Spectroscopic Study of Copper Plasma Produced by Nd: YAG Laser from The Nano and Bulk Copper Targets

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Abstract. In this paper, plasma is generated from the nano and bulk copper targets by using Nd:YAG laser with a wavelength of 1064 nm, frequency of 6 Hz and pulse duration 9 ns at atmospheric pressure. The Boltzmann plot method was used to calculate the temperature of electrons and the Stark broadening method to calculate the density of electrons in a laser-generated plasma. It was observed that increased in the laser energy from 500 to 800 mJ leads to increased the temperature of electrons from 1.8 to 2.5 eV and increased the electrons density from 3.65×10¹⁶ to 4.29×10¹⁶ cm⁻³ for nano copper plasma while increased the temperature of electrons from 1.2 to 2 eV and increased the electrons density from 2.28×10¹⁶ to 3.24×10¹⁶ cm⁻³ for the bulk copper plasma.

1. Introduction
Laser Induced Breakdown Spectroscopy (LIBS) is a powerful analytical tool that can be used in many applications [1]. When a high-energy laser pulse is focused on the target surface, the laser pulse will excite and ionize target surface atoms and generate plasma. The spectral study of the lines emitted from the plasma formed on the target surface will provide much information about the target [2]. The generated plasma depends on the properties of the laser (wavelength, energy, etc.), the properties of the material (chemical and physical), and the properties of the surrounding (gas type, pressure) [3]. The LIBS technique is one of the methods for atomic emission spectroscopic. LIBS technology has the ability to perform analyzes in laboratories or in the field. The LIBS technology provides a quick analysis, there is no sample preparation or sample destruction, easy and simplicity of installing the technology and all types of samples can be analyzed (solids, liquids and gases) [4]. LIBS is an analytical technique used to analyze and quantify elements for a wide range of materials. One of the most important applications of LIBS is the analysis of solids, food, soil and sediments. LIBS is also used in industrial processes, biomedical, medical materials, the environment, and there are other applications [5]. Researchers have tried to improve LIBS technology since its discovery, as they have recently used nanomaterials due to their unique properties [6]. Nanomaterials can be described as a wide group of material that contains particles with at least one dimension that is less than 100 nanometers. Nanomaterials have unique properties because the large surface area and nanoscale size that do not exist for the same material when they are bulk [7]. In this research, the optical properties of copper plasma generated from Nd: YAG laser with a wavelength of 1064 nm from the nano and bulk copper targets were studied. The observed spectral lines were used from copper atomic lines and extracted from them the temperature and
density of electrons. The Boltzmann plot and Stark broadening methods were used to obtain the temperature and electrons density.

2. Experimental Setup
The experiment system is shown in Figure (1). Use Nd:YAG (1064 nm) type pulsed laser with a pulse duration of 9 ns and a frequency of 6 Hz that can deliver energy from 500 to 800 mJ. The laser beam is focused on the nano and bulk copper target at atmospheric pressure by using a focal length 10 cm lens. The target is placed on a stage that can be manually rotated. To prevent the breakdown of the air surrounding the target, the distance between the lens and the target is less than the focal length of the laser lens used. The spectrum emitted from the plasma is collected by optical fiber which is connected to the (S3000-UV-NIR) model spectrometer. The copper target was used as nano and bulk materials. Copper nanoparticle powder was purchased from (Nanjing Nano Technology LTD) Company, with an average size of (10-30 nm) with a 99.9% purity. The copper nanoparticle was pressed into pellet form with a pressure of 10 ton/cm² for 10 minutes at room temperature. The diameter of the pellet is 16 mm and 5 mm thick. The bulk copper was in the form of a plate with dimensions (0.5 × 15 × 25 mm³). Bulk copper was polished with washed by 96% purity ethyl alcohol and dried before using at room temperature.

3. Result and Discussion
3.1 The Emission Spectrum
The emission spectra of the laser generated copper plasma were recorded with energy (500-800 mJ). Where the laser beams are focused perpendicular to the surface of the copper target. The emission spectrum of the copper plasma generated is recorded by the spectroscopy covering the visible region (350-750 nm). Five strong spectral lines of copper atoms (Cu) were observed in this region. These spectral lines are 465.11, 510.55, 515.32, 521.82 and 578.21 nm. The results from plasma spectra reported by Kumar in various ambients are consistent with the experimental data obtained for
the copper targets here [8]. Figures (2) and (3) show the effect of laser energy change on the intensity of the spectral lines emitted from the nano and bulk copper plasma. Where it was observed that increasing the laser energy increases the intensity of the spectral lines for the copper plasma and it is also noted that the intensity of the spectral lines for the nano copper plasma is greater than the intensity of the spectral lines for the bulk copper plasma at the same laser energy.

Figure 2. Spectrum of nano copper plasma emissions generated by a laser with energies (500,600,700 and 800 mJ).

Figure 3. Spectrum of bulk copper plasma emissions generated by a laser with energies (500,600,700 and 800 mJ).
3.2 Determination of electrons temperature

One of the most important properties of plasma is temperature. When the laser beam interacts with the target surface, the stable atoms possess very high energy. This high energy causes the bonds of atoms to break, freeing electrons and ions, which generates plasma. The plasma temperature is determined using the Boltzmann plot method using the spectral intensities emitted from the plasma. The following relationship is used to calculate the plasma temperature.

\[
\ln \left( \frac{I_{Ki}}{A_{Ki}g_k} \right) = \ln \left( \frac{N(T)}{U(T)} \right) - \frac{E_k}{kT_e}
\]

Where \(I_{Ki}\) is the intensity resulting from the transfer of the electron from the high level (K) to the low level (i), \(\lambda_{ki}\) is the wavelength of the transmission, \(A_{Ki}\) is the Probability of transition, the \(g_k\) statistical weight of the high level (K), \(N(T)\) is the total number density and \(U(T)\) is the partition function. The plot of \(\ln(\lambda_{ki} I_{Ki}/A_{Ki} g_k)\) with \(E_k\) energy gives a straight line with a slope equal to \((-1/kT_e)\) and thus the plasma temperature \(T_e\) can be determined from this slope where \(K\) is Boltzmann constant [9]. Spectral parameters such as wavelength, statistical weight, Probability of transition, transmission probability and energy of high level are listed in Table (1) and taken from Source [10] and NIST Database [11]. Figure (4) shows a Boltzmann plot for calculating the temperature of the nano and bulk copper targets. For all fitting lines of Boltzmann plot, the R\(^2\) was shown in Figure (4). R\(^2\) represents a statistical coefficient that indicates the goodness of the linear fit. R\(^2\) takes between (0, 1) and best value for R\(^2\) when approaching one [12]. When the laser energy increases from 500 to 800 mJ, it is found that in the case of the nano copper plasma, the temperature increases from 1.09 to 1.13 eV. As for the bulk copper plasma from 0.99 to 1.07 eV. Figure (5) shows the relationship between laser energy and the temperature of the nano and bulk copper plasma, as the increase in laser energy leads to an increase in the temperature of the nano and bulk copper plasma and also shows the temperature of the nano copper plasma higher than the bulk copper plasma temperature at the same laser energy.

| Table 1. The zinc I lines spectroscopic parameters for electron temperature determination. |
|---------------------------------------------|-----------------|-----------------|-----------------|
| Wavelength \(\lambda\) (nm)               | Statistical weight \(g\) | Transition probability \(A(s^{-1})\) | Energy of upper state \(E\) (eV) |
|---------------------------------------------|-----------------|-----------------|-----------------|
| 465.11                                      | 8               | 3.80E+07         | 7.74            |
| 510.55                                      | 4               | 2.00E+06         | 3.817           |
| 515.32                                      | 4               | 6.00E+07         | 6.191           |
| 521.82                                      | 6               | 7.50E+07         | 6.192           |
| 578.21                                      | 2               | 1.65E+07         | 3.786           |
Figure 4. The Boltzmann plot with best straight line fit for nano copper target (red color) and bulk copper target (blue color).
3.3 Determination of the electrons density

It is important to know the density of electrons to study the plasma generated by the LIBS method. One of the most important and reliable methods for determining the density of electrons is the Stark broadening method for the atomic spectral line emitted by the target material. The density of electrons \( N_e \) is calculated by knowing the full width at half maximum (FWHM) of the Stark broadening line \( \Delta \lambda_{1/2} \) and compensation in the following relationship [13]:

\[
\Delta \lambda_{1/2} = 2\omega \left( \frac{N_e}{10^{16}} \right) + 3.5A \sqrt{\left( \frac{N_e}{10^{16}} \right)} \left[ 1 - \frac{2}{4} N_D^{-1/3} \right] \omega \left( \frac{N_e}{10^{16}} \right) \tag{2}
\]

where \( \Delta \lambda_{1/2} \) is the Stark broadening, \( \omega \) is a parameter of electron impact width, \( A \) is the parameter of ion broadening and \( N_D \) is the particles number in Debye sphere. The first part of equation (2) indicates the broadening as a result of the contribution of the electron while the second part indicates the broadening as a result of the ion contribution and the contribution of the ion the broadening is small and can be neglected [14]. Equation (2) becomes as follows:

\[
\Delta \lambda_{1/2} = 2\omega \left( \frac{N_e}{10^{16}} \right) \tag{3}
\]

Where \( \omega \) is a value of 0.02 nm and can be obtained from the source [15]. The wavelength 521.82 nm of the copper atom (Cu I) observed from the plasma generated from the nano and bulk copper targets were used. Figures (6) and (7) represents the line for the copper atom and the use of Lorentz’s fit to extract value \( \Delta \lambda_{1/2} \) from it and replace this value in equation (2) to calculate the density of electrons from the chosen spectral line. Figure (8) represents the relationship of electron density to the nano and bulk copper with changing laser energy. The electrons density of nano copper plasma increases from 3.65x10^{16} to 4.29x10^{16} cm^{-3} as the laser energy increases from 500 to 800 mJ. As for the bulk copper plasma, the electrons density increases from 2.28x10^{16} to 3.24x10^{16} cm^{-3} when the laser energy increases from 500 to 800 mJ.
Figure 6. Represents the Lorentz fitting process for the spectral line of nano copper plasma at wavelength ($\lambda = 521.82$ nm) with different laser energies.

Figure 7. Represents the Lorentz fitting process for the spectral line of bulk copper plasma at wavelength ($\lambda = 521.82$ nm) with different laser energies.
4. Conclusion
In this paper, the Nd:YAG pulse laser at a wavelength (1064 nm) was used to study the plasma produced from nano and bulk copper targets. The electrons temperature is determined by the Boltzmann plot method, while the electrons density is determined by the Stark broadening method. It is found that the temperature of the electrons in the plasma increases with the increase in the laser energy because the electrons obtain high kinetic energy when they absorb high energy photons. It is also noted that the temperature of the plasma of nano copper target is greater than the plasma of bulk copper target at the same laser energy and the reason for this is the increase in the depth of penetration of the laser energy of the nanomaterials and the large surface area of these materials, which allows for the transfer of more energy within the nanomaterial and the higher temperature of the plasma formed from it. In addition, also observed Increasing laser radiance generates more exciting species such as ions and free electrons, which increases the electrons density in copper plasma. It is noticed at the same laser energy that the electrons density of the nano copper target is greater than of the bulk copper target due to the quantum mechanical behavior of the nanomaterials.

Figure 8. The variation electron number density with laser energies (500,600,700,800 mJ) for nano copper target (red color) and bulk copper target (blue color).
5. References

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