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Boron- and iron-bearing molecules in laser-induced plasma☆

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ABSTRACT

Boron combines with alkali-earth elements, such as Ca, Mg, and Sr and with oxygen to form molecules in LIP of boron-bearing minerals with strong and characteristic band emission. It may be supposed that those bands are of $CaBO_2$, $MgBO_2$ and $SrBO_2$ type. Besides, emission of BO, BO_2 and FeO is also detected.

1. Introduction

In laser-induced breakdown spectroscopy (LIBS), optical emission spectra of atoms and atomic ions in laser-induced plasma (LIP) are typically used to analyze solid, liquid and gaseous samples. LIBS offers excellent performance for real-time elemental analysis at atmospheric pressure, including remote applications [1–3]. Molecular analysis by LIBS has been much less investigated than elemental LIBS. The most famous molecular LIBS examples are of the CN violet system, CH, the C_2 Swan system, AlO, TiO and OH emission spectra in air [4], SrO [5] and halogens with alkali-earth elements, such as CaF and CaCl [6].

Boron is well known for its molecular BO emission, which was used for isotopic analysis [7,8]. While studying LIP of boron-bearing minerals, several bands were found in their emission that differ from those previously identified. The aim of the present work is to study molecular emission in boron-bearing minerals and materials.

2. Experimental setup

2.1. Spectroscopy

The experimental setup is a conventional confocal single-pulsed (SP) and double-pulsed (DP) laser-induced plasma configuration. The SP system contains a 1064 nm Nd:YAG laser (Quantel, Big Sky Ultra 100) with a maximum energy of 100 mJ/pulse and a pulse width (FWHM) of 7 ns. The DP system consists of two 1064 nm lasers (both Big Sky Ultra 50), with a maximum energy of 50 mJ/pulse and an FWHM of 7 ns. In our DP experiments, we used 30 mJ of energy for the second laser pulse and 3 to 30 mJ for the first laser pulse. A delay generator controlled the timing of the two laser pulses, separating them typically by 300 to 500 ns. The two laser beams were focused with a 25 cm focal length quartz lens located about 20 cm above the sample surface. The laser spot diameter was determined by the knife-edge method to be about 300 μm on the sample surface; in this way, the energy of a 10 mJ pulse resulted in a fluence of 21 J/cm^2. Emitted plasma radiation was collected by a fiber (0.22 NA) and guided to a spectrometer (Shamrock SR 303i-A) equipped with 1200 and 2400 lines/mm diffraction gratings and a gated-ICCD camera (Andor DH-720 25F-03) detector. The wavelength and spectral resolution of the spectrometer were calibrated using a low-pressure Hg lamp by measuring both the spectral positions of the lines and their spectral profiles. Using a spectrometer slit width of 10 μm, we established spectral resolutions for the 2400 l/mm and 1200 l/mm gratings as 0.1 and 0.16 nm, respectively. The time resolution of the ICCD camera was verified by analyzing the temporal profile of the laser pulse used in our experiments. For this purpose, Nd-YAG laser light, frequency-doubled and scattered by a sugar cube, was utilized to avoid complications of stray light at the fundamental frequency. Using the camera's kinetic series technique with a gate width and step of both 1 ns, the measured FWHM of the laser pulse was 5 ns, corresponding to its specified value.

Persistence data were measured by a kinetic series, an approach well suited for recording the temporal evolution of a process. It was done by measuring the intensity of emissions as a function of the acquisition

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delay between plasma formation by the laser pulse and the opening of the acquisition temporal gate, using different delays and gate widths.

The line intensities in the figures are presented in arbitrary units (au); they may only be compared within each figure, not between different figures.

A ruggedized, delayed-integration CCD spectrometer (Avantes AvaSpec) with a spectral resolution of 0.5 nm was used to evaluate feasibility for industrial applications. It has a fixed integration time of 1 ms and a variable delay starting from 100 ns.

2.2. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

Ablation was done by an ArF excimer laser (New Wave) emitting 15 ns long pulses at a wavelength of 193 nm, with repetition rate of 10 Hz, fluence of 7 J cm^{-2} and variable spot sizes of 50 to 100 μm. SRM NIST610 was used as a standard. The laser ablation chamber cell is home-designed, with a tear-shaped space, resulting in a low sample volume (4 cc). This cell consists of one gas inlet nozzle and one outlet nozzle located at the center of the cell edges. The cell was flushed with helium at a rate of 0.5 L/min. The element count rate was determined by an AGILENT (7500 CX) ORS quadrupole mass spectrometer with RF power of 1500 W, an injection tube diameter of 2.0 mm, and auxiliary gas flow of 0.9 L/min Ar.

2.3. Samples

The samples used were the minerals datolite $CaBSiO_4(OH)$, danburite $CaB_2(SiO_4)_2$, colemanite $Ca_2B_6O_{11}x5H_2O$, boracite $Mg_3B_7O_{13}Cl$, kurnakovite $MgB_3O_3(OH)_5 \cdot 5(H_2O)$, ulexite $NaCaB_5O_9x8H_2O$, ludwigite Mg_2FeBO_5, mixtures of boracite and anhydrite $CaSO_4$, colemanite with MgCl, chemically pure H_3BO_3, B, MgB_2, CaB_6 and BN compounds and mixtures of BN with CaF.

3. Experimental results and discussion

3.1. Calcium- and boron-bearing minerals

Fig. 1 shows SP-LIBS emission spectra of natural borosilicates danburite $CaB_2(SiO_4)_2$ and datolite $CaBSiO_4(OH)$. For both minerals, spectra taken with a relatively short delay of 500 ns and narrow gate of 5 μs predominantly contain narrow lines of the main elements Ca and Si and a minor element Na (Fig. 1 a, b) [9]. In spectra taken with a long delay and a broad gate width of 50 μs, emission bands peaking at approximately 563 and 595 nm were dominant (Fig. 1 c, d).

The origin of these bands is not clear. Presently two sources of band emission in LIP are known: plasma-induced luminescence (PIL) [10] and molecular emission [1–6]. Danburite and datolite are luminescent minerals with trivalent rare-earth element (REE) luminescence centers, such as Sm^{3+}, Eu^{3+}, Dy^{3+} and Tb^{3+} [11]. Such luminescence may be a source of the emission bands. To check this hypothesis, plasma emission of two non-luminescent Ca–B bearing minerals, colemanite $Ca_2B_6O_{11}x5H_2O$ and ulexite $NaCaB_5O_9x8H_2O$, were studied. Nevertheless, band emission in LIP remained for both minerals (Fig. 2a for colemanite), indicating that molecular emission was the most probable source of their band luminescence. The major elements present in all studied boron-bearing minerals — danburite, datolite, colemanite and ulexite —were boron, calcium and oxygen. Calcium is characterized by well known orange emission whose main band peaks at 620 nm, which has been ascribed to CaO molecules [12]. Such emission is actually detected in mineral calcite $CaCO_3$ (Fig. 2b), but it is markedly different from the bands detected in boron-bearing minerals. Another potential source of molecular emission is boron. Many bands have been found in its emission generated by flames and arc-induced plasma [12]. Metallic boron studied in our experimental conditions revealed several emission bands in the studied spectral range peaking at 578.7, 601.5 and 619.7 nm. Such bands are known to be present in arc-induced plasma or in a flame and have been ascribed to BO_2 molecules [12]. They were for the first time detected in LIP (Fig. 2c), but they are different from the bands under discussion. Because each relevant major element

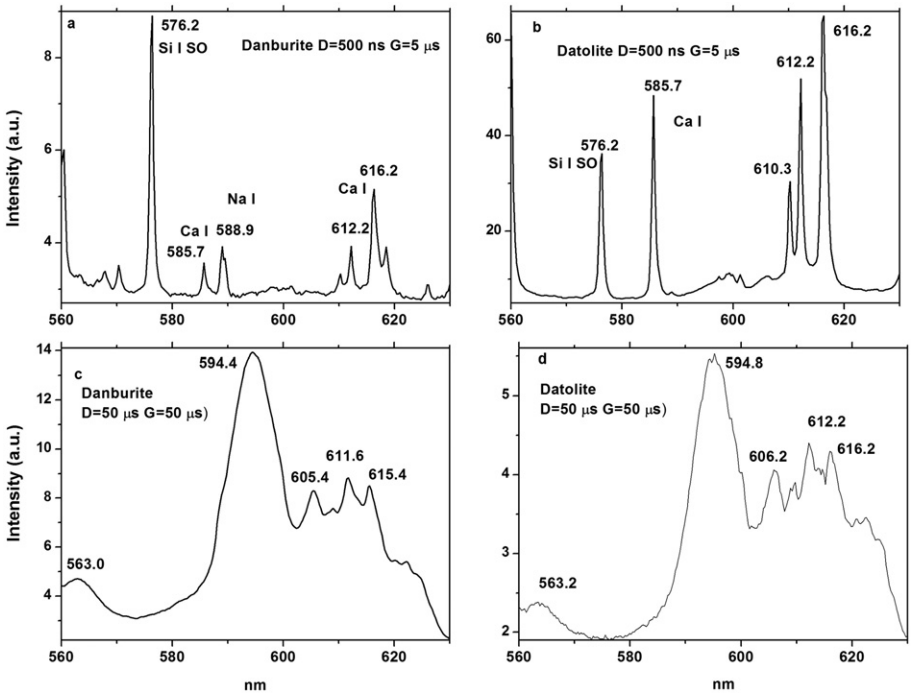

Fig. 1. Single-pulse breakdown spectra of natural danburite (a, c)and datolite (b, d) at the early (D = 500 ns G = 5 μs) and late (D = 50 μs G = 50 μs) stages of plasma life.