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Amplified spontaneous emissions from (oxalato)(dibenzoylmethanato)boron

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Abstract

Amplified spontaneous emissions (ASE) from two boron-containing organic compounds, (oxalato)(dibenzoylmethanato)boron, were obtained for the first time using a nitrogen laser as the pump source. Compared to commercially available laser dyes, there were only small red shift and minimum broadening in the peak ASE wavelength. ASE conversion efficiencies obtained were 8–10% in chloroform solution and 5% when doped in thin films of poly(methyl methacrylate).

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Keywords: Amplified spontaneous emission; Laser dye; Boron; Organic compounds

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1. Introduction

Stimulated emission from organic dyes in solution was first reported almost forty years ago by Sorokin and Lankard [1] and Schafer and Schmidt [2], and thousands of organic compounds that can exhibit strong fluorescence have been evaluated for the laser action. Research in developing new laser dyes continues, especially on those with little triplet-state loss [3] such as the quasi-aromatic [4] and the intramolecular proton transfer [5] compounds. Recently, there was an interest in synthesizing novel dyes with large two-photon absorption cross-section, which can enable up-conversion lasing [6], and are applicable to optical power limiting [7], three dimensional lithographic microfabrication [8] and optical data storage [9]. For development of solid-state dye laser, the research interest started in 1960s was renewed by doping laser dyes in different types of host materials such as polymer [10], liquid crystal [11], sol–gel [12], and organic–inorganic composite [13].

This article presents the measurements of amplified spontaneous emission (ASE) from two boron-containing organic compounds that can be classified as β-diketoboronates. The general structure of β-diketoboro-nates, as shown in Fig. 1, represents a special type of chelated boron (atomic number 5) complexes. The tetrahedrally-coordinated boron compounds having two conjugated π-entities that bind to the boron atom through their pairs of oxygen ends display an unusual type of electron delocalisation over the boron atom that occurs without the intervention of conventional π-bond resonance. The two conjugated π-entities (five- and six-membered chelates) are orthogonal to each other. Such a configuration shows a special type of electron delocalisation that has been called as spirointeraction, which was proposed on the basis of spectroscopic evidence and derived from their absorption and fluorescence spectra [14].

The preparation method for β-diketoboronate compounds from enolisable β-dicarbonyl compounds, a diol

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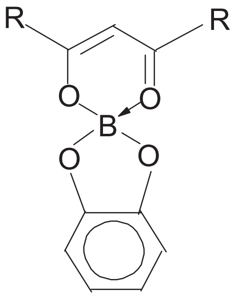

Fig. 1. General structure of β-diketoboronates.

and boric acid, were documented [15,16]. The structures of the two boron-containing organic compounds, BOC-I and BOC-II, used for this work are shown in Fig. 2. Both are structurally the same and known as (oxalato)(dibenzoylmethanato)boron except that BOC-II is deuteriated. In comparison with the conventional and commercially available laser dyes, these organic compounds have simpler structures and they can be readily synthesized by conventional organic reactions. They have also been proposed for laser action [17] but to the best of our literature search, this suggestion has yet been taken up.

2. Experimental

The boron-containing organic compounds, BOC-I and BOC-II, used in this work were prepared and given as gifts from Prof. H. Hartmann of Technische Hochschule Merseburg, Germany, whose method was already referred in the above section [15,16]. These two compounds could only be dissolved in chloroform and not in alcohol, which is a disadvantage against many commercial laser dyes. The fluorescence spectra from chloroform solution was collected using Shimadzu UV–Vis-NIR Scanning Spectrophotometer (Model UV-3101 PC) and Perkin–Elmer LS 50B Luminescence Spectrometer, so as to detect the spectral narrowing for "laser action". However, the "laser action" obtained in this work is better classified as the amplified spontaneous emission (ASE) without using a laser resonator. The ASE was obtained from chloroform solutions of BOC-I and BOC-II, contained in a 1 cm UV quartz cuvette, upon transverse pumping by a 1 mJ nitrogen laser. And the ASE energy and spectra were measured, respectively, by a pyroelectric energy meter (Ophir, model Nova PE-10) and an optical multichannel analyser (EG&G Inc., model 1461).

The ASE from BOC-I and BOC-II were also obtained when they were doped in 20 μm thin films of poly(methyl methacrylate) (Mw > 900,000), such interest arises from a stable dye-doped polymer lasers in UV-blue region [12]. The dip-coating technique was used to prepare doped PMMA thin films (20–60 μm) on the microscope slides. After a brief dipping, films coated on both sides of the microscope slide were allowed to dry in draft-free area in order in order to obtain uniform film. The ASE beam emerged from both ends of the microscope slide acting as a planar waveguide [18,19].

3. Results and discussion

The two compounds, BOC-I and BOC-II, exhibit similar fluorescence spectra but with a small difference, of about 5 nm, in their peak wavelengths. This may be attributed to deuterium in BOC-II molecular structure which causes the red shift. The full-width, half-maximum (FWHM) of their fluorescence spectra (Fig. 3) may provide a dye-laser tunable range of 30–40 nm that is comparable to most of the commercially available laser dyes. When doped in thin films of PMMA, there is an additional but relatively small red shift of (3–5 nm) in their peak fluorescence wavelengths, as compared to the many commercial dyes when doped in different types of solid hosts [10–13,19,20].

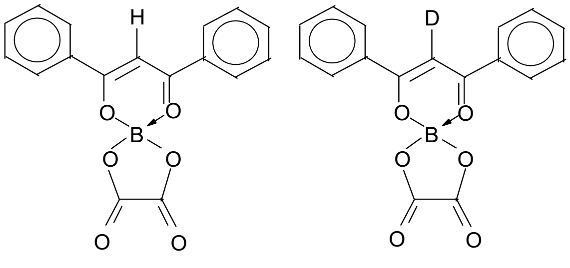

Fig. 2. Structures of boron-containing organic compound, BOC-I and BOC-II, of (oxalato)(dibenzoylmethanato)boron.

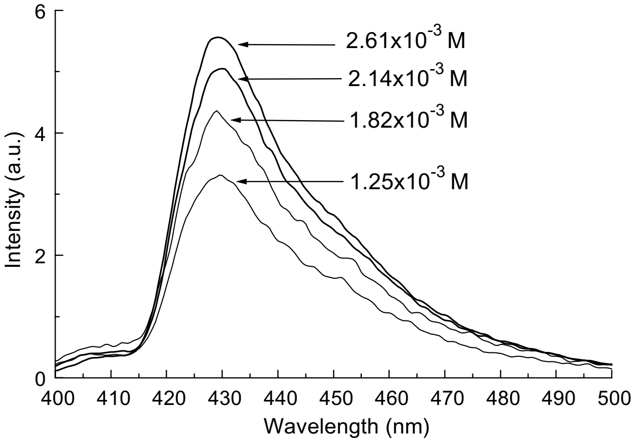

Fig. 3. Fluorescence spectra of BOC-I in chloroform.