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A comparative study of enhanced emission in double pulse laser induced breakdown spectroscopy

Rizwan Ahmed [a,*], M.A. Baig [a,b]

[a] National Centre for Physics, Quaid-i-Azam University Campus, Islamabad, Pakistan
[b] Atomic and Molecular Physics Laboratory, Quaid-i-Azam University, 45320 Islamabad, Pakistan

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ABSTRACT

We are presenting a comparative study of laser induced breakdown spectroscopy (LIBS) of copper, in single pulse and dual pulse collinear and orthogonal (re-heating) configurations, using fundamental (1064 nm) and second harmonics (532 nm) of two Nd:YAG lasers. The double pulse collinear configuration yields about fifty times and the orthogonal (re-heating) configuration yields fifteen times, signal intensity enhancement in the neutral copper lines. The difference in emission enhancements in both LIBS techniques (Collinear and orthogonal double pulse) provides an experimental evidence about the enhancement mechanism in double pulse LIBS. The effect of inter pulse delay between the two laser pulses and the ratio of their pulse energies in the double pulse spectra are reported. The variation of electron temperature with different interpulse delays, different laser pulse energies ratio and along the plume axis has been studied.

1. Introduction

During the last couple of decades, the laser induced breakdown spectroscopy (LIBS) has emerged, as a promising analytical technique for any type of materials analysis [1–5]. In this technique, multi-elemental analysis without any type of sample preparation can be performed by focusing a laser beam on a target material (solid, liquid or gas) under study. Due to the high intensity of the focused laser beam ($\approx 10^{10}$ W/cm^2), a fraction of the material is vaporized and subsequently ionized forming micro plasma. The study of the emission of atomic or ionic spectral lines in the plasma, yields elemental composition. In the initial stage of the development of this technique, a single laser pulse was used for generating micro plasma. To increase the optical emission intensity and for the better performance of LIBS, extensive work [6–11] has been devoted to the study of plasma plume dynamics. To improve the analytical capabilities of LIBS different approaches have been proposed, such as the interaction of laser plasma in the presence of electric field [31] magnetic field [32] or in modified atmosphere [33]. Piepmeier et al. [12] and Scott et al. [13] suggested a dual pulse LIBS for a better sensitivity of elemental analysis. First detail study of dual pulse LIBS was performed by Cremers et al. [14] who observed much enhanced emission signals. In a double pulse (DP) configuration, two laser pulses with inter pulse delay in the range of nano-seconds [15] to several micro-seconds [16] were used to generate plasma. In the last few years much attention has been paid towards the improvement and applications of DP LIBS [17–27]. Mukherjee et al. [28] indicated that the signal enhancement is due to the plasma plume length and the higher plasma temperature. Noll et al. [29] attributed the signal enhancement to the enlarged plasma volume and increased material ablation. Angel et al. [30] reported, nearly 40 times enhanced signal and, based on the SEM images of the plasma, concluded that the signal intensity enhancement is a result of larger plasma and increased material removal from the target.

In this work we are presenting, a comparative study of the emission from the Cu target using fundamental (1064 nm) and second harmonic (532 nm) of two Nd:YAG lasers. In collinear and orthogonal DP LIBS, the effects of interpulse delay and laser pulse energies ratio on the signal intensity enhancement factor are presented. Approximately, fifty times signal intensity enhancement was measured in collinear dual pulse configuration, while these signal intensity enhancements decrease to only fifteen times in orthogonal configuration, as compared with SP LIBS. The difference in enhancement factor in both technique provides an insight about the enhancement mechanism in double pulse LIBS as compared to SP LIBS.

2. Experimental setup

The basic experimental setup is the same as described in our earlier work [8]. Two Nd:YAG lasers (Quantel Brilliant) were used

* Corresponding author. Tel.: +92 51 2077300x524.
E-mail address: riz.phy@gmail.com (R. Ahmed).

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having 5 ns pulse width and operated at 10 Hz repetition rate. Both the laser beams were focused through a 20 cm quartz lens on the sample. The sample was mounted on a rotating stage, which was rotated to provide a fresh surface after each laser pulse to avoid deep creator. The emitted radiation from the plume was collected by a fiber optics (high-OH, core diameter of 600 μm) having collimating lens (0–45°) field view placed at right angle to the direction of plume. The LIBS detection system consists of five spectrometers equipped with 2400 lines/mm gratings, 5 μm slit width and 2048 elements of linear charge coupled device array. The detection system covers the wavelength region of 200–720 nm and its resolution ≈0.05 nm, determined by scanning a narrow bandwidth dye laser. The system has been calibrated by recording the well known lines of neon, argon, and mercury with ≈0.02 nm measurement uncertainty. All the five spectrometers installed in the LIBS2000 are manufacturer calibrated in efficiency using the DH-2000-CAL (Ocean Optics Inc) standard light source. The Q-switch of laser-I triggers the four-channel digital delay/pulse generator (SRS DG 535). One channel of the delay generator triggers the Q-switch of laser-II and the flash lamps of both the lasers were synchronized. The inter pulses delay was varied by the delay generator whereas the pulse energy was varied by the flash lamp Q-switch delay through the laser controller. In all these experiments, the time delay between the delayed laser pulse and the data acquisition system is 2.1 micro second whereas the integration time is 2 ms. The commercially available attenuators were used for varying the lasers pulse energies. For measuring the spatial variation of plasma parameters, the optical fiber having collimating lens was place at a 3D stage and its movement was controlled manually with the help of micrometers. The spatial variation of the plasma plume was registered by moving the optical fiber having collimating lens along the axis of plasma plume expansion.

3. Results and discussion

In the first set of experiment. the Nd:YAG laser pulse @ 1064 nm of energy 90 mJ was used for generating plasma and SP LIBS spectrum was registered. The spectrum reveals a number of neutral copper lines e.g. Cu I at 578.21 nm, 570.02 nm, 521.82 nm, 515.32 nm, 510.55 nm, 465.11 nm, 458.70 nm, 453.08 nm, 450.93 nm, 448.04 nm, 427.51 nm, 327.39 nm, 324.75 nm and 427.51 nm etc. The lines due to the singly ionized copper Cu II were also detected at 481.29 nm, 487.33 nm etc.

3.1. Collinear dual pulse

To register the DP LIBS spectrum in collinear configuration, two Nd:YAG laser pulses @ 1064 nm, each of energy 45 mJ were used. All the lines that appeared in the SP LIBS spectrum are also present in the DP LIBS spectrum. A portion of SP and DP LIBS spectrum is shown in Fig. 1. To get the maximum signal intensity enhancement, the inter pulse delay between the two laser pulses was optimized through a delay generator. In Fig. 2, the relative intensities of Cu I lines as a function of inter pulse delay are presented. Evidently, the maximum signal intensity enhancement was measured at 5 μs inter pulse delay. A comparison between the SP and DP LIBS spectrum at inter pulse delay 5 μs, exhibits nearly four to eight times signal intensity enhancement. Gautier et al. [34] suggested that the optimum value of interpulse delay for maximum enhancement is in the range of 5 to 10 μs, whereas Kuwako et al. [35] found maximum signal enhancements for 8 μs inter pulse delay.

To study the effect of laser wavelength on the enhancement of DP LIBS spectrum, the experiment was repeated using the second harmonics of the Nd:YAG lasers @ 532 nm of energy 60 mJ. The DP LIBS spectrum was registered using two laser pulses @ 532 nm, each of energy 30 mJ. A portion of the SP and DP LIBS spectrum is shown in Fig. 3. The spectra of SP and DP LIBS @ 532 nm are very similar to that of SP and DP LIBS @ 1064 nm and most of the lines are present in both cases. In Fig. 4, the variations in the signal intensities of Cu I lines as a function of inter pulse delay between the two lasers are presented. Interestingly, the maximum signal intensity enhancement occurs again at inter pulse delay of 5 μs, as observed already in the case of DP LIBS with the laser wavelength of 1064 nm. A comparison of SP and DP LIBS spectra reveals four to fourteen times signal enhancements in the neutral copper lines measured in DP LIBS spectrum as compared to SP LIBS spectrum. Pinon et al. [36] used dual pulses from a femtosecond laser and achieve three to ten fold enhancements in the neutral lines of copper. In the collinear double pulse configuration Cristoforetti et al. [37] also achieved enhancement factor up to 4.5.

In the second set of experiments, the effects of lasers pulse energies ratio on the signal intensity enhancement, in DP LIBS as compared to SP LIBS was studied. The interpulse delay between the two laser pulses was adjusted at 5 μs and the laser pulse energies ratio was varied continuously using commercially available attenuators. Rai et al. [38] remarked that maximum signal

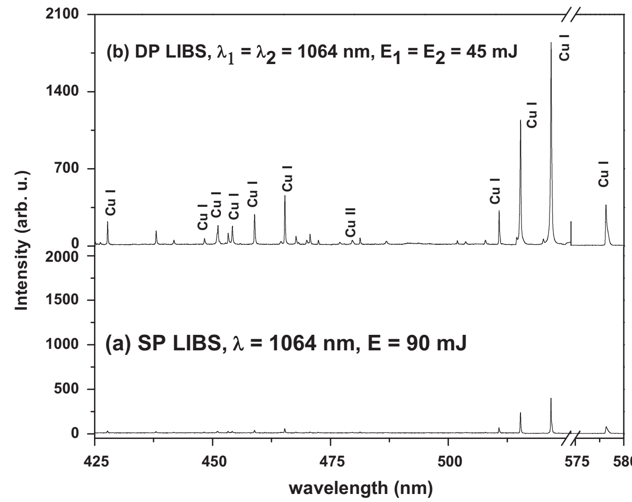

Fig. 1. A part of LIBS spectrum at laser pulse energies 90 mJ @1064 nm (a) DP LIBS spectrum with inter pulse delay 5 μs, (b) SP LIBS spectrum.

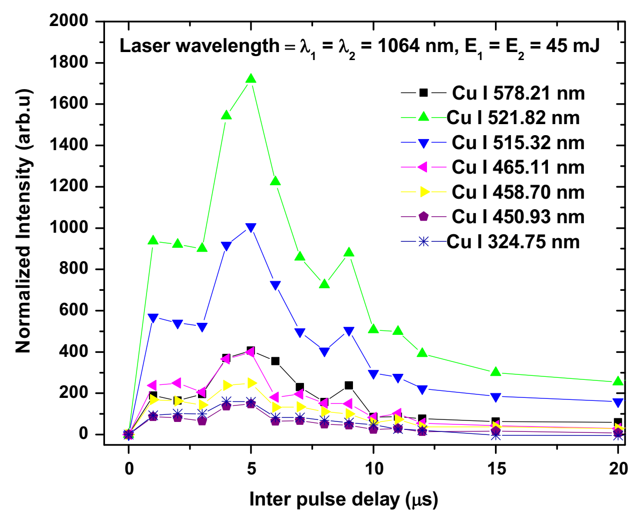

Fig. 2. Variation of signal intensity versus inter pulse delay between two laser pulses each of energy 45 mJ @ 1064 nm.