J. Bangladesh Acad. Sci. 48(2); 185-191: December 2024 DOI:https://doi.org/10.3329/jbas.v48i2.72703

Journal of Bangladesh Academy of Sciences

Journal homepage: http://www.bas.org.bd/publications/jbas.html

Research Article

Estimation of the ablation velocity of atoms in a laser-induced plasma through the Doppler effect

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ARTICLE INFO

Article History

Received: 17 April 2024
Revised: 19 June 2024
Accepted: 01 July 2024

Keywords: LIBS, Laser-Induced Plasma, Ablation velocity, Doppler Effect.

ABSTRACT

The dynamics of laser-induced plasma plumes were investigated using the Doppler effect and the spectroscopic analysis for the first time. Plasma is generated on silver, copper, and gold targets in ambient air at atmospheric pressure and room temperature using laser ablation with a Q-switched Nd: YAG laser. The laser setup included specific parameters: a pulse duration of 8 ns, a repetition rate of 10 Hz, laser pulse energies of 40 mJ, and a grating with 2400 grooves/mm. When the input end of the optical fiber is perpendicular to the sample surface, a Doppler shift in the emitted wavelength occurs. By analyzing this Doppler shift of the emission wavelengths at two distinct source-detector relative positions, we can accurately estimate the velocities of silver, copper, and gold atoms within the laser-induced plasma.

Introduction

Laser-induced breakdown spectroscopy (LIBS) is a widespread technique recognized for its rapid and effective elemental analysis (Cremers and Radziemski, 2013; Singh and Thakur, 2020; Mizioleket al., 2006). This technique harnesses the intense power of a high-energy laser pulse, channeling its focused energy onto a sample to induce the formation of a transient micro-plasma at very high temperatures. The emitted light is then analyzed using a high-resolution spectrometer coupled with a gated and intensified charge-coupled device (ICCD) to determine the sample's elemental composition.

LIBS has a wide range of applications, including ion source formation (Gammino et al., 2002; Okamura et al., 2014), nanoscale synthesis (Lin et al., 2020; Xiao et al., 2020), thin film growth (Cheung and Sankur, 1988; Harris et al., 2019) and nuclear fusion (Wu et al., 2019; Xiao et al., 2013). Therefore, a thorough understanding of the composition and dynamics of the plasma plume is crucial for optimizing performance in these fields.

Plasma velocity is critical, as it affects stability, transport properties, and wave propagation within the plasma. Knowledge of plasma velocity is essential in material processing techniques like plasma etching and deposition, as the velocity of plasma species plays a critical role in these processes; it can either accelerate thin film deposition when a certain velocity threshold is used (Shul and Pearton, 2011; Chrisey and Hubler, 1994) or compromise the integrity of the deposited film when exceeding it (Chen et al., 2021). Hence, gaining a comprehensive understanding of plasma particle dynamics, particularly in laser-induced plasma, is necessary. Additionally, measuring plasma velocity can provide valuable diagnostic information for determining plasma properties such as temperature and flow patterns.

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Previous studies have mainly focused on measuring plasma velocity using direct methods like ICCD (Anoop et al., 2014; Yuan et al., 2020). However, our study explores an alternative approach by utilizing the Doppler effect to estimate velocity. We demonstrate the capability of LIBS coupled with the Doppler effect to estimate the velocities of ablated particles within laser-induced plasma. Specifically, we estimate the velocities of copper (Cu), silver (Ag), and gold (Au) atoms within the plasma, shedding light on this crucial aspect of plasma dynamics. This is yet another novel application of LIBS.

Experimental setup

Fig. 1 shows the experimental setup for estimating the velocity of silver atoms (Haider et al., 2014). To prepare the silver plate for the experiment, a 10 mm × 10 mm × 1 mm plate of ~99.99% pure silver was mechanically polished and cleaned multiple times in an ultrasonic bath with nano-pure water to remove impurities from its surface. Similarly, copper and gold plates of similar dimensions were also polished and cleaned for conducting the velocity estimation experiment using LIBS.

The experiment utilized a Q-switched Nd: YAG laser (Spectra-Physics LAB-170-10) as the excitation laser. This laser emitted light at a fundamental wavelength of 1064 nm, with a pulse duration of 8 ns, a repetition rate of 10 Hz, and a maximum pulse energy of 850 mJ. The laser had harmonic generators capable of producing the second, third, and fourth harmonics using KDP crystals. For this experiment, we used the fundamental wavelength of 1064 nm to generate plasma. The laser beam had a Gaussian profile in the far field and a beam divergence of less than 0.5 mrad. All experiments were conducted in the air (Abedin et al., 2011).

To generate a high-intensity transient plasma, the fundamental beam of the Nd: YAG laser was focused onto the sample using a 100 mm focal length convex lens. The spot size at the sample was approximately 200 µm measured using a beam profiler. This resulted in a peak power density of approximately 16 GW/cm² for a 40 mJ pulse. The plasma was generated at a repetition rate matching the laser's frequency, occurring 10 times per second.

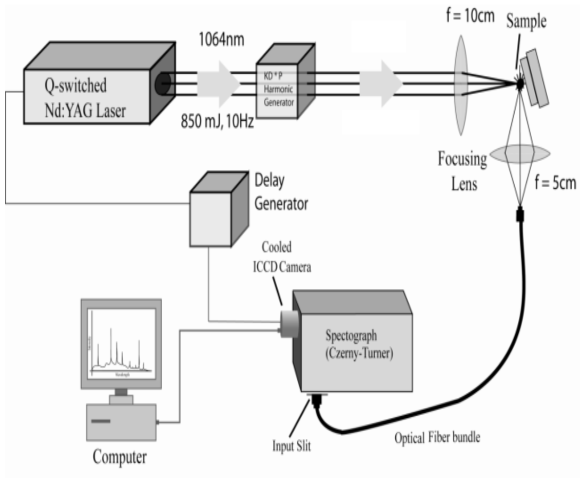

Fig. 1. Schematic diagram of the ablation velocity measurement setup.

The light emitted from the plasma was directed through a fused quartz lens with a focal length of 50 mm and collected by a 3 m long multimode silica optical fiber. This light was transmitted through the fiber to the entrance slit of a computerized Czerny-Turner spectrograph with a focal length of 750 mm (Acton Model SP-2758). The spectrograph had three interchangeable ruled gratings: 2400, 600, and 300 grooves/mm blazed at 240, 500, and 300 nm, respectively. These gratings, controlled by a computer, provided high and low-resolution spectra across a wavelength range of 200 nm to 960 nm.

For this experiment, we used a grating with 2400 grooves/mm to achieve the highest resolution for our detection system. The spectrograph output was connected to a gated ICCD camera (Princeton PI-MAX with Unigen II coating and programmable delay generator). This ICCD camera had 1024x1024 pixels and was cooled to -20°C using a Peltier cooler to minimize noise.

The synchronous pulse of the Nd: YAG laser electrically triggered the ICCD camera after applying a software-controlled adjustable time delay. This setup effectively reduced the intense background initially generated by the high-temperature plasma, enabling clearer observation of the elements' atomic/ionic emission lines. For an optimal signal, we selected a delay time (t_d) of 1.5 μs and a gate width (T_w) of 50 μs (Haider and Khan, 2012).

Typically, spectra from multiple laser shots (10 in our case) were acquired and averaged to enhance the signal-to-noise ratio. The captured spectrum from the ICCD camera was transferred to a computer via a USB cable. The manufacturer-provided WinSpec/32 software allowed complete control over all functions of the ICCD camera and the Acton spectrograph.

Results

LIBS spectra were recorded for each sample in the 200-960 nm spectral range using high-resolution gratings with 2400 grooves/mm. The wavelengths of the observed line peaks in the spectra were compared to the online database available from the US National Institute of Standards and Technology (NIST database, 2024). Since the samples primarily consisted of pure silver, gold, and copper, strong emission lines of these elements were analyzed to estimate the ablation velocity of their atoms/ions. Figs. 2(a) and 2(b) show the LIBS spectra for the Ag atom in the spectral window of 323.5 nm to 332.5 nm. In Fig. 2(a), the spectrum corresponds to a fiber input parallel to the surface of the sample, while Fig. 2(b) represents the corresponding spectra when the fiber input is perpendicular to the surface of the sample.

When the detection direction is parallel to the sample surface, the velocity component of the ablated atom/ion in that direction can be considered zero (Cremers and Radziemski, 2013). Therefore, the emitted wavelength remains unshifted (no Doppler shift). However, when the input end of the optical fiber is aligned perpendicularly to the sample surface, the emitting atom/ion moves toward the input end with a certain velocity (Kwapis et al., 2024). This results in a noticeable shortening of the wavelength due to the Doppler effect. The ablation velocities of the emitting atoms can be estimated by measuring the change in wavelengths. Table 1 illustrates the estimation of plasma plume velocity through Doppler shift analysis of emission wavelengths at different source-detector relative positions. In our work, the estimated velocity for neutral copper, silver, and gold atoms is 2.40 X 10^4 m/s, 2.29 X 10^4 m/s, and 2.21 X 10^4 m/s, respectively, at atmospheric pressure in the direction perpendicular to the sample surface.

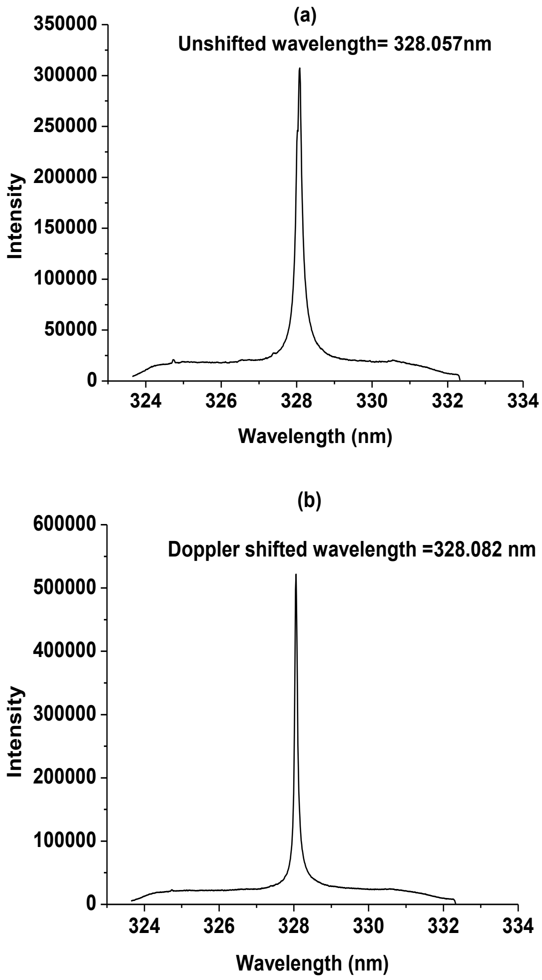

Fig. 2. Comparative analysis of emission lines from Ag I (a) Before the Doppler Shift and (b) After the Doppler Shift.

Table 1. Estimation of plasma plume velocity through Doppler shift analysis of emission wave lengths at various source-detector relative positions.

Element	Charge state	Unshifted wavelength λ (in nm) (at $\theta = 0^0$)	Doppler shifted wavelength λ' (in nm) (at $\theta = 90^0$)	The velocity of the atom in the plasma plume ($\times 10^4$ m/s)
Cu	I	324.752	324.726	2.40
Ag	I	328.082	328.057	2.29
Au	I	312.279	312.256	2.21

Discussion

When a high-power laser pulse impacts a sample surface, a fraction of the material vaporizes or ablates, creating a micro-plasma. Initially, this plasma is extremely hot and dense, which causes a broad continuum emission of background radiation. As the plasma expands and cools, ions and electrons recombine, producing excited atoms that release photons as they decay to lower energy states. By analyzing the spectrum of these emitted radiations, we can identify the different elements in the plasma that come from the target material.

The expansion of the laser-induced plasma shows an elongation perpendicular to the sample surface, resembling a pear or cigar shape. This suggests that the expansion rates vary in different directions, with the highest expansion occurring perpendicular to the surface. At laser powers of around 16 GW/cm², the plasma elongates by approximately 1 centimeter. Figure 3 provides a schematic representation of the laser-produced spark in the air, which helps visualize this phenomenon. When the detection is parallel to the sample surface, the velocity of the ablated particles in that direction is minimized because the plume primarily expands perpendicular to the surface, resulting in minimal net velocity parallel to it (Cremers and Radziemski, 2013; Singh and Thakur, 2020).

We can determine this velocity by using the Doppler effect of light. In this case, the ablated atom/ion acts as a moving source of the light wave, while the input end of the optical fiber acts as the stationary detector. When a light source moves towards an observer, the wavelengths of the emitted light waves become compressed in the direction of motion. This compression leads to an apparent increase in frequency and a decrease in the wavelength of the light observed by the observer. We can express the Doppler-shifted frequency f ' of the light as:

$$f' = f\,(1 + v / c) \qquad (1)$$

In this equation, f represents the unshifted frequency, v denotes the relative velocity between the source and the detector, c is the velocity of light, and f ' is the observed frequency. From the above equation, we derive the following relation:

$$v = c\,(\lambda' - \lambda) / \lambda \qquad (2)$$

Here, λ represents the unshifted wavelength, and λ' is the observed Doppler-shifted wavelength. By using these wavelengths in equation (2) for two different relative angular positions between the sample and the detector, we can easily determine the ablation velocity of a specific atom/ion.

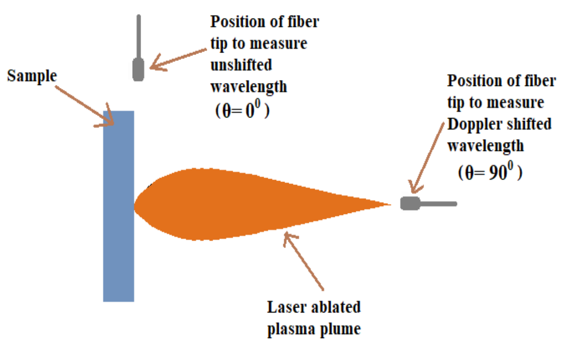

Fig. 3. Schematic shape of Laser-produced plasma plume in air.

Through this experiment, we have successfully demonstrated the capability of LIBS in estimating the velocities of ablated particles within laser-induced plasma obtained using an Nd: YAG laser. Specifically, for angles of 90 degrees between the sample surface and detector, we obtained a velocity of $2.40X10^4$ m/s for neutral copper atoms in plasma at atmospheric pressure. This contrasts with the findings of Anoop et al.(2014), who investigated the ablation of a copper target in a high vacuum using a Ti: Sapphire laser and an ICCD to image the plasma plume. They found that the peak velocity of the neutral component was 9 x 10^3 m/s. On the other hand, our study involved ablation in atmospheric conditions using a different laser and parameters, resulting in higher velocity for the neutral atom.

Additionally, our approach utilized the Doppler effect to estimate the velocity of neutral Cu atoms instead of direct measurement using ICCD.

Yuan et al. (2020) observed splitting a laser-induced plasma plume into two components at reduced pressures (50 Pa to 200 Pa). They employed a Q-switched Nd:YAG laser to ablate a copper target and imaged the plasma using ICCD. The fast component exhibited a velocity of approximately 10^4 m/s at a 200 ns delay, while the slow component had a velocity of around 10^3 m/s at the same delay. However, in our study, the background gas pressure was sufficiently high (atmospheric pressure) to maintain a continuous plume (Noll et al., 2004). Consequently, we did not observe any splitting of the plume.

Noll et al. (2004) examined the effects of collinear double pulses from an Nd:YAG laser on pure iron targets in the air. Using a long-distance microscope on a streak camera, they found that the material ablated by the second pulse expands faster, resulting in a noticeably larger plasma volume. Expansion velocities measured 60 ns after the second laser pulse were found to be $1.2x10^4$ m/s. In our measurement, however, we utilized a single pulse from a Nd:YAG laser in air and obtained different expansion velocities accordingly.

According to the Maxwell-Boltzmann distribution (though rarely this is so simple in most cases), the most probable velocity depends on both mass and plasma temperature($v_{mp} = \sqrt{\frac{2kT}{m}}$).

However, the ablation velocity of different species is influenced by a complex interplay of factors, including plasma temperature, material properties (such as density and boiling point), environmental conditions (such as constituent gases and ambient temperature), and laser parameters (such as power and spot size).

In our study, we observed that $v_{Cu}>v_{Ag}> v_{Au}$ which suggests a trend where plasma velocities decrease with atomic number. It is important to note that the plasma was generated from three different target materials with varying boiling points and densities. Additionally, the environmental conditions and laser parameters were somewhat different. Since we measured the velocity with a fairly long delay of 1.5 us for eliminating the plasma radiation background, we effectively measured the tail (lower part) of the velocity components of the atoms in the plasma plume. Therefore, our results only partially reflect significant differences in atomic mass.

Finally, while we utilized a 2400 grooves/mm diffraction grating boasting a resolution of 0.002 nm, the highest available within our experimental setup, accessing an even higher resolution (for example, using 3600 grooves/mm grating) could have yielded even greater accuracy in our results.

Conclusion

In this study, we used the Doppler Effect of light to estimate the velocities of Ag, Cu, and Au atoms within LIBS plasma for the first time. Unlike experiments conducted under reduced pressures, our study operated under atmospheric conditions to maintain a continuous plasma without splitting the plume. Using this approach, we found that the average velocities of Cu, Ag, and Au atoms were $2.40x10^4$ m/s, $2.29x10^4$ m/s, and $2.21x10^4$ m/s, respectively. The highest resolution available in our experiment was 0.002 nm. Improving the resolution and sensitivity of the spectrometer will result in more accurate measurements and better velocity estimations. This alternative method for assessing plasma species dynamics holds promising implications for optimizing performance in various fields, such as material processing, thin film deposition, and nuclear fusion. Estimating the velocity of atoms and ions in the plasma plume is another novel application of the laser-induced breakdown spectroscopic technique.

Conflicts of Interest

Concerning the publication of this paper, the authors have no conflicts of interest.

Acknowledgment

The experimental work was carried out in the Nonlinear Optics and Laser Spectroscopy Laboratory of the Center for Advanced Research in Sciences (CARS) of the University of Dhaka.

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