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Optimally enhanced optical emission in laser-induced breakdown spectroscopy by combining spatial confinement and dual-pulse irradiation

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Abstract: In laser-induced breakdown spectroscopy (LIBS), a pair of aluminum-plate walls were used to spatially confine the plasmas produced in air by a first laser pulse (KrF excimer laser) from chromium (Cr) targets with a second laser pulse (Nd:YAG laser at 532 nm, 360 mJ/pulse) introduced parallel to the sample surface to re-excite the plasmas. Optical emission enhancement was achieved by combing the spatial confinement and dual-pulse LIBS (DP-LIBS), and then optimized by adjusting the distance between the two walls and the interpulse delay time between both laser pulses. A significant enhancement factor of 168.6 for the emission intensity of the Cr lines was obtained at an excimer laser fluence of 5.6 J/cm² using the combined spatial confinement and DP-LIBS, as compared with an enhancement factor of 106.1 was obtained with DP-LIBS only. The enhancement mechanisms based on shock wave theory and reheating in DP-LIBS are discussed.

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OCIS codes: (300.6365) Spectroscopy, laser induced breakdown; (350.5400) Plasmas.

References and links


1. Introduction

Over the last few decades, laser-induced breakdown spectroscopy (LIBS) has been demonstrated as a promising and useful element analysis technique [1–8]. By focusing a powerful pulsed laser beam onto a sample surface, a hot luminous spark, forming a plasma, is generated, emission from the plasma used to identify and quantify within the sample. LIBS offers a simple and fast method of elemental analysis. The ability to form a plasma on unprocessed samples makes LIBS an amazingly versatile diagnostic tool [9–11]. It is one of the few techniques that can be used for non-contact elemental analysis, making LIBS uniquely suited to measurements of hazardous materials and materials in difficult-to-reach locations [12,13]. In recent years, LIBS has been successfully applied in many areas such as civilian and military environmental monitoring, cultural heritage analysis and characterization, biological and medical identification, and even space exploration [14–17]. Despite its obvious advantages, one of the major shortcomings of LIBS is its low detection sensitivity. Continuous studies have been made to improve the sensitivity of LIBS. These studies have led to investigations such as dual-pulse excitation and various plasma confinements [18–25].

The methods mentioned above have improved the detection sensitivity in LIBS though individual enhancement approaches. Further improvement of LIBS sensitivity will rely on
combination of these approaches. For example, dual-pulse LIBS (DP-LIBS) can be combined with spatial confinement of plasmas to effectively improve the sensitivity of LIBS. In DP-LIBS using orthogonal geometry, the first pulse is introduced onto the sample surface and the second pulse is focused parallel to the surface to reheat the plasma ablated by the first pulse. An increase in optical emission from the re-excited plasma can be observed \cite{26–28}. At the same time, along with the generation and expansion of the laser-induced plasma in air by the first pulse, a shock wave is produced. The shock wave will be reflected back when it encounters some obstacles to compress the plasma plume \cite{29}. The collision rate among the particles will be increased within the compressed plasma, resulting in an increase in the number of atoms at high-energy states, and hence, enhancing the emission intensity. Either dual-pulse excitation or plasma confinement was employed separately in previous studies. For instance, we \cite{30} studied the enhancement of optical emission plasmas confined with the combination of spatial and magnetic confinements, resulting in a maximum enhancement factor of only 24 for pure metallic Cr sample. Killinger et al. \cite{31} reported the enhancement of plasmas using a simultaneous CO\textsubscript{2} laser pulse, resulting in an increase of 60x for the Al atomic lines at 308 nm. In this study, our aim was to further improve the enhancement effects by the spatial confinement and dual-pulse in LIBS. Laser-induced plasmas with shock waves were produced and confined between a pair of parallel walls. The plasma plumes in LIBS were also investigated to study the evolution of the plasmas.

![Schematic diagram of the experiment setup.](image)

2. Experimental methods

2.1 Experiment setup

The schematic diagram of the experimental setup of the spatially confined DP-LIBS is shown in Fig. 1. The experiments were performed in ambient air. A KrF excimer laser (Lambda Physik, Compex 205, wavelength: 248 nm, pulse duration: 23 ns) was used for the first laser pulse to generate plasmas. The laser beam was reflected both by a reflector (Reflector 1) and a dichroic mirror, respectively. The laser beam was slightly focused to a spot size of about 2.6 × 0.5 mm\textsuperscript{2} to reach a laser fluence of 5.6 J/cm\textsuperscript{2}. Plasma plumes with a size of several millimeters were generated between the walls. A Q-switched Nd:YAG laser operating at 532 nm (Continuum, Powerlite Precision II 8010, pulse duration of 6 ns) with a
pulse energy of 360 mJ/pulse was introduced in parallel to the sample surfaces to reheat the plasmas generated by the first pulse. Both lasers were synchronized by a digital delay generator (Stanford Research System DG535, 5 ps delay resolution). The pulse repetition rate was set to 10 Hz. The Nd:YAG laser was focused by a convex lens (Lens 3 with f/10 cm focal length). The spatial position of the second pulse was adjusted by the Reflector 2 and Lens 3. The Nd:YAG laser was focused to a spot with a diameter of about 1 mm, around 2 mm above the sample surfaces. To avoid over ablation, the Cr target was mounted on a motorized translation stage, so that a new surface was exposed at each shot.

2.2 Spectral measurements

The optical emission from plasmas was coupled to an optical fiber by Lens 1 and another UV-grade quartz lens (Lens 2 with f/6 cm focal length). The optical fiber, with a core diameter of 100 μm, was coupled to a spectrometer (Andor Tech., Shamrock 303i) with three gratings of 150, 600, and 2400 lines/mm. The grating of 2400 lines/mm, with a spectral resolution of 0.04 nm at 435 nm, was used in this study. A 512 × 512 pixel intensified charge-coupled device (ICCD) (Andor Tech., iStar, DH-712) was attached to the exit focal plane of the spectrometer. The gate delay and width of the ICCD was adjusted so that the spectra at different time delays after the laser pulse can be obtained. Plasma reheating with different interpulse delays was studied to obtain the optimal enhancement. The spectrometer started to acquire spectra at 3 μs after the first-pulse plasma. For all experiments, the excimer laser was fired first to produce a plasma. The Nd:YAG laser at 532 nm was fired second for plasma reheating. The purity of the Cr targets is 99.95%.

![Fig. 2. Time-integrated spectra from Cr targets with combined walls and dual pulse (solid curve), with dual-pulse laser (short dashed curve) and with excimer laser only (short dotted curve). Excimer laser fluence: 5.6 J/cm²; Nd:YAG laser pulse energy: 360 mJ/pulse.](image_url)

3. Results and discussion

3.1 Time-integrated OES from the pure Cr targets

The time-integrated emission spectra of the laser-induced Cr plasmas in a spectral range of 419-432 nm were recorded with the presence of the walls in the DP-LIBS, (solid curves), DP-LIBS only (dashed curves), and excimer laser only (dotted curves), as shown in Fig. 2. The distance between the two flat walls was 13 mm. All the spectra were averaged over 30 shots to reduce the standard deviation. The time delay between the excimer laser and Nd:YAG laser was 0 μs. The gate delay and width of the ICCD detector was 3 and 30 μs, respectively. The emission intensities for the Cr atomic lines (425.44, 427.48, and 428.97 nm) were all...
obviously enhanced in the DP-LIBS with and without the presence of the walls, comparing to the excimer laser only. Enhancement factors of about 8 and 6 were obtained in the DP-LIBS with and without the walls. This clearly shows the difference cases with and without the walls in the DP-LIBS. The transition configuration for the three Cr atomic lines is $3d^5(6S)4s - 3d^5(6S)4p$, where the $3d^5(6S)4s$ is the ground state of the Cr atom.

![Graph](image)

Fig. 3. Emission intensity of Cr atomic lines (425.44 nm) as a function of time delay, using both dual-pulse and walls (square dots and solid curve), using dual-pulse (circle dots and short dashed curve) and excimer only (triangle dots and short dotted curve), at excimer laser fluence of 5.6 J/cm², Nd:YAG laser: 360 mJ/pulse.

3.2 Temporal evolution of emission intensities for Cr atomic lines from the pure Cr target

A better understanding of the process of plasma emission enhancement with walls in the DP-LIBS was obtained. Figure 3 shows the temporal evolution of the emission intensities of the Cr atomic line (425.44 nm) in DP-LIBS with the walls (square dots and solid curve), DP-LIBS without the walls (circle dots and short dashed curve), and LIBS using excimer laser only (triangle dots and short dotted). The time delay between the excimer laser and Nd:YAG laser was 9 μs. The ICCD started to acquire spectra from 3 μs after the first laser pulse and ended at 63 μs, with a gate width of 2 μs and a step of 2 μs. There were two significant enhancement peaks in the DP-LIBS with the walls. The two peaks occurred during the time periods from 7 to 17 μs and from 19 to 47 μs, while only one peak occurred from 7 to 17 μs in under DP-LIBS without the walls for comparison. The first peak was due to the enhancement by the reheating of Nd:YAG laser, whereas the second enhancement peak was due to the spatial confinement of the plasmas. Dual-pulse enhancement factors of about 12 (with aluminum walls) and 10 (without aluminum walls) have been acquired in DP-LIBS.
3.3 The optimization of the distance between the plate-walls

To optimize the distance between the two walls in the DP-LIBS, Fig. 4 shows the evolutions of the emission intensity as a function of the time delay with different wall distances of 11 (square dots and curve), 13 (circle dots and curve), 15 (pentagon dots and curve), and 17 mm (triangle dots and curve), respectively. The intensity of LIBS using excimer laser only (diamond dots and curve) was also plotted for comparison. It is observed that the emission intensities were all enhanced although the enhancement factor depends on the wall distance. The maximum enhancement factor of the second peak decreased with a longer time delay as the wall distance increased. This is because the energy of the shock wave dissipates quickly with distance, and the traveling time increases as the wall distance increases. The best distance between the two flat walls is 11 mm.

3.4 The optimization of the interpulse delay time between the excimer laser and Nd:YAG laser

After the optimization of the wall distance, the time delay between the excimer laser and Nd:YAG laser pulses was adjusted to further optimize the enhancement effects. Figure 5(a) shows the temporal evolution of DP-LIBS spectra with walls with an interpulse delay of 17 μs. The first spectrum was acquired with a delay of 3 μs after the first pulse and a gate width of 2 μs, and the following spectra were acquired with an increment of 2 μs. In Figs. 5(b) - 5(d), time-integrated LIBS spectra of Cr lines from reheating were compared with the first-pulse LIBS spectra to show the enhancement with different interpulse delays. As indicated in Figs. 5(b) - 5(d), after reheating of the plasmas, the intensity of LIBS spectra of Cr lines increased significantly compared with first-pulse LIBS spectra. Time-integrated LIBS spectra from the plasma of the Cr targets were acquired under first-pulse only condition [3 μs after plasma generation (dashed lines)] and with reheating [2 μs after second pulse (solid lines)] at different interpulse delays: Figs. 5(b) 17, (c) 25, and (d) 33 μs. It is shown that the strongest emission intensity of the Cr atomic lines appeared with an interpulse delay of 25 μs, significantly higher than shorter or longer interpulse delays.
Fig. 5. (a) Temporal evolution of DP-LIBS spectra with 50 μs interpulse delay; time-integrated LIBS spectra of plasmas from a Cr target under first-pulse only condition [3 μs after plasma generation (dashed lines)] and with reablation [2 μs after second pulse (solid lines)] at different interpulse delays of (b) 17, (c) 25, and (d) 33 μs. At excimer laser fluence of 5.6 J/cm², Nd:YAG laser: 360 J/pulse.

Table 1. The enhancement factors of emission intensity for Cr atomic lines (425.44 nm) in the DP-LIBS with and without walls

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Interpulse delay: (μs)</th>
<th>ICCD gate delay: (μs). Start to acquire from the second pulse.</th>
<th>ICCD gate width: (μs).</th>
<th>Enhancement factor VS. Excimer laser only</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP-LIBS only</td>
<td>25</td>
<td>2</td>
<td>2</td>
<td>106.1</td>
</tr>
<tr>
<td>DP-LIBS with walls</td>
<td>25</td>
<td>2</td>
<td>2</td>
<td>168.6</td>
</tr>
</tbody>
</table>

Therefore, the optimized interpulse delay time for DP-LIBS with confining walls is 25 μs. Under the best interpulse delay of 25 μs, as is shown in Table 1, the Cr line (425.44 nm) recorded by the spectrometer were acquired from 2 μs after the second-pulse plasma and with a gate width of 2 μs, the enhancement factor reached 168.6 when adding walls in DP-LIBS, while the enhancement factor was 106.1 only in DP-LIBS without confining walls. The reason can be explained by the combination of both spatial confinement of plasmas and dual-pulse reheating. When the plasma is generated by the first laser, the drastically increased pressure around the plasma induces a localized shock wave. The shock wave usually spreads out at a speed higher than the ordinary sound wave. When it reaches the walls, the shock wave is reflected by the parallel walls and travels back to the plasma center. Thus, the plasma is confined to a smaller size with increased emission intensity [32]. At the same time, the second laser pulse enters to reheat the plasma which is confined by the shock wave. As a result, the confined plasma is re-excited by the second laser pulse, leading to an increased number of excited atoms within the plasma, and consequently, temperature at the center of the plasma.
increases. Therefore, the LIBS spectra of the Cr plasmas with combined spatial confinement of plasmas and dual-pulse LIBS can be further enhanced, resulting in a high sensitivity.

4. Conclusions

In summary, the enhancement effects of optical emission in DP-LIBS with spatial confinement was studied. The significant enhancements in the atomic lines from Cr plasmas were observed. By the optimization of the distance between two Al walls and the interpulse delay time, the maximum enhancement factor for Cr atomic lines reached 168.6, as compared with an enhancement factor of 106.1 for DP-LIBS without Al walls. It is obvious that the combined enhancement effects of confinement walls and dual-pulse in LIBS is much stronger than that of DP-LIBS only. The results of this study provide a new pathway in improving the sensitivity of LIBS.

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