Re-Heating Effect on the Enhancement of Plasma Emission Generated from Fe Under Femtosecond Double-Pulse Laser Irradiation

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Abstract In this paper, we present a study on the effect of inter-pulse delay using femtosecond double-pulse laser-induced breakdown spectroscopy in a collinear geometry. The temporal evolution of spectral intensity is performed for the lines of Fe I 423.60 nm, Fe I 425.08 nm and Fe I 427.18 nm. It is found that, by selecting appropriate inter-pulse delay, the signal enhancement can be significantly increased compared with the single-pulse case. A three-fold enhancement in the current experiment is obtained. The plasma temperature and electron density are also investigated based on the theory of Boltzmann plot and Stark broadening. We attribute the main mechanism for emission enhancement to the plasma re-heating effect.

Keywords: LIBS, femtosecond laser, double-pulse, signal enhancement

PACS: 52.70.Kz, 52.50.−b, 33.20.Kf

DOI: 10.1088/1009-0630/18/12/09

(Some figures may appear in colour only in the online journal)

1 Introduction

Laser-induced breakdown spectroscopy (LIBS) or laser-induced plasma spectroscopy, is a very promising spectrum analysis technology for detecting element composition\textsuperscript{[1]}. LIBS, in short, is that a bunch of high energy laser pulses are focused onto the sample, producing a plasma plume, then the spectrum is recorded, and finally the neutral and ionic lines in the plasma spectroscopy are analyzed\textsuperscript{[2,3]}. In the second half of the 20th century, more and more attention has been paid to the emergence of this LIBS technique by many researchers, for it has a series of main advantages. They are respectively rapid quantitative analysis\textsuperscript{[4]}, null sample preparation\textsuperscript{[5,6]}, low invasiveness\textsuperscript{[7]}, in situ\textsuperscript{[8]}, small quantity of ablated mass\textsuperscript{[9]}, and no chemical procedures for dissolution\textsuperscript{[10]}. Utilizing the above advantages, it has been successfully applied in a variety of fields, including environmental monitoring\textsuperscript{[11,12]}, biological agents\textsuperscript{[13]}, fast and remote detection\textsuperscript{[14]}, cultural heritage conservation\textsuperscript{[15]} and lighting control\textsuperscript{[16]}. Based on a large number of applications in scientific research and real life, the study of the basic LIBS technique is an important task. What mainly limits the application of the LIBS technique is that it has low sensitivity in detecting the concentration of element, which seriously prevents the improvement of the detection limit and the rapid development of this technique\textsuperscript{[3]}. In order to enhance the sensitivity of LIBS, several different methods have also been presented. One of them is focused on the double-pulse (DP) LIBS scheme, the term “double-pulse” is defined as two lasers or two pulses from a single pulse (SP) laser used for LIBS excitation, which are separated in time and then successively spread, the inter-pulse delay usually ranges from picosecond to hundred microseconds\textsuperscript{[17]}. It has been proved, DP-LIBS can effectively improve the sensitivity of the technique, and enhance the signal intensity more significantly compared with the SP case. Adopting the DP scheme can enhance the emission line intensity of plasma for different pulse durations. So far, for this scheme, several researchers have conducted a more detailed classification according to the different geometrical configuration, including collinear, crossed beam, and orthogonal configuration\textsuperscript{[18]}. In the collinear case, two laser beams separated by a certain time propagate along the same direction and are focused onto the target. In the crossed beam case, both laser pulses irradiate to the target surface with a certain angle. Orthogonal configuration is divided into two kinds based on the different inherent physical mechanisms. One is the orthogonal re-heating configuration. The first laser...
pulse is used to focus on the target surface, generating the plasma plume, and the second laser pulse parallel to the surface re-heats the plasma plume. Another one is the orthogonal pre-ablation configuration, which is different from the re-heating configuration; the order of two laser pulses is changed. It refers to generate a laser-induced plasma in the ambient atmosphere, while the delayed laser pulse is used to ablate the target \cite{18−20}. Generally, the collinear configuration is the simplest approach from the practical point of view.

From the published papers, we find that most of them are all about nanosecond DP-LIBS. For example, Cremer et al. had investigated the enhancement of liquids emission lines by a Nd:YAG laser and it was a first detailed study \cite{21}. Shoushheini et al. studied the Cu emission lines of a micro-plasma, large enhancement of the emission lines was achieved at a higher temperature \cite{22}. Cristofoletti et al. used a Nd:YAG laser to ablate a brass sample at different air pressures to study single-pulse and double-pulse laser-induced breakdown spectroscopy experiments \cite{23}. Sattmann et al. reported a two-fold enhancement of the Fe I line on a steel sample using a Nd:YAG laser \cite{24}. Even though numerous works are dedicated to improve signal intensity of DP-LIBS, until now rather few works are focused on studying the effect of time separation using femtosecond laser pulse. As is well known, the laser pulse duration can greatly influence the performance of LIBS. Compared with the nanosecond laser, a femtosecond laser pulse has a shorter duration, which provides the better control and a much higher quality ablation crater. For the femtosecond laser, the duration of the pulse is shorter than the interaction between electrons and phonons in terms of time scale, therefore, the pulse energy has already been completely absorbed before any ejection in the surface of samples, thereby increasing the repeatability \cite{25}. This is a major advantage of the femtosecond laser itself, there is also a big advantage compared to the nanosecond laser in the produced spectra. Femtosecond laser-induced plasma spectroscopy has the characteristics of high resolution and low background emission, allowing the signal accumulation with a large number of pulses \cite{2}. In addition, femtosecond laser also has many other advantages, for example, it reduces the re-deposition and improves the ablation efficiency \cite{26}. Therefore, more and more attention has been paid on researching femtosecond LIBS in recent years. Singha et al. presented that the spectrally resolved plasma emission was measured as a function of laser fluence and pulse delay by dual femtosecond laser pulses \cite{27}. Hermann et al. investigated the composition of plasmas produced by laser ablation of metals with two time-delayed ultrashort laser pulses \cite{28}. Noël et al. experimentally reported the results of laser ablation of copper and gold with two time-delayed femtosecond laser pulses \cite{29}. Liu et al. studied the effect of laser pulse energy on orthogonal femtosecond double-pulse laser-induced breakdown spectroscopy in air \cite{17}. Penczak et al. investigated the role of plasma shielding in collinear double-pulse femtosecond laser-induced breakdown spectroscopy \cite{30}. In order to clarify the contributing processes responsible for the signal enhancement, an experimental study of collinear geometry double-pulse femtosecond LIBS was performed on a Ni sample in ambient air by Shen et al. \cite{31}. Therefore, we put forward the femtosecond double-pulse scheme.

In this paper, we combine femtosecond laser and a double-pulse scheme; the key is to explain the underlying physical processes and understand the evolution of the plasma temperature and electron density. The emission line intensity is studied by varying the time separation of the femtosecond double-pulse. The Boltzmann plot method is employed for plasma temperature. The measurement of electron density is from the Stark broadening. The plasma temperature and the electron density are obtained at different time separation. We expect that this study can provide a better understanding on femtosecond DP-LIBS.

2 Experiment

The basic components of the experimental setup are shown in Fig. 1. The laser system is a regenerative amplified Ti:sapphire laser (Coherent Libra). The full-width at the half maximum (FWHM) is 50 fs, the repetition rate is 1 kHz, and the fundamental wavelength is 800 nm. In brief, a beam splitter is used to split two beams from a laser source. One of them via a series of mirrors is directed to the target. The light path of this laser beam is fixed, considered to be the main pulse, so we define this laser pulse as the time zero. The other laser beam is merged with the first laser beam by another dichroic mirror after a computer-controlled translation stage (Physik instrumente, M-505). The inter-pulse delay is varied by this stage. The laser beam is slightly focused through a 25 cm focal length plano-convex lens onto the target material. The spot diameter at the surface of the sample is about 40 µm. The target is equipped with a 3-D micrometer resolution motorized translation stage (Thorlabs, PT3/M-Z8), which is moved to provide a new surface before each laser shot. Then plasma emission is collected through two lenses (BK7) and focused into an optical fiber. The spectrometer (Spectra Pro 500, PI Acton, the grating is 1200 grooves/mm) is fitted by an intensified charge-coupled device (ICCD, PI-MAX, Princeton Instruments). Its resolution of pixels is 1024×256. The system has been calibrated by recording the well known lines of mercury. By setting the ICCD gate width, gate delay and a digital delay generator, the generation of the plasma and the collection of spectral emission signal are synchronous. In order to enhance the signal-to-noise(S/N), we set the fixed gate delay of 580 ns (synchronization with the signal delay generation of laser system) and a gate width of 5 µs, and each spectral data point is typically an average of 20 shots to minimize the effect of the fluctuation in this

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3 Results and discussion

3.1 Spectral intensity evolution

In order to understand the characteristics of the plasma, we focus the 800 nm laser beam onto the sample surface to produce plasma spectroscopy and record the emission intensity. The spectra are obtained from an Fe sample. Fig. 2 shows the role of inter-pulse delay for signal enhancement in the collinear femtosecond double-pulse arrangement, and from it we can see the well-resolved iron lines and a multi-peak structure. Besides, the spectral signal intensity at three different time separations is compared, the time separations are 0 ps, 50 ps, and 150 ps. It can be seen from Fig. 2 that the spectrum corresponding to the case of 50 ps is highest, and the one corresponding to the case of 0 ps is weakest. In this experiment, the single-pulse is equivalent to the double-pulse with the time separation of 0 ps. The whole laser energy is 270 µJ, the power density is $4.28 \times 10^{14}$ W/cm$^2$, the whole laser fluence is 21.4 J/cm$^2$, and the fluence of each sub-pulse is 10.7 J/cm$^2$. It verifies that the femtosecond DP-LIBS is an effective method to improve the signal emission intensity of femtosecond LIBS. Fig. 3 presents the distribution of spectral intensity obtained from the Fe sample at the time delay ranging from $-150$ ps to 150 ps, and spectra range from 400 nm to 440 nm. As is shown in Fig. 3, compared with the case of 0 ps, the spectra are much stronger for other time separations. Several mechanisms have been proposed to explain the signal enhancement in the collinear DP-LIBS arrangement. They are: (a) reheating the plasma plume by second pulse; and (b) the more removed material \[32,33\]. Under certain conditions, the mechanism to occupy the dominant fact is associated with the inter-pulse delay. When the inter-pulse delay is a relative short value, the first laser beam irradiates to the sample surface to generate plasma, meanwhile, the electron density in plasma is high, followed by a second laser beam, and the energy of the second pulse will be absorbed by the plasma with high electron density, therefore the re-heating effect is more effective. However, when the inter-pulse delay is longer, with the increase of time delay, plasma expands, and when the second beam pulses arrives, the electron density of the pre-plume has been in a downward trend, therefore the interaction of the laser-sample coupling has been enhanced, leading to the more removed material \[19\].

Fig. 2 Plasma spectra produced by femtosecond double-pulse ablation at three different inter-pulse delays. They are respectively 0 ps (solid line), 50 ps (dashed line) and 150 ps (dotted line). The whole laser fluence is 21.4 J/cm$^2$ (10.7+10.7 J/cm$^2$)

Fig. 3 Three-dimensional profile of plasma spectrum emission. Spectral intensity of iron sample obtained by femtosecond DP-LIBS with $-150$ ps–150 ps time separation at the range of 400–440 nm. The whole laser fluence is 21.4 J/cm$^2$ (10.7+10.7 J/cm$^2$)

Fig. 4 shows the temporal evolution of emission intensity for different wavelengths of 423.60 nm, 425.08 nm, and 427.18 nm, respectively. Apparently, the spectral line intensity at 427.18 nm is greater than the others. For the same two laser pulses, the positive and negative delay time is not much different, therefore we only discuss the positive delay time. From this plot, two main regimes could be observed at the positive delay time. The first regime is observed in the range from 0 ps to 50 ps. The intensity of the plasma emission lines increases steadily with the increase of the time delay. The maximum enhancement appears at approximately $\Delta t = 50$ ps. This effect can be mainly
attributed to the re-heating effect of the second beam pulse. In the second regime a declining trend is observed from 50 ps to 150 ps. It is caused by the expansion of the plasma and the reduction of plasma density with the increase of time.

![Fig. 4](image)

**Fig. 4** Temporal evolution of plasma spectral intensity for three different wavelengths. They are 423.60 nm, 425.08 nm, and 427.18 nm, respectively. The laser fluence is 21.4 J/cm² (10.7+10.7 J/cm²)

### 3.2 Temporal evolution of plasma temperature and electron density

The plasma temperature and electron density are two important parameters to describe the plasma characteristics. Five spectral lines (419.91 nm, 420.20 nm, 426.04 nm, 427.18 nm and 432.58 nm) are selected to calculate the plasma temperature. Since these lines are much stronger than the other lines, and the corresponding upper levels ($E_i$) have a wide range. Their parameters are shown in Table 1 from the NIST database. In the following sections, we will discuss two parameters in detail. Firstly, the plasma excitation temperature is widely calculated using the Boltzmann plot method, assuming that the local thermodynamic equilibrium and optically thin exist in the plasma.

$$\ln \left( \frac{\lambda_{ij} I_{ij}}{g_i A_{ij}} \right) = -\frac{E_i}{k_B T} + \ln \left( \frac{\hbar c N}{U} \right),$$  

(1)

where $i$ and $j$ represent the upper and lower atomic levels, $\lambda_{ij}$ is the wavelength of the spectral line, $I_{ij}$ is the spectral line intensity, $g_i$ is the statistical weight for the upper level, $A_{ij}$ is the transition strength, $E_i$ is the upper level energy, $k_B$ is the Boltzmann constant, $T$ is the plasma temperature, $h$ is Planck’s constant, $c$ is speed of light, $N$ is the total number density of atoms, and $U$ is partition function. The second term on the right side of the equation is considered as a constant. To obtain the plasma temperature, we need to calculate the slope of the function $(-1/k_B T)$ in Eq. (1). Then the temperature $T_e$ is calculated through the slope value. Fig. 5 shows the Boltzmann plot obtained by using the selected lines. We select two points of inter-pulse delay in femtosecond DP-LIBS for comparison, the delays are 0 ps, and 100 ps. It can be seen from the figure that the slopes of two inter-pulse delays are different. For the inter-pulse delay time of 100 ps, it is slightly smaller than the value of 0 ps. The temporal evolution of plasma temperature can be seen in Fig. 6. The solid lines show the fitting over the experimental data points. It shows a trend of a rise at first and then a drop with the increase of inter-pulse delay. The increase in the plasma temperature may be attributed to the arrival of the second pulse and the absorption of the energy. The drop results from the expansion of the plasma plume and a rapid conversion of the energy: thermal energy of the plasma transfers into kinetic energy of the particles. However, it is worth noticing that the time separation of the intensity maximum is not the time separation of the temperature maximum. For plasma temperature, the position of the highest temperature is the maximum position of plasma electron density. In other words, the temperature reaches its maximum because the absorbed laser energy reaches a maximum. For spectral intensity, firstly, the intensity distribution of femtosecond pulse is a Gaussian behind a focusing lens. Initially, plasma occurs in the center of the Gaussian intensity distribution range. As a result, the inverse bremsstrahlung (IB) processes can only absorb a portion of the second center laser. As the time increased, influenced by the expansion of the ionization region, IB processes will absorb more and more energy of the second pulse, until the region of the plasma and laser focus areas are equal, and at this time, the absorption of air plasma reaches a maximum, for this reason, the spectral intensity is the highest. However, due to the expansion of the plasma and electrons recombination, the free electron density is not the maximum value and begins to decrease. Therefore, the time separation of the intensity maximum appears after the time separation of plasma temperature maximum.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Upper-level energy (eV)</th>
<th>Transition probability $A_{ij}$ ($10^8$ s⁻¹)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>419.91</td>
<td>6.00</td>
<td>5.41</td>
<td>$3d^7(2G)4s - 3d^7(2G)4p$</td>
</tr>
<tr>
<td>420.20</td>
<td>4.43</td>
<td>0.74</td>
<td>$3d^7(4F)4s - 3d^7(4F)4p$</td>
</tr>
<tr>
<td>426.05</td>
<td>5.31</td>
<td>4.39</td>
<td>$3d^7(4D)4s4p(3P^0) - 3d^7(4D)4s(6D)5s$</td>
</tr>
<tr>
<td>427.18</td>
<td>4.39</td>
<td>2.51</td>
<td>$3d^7(4F)4s - 3d^7(4F)4p$</td>
</tr>
<tr>
<td>432.58</td>
<td>4.47</td>
<td>3.61</td>
<td>$3d^7(4F)4s - 3d^7(4F)4p$</td>
</tr>
</tbody>
</table>

Table 1. Spectral lines corresponding to the relevant parameters. They are used to calculate plasma temperature.
In the laser-induced plasma experiment, the line broadening includes the Stark broadening ($\Delta \lambda_{1/2}$), the Doppler broadening ($\Delta \lambda_{\text{FWHM}}^D$), the instrument broadening ($\Delta \lambda_{\text{FWHM}}^\text{instrument}$), and the natural broadening ($\Delta \lambda_{\text{FWHM}}^N$). We know that a relationship among them, i.e. $\Delta \lambda_{1/2} = \Delta \lambda_{\text{observed}} - \Delta \lambda_{\text{instrument}} - \Delta \lambda_{\text{FWHM}}^D - \Delta \lambda_{\text{FWHM}}^N$. In this experiment, the instrument broadening is approximated 0.04 nm. The Doppler broadening is approximated $4.2 \times 10^{-4}$ nm. The natural broadening is approximated $1.19 \times 10^{-5}$ nm. Because the atoms or other particles are subjected to electron impact, and the interaction of such collisions not only dominates the broadening of the plasma spectral lines, but also makes the center line of the plasma spectrum move. Therefore, the Stark broadening plays a predominant role among the broadening mechanisms. The electron density can be calculated from the measured value of the FWHM of the Stark-broadened lines $\Delta \lambda_{1/2}$ [36]:

$$\Delta \lambda_{1/2} = 2\omega \frac{N_e}{10^{16}},$$  

here $\Delta \lambda_{1/2}$ is the FWHM of spectral lines, $N_e$ is the electron number density and $\omega$ (0.011 nm at 426.04 nm [37]) is the electron impact parameter. In this work, we use Fe I lines (426.04 nm) to calculate the electron density. As shown in Fig. 7, it shows the evolution of the electron density as a function of the inter-pulse delay. However, the electron density has merely a slight variation at different inter-pulse delays, it remains relatively flat from $\sim 150$ ps to 150 ps. This may be due to the fact that time resolution chosen is longer, and it is an integral result.

4 Conclusions

In conclusion, we demonstrate the enhancement of the LIBS signal by the collinear femtosecond double-pulse LIBS. In comparison with single-pulse, enhancement of three-fold has been found in this study. The effect of inter-pulse delay is investigated by changing the time separation of femtosecond double-pulse. It has been observed that to realize the optical emission enhancement, the inter-pulse delay between the two laser pulses should be optimized. The results show that by choosing the appropriate inter-pulse delay, the plasma spectral intensity can be improved. At the local thermal equilibrium and optically thin, the electron temperature is very sensitive to the inter-pulse delay of double-pulse, while electron density is almost constant. We attribute the dominant mechanism for emission enhancement to the plasma re-heating effect.

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(Manuscript received 20 January 2016)
(Manuscript accepted 17 May 2016)

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