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Spectroscopic Diagnostics of Laser-Induced Silver Plasma Using LIBS at Different Laser Energies

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Abstract: Laser-induced breakdown spectroscopy (LIBS) has been used to investigate the plasma generated from a silver target by the Nd:YAG laser system at a wavelength of 1064 nm. The plasma was produced at different laser pulse energies (500, 600, 700, and 800 mJ) to study the effect of laser energy on plasma parameters. The electron temperature (Te) was determined using the Boltzmann plot method, while the electron density (ne) was calculated using Stark broadening of the spectral lines. Moreover, other plasma parameters such as plasma frequency (f_p), Debye length (λ_D), and Debye number (N_D) have been evaluated. The results showed that the electron density increased from 3.11×10^{17} cm^{-3} to 5.32×10^{17} cm^{-3} with increasing laser energy, while the electron temperature increased from 0.64 eV at 500 mJ to 0.84 eV at 800 mJ. The plasma frequency also increased from 5.01×10^{12} Hz to 6.55×10^{12} Hz, whereas the Debye length decreased from 3.37×10^{-7} cm to 3.06×10^{-7} cm. The Debye number (ND) was greater than unity, confirming that the generated plasma satisfies the basic conditions of a stable ionized plasma. These results indicate that increasing laser energy significantly influences excitation, ionization processes, and overall plasma characteristics.

Keywords: LIBS, Ag plasma, Stark broadening, plasma parameters, Laser-induced plasma.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a versatile spectroscopic technique that analyzes the spectral emission from laser-generated plasma, resulting in the rapid detection of the elements of matter. Recent literature has increased the application of LIBS in many research works [1] as it is very fast and can be used to conduct tests without having to move the sample. The effectiveness of this technique depends on several factors such as the wavelength of the laser, the number of pulses, pulse repetition rate and energy. The principle of operation can be seen as the repair of the sample, followed by irradiation with a laser of a certain energy level. This process takes out a small portion of the sample and produces a hotter plasma [2,3]. Plasma usually consists of ions and electrons. It is the collision of these ions that causes them to achieve a high energy level which is then dropped back to a lower energy level to cause the production of certain radiation. The light emitted is then imaged using a spectrometer to analyze its components and concentration [4]. The particularities of silver nanoparticles have made them essential and very relevant in studies and research as they are applicable to a wide range of fields and applications, including biological

applications and drug delivery [5], optics, and medicine [6]. The use of silver nanoparticles has also been widely felt in day-to-day life, including coating most of the surfaces of household appliances and equipment, because of their antibacterial effect and the capability to prevent the growth of fungi [7]. One of the key techniques that may be used to investigate the impact of lasers on plasma during the process of ablation is LIBS technology, which will help in enhancing the properties of the photoemission [8].
Past research studies have revealed that silver nanoparticles are antibacterial because of their large total surface area and nano capacity, since nanoparticles are more effective in killing bacteria than the larger nanoparticles, thus making them indispensable in biological applications. [9]. Rajaa N. Ketan, Muayyed J. Zoory, and others have demonstrated that pulse-coupled analysis and uncalibrated analysis are among the most important factors upon which LIBS technology depends [10]. As Wisam D. Jalal, Mohanad A. Aswad, and others have shown, LIBS is one of the most important technologies in medicine. They used LIBS and other techniques to study children's teeth using an Nd-YAG laser with a wavelength of 1064 nm and a specific energy to record the emission spectrum. They proved that LIBS is more accurate and comprehensive than other techniques for practical and academic dental applications [11].

The elemental composition and emission lines of silver plasmas produced by laser ablation at various energies (500,600,700,800mJ) help to evaluate the parameters and behavior of the plasmas, including density and temperature of the electrons, which are important aspects of successful analysis. The spectroscopic characterization is aimed at measuring the spectrum emitted to identify silver atoms and ions, to study the excitation mechanism of plasma, and the influence of the laser on the material and its effects on the formation of plasma. The value of this characterization is that it exhibits high analysis speed, enhanced laser properties, and the synthesis of nanoparticles, which are useful in the biological domain.

Even though LIBS has been widely used in plasma diagnostics, little is known systematically on the silver plasma produced at relatively high laser energies. In this study, the plasma properties of silver were studied in the range of laser energy of 500-800 MJ with LIBS. The research aims at measuring the most important plasma parameters, including electron temperature, electron density, plasma frequency, Debye length, and Debye number. The results obtained give a better picture about the impact of the laser energy on the behavior of the plasma and its spectroscopic characteristics.

2. Materials and Methods

Figure 1 presents the schematic diagram of the experimental setup used for LIBS plasma generation. A Q-switched Nd:YAG laser operating at a wavelength of 1064 nm was used to generate plasma. The laser beam was focused perpendicularly onto a high-purity silver target (Ag, 99.99%). The silver sample had an approximate thickness of 1 mm and was carefully cleaned prior to the experiment to remove any surface contamination. The target was mounted on a fixed holder, and the distance between the focusing lens and the sample surface was maintained at approximately 10 cm. Plasma was generated using different laser pulse energies of 500, 600, 700, and 800 mJ, while the number of laser pulses was kept constant at 300 pulses for all measurements.

At the point of interaction between the laser beam and the silver surface, the rapid heating and ablation processes took place, which resulted in the appearance of the high temperature plasma plume consisting of excited atoms, ions, and free electrons. An optical fiber probe has been placed at a proper angle to the plasma to prevent exposure to the laser beam to gather the optical emission of the plasma plume.

The emission obtained was passed to a spectrometer that was linked to a computer to acquire spectral data and analyze it. The emission spectra, which indicated the association between the intensity of emission and wavelength, were demonstrated on the spectrometer, and the achieved spectra were analyzed with the aid of special analysis software. The spectrometer had a wavelength error of about 0.02 nm. According to the spectral resolution and the procedures that were applied during the analysis of the Boltzmann plot and Stark broadening, the error of the determined plasma parameters was determined to be approximately 5 percent.

The laser pulse energies (500-800 mJ) selected were to make sure that there would be enough plasma formation and high emission intensity that could be analyzed using spectroscopy. At lower energies, the plasma emission can be weak and unstable, and consequently, the measurement of plasma parameters (e.g., electron temperature, electron density) is less precise. Thus, comparatively large laser energies have been utilized in the given study to increase the ablation efficiency, the population of additional exciting species in the plasma plume and achieve emission lines with sufficient strength to permit a more stringent spectroscopic diagnostic.

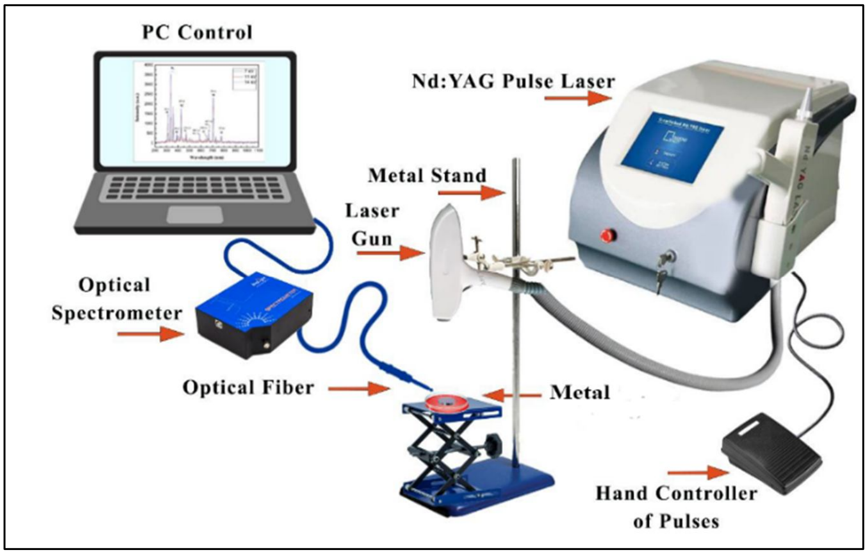

Fig. 1: Schematic diagram of the LIBS experimental setup using an Nd:YAG laser (1064 nm) [12].

2.1. Plasma Parameters Calculation

The plasma parameters have been calculated from the emission spectra using several well-known spectroscopic relations. The electron temperature (Te) was determined using the Boltzmann plot method according to the following relation [13]:

$$\ln\left[\frac{\lambda_{ji} I_{ji}}{hcA_{ji} g_j}\right] = \frac{1}{k_B T}(E_j) + \ln\left[\frac{N}{U(T)}\right] \quad (1)$$

where Iji is the emission line intensity, lambda_ji is the wavelength of the spectral line, Aji is the transition probability, gj is the statistical weight of the upper level, h is Planck's constant, c is the speed of light, Ej is the upper energy level, kB is the Boltzmann constant, Te is the electron temperature, N is the total number density of emitting species, and U(T) is the partition function.

The electron density (ne) was calculated using the Stark broadening method according to [13]:

$$n_e = \left(\frac{\Delta\lambda_{FWHM}}{2w}\right) N_r \quad (2)$$

where $\Delta\lambda_{FWHM}$ is the full width at half maximum of the spectral line, w is the Stark broadening parameter, and Nr is the reference electron density.

The plasma frequency was calculated using [13]:

$$f_p = \sqrt{\frac{e^2 n_e}{\varepsilon_0 m_e}} \quad (4)$$

Where e is the electron charge, ε0 is the permittivity of free space, and me is the electron mass.
The Debye length was calculated from [14]:

$$N_D = \frac{4}{3}\pi n_e \lambda_D^3 \quad (5)$$

3. Result and discussion

Figure (2) represents the emission spectra of silver plasma generated using LIBS technology at different energies ranging from (500 to 800mJ). The figure represents the relationship between emission intensity and wavelength, which ranges from (200 to 800 nm). The visible lines represent sharp peaks belonging to silver atoms and ions resulting from electronic transitions between different energy levels. It was found that the emission intensity is affected by changing laser energy, as increasing the laser energy leads to an increase in emission intensity (the emission intensity at (800mJ) was observed to be higher than at (500mJ). This is because the increased energy leads to increased evaporation of the material from the sample surface and the generation of a hotter plasma, in addition to increased electronic transitions between silver atoms and ions. It was also found that the positions of the spectral peaks did not change despite the change in laser energy; only the intensity of the radiation changed.

This promotes the production of a more stable plasma in terms of elemental composition, in addition to the fact that silver is a pure element without any additional impurities. These results are coherent with the changes in Figure 3, which shows the relationship between the electron density ne measured in ($\times 10^{17}$ cm^{-3}) and the electron temperature Te measured in (eV). It was observed that the density and temperature of electrons are directly proportional to the change in laser energy; there is a direct relationship between the emission intensity and the temperature and density of electrons, and this proves that the properties of the plasma depend on the laser energy. This is one of the features that indicates an improvement in plasma properties, in addition to its suitability for spectral diagnosis**.**

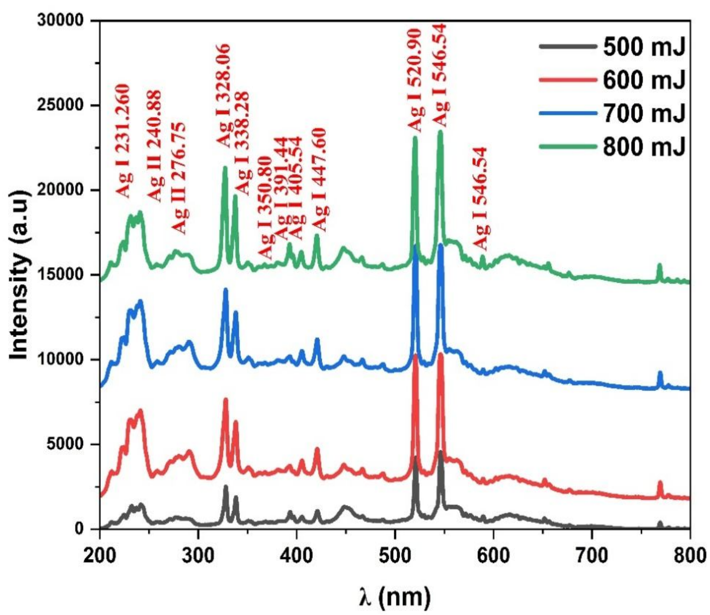

Fig. 2 Emission spectra of Ag plasma at different laser energy.

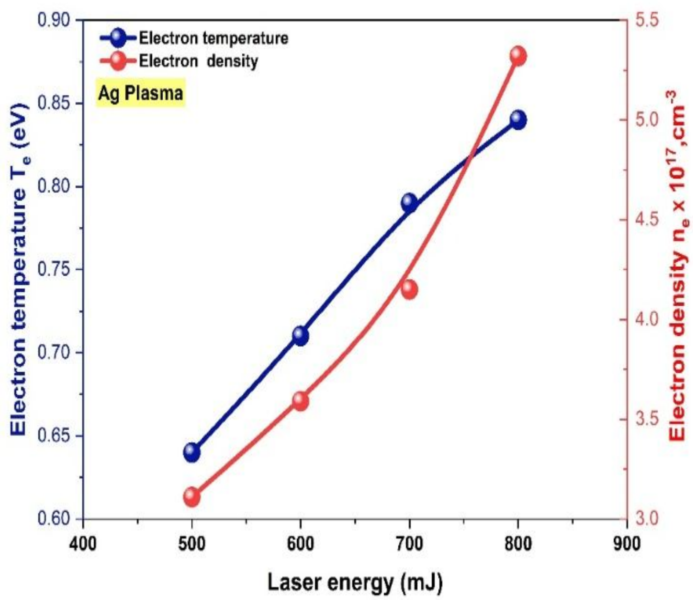

Fig. 3 The relationship between electron density and temperature at different laser energies.

Figure 4 illustrates the Boltzmann chart of silver plasma with a varying laser energy (500, 600, 700, and 800 mJ). The electron temperature was determined using these plots using the intensities of the Ag spectral lines created by the emission. The logarithmic function ln (I ln /Ag) is plotted against the vertical axis, and the maximum energy level of the transition is plotted against the horizontal axis. There is a line and the slope of the line (slope = -1/kTe) is taken to determine the temperature of the electrons.

This is demonstrated in the results that the electron temperature rises with the increase of laser energy, with maximum and minimum values at 800 mJ and 500 mJ. The increased value of the R 2 (>0.90) is a good fit linear and it shows that the plasma meets the LTE condition. Such findings indicate that the higher the laser energy, the higher the plasma excitation and ionization increases the emission intensity,
as indicated by the spectra in Figure 2.

Figure 5 shows the Stark Broadening of the silver (Ag I) spectral line, centered approximately at a wavelength of 547 nm, at multiple energies ranging from (500 to 800mJ). It shows that the penetrating intensity is proportional to laser energy (increasing the laser energy leads to a rise in the number of free electrons, a rise in the amount of ionized material, a rise in the spectral peak intensity, and an increase in the full width at half maximum (FWHM).

This peak has been used to calculate the electron charge because the broadening of the line indicates an increase in electron density. It was observed that at 500mJ, the FWHM is narrow, indicating weak plasma ionization, while at 800mJ, the FWHM, or Stark broadening, is wide, demonstrating strong plasma ionization. This proves that laser energy has a clear effect on the Stark effect due to collisions between ions and electrons of the silver element, resulting in a high-density plasma [14].

To verify the validity of the local thermodynamic equilibrium (LTE) condition in the plasma, the McWhirter criterion was applied. According to the McWhirter criterion, the electron density must satisfy the following conditions:

$$n_e \geq 1.6 \times 10^{12} T_e^{\frac{1}{2}} (\Delta E)^3 \text{cm}^{-3}$$

where T is the temperature of the electrons (in eV), and 0 is the difference in the energy of the relevant energy levels (in eV).

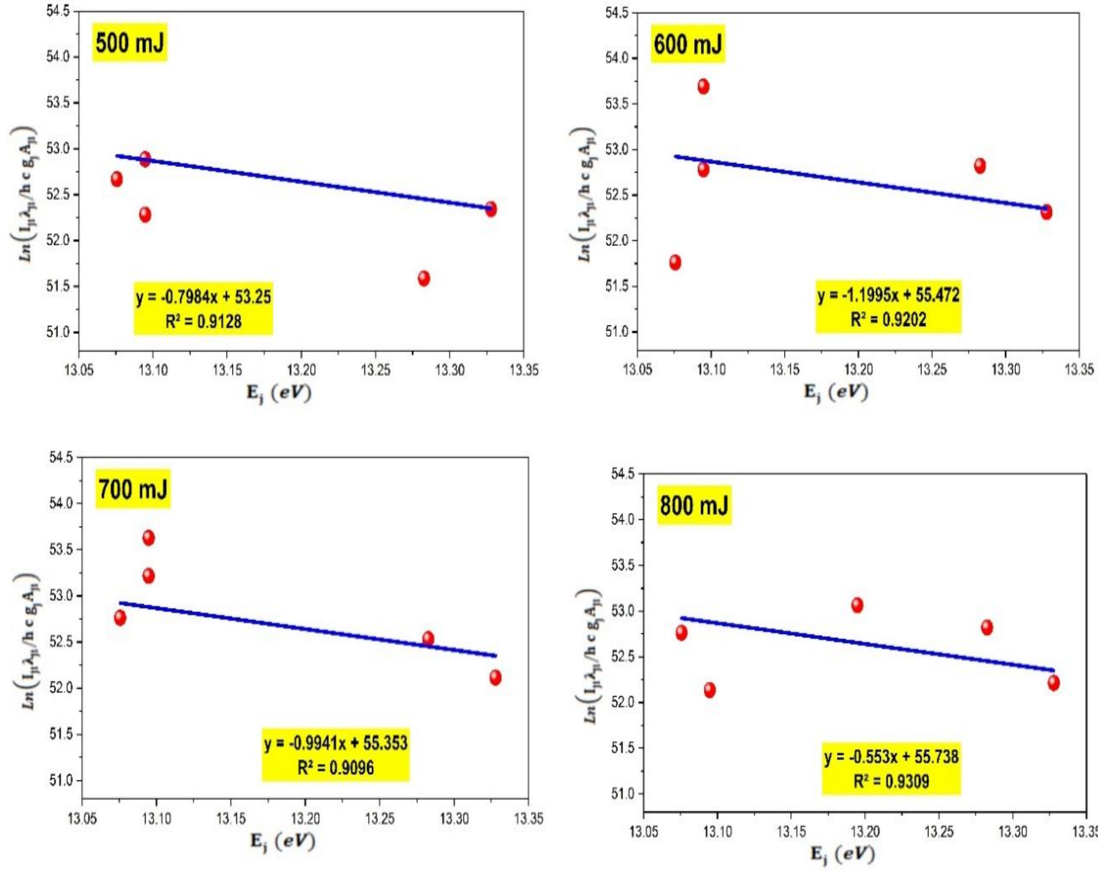

Fig. 4 Boltzmann plots of Ag plasma at different laser energies (500–800 mJ) used to determine the electron temperature (Te).

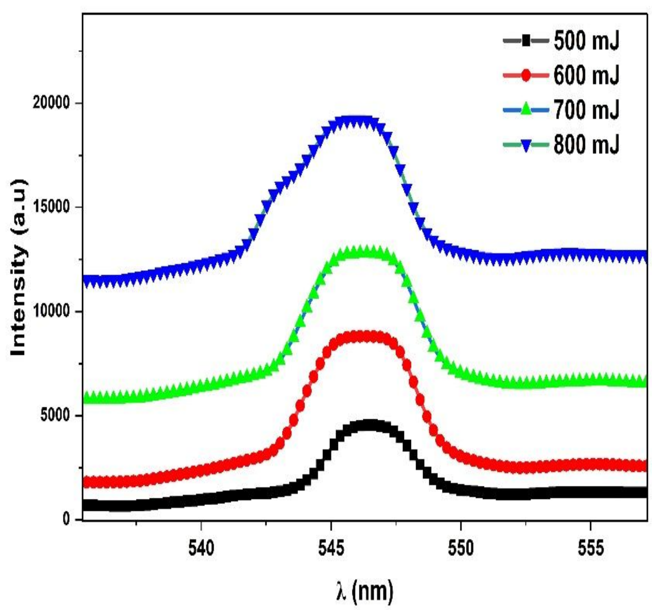

Fig. 5 Stark Broadening of the Ag spectrum

This study determined the minimum electron density necessary to satisfy the LTE condition using the obtained parameters of the plasma and found that the value was quite lower than the experimental values of electron densities. The McWhirter criterion is easily fulfilled since the values of the measured electron density are of the order of 10^{17} cm^{-3}. Thus, it may be concluded that the plasma produced in this experiment may be in the local thermodynamic equilibrium.

Table 1 summarizes the main plasma parameters of silver plasma, including electron temperature (Te), electron density (ne), plasma frequency (fp), Debye length (λD), and Debye number (Nd), and their dependence on laser energy. It can be observed that the electron temperature increases from 0.64 eV at 500 mJ to 0.84 eV at 800 mJ. Similarly, the electron density increases from 3.11×10^{17} cm^{-3} to 5.32×10^{17} cm^{-3} with increasing laser energy. This behavior is attributed to the higher laser energy, which enhances the ablation rate of the target material and increases the number of excited and ionized particles in the plasma plume. The plasma frequency (fp) also increases with increasing electron density, since the plasma frequency is proportional to the square root of electron density ($fp \propto \sqrt{ne}$). As the number of free electrons increases, the collective oscillation frequency of electrons in plasma increases accordingly.

On the other hand, the Debye length (λD) decreases gradually from 3.37×10^{-7} cm at 500 mJ to 3.06×10^{-7} cm at 800 mJ. The Debye length represents the characteristic shielding distance in plasma and depends on both electron temperature and electron density according to the relation $\lambda D \propto \sqrt{(Te / ne)}$. Therefore, the increase in electron density at higher laser energies leads to a reduction in the Debye length, indicating stronger electrostatic shielding and a more confined plasma environment. Moreover, with rising laser energy, the increase in Debye number (Nd) is caused by a rise in the electron density and a drop in Debye length. The values of Nd obtained are bigger than unity, which means the produced silver plasma meets the minimum plasma requirements and the behavior of a stable and well-ionized plasma.

Table 1. Laser-induced plasma parameters of Ag Plasma at different laser energy

E (mJ)	Te (eV)	ne (cm^{-3})*10^{17}	fp (Hz) *10^{12}	λD (cm) *10^{-7}	Nd*10^3
500	0.64	3.11	5.01	3.37	1.48
600	0.71	3.59	5.38	3.32	1.65
700	0.79	4.15	5.74	3.29	1.82
800	0.84	5.32	6.55	3.06	1.93

The uncertainty in the calculated plasma parameters mainly arises from the spectral measurement accuracy and the fitting procedures used in the Boltzmann plot and Stark broadening methods. The wavelength resolution of the spectrometer was approximately ±0.02 nm, which introduces a small uncertainty in determining the spectral line positions and widths. Consequently, the estimated uncertainty in the calculated electron temperature and electron density is about ±5%.

The practical applications of silver in (medical and biological) applications can also be related to the obtained plasma parameters. The antimicrobial activity of silver made it be popular in the application of antibacterial coating on medical devices, wounds, and antibacterial dressings. It is important to understand the plasma characteristics like the electron temperature and the electron density since these are the parameters that directly affect the ablation efficiency, ionization, and the silver species that form when the laser interacts with the material. Increased electron temperature and density show greater excitation of the plasma and better ablation of material which will be useful in increasing the control of silver particle formation and surface modification process. Thus, spectroscopic diagnostics introduced in the present paper will help to understand better the interaction of laser with silver that would facilitate optimization of laser-based procedures in the preparation of antimicrobial coatings, biomedical sensors, and silver-based nanomaterials. The parameters of plasma retrieved in the current research are affirmative of other LIBS studies carried out in the past. Subsequent rises in electron temperature and electron density under rising laser energy are consistent with the findings of studies done on the spectroscopic diagnostics of CuZn plasma produced by a Nd:YAG laser, in which both parameters increased substantially with laser pulse energy owing to greater laser–matter interaction and excitation interactions (Shaltout et al., 2010) [17]. Besides, the recent LIBS experiments on metallic targets proved that the more laser energy is used, the more plasma excitation is developed and, as a result, the higher the temperature of electrons and their density and the intensity of spectral emissions (Azam et al., 2025) [18]. Moreover, recent spectroscopic studies of laser-induced plasma in metallic materials observed electron densities of the order of 1017 cm -1 and demonstrated that the parameters of the plasma strongly depend on the laser energy and the conditions of the experiment (Abed et al., 2025) [19]. Thus, the findings made in the current research are well consistent with the already existing and published experimental research on laser-induced plasma diagnostics.

4. Conclusion

During this study, a sample of silver plasma has been prepared by irradiating the sample with multiple energies ranging from 500 to 800mJ and 300 pulses. The expansion of the silver emission line was observed due to the strong integration between electrons and ions in plasma, in addition to clear changes in plasma parameters. The Boltzmann diagram method was used to determine the electron heat (Te), and it was observed that Te is directly proportional to the laser energy, as the value of Te gradually increased with the increase in laser energy. Similarly, for the electron density (n_e), its value was shown to rise with a rise in laser energy, and it was characterized using the Stark Broadening method. The results showed that all plasma parameters increase with the increase in laser energy, and this is evidence of an increase in plasma density and the ablation rate with higher energies, in addition to an increase in plasma temperature and in coherence, except for the Debye length(λD), whose value decreases with the increase in energy, because the increase in density of electron leads to the proximity of the particles, and thus the expansion in the internal electric field decreases. The results obtained confirm that laser energy is a key factor in controlling the properties of the silver plasma, as increasing the energy leads to improved excitation and ionization within the plasma. In the Boltzmann diagram that used to calculate electron heat (T_e) from the slope of the straight lines, all diagrams showed that the value of R^2 is greater than 0.90, which confirms the fulfillment of the thermal equilibrium condition (LET) and the possibility of using the Boltzmann method to determine the electron heat.

Author Declaration

The authors declare that this work is original, has not been published before, and is not under consideration elsewhere. All authors approved the final manuscript.

Ethics Approval and Consent for Authors

This study does not involve humans or animals; therefore, ethical approval is not required.

Authors Contribution

Dalal Y. Sarhan performed the experiments and wrote the manuscript. Kadhim A. Aadim supervised the work and revised the manuscript. All authors approved the final version.

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التشخيص الطيفي لبلازما الفضة المحفزة بالليزر باستخدام تقنية التحليل الطيفي بالليزر عند طاقات ليزر مختلفة

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الخلاصة: في هذا العمل استخدمت تقنية التحليل الطيفي بالانهيار المستحث بالليزر (LIBS) لدراسة البلازما المتولدة من هدف فضة باستخدام ليزر Nd:YAG بطول موجي 1064 نانومتر. تم توليد البلازما عند طاقات ليزر مختلفة لدراسة تأثير طاقة الليزر في معاملات البلازما. حسبت درجة حرارة الإلكترون باستخدام طريقة مخطط بولتزمان، بينما حسبت كثافة الإلكترونات باستخدام اتساع ستارك لخطوط الطيف. كما تم تقييم بعض معاملات البلازما الأخرى مثل تردد البلازما وطول ديباي وعدد ديباي. أظهرت النتائج أن زيادة طاقة الليزر تؤدي إلى زيادة درجة حرارة الإلكترون وكثافة الإلكترونات وشدة الانبعاث الطيفي، في حين ينخفض طول ديباي مع زيادة كثافة البلازما. وتشير قيم عدد ديباي إلى أن البلازما المتولدة تحقق شروط البلازما المستقرة. تؤكد هذه النتائج أن طاقة الليزر تعد عاملا مهما في تحديد خصائص البلازما المتولدة من الفضة باستخدام تقنية LIBS.