Generation of high-temperature and low-density plasmas for improved spectral resolutions in laser-induced breakdown spectroscopy

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Abstract: Improved spectral resolutions were achieved in laser-induced breakdown spectroscopy (LIBS) through generation of high-temperature and low-density plasmas. A first pulse from a KrF excimer laser was used to produce particles by perpendicularly irradiating targets in air. A second pulse from a 532 nm Nd:YAG laser was introduced parallel to the sample surface to reablate the particles. Optical scattering from the first-pulse plasmas was imaged to elucidate particle formation in the plasmas. Narrower line widths (full width at half maximums: FWHMs) and weaker self-absorption were observed from time-integrated LIBS spectra. Estimation of plasma temperatures and densities indicates that high temperature and low density can be achieved simultaneously in plasmas to improve LIBS resolutions.

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References and links


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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) has been developed into a very popular and useful elemental analysis technique in recent years. When powerful laser pulses are focused on solid, liquid, or gas targets, luminous hot sparks (or laser-induced plasmas) are generated. By spectrally analyzing the line emissions from the luminous plasmas, the elemental compositions can be deduced. LIBS has been applied in a wide range of applications, such as aerosol detection [1], artwork diagnostics [2], and remote elemental analysis [3]. LIBS is also a potential tool for real-time monitoring of radioactive materials [4].

A number of techniques, such as introduction of purge gas [5] and dual-pulse excitation [6–18], have been used to improve the sensitivity of LIBS. A higher temperature of plasmas is beneficial to the sensitivity of LIBS. However, plasmas in typical LIBS also have high densities correlated to their high temperatures. High plasma density gives rise to the widened line widths and increased self-absorption of atomic lines, therefore, results in lower spectral resolutions. Spectral resolution of LIBS is very important for element analysis. Higher spectral resolution will improve the accuracy of element determination. To improve the LIBS resolution, low density and high temperature in plasmas need to be achieved simultaneously. The profile of a line is the result of many effects, but under typical LIBS conditions the main contribution to the line width comes from the Stark effect (see Gornoshkin et al. [19], for a discussion of the different broadening effects influencing the spectral line shape in LIBS). In fact, the electric field generated by electrons in plasma perturbs the energy levels of ions, thereby broadening the emission lines from these upper (or excited) levels. Thus the Stark broadening has a well established relation with plasma density (or plasma electron density). On the other hand, the self-absorption effect [20], in which some of the radiation emitted by a material is absorbed by the material itself, also takes place in the radiation from laser-induced plasmas.

Dual-pulse LIBS (DP-LIBS) originated in research performed more than 20 years ago, in which spatially overlapping laser-induced plasmas formed in bulk aqueous solution could improve the detection limits by orders of magnitude over those seen in nanosecond single-pulse LIBS [6]. Collinear and orthogonal reheating multipulse LIBS of solids were examined in air [7,8]. Orthogonal pre-ablative spark dual-pulse configuration was also characterized [9–14]. The fundamental physics of laser ablation and the recent explosion of applications of single- and dual-pulse LIBS have been discussed in the literature [15–18].

In conventional reheating DP-LIBS, optical emission drops drastically with interpulse delays (the delay between the two pulses in DP-LIBS) of more than 100 μs due to the limited...
plasma lifetime [21]. However, when the laser fluence is sufficiently large, there is an appreciable amount of laser-induced particles. With delays up to milliseconds, a second pulse can reablate the laser-induced particles to generate plasmas with high temperature but low density properties for improved spectral resolutions in LIBS.

With the aim to improve the spectral resolution of LIBS through the generation of high-temperature and low-density plasmas, we studied the reablation of laser-induced particles by introducing the second pulses with delays up to milliseconds. Fast imaging of optical scattering from particles generated by the first pulse was investigated to study the evolution of the first-pulse plasmas and the formation of the laser-induced particles. Time-integrated LIBS spectra of plasmas produced by reablation were studied. Plasma temperatures and densities, estimated using the emission intensities and line widths of atomic spectral line, were plotted to show the high-temperature and low-density properties of the plasmas generated.

2. Experimental methods

2.1 Experimental setup

The schematic diagram of the experimental setup used in this study is shown in Fig. 1. A KrF excimer laser (Lambda Physik, Compex 205, 248 nm, pulse duration 23 ns) that can deliver a pulse energy of 100–600 mJ was used in the experiments. The laser beam was reflected by a dichroic mirror, which is reflective to the laser light but transparent to the other wavelengths studied. The laser beam was focused normally onto an Al alloy target by an ultraviolet (UV) grade quartz lens (Lens 1 with f/15 cm focal length). The laser beam was slightly defocused to a spot size of about 2.5 × 0.5 mm². The laser fluence was 16 J/cm². A Q-switched Nd:YAG laser operating at 532 nm (Continuum, Powerlite Precision II 8010, pulse duration of 6 ns) with a 5.5 mJ/pulse energy for optical scattering of laser-induced particles or with a 200 mJ/pulse energy was introduced in parallel to sample surfaces for reablation of particles. Both lasers were synchronized by a digital delay generator (Stanford Research System DG535, 5 ps delay resolution). The pulse repetition rate was set to 6 Hz to minimize possible heating of the target. The Nd:YAG laser was focused by a convex lens (Lens 3 with f/10 cm focal length). The Nd:YAG laser beam was focused to a spot size of about 50 μm. The distance between the Nd:YAG laser and sample surfaces was optimized to about 1 mm. The Nd:YAG laser was focused at about 2 mm beyond (overshoot) the excimer laser focal point (see Fig. 3). The experiments were performed in open air. To avoid over ablation, the Al alloy target was
mounted on a motorized one-dimensional translation stage. The plume size was around several millimeters.

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/5 cm focal length). The optical fiber with a core diameter of 100 μm was coupled to a spectrometer (Andor Tech., Shamrock 303i). The spectrometer has three gratings of 150, 600, and 2400 lines/mm, respectively. The spectral resolution for the 2400-line grating is 0.04 nm at 435 nm and the spectral region is 190–800 nm. A 512 × 512 pixel intensified charge-coupled device (ICCD) (Andor Tech., iStar, DH-712) was attached to the exit focal plane of the spectrograph. The gate delay and gate width can be adjusted so that the spectra at different time delays after the laser pulse can be obtained. In fast imaging, a Nikon micro lens (105 mm, f/2.8 D) was attached to an ICCD (Andor Tech., iStar, DH-734). During laser scattering experiments, a 532 nm bandpass filter was placed before the ICCD camera.

Optical scattering from laser-induced particles used delays of 1, 2, 5, 10, 20, 30, 40, 50, 60, 80, 100, 200, 300, 500, 1000, 2000, 5000, and 12000 μs between the two laser pulses to monitor the temporal evolution of the particles formation process. The ICCD camera was synchronized to the pulse used for optical scattering. Particle reablation process used interpulse delays of 15, 40, 60, 80, and 12000 μs. The spectrometer started to acquire spectra from 3 μs after the first-pulse plasma. For all delay experiments, the normal excimer laser was fired first to produce a plasma, and the 532-nm Nd:YAG laser was fired second for either optical scattering or particle reablation.

3. Results and discussion

3.1 Fast imaging of optical scattering from laser-induced particles

Particle formation was observed through optical scattering using pulses from the 532 nm Nd:YAG laser. The excimer laser with a pulse energy of 200 mJ/pulse was focused normally onto the Al sample to generate first-pulse plasmas. A laser pulse of 5.5 mJ from the Nd:YAG laser was introduced in parallel with the target surface for optical scattering of the particles. The gate width for scattering was set to 200 ns, considering the fact that the duration of the scattering from particles usually lasts for ~60 ns.

In Fig. 2, optical scattering images with a relative intensity scale were acquired with laser pulses produced by the Nd:YAG laser at different delays. The ICCD was synchronized with the Nd:YAG laser. The first image was taken at a delay of 1 μs and the following images were taken with increasing time delays. At a delay of 1 μs, the first-pulse plasma still has strong emission, which can be observed through the 532 nm bandpass filter in front of the ICCD camera. The plasma emission disappeared at a delay of 5 μs. At a delay of 20 μs, particles were observed with low concentration. The concentration of particles increased gradually after 20 μs and reached a maximum at a delay of 200 μs. The particle concentration remained high from 200 to 500 μs, after which the particle concentration gradually decreased. As shown in Fig. 2, particles stayed in the plasma-plume region for up to milliseconds before eventually drifting away. The optical scattering from dusts in air was too small to be detected, because we cannot see any Al lines only with Nd:YAG laser (not shown). The particle formation process includes two steps. The first step is the cool down process of the plasma, during which, material will be condensed to form particles. The second step is the drifting movement of particles, which causes the concentration of particles to decrease. This phenomenon provides an opportunity to obtain high-temperature and low-density plasmas by reablation of the particles to improve spectral resolutions in LIBS. The reablation of particles was investigated using temporal and spectral analysis, followed by temperature and density calculations.
The spatial distribution of the particle changed with different interpulse delays. With delays under 80 μs, particles distributed in two area, above and below plasma-plume region. The focused laser beam was used for optical scattering, only scattering from particles in the beam path were captured. The actually distribution of the particles should be surrounding the plasma-plume region. This was primarily due to the low pressure produced by the evacuated shock-wave volume [22]. With longer delays, the plasma disappeared with the volume returning to atmospheric pressure. As seen in Fig. 2, after 80 μs, the pressure in the plasma-plume region recovered to atmospheric pressure. Therefore, particles appeared in the plasma-plume region.

3.2 Temporal analysis

After the generation of first-pulse plasmas, the particles formed during and after the plasmas were reablated by a second pulse with an energy of 200 mJ/pulse from the Nd:YAG laser operating at 532 nm in parallel with the target surface when the concentration of the particles was sufficiently high. With the Nd:YAG laser pulse, an air spark (or air plasma) can be formed, the LIBS spectra of which disappear within 2 μs. The center of air plasma was ~2 mm below the center of the first-pulse plasma. On the pathway of this pulse, particles were reablated. By adjusting the delay and gate width of the ICCD, the LIBS spectra at different delays were acquired.

From Fig. 3 (a), temporal evolutions of emission peak intensity at 394.4 nm with different focal point locations were plotted. The first data point was acquired with a delay of 3 μs and a gate width of 2 μs. The following data points were acquired with increasing delays by a step of 2 μs and a gate width of 2 μs. Square symbols represent temporal evolution under first-pulse-only condition, that is, first-pulse plasma without reablation process. Circle symbols show temporal evolution when the focal points of the two lasers were overlapped (see Fig. 3 (b)), while the triangle symbols show temporal evolution when the focal point of the Nd:YAG reablation pulse were ~2 mm beyond (overshoot) the focal point of the excimer laser (see Fig.
When the focal points of the Nd:YAG laser and the excimer laser overlapped, the enhancement of emission was much less than that with ~2 mm overshooting. This was mainly due to the low pressure generated in the evacuated shock-wave volume (as mentioned in part 3.1). When the interpulse delay became larger (>80 μs), the pressure of the shock-wave volume recovered to atmospheric pressure. The Nd:YAG laser was also focused 2 mm before the focal point of the excimer. Although there were enhancements, they were not as good as overshooting. Thus we just consider overshooting condition. We fixed the focal point of the Nd:YAG laser at ~2 mm overshooting position during the experiments.

![Figure 3](image)

Fig. 3. (a) Temporal evolutions of emission intensity at 394.4 nm with first-pulse plasma only (square symbols), with focal points of the Nd:YAG laser and the KrF excimer laser overlapped (circle symbols), and with focal points of the Nd:YAG laser overshoot 2 mm (triangle symbols); (b) Schematic diagram of overlapped focal points of the Nd:YAG laser and the excimer laser; (c) Schematic diagram of ~2 mm overshoot of the Nd:YAG laser (the focal point of the Nd:YAG laser was ~2 mm beyond the focal point of the excimer laser).

As shown in Fig. 4, temporal evolutions of emission peak intensity at 394.4 nm with different interpulse delays of 15, 40, 60, and 80 μs for reablation of laser-induced particles were plotted. The first data point was acquired with a delay of 3 μs and a gate width of 2 μs. The following data points were acquired with increasing delays by a step of 2 μs and a gate width of 2 μs. The inset graph shows temporal evolution of the intensity with an interpulse delay of 12 ms. The lifetime of the first-pulse plasma is around 50-60 μs, after which the emission from the plasmas drops to zero (not shown). There was enhancement of emissions before particle formation. The enhancement occurred with interpulse delays less than 20 μs, mainly due to the reheating process [21]. However, the enhancement of emission with interpulse delays longer than 20 μs was a combination of reheating effects and reablation of particles. With interpulse delays longer than 60 μs, the Al atomic emission was mainly comprised of reablation effects, which can be observed with interpulse delays up to milliseconds. The reablation laser pulse did not ablate sample surface, because no Al lines were seen from the spectra with second pulse (the Nd:YAG laser pulse) only (not shown).

### 3.3 Spectral analysis

Figure 5 (a) shows the temporal evolution of LIBS spectra from the reablation with an interpulse delay of 50 μs acquired using the 2400 line/mm grating. The first spectrum was acquired with a delay of 3 μs and a gate width of 2 μs. The following spectra were acquired with a step of 4 μs. In Fig. 5 (b), time-integrated LIBS spectra of Al lines from reablation were compared to first-pulse LIBS spectra to show reduced atomic line widths. All of the
spectra were accumulated for 30 pulses to reduce the standard deviation. As indicated in the diagrams, after reablation of particles, the line widths of Al lines decreased significantly compared with first-pulse LIBS spectra. Time-integrated LIBS spectra from the plasmas of the Al target were acquired under conditions of first-pulse only condition (first-pulse LIBS) [3 μs after plasma generation (dashed lines)] and with reablation [1 μs after second pulse (solid lines)] at different interpulse delays: Figs. 5 (b) 20, (c) 50, and (d) 100 μs. The line widths gradually reduced from ~0.32 nm (dashed curve) to ~0.09 nm (100 μs). The Al atomic lines show some self-absorption in first-pulse LIBS spectra. The self-absorption effect usually occurs when the plasmas are optically thick (high plasma density). Comparing the spectra, self-absorption was reduced significantly in the high-temperature and low-density plasmas produced by the second pulse.

![Graph](image)

Fig. 4. Temporal evolutions of emission intensity at 394.4 nm with different interpulse delays: 15, 40, 60, and 80 μs. Inset: intensity temporal evolution with 12 ms interpulse delay.

### 3.4 Plasma temperature and density

According to the local thermodynamic equilibrium (LTE) assumption, plasma temperatures can be deduced from the ratio of relative intensities of the spectral lines from the same element and ionization stage, which is expressed as [23]

$$
\frac{I_1}{I_2} = \frac{g_1 A_1}{g_2 A_2} \frac{\lambda_2}{\lambda_1} \exp \left[ \frac{-(E_i - E_f)}{kT_e} \right],
$$

where indices 1 and 2 refer to the first and second spectral lines of interests, respectively. $I_i$, $\lambda_i$, $g_i$, $A_i$, and $E_i$ ($i = 1, 2$) refer to the line intensity, the wavelength, the statistical weight factor for the upper states, the Einstein transition probability, and the energy of the upper states of the two spectral lines, respectively. $k$ is Boltzmann constant, and $T_e$ is the electron temperature of the plasma. The 150 line/mm grating was used to acquire a pair of spectral lines: 309.25 nm (from Al I 308.22, 309.27, and 309.28 nm) and 396.13 nm (from Al I 394.40 and 396.15 nm) (see Table 1) [24]. Within each spectral line (309.25 or 396.13 nm), atomic
lines will not be distinguished from each other due to the low spectral resolution of the 150 line/mm grating. Therefore, the multiplications of $A_i$ and $g_i$ of each atomic line were added together for 309.25 and 396.13, respectively. An efficiency curve was measured and used for correction of spectrometer efficiency.

Fig. 5. (a) Temporal evolution of LIBS spectra with 50 μs interpulse delay; time-integrated LIBS spectra of plasmas from an Al target under first-pulse only condition [3 μs after plasma generation (dashed lines)] and with reablation [1 μs after second pulse (solid lines)] at different interpulse delays of (b) 20, (c) 50, and (d) 100 μs.

<table>
<thead>
<tr>
<th>Wavelength $\lambda_i$ (nm)</th>
<th>Upper level energy $E_i$ (cm$^{-1}$)</th>
<th>Degeneracy $g_i$</th>
<th>Transition probability $A_i$ (s$^{-1}$)</th>
<th>Configurations</th>
</tr>
</thead>
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<tr>
<td>308.22</td>
<td>32435.453</td>
<td>4</td>
<td>6.3e + 07</td>
<td>3s$^2$3p - 3s$^2$3d</td>
</tr>
<tr>
<td>309.27</td>
<td>32436.796</td>
<td>6</td>
<td>7.4e + 07</td>
<td>3s$^2$3p - 3s$^2$3d</td>
</tr>
<tr>
<td>309.28</td>
<td>32435.453</td>
<td>4</td>
<td>1.2e + 07</td>
<td>3s$^2$3p - 3s$^2$3d</td>
</tr>
<tr>
<td>394.40</td>
<td>25347.756</td>
<td>2</td>
<td>4.93e + 07</td>
<td>3s$^2$3p - 3s$^2$4s</td>
</tr>
<tr>
<td>396.15</td>
<td>25347.756</td>
<td>2</td>
<td>9.8e + 07</td>
<td>3s$^2$3p - 3s$^2$4s</td>
</tr>
</tbody>
</table>

Under typical LIBS conditions, the main contribution to the line width comes from the Stark effect [19]. The Stark broadening of a well-isolated line is thus a useful tool for estimating the electron density. The Stark broadening of a line, expressed as the FWHM in nanometers, is given with an accuracy of 20-30% [11] by [25]

$$\Delta \lambda_{\text{Stark}} = 2w \left( \frac{n_e}{10^{16}} \right) + 3.5A \left( \frac{n_e}{10^{16}} \right)^{1/4} \left[ 1 - BN_D^{-1/3} \right]w \left( \frac{n_e}{10^{16}} \right),$$  \hspace{1cm} (2)
in which, value of \( w \), the electron impact half-width, can be found in the extensive tables given by Griem [26]. \( n_e \) is plasma electron density with a unit of \( \text{cm}^{-3} \) and \( N_D \) is the Debye shielding parameter. \( B \) is a coefficient equal to 1.2 or 0.75 for ionic or neutral lines, respectively. The first term on the right side comes from the electron interaction, while the second one is resulted from the ion interaction. For typical LIBS conditions, the contribution from ion broadening is negligible, and thus Eq. (2) becomes

\[
\Delta \lambda_{\text{Stark}} = 2w \left( \frac{n_e}{10^6} \right),
\]

from which, assuming that other sources of broadening (natural, Doppler, etc.) are negligible (i.e. \( \Delta \lambda_{\text{line}} \approx \Delta \lambda_{\text{Stark}} \)).

As shown in Fig. 6, the temperature temporal evolution of first-pulse plasma was plotted. Plasma temperatures and densities at delays of 3, 10, 20, 30, 40, 50 \( \mu \text{s} \) were estimated from LIBS spectra using Eq. (1). The atom lines were too weak for temperature and density estimation with delays longer than 50 \( \mu \text{s} \). The temperature at 3 \( \mu \text{s} \) delay was around 6400 K, and decreased drastically to 3200 K at 50 \( \mu \text{s} \) delay. At the same time, plasma density decreased almost the same trend as temperature, from \( -1.2 \times 10^{18} \) (at 3 \( \mu \text{s} \)) to \( -3.4 \times 10^{17} \text{ cm}^{-3} \) (at 50 \( \mu \text{s} \)). Lower density means improved spectral resolution, however, with first-pulse LIBS we can get low density only when the temperature of plasmas was sufficiently low. Therefore, we tried to used a second pulse to reablate the laser-induced particles for generation of high-temperature and low-density plasmas.

Fig. 6. Temporal evolutions of the temperature (hollow square symbols) and density (hollow circle symbols) of first-pulse plasma.

In Fig. 7, hollow square symbols represent temperatures of Al plasma from reablation, obtained 1 \( \mu \text{s} \) after the second pulse, with different interpulse delays. Hollow circle symbols are electron densities calculated from spectra, acquired 1 \( \mu \text{s} \) after a second pulse, with different interpulse delays. The solid symbols (indicated by the dotted line) show data points obtained at 3 \( \mu \text{s} \) after first-pulse plasma without reablation. The temperature of the plasma produced by the second pulse increased several hundred Kelvin from the first-pulse plasma (~6400 K) because of the reheating process. The temperature decreased to ~6300 K with an interpulse delay of 70 \( \mu \text{s} \) due to the lifetime of Al plasmas that were reheated. The temperatures with interpulse delays longer than 70 \( \mu \text{s} \) decreased slightly. The plasma density, however, decreased drastically from \( -1.2 \times 10^{18} \) (first-pulse plasma) to \( -3.3 \times 10^{17} \text{ cm}^{-3} \)
(plasma by reablation with an interpulse delay of 100 μs). The temperature with an interpulse delay of 100 μs was ~6200 K, which was almost the same temperature as the first-pulse plasma (~6300 K). Low plasma density was obtained while the plasma temperature was still high. Therefore, high-temperature and low-density plasma was achieved for improved spectral resolution for LIBS.

Fig. 7. Temporal evolutions of the temperature and density of the reablation plasma. Hollow square symbols in the solid curve: temperatures of Al plasma acquired 1 μs after second pulse with different interpulse delays. Hollow circle symbols in the dashed curve: Al plasma electron densities 1 μs after second pulse with different interpulse delays. The solid symbols indicated by the dotted line shows data point 3 μs after the generation of first-pulse plasma without reablation.

4. Conclusions

High spectral resolutions in LIBS were achieved by generation of high-temperature and low-density plasmas through reablation of laser-induced particles. Particles were formed using a KrF excimer laser to irradiate on an Al target. The particles were then reablated by a 200 mJ pulse from a 532 nm Nd:YAG laser. The line widths of plasmas decreased from ~0.32 nm (first-pulse plasmas) to ~0.09 nm (plasmas by reablation with an interpulse delay of 100 μs). The temperatures of plasmas in DP-LIBS increased due to the reheating process and then decreased gradually with longer interpulse delays. The plasma electron density, however, was significantly reduced from ~1.2 × 10^{18} to ~3.3 × 10^{17} cm^{-3}. The temperature of reablation plasma was as high as the temperature of first-pulse plasma. The temperature of first-pulse plasma was ~6400 K with a plasma density of ~1.2 × 10^{18} cm^{-3}. The temperature of the reablation plasma, for instance, with an interpulse delay of 100 μs, was ~6200 K. However, the plasma density was ~3.3 × 10^{17} cm^{-3}, much lower than the density of first-pulse plasma. Therefore, high-temperature and low-density properties in plasmas were simultaneously achieved for improved spectral resolutions in LIBS.

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