

Laser Breakdown Spectroscopy of BO Molecule

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a variant of the classic technique of electric spark spectroscopy. The process of laser-induced breakdown has been studied extensively since the discovery of the laser [1-3]. Practical applications of LIBS were demonstrated [4-6] for the detection of atomic constituents in gases and gas-entrained particulates and for the analysis of metals.

We have investigated the applicability of LIBS to the measurement of boron isotopic ratio. Spectral resolution of LIBS is not high enough to resolve the atomic emission lines from the different isotopes. However, the BO molecule is known to have large isotope shift in its emission spectrum. In this study we concentrated on observing and analyzing the emission spectra from BO molecules which were produced by the recombination in the laser-generated plasma. The emission bands of BO lying in the visible and the ultraviolet region have been well investigated so far to determine the rotational and vibrational constants [7]. By using these molecular constants we developed a computer calculation code to reconstruct the emission spectrum under the relatively low spectral resolution. By analyzing the observed spectrum comparing with the calculated result the evaluation method of the isotopic ratio and its accuracy were discussed.

2. Experimental set-up

The experimental set-up is shown in Fig.1. A boron disk ($20\text{mm } \phi$) was used as a sample which was placed in the depressurized chamber. The output energy of 130 mJ from a Q-switched Nd:YAG laser was used as light source. The pulse width and the repetition rate were 7ns and 30Hz, respectively. The laser light was focused on the surface of the sample using the lens with the focal length of 10cm. The drilling effect was avoided by rotating the sample.

The hemispheric visible emission was observed through the side window, the radius of which was

increased as the ambient air pressure was decreased. The radius of the plasma was typically about 15mm at the air pressure of 4hPa. The laser-induced plasma was imaged onto the entrance slit of the monochromator by a lens with the focal length of 10cm to obtain the spatially resolved spectrum. The light signal was detected by a photomultiplier, averaged by a boxcar and fed to a chart recorder. The slit width of the monochromator was set to 0.5mm corresponding to the spectral resolution of 0.4nm which was sufficient to observe the band contours of the BO spectra. The rotational lines involved in each band, however, were not resolved due to the collisional broadening of the emission source.

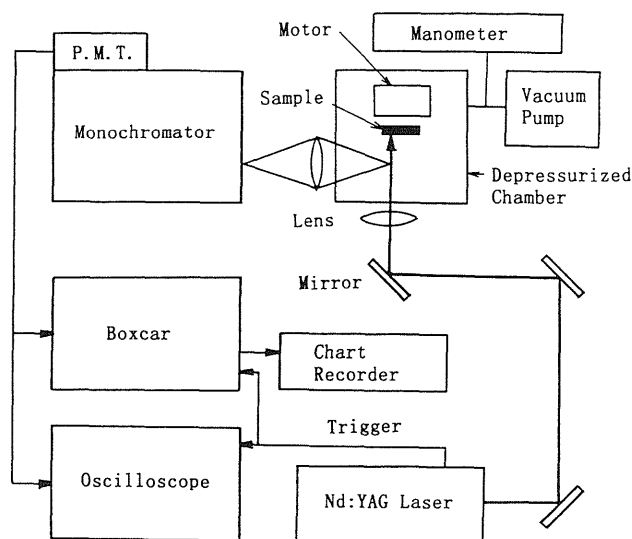


Fig 1 Experimental set-up

3. Results

The emission spectra taken at the distance from the sample surface between 5mm and 15mm showed the BO emission bands clearly when we measured them at the delay time between $7\mu\text{s}$ and $15\mu\text{s}$ after the laser shot. The BO band spectra were observed in the wavelength region from 330nm to 560nm. By

analyzing the band contours and their spectral positions twelve bands of the $A-X$ transition were identified in this wavelength region. Of these bands the (0-2) band was observed without interference of neighboring bands. Furthermore, the isotope shift of this band is larger than those of intense bands below 500nm. [7]. These characteristics are suitable for the analysis of the isotopic abundance ratio. Therefore, the analysis was mainly performed on this (0-2) band.

In order to explain the structure of the band spectrum of BO an example of the calculated results is shown in Fig.2. The calculation was done for the (0-2) band with the spectral width of 0.5nm and the temperature of 1,000K. The abundance ratios of ^{10}BO and ^{11}BO were assumed to be equal to each other (50% : 50%) in this calculation. The both contributions of ^{10}BO and ^{11}BO and the whole band spectrum are shown in the figure. The band contours of two isotopic molecules seem to be quite similar to each other except for the spectral positions because the differences in the values of the molecular constants used in the calculation are very small except for the band origin. The band contour of one isotopic molecule consists of two wide peaks. One peak in the shorter wavelength side is the contribution of the $^2\Pi_{3,2} - ^2\Sigma$ sub-band and the other is $^2\Pi_{1,2} - ^2\Sigma$ sub-band. The slope in the shorter wavelength side of the peak is steeper than that in the other side. This is because the band head of each sub-band lies in the shorter wavelength side of each peak. The peaks of the small fluctuations in the longer wavelength side are scarcely resolved emission lines. The frequency difference between the band origins of ^{10}BO and ^{11}BO (isotope shift) is 2.87nm [7] for this band, which coincides with the frequency difference between two sub-band peaks. Therefore, three peaks are observed in the whole band spectrum.

Figure3 shows the experimentally observed (0-2) band spectrum and the calculated result. The spectral width in the calculation was set to be 0.4nm corresponding with the experimental condition. The spectrum calculated with 1,500K was found to fit the experimental result. The evaluation method of the isotopic ratio and its accuracy were discussed elsewhere [8].

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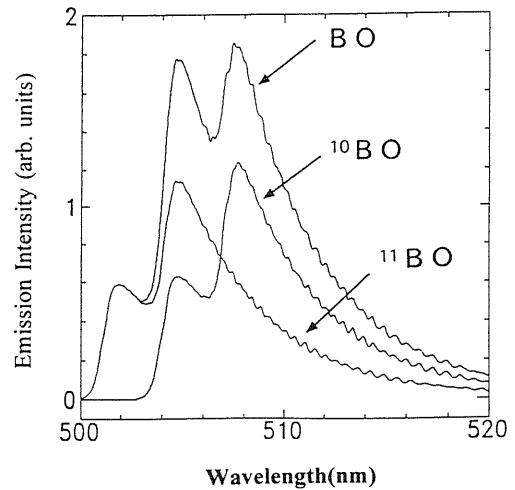


Fig.2 Calculated (0-2) band spectrum of BO

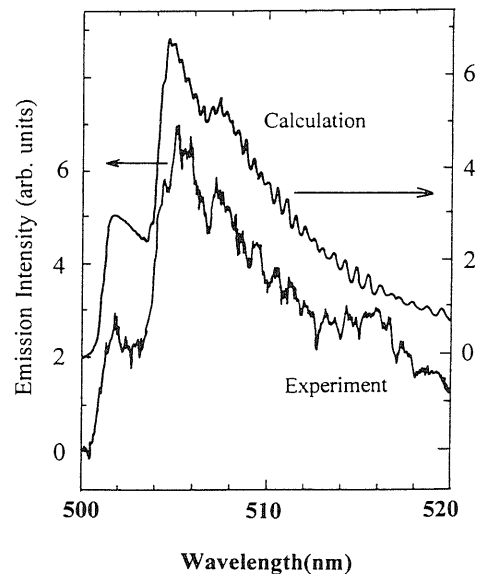


Fig.3 Observed and calculated (0-2) band spectrum

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