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Issues in deep ocean collinear double-pulse laser induced breakdown spectroscopy: Dependence of emission intensity and inter-pulse delay on solution pressure ☆

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ABSTRACT

Double-pulse laser-induced breakdown spectroscopy (DP-LIBS) with a collinear laser beam orientation is shown for high-pressure bulk aqueous solutions (up to 50 bar) along with bubble and plasma images. These investigations reveal that the emission plasma is quenched much more rapidly in solution requiring much shorter detector gate delays than for typical LIBS measurements in air. Also, the emission is inversely proportional to solution pressure, and the most intense emission at all pressures occurs when the laser-induced vapor bubble is at a maximum diameter. It is also shown that the laser-induced bubble grows initially at the same rate for all solution pressures, collapsing more quickly as the pressure is increased. Intense emission is best obtained for conditions where the laser-induced bubble formed by the first laser pulse is small and spherically shaped.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS), first reported by Brech and Cross in 1962 [1], is a relatively simple spectroscopic technique that allows rapid multi-elemental analysis of solids, liquids and gases with little or no sample preparation. As only optical access is required for the analysis, LIBS is well suited for *in situ*, non-contact and remote elemental analysis [2–20], and LIBS is particularly useful for applications in extreme, hostile, and inaccessible environments [10–18,21–33]. Of particular interest to our research group is using LIBS for multi-elemental analysis of high-pressure aqueous solutions, with the goal of applying LIBS to *in situ* elemental analysis in the deep ocean [31–33].

In previous work we reported double-pulse LIBS (DP-LIBS), first introduced by Cremers *et al.* in 1984 [34], to increase the range of elements in high-pressure aqueous environments [32]. It was shown previously that significant DP-LIBS emission enhancements are achieved by exciting the vapor bubble that is formed in solution by a previous laser pulse [34–42]. It was also reported that when a second laser pulse is focused onto the laser-induced vapor bubble, less energy goes into vaporization of the bulk solution, leaving more energy for excitation of the second plasma and as a result, the rapid rate of quenching associated with SP-LIBS in bulk solution slows considerably. In our earlier orthogonal DP LIBS studies, it was found that increasing the solution pressure reduced the amount of DP-LIBS emission produced in the bulk solution, such that little or no DP-LIBS emission enhancements were observed above approximately 100 bar [32].

In the current collinear DP LIBS work, we utilize plasma and bubble imaging in high-pressure solutions to better understand the processes that lead to the observed decrease in DP-LIBS emission with increasing solution pressure. Although it is intuitive that pressure effects on DP-LIBS enhancements are related to the conditions of the vapor bubble, our results show a direct relationship between the size and lifetime of the laser-induced bubble with increasing solution pressure and the resulting DP-LIBS emission.

2. Experimental

The experimental system used to obtain LIBS spectra and shadowgraph images of the laser-induced plasmas and bubbles is shown schematically in Fig. 1. Two Nd:YAG laser beams (Continuum Surelight III, 5-ns pulses, 1064 nm, 1 Hz) were collinearly aligned and focused into a previously-described [31,32], high pressure stainless steel sample chamber. A 5-cm focal-length, spherical fused silica lenses (L_1 in Fig. 1) was used to focus the laser pulses into the cell. L_1 was also used to collect plasma emission and L_2 was used to focus the plasma emission onto a collection optical fiber (FO). For some studies, the lenses were replaced with high quality fused silica achromats, of the same focal lengths. Unless otherwise stated, the energies of the first and second laser pulses were 8 and 25 mJ at the laser, respectively, measured as the energy incident on L_1. The e-folding scale (*i.e.*, the distance over which the laser power attenuates by 1/e) for pure water at 1064 nm is

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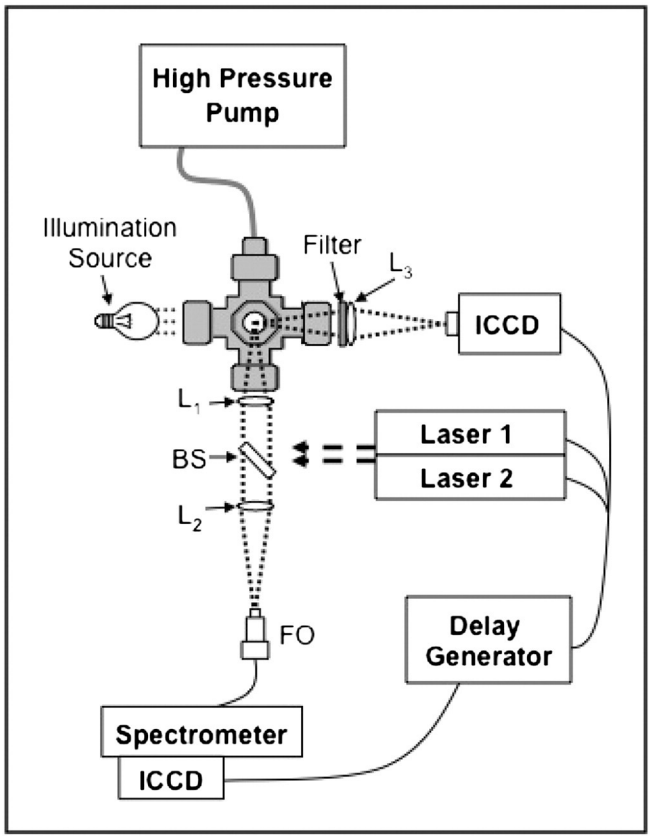

Fig. 1. Schematic diagram of LIBS spectrographic and shadowgraphic apparatus. The two laser beams were collinearly aligned along the same path. The labels L, BS, and FO indicate lens, beamsplitter, and fiber optic, respectively.

about 2.2 cm [43], and therefore at the laser focus (~3-cm into the bulk solution) approximately 24% of the laser energy (including reflection losses) incident on the focusing lens reaches the laser focus region inside the sample chamber. Thus, the effective energies of the first and second laser pulses (E_1 and E_2) in solution were approximately 2 and 6 mJ/pulse, respectively.

Spectral measurements were obtained using a Chromex spectrograph (Model 250IS/RF, 0.25-m, f/4) with a 1200 groove/mm grating blazed at 500 nm to provide 0.1 nm spectral resolution using a 25 μm-slit, coupled to a 1-mm core diameter collection optical fiber (Polymicro Technologies, Model JTFSH100010351400), and an intensified CCD (ICCD) camera (Princeton Instruments I-Max 1024E), controlled with WinSpec/32 version 2.5.7.3 software. Detector gating was controlled using a pulse timing generator (Roper Scientific ST-133A), and a delay generator (Berkley Nucleonics Corporation Model 555) was used to synchronize laser timing for spectral measurements with image acquisition. Shadowgraph images of the laser-induced plasma and bubble were obtained by passing a broadband light source (Fiberoptic Technology Inc., Model FO-150) through the laser focal volume orthogonal to the incident laser pulse (see Fig. 1). A camera lens (Nikon series E, 50 mm, f/1.8) (L_3 in Fig. 1) was used to image light from the plasma region (the laser focus) directly onto a gated, intensified charge-coupled detector (ICCD) (Princeton Instruments, Model ITEA/CCD-576-S/RB-E). The imaging lens was positioned approximately 6 and 9.5 cm from the plasma region and imaging ICCD, respectively, providing an image magnification of approximately 1.6 (corresponding to a field of view of ~16 microns per CCD pixel) and a total imaged area of 9 × 6-mm around the plasma breakdown region. A neutral density filter (OD 2) was positioned in front of the imaging lens (L_3 in Fig. 1) to reduce the amount of light incident on the detector. Imaging detector timing was controlled using a Princeton Instruments Model PG-200 pulser and Model ST-138 detector controller.

In the discussion of these experiments, t_d, t_b, and Δt, refer to the interval between the second laser pulse and collection of the plasma emission (t_d), the ICCD gate width which determines the duration of the plasma emission integration (t_b), and the inter-pulse delay which is the delay between the two sequential laser pulses (Δt), respectively. Unless otherwise stated, bubble and plasma images were acquired using a 1-μs integration time (the smallest window that provided significant image contrast between the laser-induced bubble and the background illumination) and a detector delay, t_d, of 200 ns (the shortest delay time after the laser pulse that emission could be easily recorded with the imaging ICCD). Similarly, all plasma emission was recorded using a similar detector delay, t_d, of 200 ns and an integration time, t_b, of 1 μs, in order to ensure that SP- and/or DP-LIBS plasma emission was collected over a significant duration of the plasma lifetime (the plasma emission decreased to negligible levels within several μs).

Sample solutions for each element were prepared using sulfate or bromide salts dissolved in de-ionized water. All spectra were averaged over five replicate measurements, each the sum of 100 accumulations (*i.e.*, 100 laser pulses or pulse pairs). The LIBS emission intensities were calculated by averaging the baseline-subtracted emission intensity for the five replicate emission spectra. Baseline subtraction was performed using a local baseline subtraction, in which the average background signal on either side of the peak was subtracted from the maximum peak intensity. Bubble volumes were calculated by averaging the estimated volume for ten replicate bubble images, each recorded following a single laser shot, and assuming that the bubbles were symmetrically shaped.

3. Results

In DP LIBS of liquids two consecutive laser pulses are used with the emission measured at time Δt, the inter-pulse delay time, after the second laser pulse. The first pulse breaks down water at the focus and the resulting high plasma temperature and pressure (6000–15,000 K and 20–60 kbar, respectively) causes thermal expansion of the plasma and consequent formation of vapor bubbles or cavities (*i.e.*, thin layers of vapor and diffused gas) around the plasma volume [38,44]. The single-pulse (SP) plasma quickly decays and cools (within <1 μs), and after tens of microseconds a relatively large vapor bubble forms. A large literature discusses the rapid recombination and cooling of the SP-LIBS plasma formed in bulk solution [36–39,45,46]. In DP LIBS, the second laser pulse focused in the region of the vapor bubble excites another plasma which can rapidly fill the vapor bubble. The second plasma is isolated from quenching by water and thus the resulting emission of the previously vaporized material is stronger than the plasma generated by the first laser pulse.

Fig. 2 shows a comparison of SP and collinear DP LIBS at 1 bar of a solution containing 5000 ppm Zn and Mn in bulk aqueous solution. Though the solution contained very high concentrations of Zn and Mn, no SP LIBS Zn or Mn emission was observed using SP LIBS (SP, lower traces in a and b). However, when a 6 mJ second pulse with an inter pulse-delay (Δt) of 60 μs was used, the emission intensity increased dramatically, revealing several Zn(I), Mn(I), H_β, O(I) and O(II) spectral features (DP, upper traces in a and b). No SP emission was observed from Mn or Zn, or from O and H for any laser energy between 8 and 100 mJ/pulse, using a 200 ns inter-pulse delay. Very short delay times are required in DP LIBS of bulk aqueous solution because of rapid plasma quenching by water. Although shorter inter-pulse delay times could be used to measure H and O SP LIBS emission, in this study a single inter-pulse delay of 200 ns was used to match the timing of the imaging camera, used to study the relationship between the growth rate, size and shape of the laser induced bubble and the corresponding DP LIBS emission.