The effect of excitation wavelength on plasma spectrum of metals in vacuum condition

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Abstract. Pure metals Aluminum (Al), Copper (Cu) and Brass (CuZn) have been detected using laser-induced plasma spectroscopy technique using nanosecond laser. A Q-switch pulsed Nd:YAG laser operating at infrared (1064 nm), visible (532 nm) and ultraviolet (355 nm) wavelengths have been used. The energy laser used was 12 mJ and the experiment was carried out in vacuum condition (5 Torr). The plasma generated by a focused Nd:YAG laser beam was detected by a spectrometer to identify trace elements quantitatively. The result of quantitative trace element of pure metals at three different wavelengths gave the different results. Al metal excited by 355 nm, 532 nm and 1064 nm wavelengths has 5, 2 and 13 Al emission peaks, respectively. Whereas the analysis of Cu showed 5, 7 and 6 emission peaks upon excitation by 355 nm, 532 nm and 1064 nm wavelengths, respectively. Finally, CuZn metal produced 7 Cu lines and 2 Zn lines upon excitation by 355 nm wavelength, 8 Cu lines and 1 Zn line when excited by 532 nm wavelength, and 8 Cu lines and 3 Zn lines when excited by 1064 nm wavelength.

1. Introduction

When a powerful pulsed laser is focused onto a surface, a tiny amount of the material is vaporized and through further photon absorption, it is heated up until it ionizes and creates a dense area of high energy ions/atoms/electrons which we call as a plasma. This laser-induced plasma is a micro-source of light that can be analyzed by a spectrometer. The obtained spectra consist of lines corresponding to the elements evaporated from the sample surface. This is the principle of laser-induced plasma spectroscopy (LIPS) and it has proven to be a powerful surface analytical technique, capable of performing trace element measurements in any kind of solid material [1-3] as well as in liquids [4-5]. A variety of phenomena in laser interaction with material including heating, melting, evaporation, atomization, excitation and ionization are involved [6].

The efficiency of plasma is described by the ablation rate, which gives the maximum layer thickness ablated during the irradiation with a laser pulse [7]. The ablation rate is strongly influenced not only by the laser beam characteristics (laser spot diameter, laser fluence, laser wavelength, a number of pulses and pulse duration), but also by the optical and thermal properties of the processed material surface (optical absorption, surface reflectivity, thermal conductance and mass density) [8-9]. The influence of laser fluence on ablation rate is more significant when the laser fluence exceeds its threshold value \( F_{th} \) [10]. Plasma formation requires vaporization of the material surface as a first step. The vaporization of the sample occurs when the energy deposited on the target exceeds the latent heat of vaporization of the target, \( L_v \). Threshold fluence \( F_{th} \), \( F_{th} = \rho L_v a^{1/2} t_e^{1/2} \), where \( \rho \) is the sample density, \( a \) is its thermal diffusivity \( (a = K/\rho C_p) \), where \( K \) and \( C_p \) are the thermal conductivity and specific heat, respectively, and \( t_e \) is the laser pulse width. The initiation of plasma over the target surface begins in the hot vapor and is...
generated by inverse bremsstrahlung absorption during collisions among sampled atoms and ions, electrons and gas species. Theoretical considerations on plasma production and heating by means of laser beams have been discussed by several authors [11].

Here, we experimentally explored the influence of the laser wavelength on the plasma spectrum for material analysis of pure metals. We use three pure metals (Al, Cu and CuZn) that were ablated by three different laser wavelengths from Nd-YAG laser (355 nm, 532 nm and 1064 nm) in vacuum condition.

2. Materials and methods

2.1. Materials
Three pure metal samples used in this research are 99% Aluminum (Al), 99% Copper (Cu) and 99% Brass (CuZn). Samples are high purity metals for research and industry. Samples were cut into $2 \times 2$ cm dimension.

2.2. Methods
The schematic diagram of the experimental setup used in this research is shown in figure 1. A Nd:YAG laser source (Q-Smart 850, Quantel) with a pulse repetition rate of 10 Hz and pulsed width of 6 ns was used in this experiment. Three optional wavelengths were available, i.e. fundamental (1064 nm), second harmonic generation (SHG) (532 nm) and third harmonic generation (THG) (355 nm) modes. The output of laser beam was focused by a convex lens with a 100 mm focal length onto a copper target mounted on a rotating table in the vacuum chamber. Energy laser used was fixed at 12 mJ/pulse. Plasma emission generated from the laser-sample interaction was collected through a high-resolution fiber optic spectrometer (HR 2000, Ocean Optics). This spectrometer has a detection range from 200 nm to 1050 nm. The experiments were carried out in vacuum condition (5 Torr).

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

3. Results and discussion

Our research purpose was to analyze three pure metals (Al, Cu and CuZn) with LIPS technique and to observe the effect of laser wavelength on plasma spectrum for material analysis. We used three different laser wavelengths, i.e., infrared (1064 nm), visible (532 nm) and ultraviolet (355 nm).

3.1. Information about sample properties of Aluminum (Al), Copper (Cu) and Brass (CuZn)
When a laser beam is focused on a solid sample surface, a plasma is formed. The plasma consists of atoms, ions, electrons. When pulsed laser interacts with material, a certain amount of energy is absorbed by metals and converted into heat, causing analyte vaporization as the local temperature exceeds the
boiling point of the sample material. The timescale of this interaction is so small that it has been considered for the optical energy is converted into heat instantaneously at the point of absorption [8]. Hence, plasma plume is strongly influenced by the properties of material. The physical properties of Al, Cu and CuZn, especially thermal features such as boiling point, melting point and thermal conductivity are shown in table 1 [12].

### 3.2. Influence of laser wavelength on analysis of materials

The formation of plasma is also influenced by threshold fluence ($F_{th}$) and $F_{th}$ strongly influences the ablation rate ($\Delta h$). The dependency of the ablation rate and the threshold laser fluence on the laser wavelength arises from three interrelated phenomena: the decrease in the sample’s intrinsic absorption, the increase in the surface reflectivity and the enhancement of the absorptivity of the produced plasma with increasing the laser wavelength. The interplay of these three phenomena drives to a larger ablation rate and smaller threshold fluence for the visible than for infrared laser pulses. The enhancement of absorptivity of the produced plasma with increasing the laser wavelength relate with the dependence of the plasma coefficient ($\alpha_{IB}$) on the wavelength ($\lambda$) is showed in equation (1), implies that the attenuation of the incoming laser beam into the ignited plasma-plume via the inverse-Bremsstrahlung effect is significantly stronger in longer wavelengths [11].

$$\alpha_{IB} \approx \lambda^3$$  \hspace{1cm} (1)

In our case, we wanted to observe the effect of laser wavelength (1064, 532 and 355 nm) on plasma spectrum for material analysis of three pure metals: Al, Cu and CuZn. When laser interacts with materials, the plasma is generated and the plasma spectrum are collected and analyzed by HR 2000 spectrometer from Ocean Optics. We used the standard table from MIT to analyze the emission spectrum of metals. The Al analysis result is shown in figure 2, the result of analysis Cu is shown in figure 3 and the result of analysis CuZn is shown in figure 4.

![Figure 2](image-url) 

**Figure 2.** The emission spectrum of Al generated by three different wavelengths (a) 355 nm, (b) 532 nm and (c) 1064 nm, in vacuum condition (5 Torr) and laser energy 12 mJ.

### Table 1. Thermal and physical constants of the metals used in this work$^a$

| Element | $T_b$ (K) | $T_f$ (K) | $\rho$ (g cm$^{-3}$) | $L_v$ (J g$^{-1}$) | $L_f$ (J g$^{-1}$) | $C_p$ (J K$^{-1}$ kg$^{-1}$) | $K$ (W m$^{-1}$ K$^{-1}$) | $\alpha$ (cm$^2$ s$^{-1}$) |
|---------|-----------|-----------|----------------------|-------------------|-------------------|--------------------------|--------------------------|-----------------|
| Al      | 2740      | 933       | 2.70                 | 10800             | 388               | 900                      | 237                      | 0.97            |
| Cu      | 2840      | 1356      | 8.96                 | 4796              | 205               | 385                      | 401                      | 1.16            |
| Zn      | 1180      | 692       | 7.14                 | 1748              | 111               | 388                      | 116                      | 0.41            |

$^a$ $T_b$, boiling point; $T_f$, melting point; $\rho$, density; $L_v$, latent heat of evaporation; $L_f$, latent heat of fusion; $C_p$, specific heat; $K$, thermal conductivity; $\alpha$, thermal diffusivity
Figure 3. The emission spectrum of Cu generated by three different wavelengths (a) 355 nm, (b) 532 nm and (c) 1064 nm, in vacuum condition (5 Torr) and laser energy 12 mJ.

Figure 4. The emission spectrum of CuZn generated by three different wavelengths (a) 355 nm, (b) 532 nm and (c) 1064 nm, in vacuum condition (5 Torr) and laser energy 12 mJ.

Figure 2 shows that different emission spectrum of Al ablated by three different laser wavelengths. The same result is also shown in figure 3 for Cu and in figure 4 for CuZn. Al metal excited by 355 nm, 532 nm and 1064 nm wavelength generated 5, 2 and 13 Al emission peaks, respectively. While the analysis of Cu showed 5, 7 and 6 emission peaks upon excitation by 355 nm, 532 nm and 1064 nm wavelength, respectively. Finally, CuZn metal produced 7 Cu lines and 2 Zn lines upon excitation by 355 nm wavelength, 8 Cu lines and 1 Zn line when excited by 532 nm wavelength, and 8 Cu lines and 3 Zn lines when excited by 1064 nm wavelength. The number of detectable elements peaks depends on the ablation wavelength as predicted by equation 1. Emission spectrum of Al, Cu and CuZn ablated using 1064 nm wavelength yield the most number of element peaks. However, our results do not show cubic dependency between element peaks and wavelength as predicted by equation 1. It is believed that our fiber-optic spectrometer was not sensitive enough to detect and differentiate element peaks due to two reasons. First, some element peaks are similar to the noise level, i.e., high signal-to-noise ratio. Second, the resolution of our spectrometer is limited to differentiate two coinciding peaks. Nevertheless, this results show the trend of wavelength influence.

The emission spectrum of Al, Cu and CuZn generated by three different wavelengths in figure 2, 3 and 4 are the optical emissions from the relaxation of excited species within plasma, which provides information regarding the composition of the material. Therefore, spectroscopic analysis of the optical emission from the excited species is able to identify and reveal pure elements in the material. A spectral line emission occurs when a bound electron in an excited state relaxes to a lower energy state, emitting
photons of a specific wavelength in the process. The continuum emission is caused by free-free transitions (also called ‘Bremsstrahlung’ radiation) and free-bound transitions (also called recombination radiation).

The influence of wavelength on emission spectrum is briefly described as follow. A previous study revealed that there is a correlation between the fluence of wavelength and plasma threshold in different metals [13]. The initiation of plasma over the target surface begins in hot vapor and the plasma is generated by inverse Bremsstrahlung absorption during collisions among sampled atoms and ions, electrons and gas species. In the case of metal sample, generation of initial electrons, which promotes the plasma process, is produced by a thermal ionization mechanism. It is known that metals have a low ionization potential, high absorption coefficient and high electron number density. Using short laser pulses, which have small thermal diffusion into the material, the generated vapor is rapidly ionized [6]. Consequently, the laser induced breakdown occurs easily. Previous study also revealed that the cascade-like growth of the electron number density is considerably more favorable in the IR than in the UV [13]. Another study reported that the \( F_{th} \) in the case of infrared pulse laser is twice as large as \( F_{th} \) corresponding to the visible pulse laser [14]. In this work, although we could not show calculation of ablation rate and threshold value, we have clearly showed the influence of spectra emission due to ablation wavelength.

4. Conclusion
The analysis of Al, Cu and CuZn has been done by means of LIPS system. The different ablation wavelengths (1064, 532 and 355 nm) of nanosecond laser were used in this experiment. The results show that wavelength 1064 nm produced the most emission peaks spectra. This phenomenon is influenced by properties of sample material, laser fluence and laser wavelength. Further observations and experiments can be done further if we want to know and learn about the accuracy of the material analysis. If we are able to observe the environmental effects of laser, energy laser and the relationship about the ablation threshold fluence, ablation rate, the impact of the laser spot diameter and with plasma formation, we hope we can explain this phenomenon more detail.

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