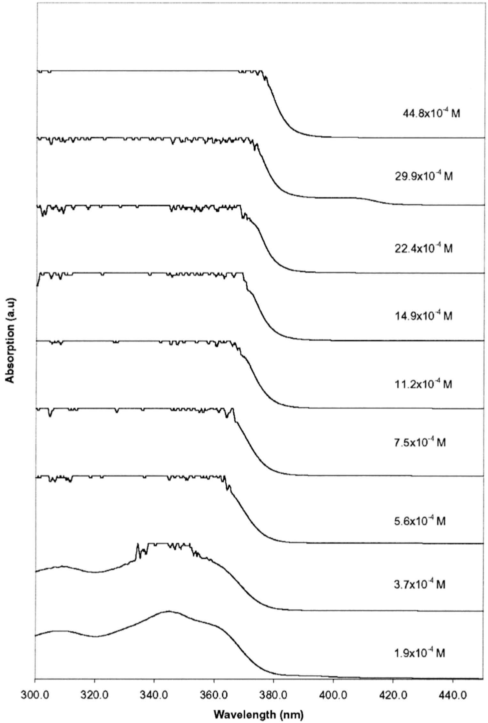

Figure 4.2. Absorption spectra of a solution of compound **(5)** in chloroform at different concentrations

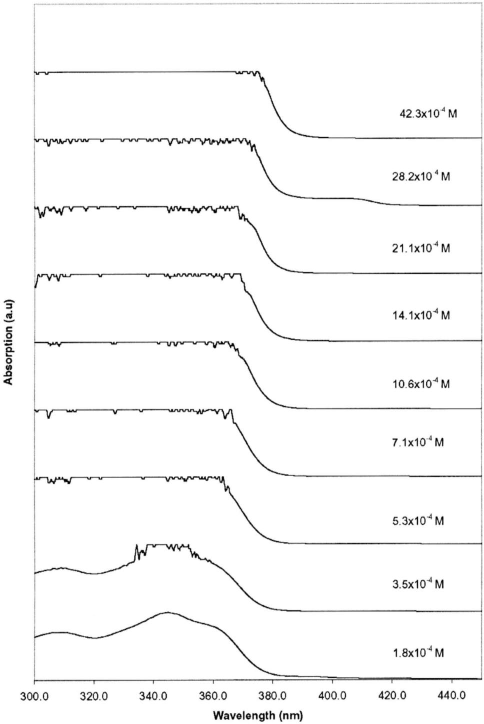

Figure 4.3. Absorption spectra of a solution of compound **(6)** in chloroform at different concentrations

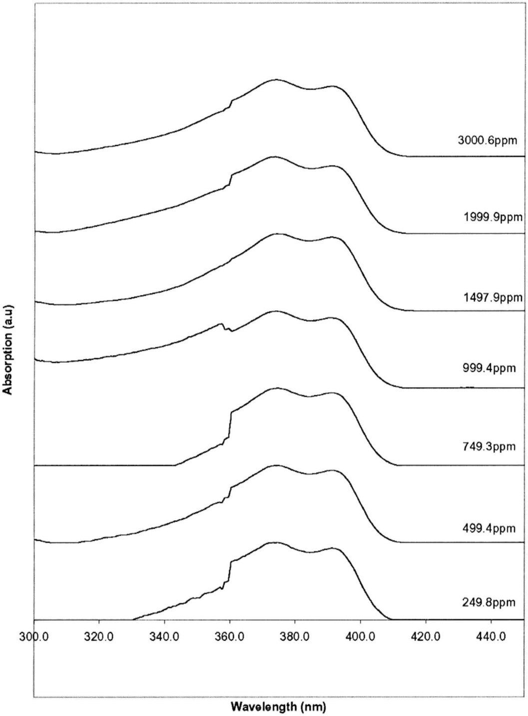

Figure 4.4. Absorption spectra of a slide of compound **(1)** doped in PMMA at different concentrations

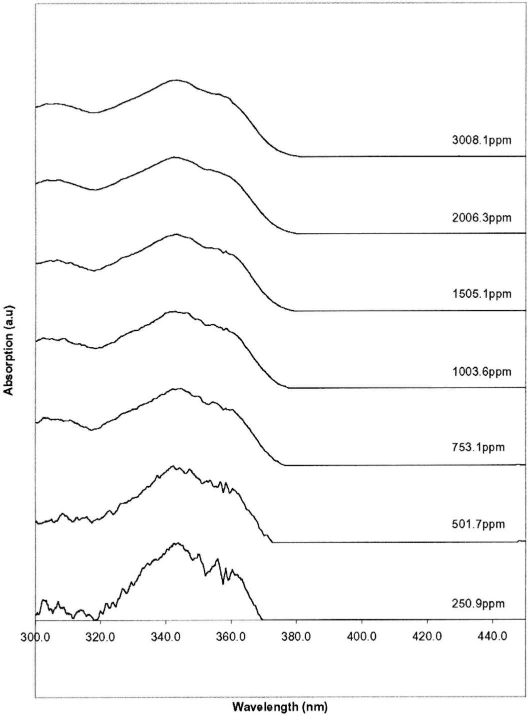

Figure 4.5. Absorption spectra of a slide of compound **(5)** doped in PMMA at different concentrations

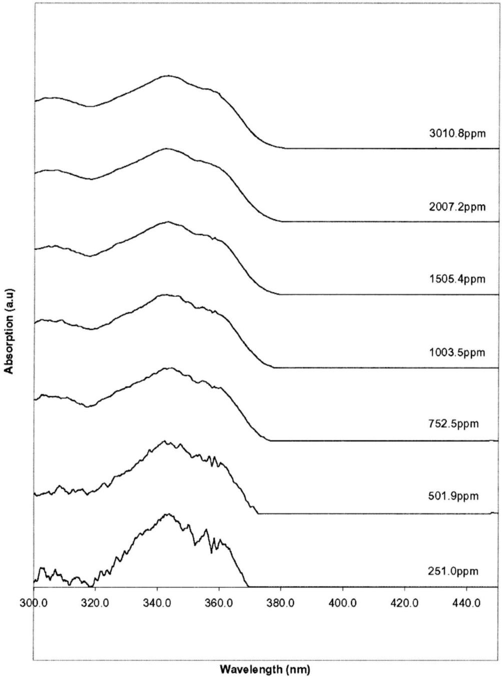

Figure 4.6. Absorption spectra of a slide of compound **(6)** doped in PMMA at different concentrations

## 4.2 ENVIRONMENT AND CONCENTRATION EFFECT ON LASER WAVELENGTH

As a function of concentration, the laser spectra of compound (flavonolato)(oxalato)boron **(5)**, (flavonolato)(catecholato)boron **(6)** and (diphenylpropen-1,3-dialato)(oxalato)boron **(1)** in liquid phase (chloroform) are shown in Figures 4.7 – 4.9 and in thin film PMMA solid phase in Figures 4.10 – 4.12. The laser spectra of compound **(1)** in the PMMA slab is shown in Figures 4.13. The summary of the maximum peak wavelength versus concentration can be obtained in Figures 4.14 – 4.20.

The laser bands of the β-diketoboronates were much narrower than the absorption bands. The compounds in the liquid phase showed very small bathochromic shifts (less than 1 nm) in the maximum peak wavelength in the laser spectra with increasing concentration. For the compounds doped in the PMMA matrix, the maximum peak wavelength of the laser bands was shifted to the longer wavelengths by 2-3 nm. The rigidity of PMMA reduced the structural mobility and hence resulted in the higher wavelength shift (2-3 nm).

At the same laser excitation wavelength of 355 nm, the bands for (flavonolato)(oxalato)boron **(5)** and (flavonolato)(catecholato)boron **(6)** were shifted to larger wavelength as compared with that of (diphenylpropen-1,3-diolato)(oxalato)boron **(1)**. This was further supported by the observation that the bathochromic shifts were greater with increasing conjugation of the structure [38, 27]. A similarity of the bathochromic shift (± 1 nm) for compound **(5)** and **(6)** was observed and suggested that the $C_6H_5COCH_2COC_6H_5$ unit (in compound **(1)**) and $C_6H_5C_9H_4O_3$ unit (in compounds **(5)** and **(6)**) provided the major contribution of laser action.

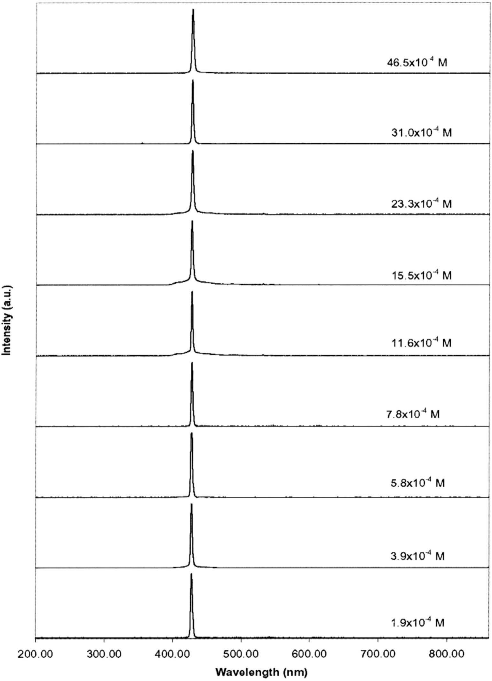

Figure 4.7. Output laser spectra of solution compound **(1)** in chloroform at different concentrations

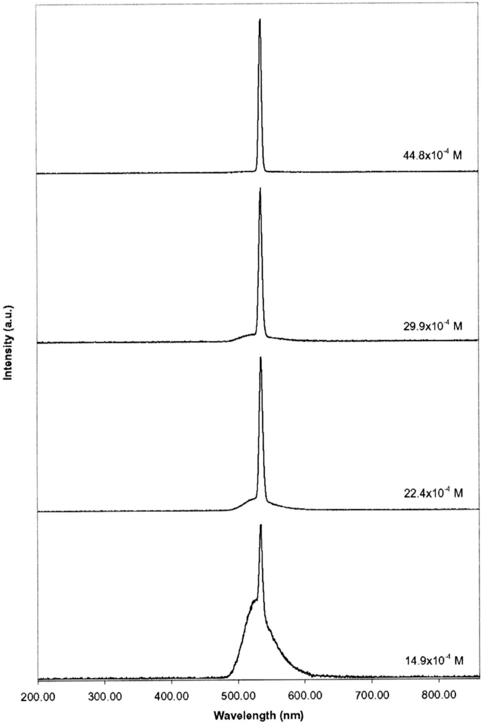

Figure 4.8. Output laser spectra of solution compound **(5)** in chloroform at different concentrations

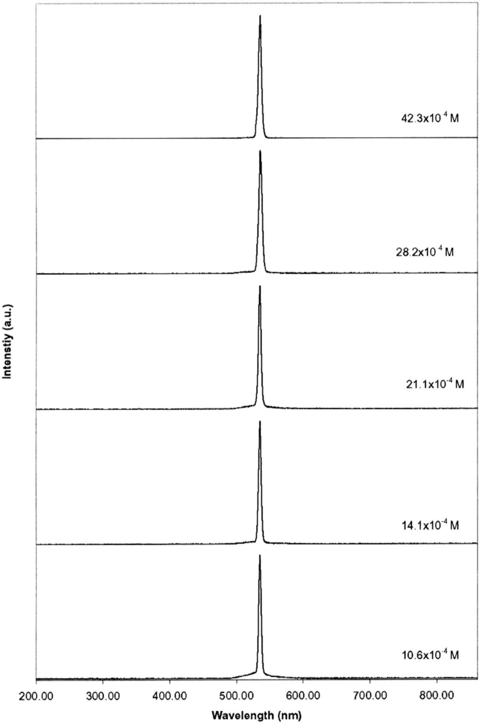

Figure 4.9. Output laser spectra of solution compound **(6)** in chloroform at different concentrations

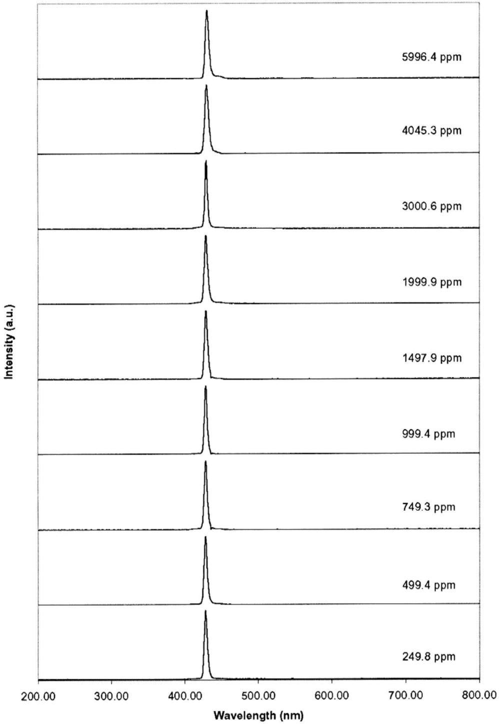

Figure 4.10. Output laser spectra of slide compound **(1)** doped in PMMA at different concentrations

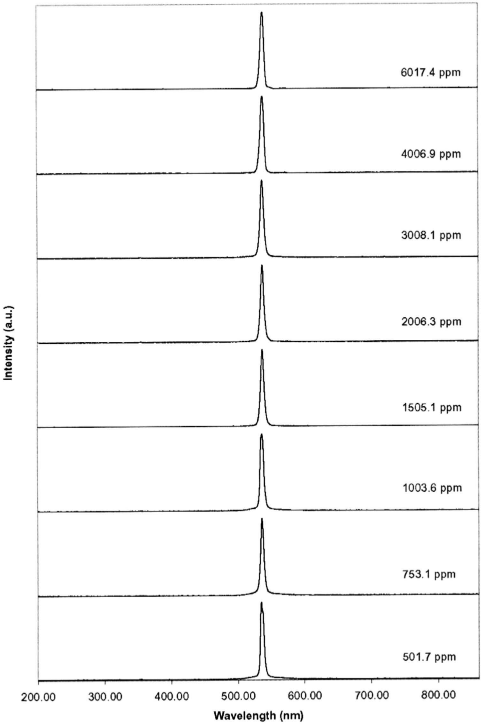

Figure 4.11. Output laser spectra of slide compound **(5)** doped in PMMA at different concentrations

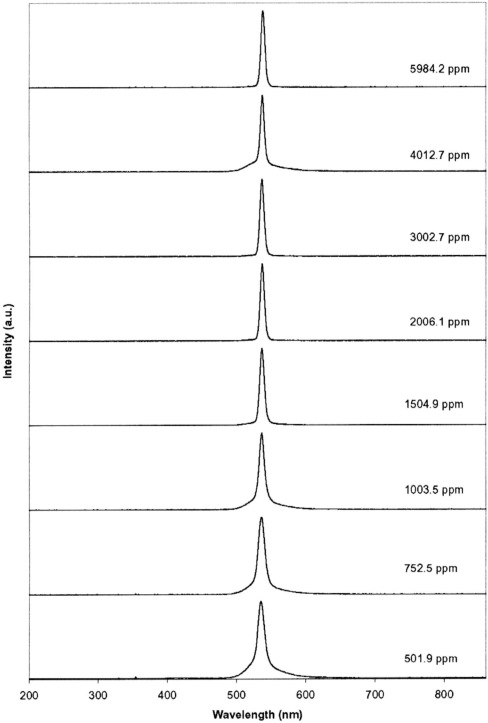

Figure 4.12. Output laser spectra of slide compound **(6)** doped in PMMA at different concentrations

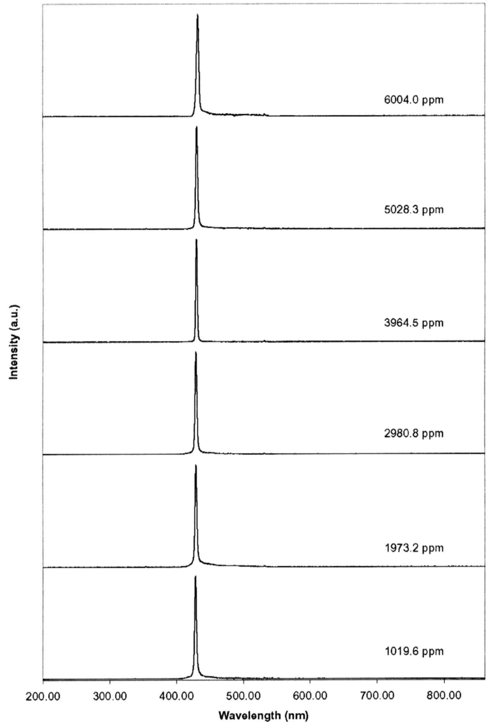

Figure 4.13. Output laser spectra of slab compound **(1)** doped in PMMA at different concentrations

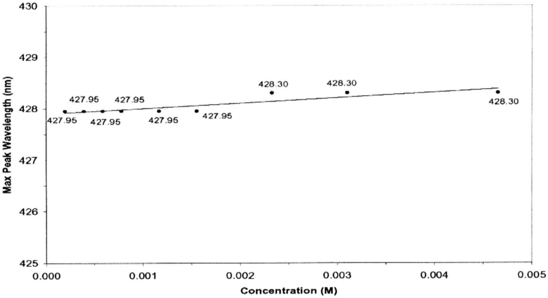

Figure 4.14. Maximum peak wavelengths of compound **(1)** in chloroform at different concentrations

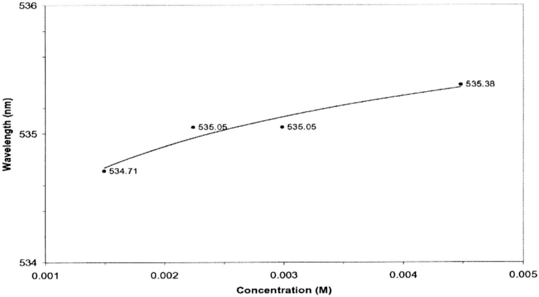

Figure 4.15. Maximum peak wavelengths of compound **(5)** in chloroform at different concentrations

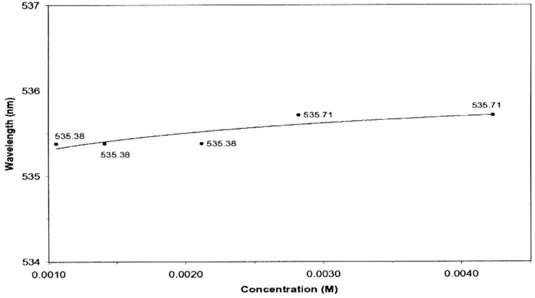

Figure 4.16. Maximum peak wavelengths of compound **(6)** in chloroform at different concentrations

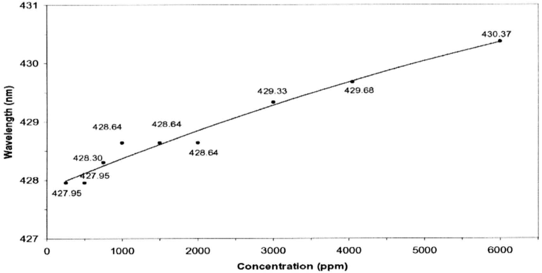

Figure 4.17. Maximum peak wavelengths of compound **(1)** doped in PMMA on a slide at different concentrations

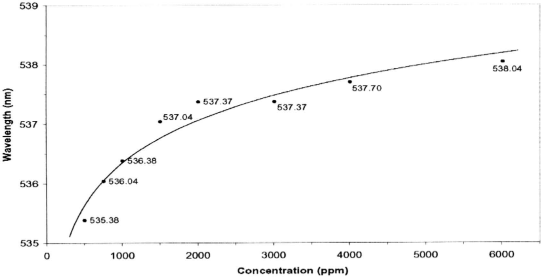

Figure 4.18. Maximum peak wavelengths of compound **(5)** doped in PMMA on a slide at different concentrations

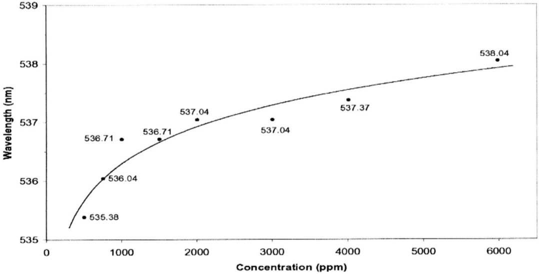

Figure 4.19. Maximum peak wavelengths of compound **(6)** doped in PMMA on a slide at different concentrations

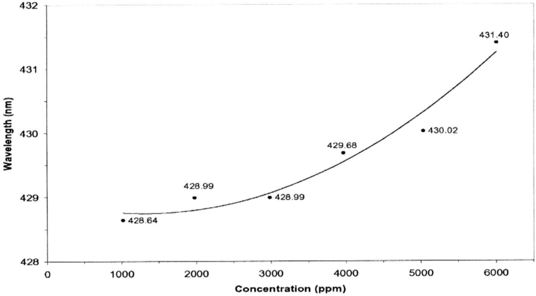

Figure 4.20. Maximum peak wavelengths of compound **(1)** doped in PMMA slab at different concentrations

## 4.3 ENVIRONMENT AND CONCENTRATION EFFECT ON LASER EFFICIENCY

Figures 4.21 – 4.27 show the laser conversion efficiency of the β-diketoboronates in chloroform, thin-film PMMA and slab PMMA. The laser conversion efficiency is defined as the ratio of the energy of dye laser output to the output energy of the pulsed ND:YAG laser incident on the sample surface with the minimum excitation energy producing dye laser emission [39].

If the concentration of dye was increased, the laser performance of compounds **(1)**, **(5)** and **(6)** increased to a lasing threshold limit such that solubility of dyes was saturated. In lower concentration range, the increase in the laser conversion efficiency maximum was assisted by the increase of fluorescence lifetime due to the effect of radiation trapping [50], i.e., absorption-re-emission that also increased the maximum peak lasing wavelength. If the concentration was further increased, a reduction of laser performance was observed that could be attributed by concentration quenching, photoquenching, aggregation, intersystem crossing [40-42]. A further increase in dye concentration gives rise to reduction of host free volume that resulted in the dye molecules not being able to penetrate completely into the free volume space and dimers aggregation probably resulted [43].

In the comparison study of the medium or host effect, the β-diketoboronates in PMMA host showed better laser efficiency as compared liquid medium with the structural mobility is the major contribution to deactivation of structural deformation caused by thermal equilibrium during the radiative lifetime of a few nanoseconds; the planarity of the β-diketoboronate dye before light emission is maintained [41].

As the thickness of the active region was increased, the relative laser conversion efficiency was also increased [41]. A maximum laser conversion efficiency of 7.9% was observed in this work for compound **(1)** in thin film PMMA at 20 – 30 μm thickness on each side of glass slide. A larger increase in thickness (approximately 1 cm) led to the absorption of all the incident laser energy and therefore the maximum laser conversion efficiency result of the compound **(1)** in PMMA slab was 28.5% at a concentration of 3000ppm.

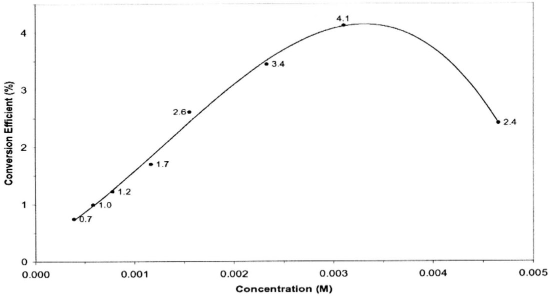

Figure 4.21. Conversion efficiency of compound **(1)** in chloroform at different concentrations

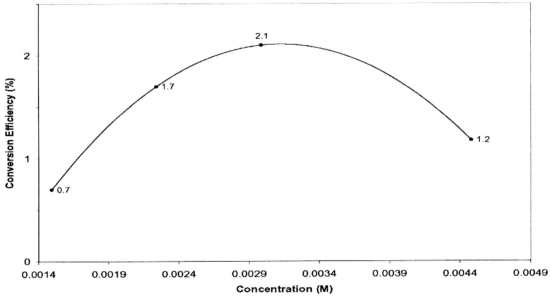

Figure 4.22. Conversion efficiency of compound **(5)** in chloroform at different concentrations

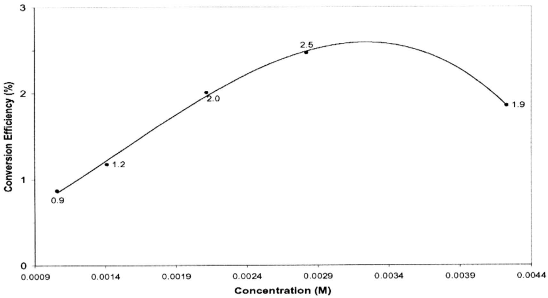

Figure 4.23. Conversion efficiency of compound **(6)** in chloroform at different concentrations

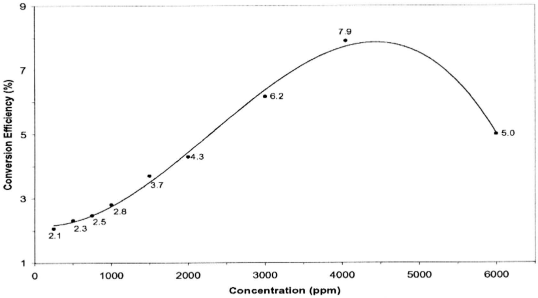

Figure 4.24. Conversion efficiency of compound **(1)** doped in PMMA on a slide at different concentrations

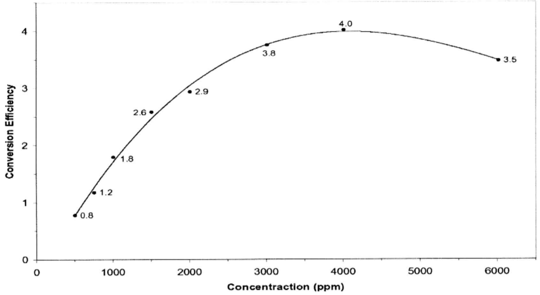

Figure 4.25. Conversion efficiency of compound **(5)** doped in PMMA on a slide at different concentrations

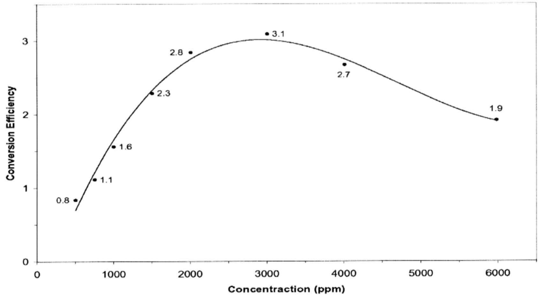

Figure 4.26. Conversion efficiency of compound **(6)** doped in PMMA on a slide at different concentrations

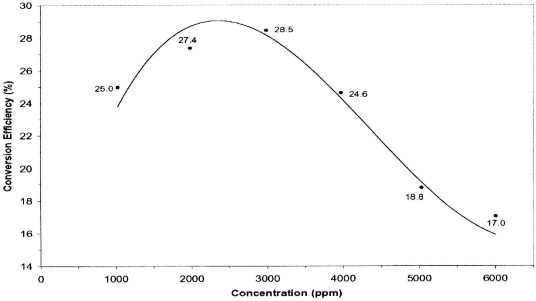

Figure 4.27. Conversion efficiency of compound **(1)** doped in PMMA slab at different concentrations

## 4.4 PHOTOSTABILITY

The dye laser conversion efficiency for compounds **(1)**, **(5)** and **(6)** in thin film PMMA gradually decreased with increasing number of pulses. The reduction of the efficiency can be attributed to the photodegradation of the dyes [41].

The photostability of the dyes in PMMA is defined by the bleaching efficiency, which is the ratio of the optical density of the dye in the initial stage to that in the bleached state. Low values are due to the aggregation of the dye molecules into dimers, trimers and oligomers; generally the dye dissolves only sparingly in PMMA. The dye can also be excited to form free radicals that then react with neutral molecules. Ideally, free radicals and their reaction products should not be present [30].

Figures 4.28 to 4.31 show the plots of conversion efficiency of each concentration versus the number of pulses. At constant absorption energy, compounds **(1)**, **(5)** and **(6)** show decreasing emission energy with increasing pulses, which is attributed to energy being converted for other non-radiative processes. Similar conditions are observed for different concentrations, but increase concentration will give rise to initial higher conversions until the stage that further increase in concentration leads to formation of dimers, which will absorb energy without radiative emission [43].

The optimum concentration for compound **(1)** gave rise to a higher degradation rate at the initial stage. The degradation rate was gradually slowed down on further excitation pulse. The photostability for compound **(5)** and **(6)** was better than that of compound **(1)** because compound **(1)** took less pumping pulse to reduce 50% of the starting laser conversion efficiency.

Although variations of dyes degrade in different manners, the mechanisms themselves can be categorized into several primary factors that include thermal destruction during fabrication or upon irradiation, chemical interaction of the dye molecules and macromolecules and viscosity of the host medium [31, 6].

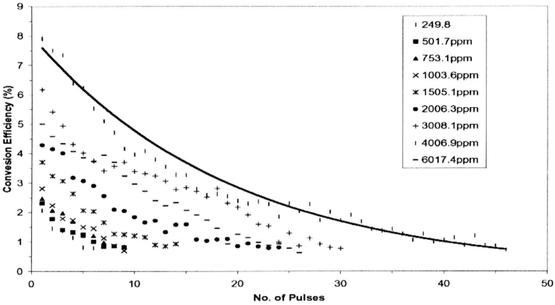

Figure 4.28. Degradation versus pump pulses for compound **(1)** doped in PMMA on a slide at different concentrations

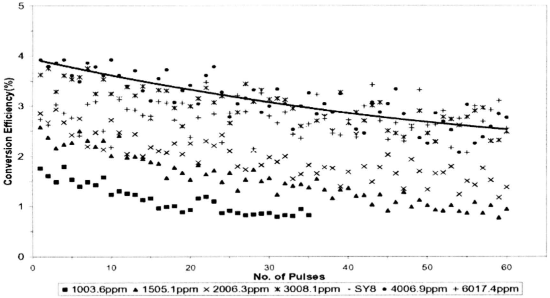

Figure 4.29. Degradation versus pump pulses for compound **(5)** doped in PMMA on a slide at different concentrations

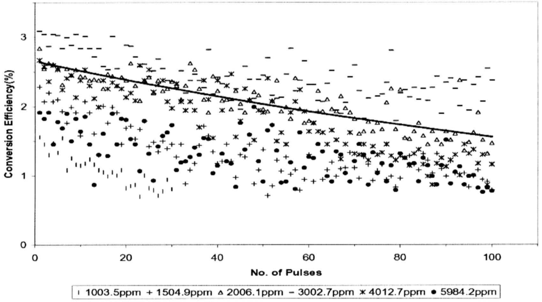

Figure 4.30. Degradation versus pump pulses for compound **(6)** doped in PMMA on a slide at different concentrations

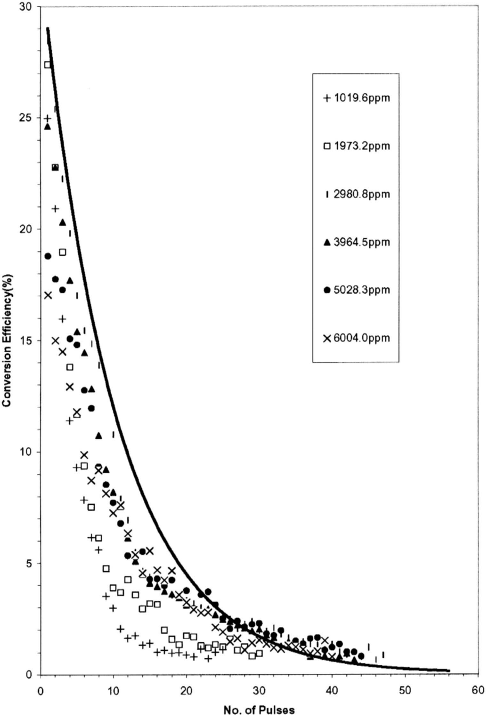

Figure 4.31. Degradation versus pump pulses for compound **(1)** doped in PMMA slab at different concentrations

## 4.5 CONCLUSIONS

The β-diketoboronates, (diphenylpropen-1, 3-dialato)(oxalato)boron **(1)**, (flavonolato)(oxalato)boron **(5)** and (flavonolato)(catecholato)boron **(6)**, have the dye laser characteristics. Three other β-ketoboronates (RCOCHCOR')(O2CCO2)B where (R = R' = t-butyl **(2)** ; R = methyl, R' = phenyl **(3)** and R = R' = 2-pyridyl **(4)**) do not laze. Compound **(1)** has much better laser efficiency as compared with compounds **(5)** and **(6)**. Even though the maximum laser efficiency of 28.5% was achievable from the compound **(1)** doped in PMMA slab, the optimum concentration gave rise to an unrealistic degradation rate. For compounds **(5)** and **(6)**, the maximum laser efficiency was 4.0% and 3.1% in thin-film PMMA. As a comparison, maximum laser efficiency of 7.9% was observed for the compound **(1)** doped in PMMA on a slide.

The higher bathochromic shift for the maximum peak wavelength in the laser spectra clearly depended on the substitution of the diphenylpropen-1, 3-dialato units. The maximum peak wavelength for compounds **(5)** and **(6)** did not show much difference in the replacement of the oxalato unit by the catecholato unit.