Effect of sample temperature on spectroscopic investigation of laser-induced aluminum and copper plasma

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Abstract. In this work, the influence of samples temperature and laser energy on the optical emission spectra and plasma parameters of laser-induced breakdown spectroscopy for aluminum and copper metallic target is investigated. The samples are uniformly cooled down to -70 °C and heated up to 200 °C by an external liquid nitrogen and ceramic heater, respectively. The plasma formed is generated by ablating the surface targets using Nd:YAG laser with laser energies of 100 mJ, 200 mJ and 300 mJ. The emission spectra at ambient atmospheric pressure are recorded using HR4000 spectrometer. From these spectra, plasma temperatures and electron densities are determined by using Boltzmann plot and Stark broadening methods, respectively. A significant increase in the peak intensity of spectral lines is observed with increase in the laser energy as well as sample temperature for both elements. Both of these parameters have shown a clear influence on dynamics of laser-induced plasma for each species. In brief, both laser energy and sample temperature affect the emission intensity, temperature and density of the laser-induced plasma generated from aluminum and copper samples.

1. Introduction

Over the last decades, the development of laser technology has been rising rapidly and the applications beneficially can be found in engineering, medicine, and physical sciences. Naturally, physical interaction of energetic laser light with materials will induced plasma plume formation. The emission of plasma formed signify the properties of plasma itself and composition information of atomic or molecular forms on that material, which can be implied in the quantitative and qualitative analysis study. This phenomenon is widely used in technique known as laser induced plasma spectroscopy (LIPS) or laser induced breakdown spectroscopy (LIBS). Nowadays, this technique has become one of the leading research directions for researchers in direct analysis or as an alternative elemental analysis of various materials and applications such as addictive manufacturing, material processing, pharmaceutical processing, thin film deposition, explosive materials recognition, etcetera [1–7]. Furthermore, our
previous work successfully demonstrated automated system for real-time LIBS analysis which capable to improve and speed up the data acquisition and analysis [8].

A critical understanding of plasma properties such as plasma temperature, electron density, or gas temperature is important in order to improve the application of LIBS. The properties of plasma are directly influenced on the emission signals by the state of the samples such as gas, liquid, or solid [9–11]. Moreover, the experimental parameter such as laser parameter (type of laser, laser pulse duration, wavelength, and irradiance) [12–15] or pressure and composition of the surrounding atmosphere [16–18] also technically affected the plasma properties. Metals show wide-ranging applications in industry with interesting targets to investigate due to their high number of free electrons that will readily interacting with the laser beam. Composite materials based on metals such as aluminum and copper are widely used as contact materials on electrical component in electric industry applications. Furthermore, the Al-Cu metallic composite possess attractive properties in particular on high electrical conductivity, thermal conductivity, and mechanical strength [19,20].

Previous works on laser induced aluminum and copper plasma are mainly focus on laser parameter and surrounding environment. Gojani et al. reported the effects of laser power on aluminum and copper targets have influenced the plasma and crater depth formation [21]. Dawood et al. have studied the influenced surrounding gas, composition, and pressure on laser-induced aluminum plasma towards dynamical plasma plume formation [22]. Further information on plasma properties of spectral line for aluminum and copper species have been analyzed in details by Babich et al. [23] and Ciobanu et al. [24], respectively. In addition, the effect of sample temperature on plasma properties such as on titanium species has been demonstrated successfully [25]. However, the knowledge of the effect of samples temperature on the plasma properties for aluminum and copper species is still unclear. The main aim of this paper is to investigate the plasma properties of laser induced plasma of aluminum and copper materials with various temperature target. In present work, we were focused on collecting spectral data at low (< 0 °C) and high temperatures from aluminum and copper samples with different laser energies. Both samples experienced similar temperature variations in range of -70 °C to 200 °C. The laser energies used in this research are 100 mJ, 200 mJ, and 300 mJ. The electron density and plasma temperature were estimated for each variation in experimental parameters using Stark Broadening and Boltzmann-Plot methods, respectively, to investigate the relationship of plasma dynamics with sample temperature and laser energy.

2. Experimental
Aluminium and copper samples were polished with sandpaper of six different roughness grades followed by cleaning with acetone to remove any dirt or oils, to make sure the samples surfaces are smooth and clean. The schematic of experimental arrangement is illustrated in figure 1. Sample was placed on a ceramic heating element to heat from 50 °C to 200 °C and the temperature was monitor using a thermocouple. Whereas for ≤ 0°C temperatures (-70 °C to 0 °C), the sample was immersed in liquid nitrogen and waited for the desired temperature to reach before ablating to record the data. In addition, the samples target at standard room temperature was used as reference. The temperature of sample surface was monitored using IR thermometer and a thermocouple. Nd:YAG Laser (1064 nm, 8 ns) was focused vertically on the sample surface by a focusing lens to ablate the sample surface with 100 mJ, 200 mJ and 300 mJ energies. The focusing lens of 10 cm was used to generate the plasma. The radiations emitted from the ablation plasma were collected by a fibre optic cable and delivered to spectrometer. The spectrometer (OceanOptics HR4000) resolved radiations into constituent wavelengths and Spectrasuite software stored the spectra on a computer hard disk.
3. Results and Discussion

3.1. Spectral Analysis

Each of the element has its characteristic emission lines due to unique energy band gaps. Figure 2 shows LIBS spectra of both aluminium and copper recorded by the spectrometer. Spectral lines of elements are identified by matching with Atomic Spectral Database of NIST [26] and the published literature as discussed in section 1. Six sharp copper lines appear at 324.75 nm, 327.40 nm, 330.12 nm, 510.55 nm, 515.32 nm, and 521.82 nm. Also, six sharp aluminum lines observed in the spectrum are; 281.61 nm, 308.22 nm, 309.27 nm, 358.65 nm, 394.40 nm, and 396.15 nm.

Figure 3 shows the graphs of intensity versus sample temperature for aluminum and copper lines at 100 mJ, 200 mJ, and 300 mJ laser energies while the sample temperature varies as 28 °C, 100 °C, 150 °C and 200 °C. The blue line in the graph figure 3 (b) is a straight line because the emission intensity of Cu I 521.28 nm saturated the detector response at whole range of sample temperatures when ablated with 300 mJ of laser energy. It is observed that as the laser energy is increased, the intensity of spectral line for both elements also increasing. It also depicts that with rise in target temperature, the spectral line emissions are also enhanced significantly. Therefore, it can be concluded that emission intensities of spectral lines depend on laser energy as well as sample temperature.

![Figure 1. Schematic diagram of the experimental setup.](image)

![Figure 2. LIBS spectra of (a) copper and (b) aluminum.](image)
Figure 3. Emission intensity vs sample temperature for (a) Al I 309.27 nm and (b) Cu I 521.28 nm emission line obtained with different laser energies.

3.2. Plasma Parameters

The electron density and plasma temperature are estimated using Stark broadening and Boltzmann-plot method respectively. In doing for these methods, spectral lines for aluminum and copper species at 308.2 nm and 510.6, respectively, are selected for the diagnostics due to the sufficient intensity and optically thin spectral line with well isolated in the emission spectra.

3.2.1. Plasma Temperature. Plasma temperature can be determined based on Boltzmann distribution law, which described the relative population of excited and levels of an atom or ion [27]. Eventually, the Boltzmann plot are used to calculate the plasma temperature by linear fit the data \( y = mx + c \) with the function is defined as follows;

\[
\ln \left( \frac{I}{gA} \right) = - \frac{E}{kT} + \text{constant}
\]  

(1)

Where \( I \) and \( \lambda \) are the intensity and wavelength to the corresponds species, \( g \) is the statistical weight of upper energy level, \( A \) is the transition probability of species, \( T \) is plasma temperature, and \( k \) is Boltzmann constant (8.617 x 10^{-5} eV/K). In order to obtain plasma temperature, the determined slope of the plot was used as follows,

\[
T = \frac{1}{mk}
\]  

(2)

The calculated plasma temperature with laser energy of 100 mJ for aluminum and copper plasma are summarized in table 1 and table 2. Figure 4 and figure 5 illustrate the plot of plasma temperature vs sample temperature for aluminum and copper with various laser energy, respectively. It is clear that plasma temperature increases when the target sample is ablated with higher laser energy. Figure 4 (a) and figure 5 (a) show the trend of aluminum and copper for -70 °C to 200 °C of samples temperature with 100 mJ laser energy. Both target experienced inconsistent pattern for temperature below 0 °C, which is not suitable to be applied on 200 mJ and 300 mJ laser energy due to the insensitivity of the plasma correspond with laser energy.

For samples temperature above 0 °C, laser energy of 200 mJ and 300 mJ are applied with the plasma temperature show good trend. It obviously can be seen that as the samples temperature of aluminum target increase, the plasma temperature also increasing as shows in figure 4 (b). However, aluminum
target with laser energy of 200 mJ shows plasma temperature dropped after 150 °C, which possibly due to the increase of collisions between species inside the plasma. Figure 5 (b) shows plasma temperature increase with the increasing of copper target temperature and achieved the highest plasma temperature at 150 °C. Eventually, the plasma temperature slightly drops for after 150 °C.

Table 1. Plasma temperature for aluminum target, irradiated by 100 mJ laser energy at different sample temperature.

| Temperature (°C) | Slope (eV)^{-1} | Plasma Temperature (K) |
|------------------|-----------------|------------------------|
| -70              | -2.64356        | 4389                   |
| -50              | -2.64356        | 4389                   |
| -40              | -4.01222        | 2892                   |
| -20              | -2.66857        | 4349                   |
| 0                | -2.66521        | 4354                   |
| 28               | -2.91440        | 3982                   |
| 100              | -2.90415        | 3996                   |
| 150              | -2.84517        | 4079                   |
| 200              | -2.19385        | 5289                   |

Figure 4. Plasma temperature for aluminum with sample temperature of (a) -70 °C to 200 °C on 100 mJ laser energy and (b) room temperature with the heating conditions start from 100 °C to 200 °C on 100 mJ, 200 mJ, and 300 mJ laser energies.
Table 2. Plasma temperature for Cu target, irradiated by 100 mJ laser energy at different sample temperature.

| Temperature (°C) | Slope (eV)$^{-1}$ | Plasma Temperature (K) |
|------------------|-------------------|------------------------|
| -70              | -1.27893          | 9074                   |
| -50              | -1.13042          | 10266                  |
| -40              | -1.21179          | 9577                   |
| -20              | -1.17397          | 9885                   |
| 0                | -1.16660          | 9948                   |
| 28               | -1.22994          | 9435                   |
| 100              | -1.12532          | 10313                  |
| 150              | -1.08335          | 10712                  |
| 200              | -1.12897          | 10279                  |

Figure 5. Plasma temperature for copper with sample temperature of (a) -70 °C to 200 °C on 100 mJ laser energy and (b) room temperature with the heating conditions start from 100 °C to 200 °C on 100 mJ, 200 mJ, and 300 mJ laser energies.

3.2.2. Electron Density. Electron density for both elements were determined from Stark broadening considerations. The spectrum broadening appears due to splitting of energy levels of atoms due to the presence of an external electric field because of surrounding electric charges. Electron density of the sample target was calculated by using equation as follows;

$$\frac{\Delta \lambda_{1/2}}{\lambda_{1/2}} = 2w \left( \frac{n_e}{10^{17}} \right)$$

Where $n_e$ is electron density, $\lambda_{1/2}$ is value at full width half maximum (FWHM) and $w$ is electron impact parameter. The value of FWHM is obtained from non-linear fitting of the emission line while the value for $w$ was obtained from the literature. Figure 6 shows that the electron density increases with increase in the laser energy as well as sample temperature. The laser pulse used for ablation in this experiment has a nominal duration of 8 ns. Since, plasma is typically initiated within a nanosecond after the laser pulse hits the sample surface, major portion of the rest of the laser pulse (~7ns) is absorbed within the plasma plume. It further excites the plasma species which drive to the increasing in temperature. Meanwhile the degree of ionization which resulting to the increase of the electron density in the plasma. When the sample is hot, the atoms at the surface are already excited before the laser pulse hits the sample surface. It assists the laser ablation process by ejecting more excited material into the
plasma. In turn, it increases both density and temperature of the plasma which can be proved in our results.

**Figure 6.** Plot of electron densities calculated from Stark broadening of (a) Al I 308.2 nm and (b) Cu I 510.6 nm emission lines at different sample temperatures and laser energy.

4. Conclusion

Aluminum and copper samples were ablated with 100, 200 and 300 mJ of laser energies at sub-zero (up to -70°C) and high sample temperatures (up to 200°C). The LIBS spectra were recorded and analyzed to study the effect of sample temperature and laser energy on plasma parameters. The intensities of the spectral lines of aluminum and copper are found increase with the increasing in laser pulse energy as well as the sample temperature. Electron density and plasma temperature are varied for each sample temperature and laser energy with an overall increasing trend. It shows that the sample temperature and laser energy have influence on the plasma parameters. It can be concluded from the results that the overall variation trend in spectral intensity and plasma parameters for change in sample temperature and laser energy are similar for aluminum and copper. However, to generalize this conclusion further investigations are needed by including much larger set of elements.

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