Measurements and Calculations of parameters of Zinc Oxide Plasma Produced by Laser induced Breakdown Spectroscopy

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Abstract
In this work, the optical emission characteristics of the ZnO plasma were presented. The plasma parameters: electron temperature \(T_e\), electron density \(n_e\), plasma frequency \(f_p\) and Debye length \(\lambda_D\) were studied with a spectrometer that collects the spectrum ZnO plasma in air produced by Nd:YAG laser, \(\lambda=1064\,\text{nm}\) at ratio \(X=0.5\) in the range of energy of \((700-1000\,\text{mJ})\), duration \((10\,\text{ns})\). The Boltzmann plot method was employed to calculate the electron temperature \(T_e\), while the Stark broadening was used to determine the electron density \(n_e\), Debye duration \(\lambda_D\), and plasma frequency \(f_p\). \(T_e, n_e, \text{ and } f_p\) were found to increase with the increase of laser energy. In contrast, \(\lambda_D\) decreased with laser energy increase. The resulting electron temperature calculation value was \((1.908-2.084)\,\text{eV})\.

Keywords: Optical Emission Spectroscopy (OES), Laser-Induced Plasma Spectroscopy (LIPS), Zinc oxide (ZnO), Nd: YAG laser.
1. Introduction

An atomic emission spectroscopy technique that uses a high energy laser pulse to excite a specimen is known as Laser-Induced Breakdown Spectroscopy (LIBS). The impact of focused laser pulses on a target creates plasma plume [1]. Irradiance, wavelength and pulse duration of the laser, target composition, and atmospheric conditions all influence the characteristics of a plasma plume [2-4]. To evaporate and excite the analyze producing plasma, a pulsed laser source is used [5]. An ablation process occurs when the laser beam impact the target surface leading to quick ionization of the sample surface which produces the plasma. This happens in a short time frame compared with laser pulse period. The plasma, which expands isothermally, efficiently absorbs the laser energy [6-7]. For analysis of plasma, many diagnostic techniques such as optical emission, absorption, fluorescence, and resonance ionization spectroscopy are used [8-9]. The optical emission spectroscopy (OES) is a non-invasive, simple to use method and provides quick results. It is based on the recording of light emitted by the plasma [10]. Plasma particles are stimulated to higher electronic states as a result of collisions with electrons. Photons are emitted due to the relaxation of the excited particles to lower energy states [11].

Boltzmann plot method is the method utilized for spectral measurements. It depends on measuring the relative density for one line of the same element. Nevertheless, to apply the Boltzmann method to measure electron temperature, the level of excitement must be reached under local thermal equilibrium (LTE). The last allows the use of the traditional Boltzmann plot technique to calculate \( T_e \) using the following equation [12]:

\[
\ln \left( \frac{\lambda_{ji} I_{ji}}{\kappa_e A_{ji} g_j} \right) = \frac{1}{k_B T} (E_j) + \ln \left( \frac{N_i}{U(T)} \right) \quad \text{...........(1)}
\]

Where \( A_{ji} \) is a transition probability from upper level \( j \) to lower level \( i \), \( I_{ji} \) is the intensity of the spectral line corresponding to the transition from \( i \) to \( j \) levels, \( \lambda_{ji} \) is the wavelength of the emitted light, \( g_j \) a statistical weight of the \( j \) level, \( h \) is Planck constant, \( c \) is the speed of light, \( E_j \) energy of the upper level \( j \) (in electron volts), \( k_B \) is Boltzmann constant, \( N \) state population densities and \( U(T) \) is the partition function[13]. However, regarding the electron density, it can be determined by the Stark broadenning of an emission line or using the linear density ratio of different emissions for the same element [14]. Electron density can be determined using the Stark broadenning method (in \( \text{cm}^{-3} \)) [15]:

\[
n_e = \left( \frac{\Delta \lambda_{\text{FWHM}}}{2 \omega} \right) N_r \quad \text{........(2)}
\]

\( \omega \) A theoretical line full-width stark broadenning parameter, calculated at the same reference electron density \( N_r \approx 10^{17} \text{cm}^{-3} \). The responses of a charged particle (ions and electrons) for decrease impact of electric fields applied to it is called Debye shielding. This shielding granted quasi-neutrality particular property for plasma. A distance \( \lambda_D \), the Debye length, can be calculated from the following equation [16]:

\[
\lambda_D = \sqrt{\left( \frac{\varepsilon_0 k_B T_e}{n_e e^2} \right)} \quad \text{........(3)}
\]

Where \( \varepsilon_0 \) is the free-space permittivity, \( e \) is the electron charge, and \( T_e \) is the electron temperature. While the frequency of plasma is defined, any disturbance from quasi-neutral equilibrium in the plasma will create electric fields. This frequency, which only depends on the density of the plasma, is one of the most important plasma parameters. It is very high due to the small size of the electron mass \( m_e \). A plasma frequency is calculated from the given equation [17-18].
\[ f_p = \sqrt{\frac{e^2 n_e}{\varepsilon_0 m_e}} \] ............ (4)

Where \(\varepsilon_0\) is the permittivity of the free space; \(e\) is the electron charge, \(n_e\) is the density of the number, \(m_e\) is the mass of the electron. Also, the number of particles \((N_D)\) in a Debye sphere can be found using the equation [19].

\[ N_D = \frac{4}{3} \pi n_e \lambda_D^3 = 1.38 \times 10^6 \frac{T_e^{(2)}}{n_e^2} \] ............ (5)

This paper primary goal is the analysis of the optical emission of the ZnO plasma created by the fundamental harmonic of the Nd: YAG laser(1064 nm). The LIBS technique and the Boltzmann plot method were used to derive the electron temperature \((T_e)\). While, the Stark broadening parameter was used to calculate the electron number density \((n_e)\). In addition, the changes of temperature and number density of electrons with the increase of the laser energy were investigated.

2. The Specimen

Zinc Oxide Powder and its Pellet (99 percent purity) were provided by BDH chemicals Ltd Poole, -USA. Just a smidgeon of it, the samples were introduced as pressed pellets for LIBS analysis. Depending on the amount of material, pressing with a hydraulic press at 6 Pa for 10 minutes produced pellets of 20mm diameter and a thickness of 20 mm (usually 3gm weight was needed for a pellet of approximately 15 mm of thickness).

3. The Experimental Setup

In this experiment, the optical emission plasma spectra of ZnO target were recorded for different laser energies(700- 1000 mJ) using the experimental setup of laser-induced plasma spectroscopy (LIPS) shown in Figure 1 (a,b). It was made up of a pulsed Nd: YAG laser with a wavelength of 1064 nm, duration of 10 ns, and a frequency of 6 Hz pulse repetition. The laser beam was focused on the surface of the irradiated sample by a converging lens of 10cm focal length. An optical fibre carrying a photo-detector was rotated 45 degrees, with the beam path set at 5 cm from the plasma-generating sample. The optical emission spectrometer (OES) was utilized to calculate the results. The temperature of electrons, densities, and then plasma frequency and the Debye length and the Debye number were all calculated mathematically. The spectra emitted from ZnO plasma were studied with a spectrum analyser within a spectral range of (300-800) nm. The light emitted from the sample surface bombarded by a pulsed laser was analysed with a spectrometer(Surwit S3000-UV-NIR spectrometer).The results were analyzed and compared with data from the the National Institute of Standards and Technology (NIST) database [20].

![Figure 1- (a) The conventional LIBS system set-up (b)Photo of LIBS experiment](image-url)
4. Results and Discussions
The laser ablation process can be classified into three categories, evaporation of the target material, the interaction of the evaporated cloud with incident laser beam resulting in cloud heating, plasma formation, and expansion and rapid cooling of the plasma. Figure 2 shows the emission spectra of laser-induced ZnO plasma at X=0.5 percentage in air at a spectral range (300-800 nm) with different laser energies (700- 1000) mJ. It can be seen that the intensity of the peaks of ZnO plasma spectra increases with increased laser energy. This is due to the increase absorption of laser by the plasma. This result agrees with that of Hussain and Al-Razzaq [21].

Figure 2- Emission spectra of laser-induced ZnO plasma at X=0.5 with different laser energies.

Understanding the atomic ionization and excitation processes occurring inside the plasma requires knowledge of the plasma temperature and density of the plasma species. Boltzmann plot method was used to determine the electron temperature values as in Equation (1). Three peaks from the same atomic species and ionization process are required for the Boltzmann plot. These were chosen at (472.22 nm, 481.05 nm, and 636.23458 nm) for ZnI for a zinc oxide target.

Figure 3 shows the plots of \( \frac{\lambda_i \lambda_j}{hc} A_{ij} g_{ij} \) versus E for the different laser energy. These are straight lines each with a gradient of \( \frac{1}{K_B T} \). The plasma temperature can be calculated using several simultaneously measured emission lines. The fitting equations and all fitting lines \( R^2 \) values (\( R^2 \) is a coefficient of statistical indicating the quality of linearity) are given in the figure. \( R^2 \) value is closer to 1 in the better one.

As shown in Figure 3, the value of electron temperature ranged from 1.908 to 2.048 Evi as listed in Table 1. Electron temperature increased with the increase of the laser energy due to the increase in the mass-ablation rate. As the laser energy increases the heating of the material rises, the glow of the plasma increases, the kinetic energy increases, and thus the temperature of the electron increases due to the absorption of the laser energy by the plasma. This agrees with the results of Hamada et al.[22] and of Shaik et al. [23].
Collisions of charged species induce a sharp broadening of spectral lines in plasmas, resulting in broadening of the line which is related to electron density. The electron density ($n_e$) was determined using the Stark broadening method as in Equation 2. Figure 4 shows the Stark broadening at 472.22 nm line of Zn II which was used to determine the electron density. The electron density ranged from $4.98 \times 10^{17}$ to $6.036 \times 10^{17}$ cm$^{-3}$. The electron density increased with laser energy due to an increase in the mass ablation, also due to the increase of the temperature of the electron. This agrees with the results of Fikry et al. [24].
Figure 4-Stark broadening at 472.22 nm for ZnO plasma at various laser energies

Figure 5 shows that electron temperature and electron density increases with the increase of the laser pulse energy; this shows that the laser peak energy has a significant impact on the intensity of the emission lines in all metals. $T_e$ since the plasma becomes opaque to the laser beam shields the target when the peak energy is higher. It gets close to being stable. When the plasma reduces the laser peak power transmission along a beam path, this is known as plasma shielding [25].

Figure 5-Variation of ($T_e$) and ($n_e$) of ZnO plasma at different laser energies.

Other fundamental plasma parameters can be measured depending on the electron temperature and electron density; these parameters are plasma frequency and Debye length. The Debye length was calculated from Equation (3). Figure 6 displays the decrease of Debye length with the increase of laser energy.
The plasma frequency was calculated according to Equation (4). Figure 7 shows the variation of plasma frequency with laser energy. It can be seen that plasma frequency increases with laser energy due to the direct proportionality with electron density, as listed in Table 1.
Table 1-Plasma parameters for a pure (ZnO) with different laser energies.

<table>
<thead>
<tr>
<th>Laser energy (mJ)</th>
<th>$T_e$ (eV)</th>
<th>$n_e (\text{cm}^{-3}) \times 10^{17}$</th>
<th>$f_p (\text{Hz}) \times 10^{12}$</th>
<th>$\lambda_0 (\text{cm}) \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1.908</td>
<td>4.98</td>
<td>6.3</td>
<td>1.5</td>
</tr>
<tr>
<td>800</td>
<td>1.960</td>
<td>5.51</td>
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<tr>
<td>1000</td>
<td>2.048</td>
<td>6.036</td>
<td>7.0E</td>
<td>1.4</td>
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</tbody>
</table>

5. Conclusion
A Q-switched Nd: YAG laser with a wavelength of 1064 nm and with various energies (700 - 1000 mJ) was used to produce plasma ZnO. To establish the dependency of plasma parameters such as electron density and electron temperature, optical emission spectroscopic (OES) studies were conducted. The plasma parameters were calculated based on their relationship to the laser energy. The results showed that when laser energy in air increased, the values of $T_e$, $n_e$, and $f_p$ increased, but the values of $\lambda_0$ decreased. The rate of material ablation increases as the laser energy increases.

References


