SPECTROSCOPIC STUDY OF (TiO\textsubscript{2})\textsubscript{1-x}(CuO)\textsubscript{x} PLASMA GENERATED BY Nd:YAG LASER

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ABSTRACT
Laser-induced (TiO\textsubscript{2})\textsubscript{1-x}(CuO)\textsubscript{x} plasma, which is produced by laser. A pulse of Nd:YAG laser is supplied for duration 10 ns produce plasma from a planar (TiO\textsubscript{2})\textsubscript{1-x}(CuO)\textsubscript{x} sample placed in a vacuum having a pressure of 10\textsuperscript{-3} mbar. The temperature of the plasma electrons is calculated by the Boltzmann plot methodology from of Ti and Cu emission lines of singly ionized, and the density of plasma electron is calculated with the use of Stark broadened profiles. As well as the electron temperature is calculated within the values of (0.699 - 0.78 1) eV, and the density of electron is measured in the values of (34.7\times10\textsuperscript{18} - 50.5\times10\textsuperscript{18}) cm\textsuperscript{-3}.

Keywords: boltzmann plot, plasma diagnostic, optical emission spectroscopy.

1. INTRODUCTION
The knowledge about free electron number densities, Ion, atom and their temperatures is very essential to describe the laser-induced plasma (LIP) which is crucial for modeling and analytical objectives. The above parameters are usually determined indirectly through the assistance of optical emission measurements, under the hypotheses is that plasma in local thermodynamic equilibrium (LTE) [1, 2, 3, 4]. Laser-induced plasma can constitute from the interaction of high-power Nd:YAG laser with solid medium. The produced laser can be utilized in many fields for instance, the elemental analysis that is depend on atomic lines intensities. [13].

In this work, the method of Boltzmann plot is utilized in order to calculate the electron’s temperature \( T_e \) which is taken from the gradient of this method. By the same token, the peaks of this approach are very essential to calculate \( T_e \). These peaks can be obtained by the identical stage of ionization and the identical atomic species. However, the latter method is superior to the ratio method because the lines having greater optical thickness can be readily localized amongst the large deviation of the data points.

The line intensity of spectral is calculated by [14]:

\[
I_{ij} = \frac{hc}{\lambda_{ij}} \frac{n}{g_j} \frac{\varepsilon_i}{U(T)} e^{\frac{-\varepsilon_i}{kT}} \quad (1)
\]

where \( I_{ij} \) and \( \lambda_{ij} \) denote the intensity and wavelength that match the transition from \( i \) to \( j \) respectively, \( h \) is the Planck’s constant, \( c \) is the light of speed, \( n \) is the number density of emitting species, \( U(T) \) refers to partition function, \( A_{ij} \) means the transition probability between level \( i \) and \( j \). Boltzmann’s constant \( k \), excitation temperature \( T \), \( g_j \) stands for the statistical weight of upper energy level and \( E_j \) means upper energy level [14].

From equation (1), minor rearrangement yields:

\[
\frac{\lambda_{ij} I_{ij}}{hc \ A_{ij} g_i} = \frac{n}{U(T)} \frac{\varepsilon_i}{e^{\frac{-\varepsilon_i}{kT}}} e^{\frac{-\varepsilon_i}{kT}} \quad (2)
\]

From the above equation, getting the natural logarithm on both sides, the result will be:

\[
\ln \left( \frac{\lambda_{ij} I_{ij}}{hc \ A_{ij} g_i} \right) = -\frac{1}{kT} \varepsilon_j + \ln \left( \frac{N}{U(T)} \right) \quad (3)
\]

Equation (3) gives linear relationship when \( \ln \left( \frac{\lambda_{ij} I_{ij}}{hc \ A_{ij} g_i} \right) \) is plotted viruses \( E_j \) [14].

2. ELECTRON TEMPERATURE CALCULATION
All types of internal energy (vibrational, rotational and electronic) represent a single temperature in LTE plasmas, the temperatures of Boltzmann and LET depend on atomic lines intensities. [13].

In comparison to other numerous diagnostic techniques that recognizes other transient processes/occurrences, the optical emission spectroscopy (OES) has many advantages, such as obtaining information of the constituted elements, in addition of studying plasma expansion dynamics [7]. Normally, LIBS has the capacity to be utilized for the purpose of chemically describing the majority of the samples, which can include of metals, rocks, glasses, etc. The applications of LIBS “under gaseous condition” have shown considerable developed in the field of scientific research [8]. Showing a great capacity for development as a tool for space exploration, it is also considered as an accepted form of analysis in challenging applications[9]. In the case of high-speed practices, flow control process of laser-based has numerous merits with regards flow control applications [10]. In LIBS measurement, there are two main factors to explain laser-induced plasma: plasma temperature, as well as electron density. In terms of diagnostic techniques, temperature plasma can be clarified by integrated line intensities ratio, line intensity ratio to accompanying continuum, and the continuum spectrum shape [11,12].
3. ELECTRON DENSITY CALCULATION

The spectral line width and its final shape are influenced by numerous mechanisms such as of broadening types (natural, Doppler, Stark and instrumental). However, the Stark broadening which is related to the local electric fields developed by the adjacent particles which are charged, specially the electrons which are found in the vicinity of the emitting atoms, as a function of their density and energy is important and hence allows a more convenient manner to assess the density of the density of the electrons and the field strength. Hence, in plasma spectroscopy field, Stark broadening regarded as the single most important aspects of spectral line broadening which supplies the electron density with the known electron temperature of the plasma [15].

The density of the electron can be outlined by the equation:

\[ \ln n_e = 1.2 \ln(\Delta \lambda_{1/2}) + 44.2476 - 0.60 \ln(T_e) \]  
\[ T_e \] refers to the electron temperature in Kelvin, \( n_e \) refers to the electron number density in \( \text{cm}^{-3} \) [16].

\[ \Delta \lambda_{1/2} = 2\left[1 + 1.75\alpha (1 - 0.75r)\right]\omega \]  
\( \alpha \) is the ion broadening parameter in nanometers, \( r \) is the mean distance between ions divided by the Debye length [15].

4. DEBYE LENGTH MEASUREMENTS

Debye length is the measure of the penetration depth of the external electrostatic fields, i.e. of the thickness of the boundary sheath over which charge neutrality may not be maintained [17].

The Debye length \( \lambda_D \) can be calculated by the applied electrical potential and as shown in the following equation [16]:

\[ \lambda_D = \sqrt[1/2]{\frac{\varepsilon_0 k_B T_e}{n_e e^2}} \]  
where \( n_e \) is the density of the electrons \( \left( \text{m}^{-3} \right) \), \( \varepsilon_0 \) is permittivity of free space.

The foremost condition for the existence of plasma is the Debye length, which should be minute when compared to the system dimension (L) i.e. \( \lambda_D < < L \) [18].

5. DEBYE NUMBER \( N_D \) MEASUREMENT

An additional plasma parameter which has an association with the Debye length is the particles number \( (N_D) \) in a Debye sphere has a radius equal to \( \lambda_D \). When the Debye sphere includes many electrons, the effect shielding can form.

Depending on Debye sphere and number of electrons, it is easy to calculated Debye number as given in the following equation [19]:

\[ N_D = \frac{4}{2} \pi n_e \lambda_D^3 \]  

6. EXPERIMENTAL DETAILS

The pellets \( (\text{TiO}_2)_{1-x}(\text{CuO})_x \) has been prepared from Nano shell Company with a purity 99.99% and Copper oxide with purity 99.99% were mixed at different concentrations Copper oxide of \( (x= 0.0, 0.05, 0.1, 0.15, 0.2) \) Wt. %. Optical emission spectroscopy measurements are performed to obtain the electron temperature and electron number density of Plasma Generated by Laser- the pellets \( (\text{TiO}_2)_{1-x}(\text{CuO})_x \) interaction under the vacuum of \( (10^{-3}\text{mbar}) \), by PLD technique, Nd:YAG laser was utilized to deposited thin films from TiO\(_2\)-CuO. The characteristic features of Nd:YAG laser were \( (\lambda= 1064 \text{ nm}) \) SHG Q-switching laser beam at 800 mJ, repetition frequency (6Hz) for 500 laser pulse is incident on the target surface making an angle of 45° with it as shown in Figure-1. Emission spectrum ranging from \( (100-1100 \text{ nm}) \) is recorded in axial and radial directions by using ocean spectrometer (S3000-UV-NIR). The electron temperature is determined from the slope of Boltzmann’s plot that uses the intensity of several spectral lines versus their corresponding excitation energies.

![Figure-1. PLD set up using Nd:YAG with \( \lambda=(1064 \text{ nm}) \) under the vacuum of \( (10^{-3}\text{mbar}) \).](image)

7. RESULTS AND DISCUSSIONS

Plasma composition can be detected by OES by the careful monitoring of electronically the stimulated species and their intensities in the discharges produced by Ar plasma torch. Within the range \( (200 -1100) \text{ nm} \) and utilizing a spectrometer (S2000), the spectra were detected. The S2000 is of great sensitivity, receives light energy emitted via optical fiber and spreads it through a fixed grating across the detector. The emission spectrum that covering the region of spectral \( (200 – 1000) \text{ nm} \) that belongs to neutral \( (\text{Ti I}, \text{Cu I}, \text{OI}) \) and singly ionized \( (\text{Ti II}, \text{Cu II}, \text{O 5II}) \) as a function wavelength were reproduced in Figure-2.
Figure-2. Illustrates the intensity of spectral line in $(\text{TiO}_2)_{1-x}(\text{CuO})_x$ plasma as a function of wavelength.

Figure-3 Shows samples of the method of Boltzmann plots, which are calculated various plasma energy levels, starting from 400 mj - 1000mj. According to the linear nature shown by the Boltzmann plots, it is concluded that an equilibrium state was made between neutral species and the electrons. The high energy states of nonstationary conditions clarified the discrepancies with ion species LTE. This result was backed up by the ionization energy that resulted to be higher than the characteristic energy of plasma expansion.
Figure-3. Clarify plots of Saha Boltzmann depicting the LIP produced by a Nd:YAG laser from an
Titanium Oxide and copper Oxide target at different energies: (a) 400 mj, (b) 500 mj,
(c) 600 mj, (d) 700 mj, (e) 800 mj, (f) 900 mj, and (g) 1000 mj

Figure-4. Illustrates the predicted values of the Lorentzian fit on the Cu I Ti I and Ti II transition lines as a
function wavelength at different laser energies. Under the hypothesis of local thermodynamic equilibrium (LTE), the
parameters such as electron number density and plasma temperature have been calculated by utilizing Boltzmann
plot method. The plasma-emitted spectral line’s shape and width are determined via the perturbing collision processes
of the emitted atoms and ions. Therefore, the density of the plasma can be determined from the profile of the line
spectra. The FWHM of the Stark broadened profile of Cu I Ti I and Ti II lines have been utilized to estimate the
density of electron number [7, 10]. The parameter of Stark broadening was obtained from past studies and papers [9].
Depending on the NIST database, spectroscopic constants of Cu I, Ti I and Ti II lines have been utilized to estimate the temperature [11].

![Figure 4](image)

**Figure-4.** Shows the estimated values of the Lorentian fit on the Cu I, Ti I lines.

![Figure 5](image)

**Figure-5.** Shows the dependence of Te and Ne of the Ti and Cu plasma with laser energies.

Figure-5 depicts the predicted values of the plasma temperature and number density of the Ti plasma that depend on the intensity of laser. It is noticed that the $T_e$ which was between the range of (0.699 – 0.781) eV, showed an increase by the factor of 1.11 and the Ne fell which was in the range of (34.7×10^{18} – 50.5×10^{18}) cm^{-3}, rose by the factor of 1.45 along with the rise in the laser energy from 400 to 1000 mj. Along with the rise in laser irradiance, the temperature as well as the number density were found to rise to a level of 1000mj irradiance of laser and to saturate later on. The temperature’s saturation along with the number density which was over the 1000mj radiance level is thought to occur due to the effect of shielding of plasma. In other word, it means absorption and/or reflection laser photons mode by the plume of plasma.
8. CONCLUSIONS

This paper has critically evaluated the development which has been made experimentally on properties of laser-induced plasmas. This was achieved by utilizing OES to determine plasma physical parameters. In addition, this paper studied the Nd:YAG laser intensity effects $T_e$ and $N_e$ of the Ti and Cu plasma. The changes in the aforementioned parameters with irradiance of laser indicated that $T_e$ and $N_e$ increase with the increase in intensity of laser. It is also noticed that the $T_e$, which was between the range of (0.699 - 0.781) eV, showed an increase by the factor of 1.11 and the $N_e$ fell, which was in the range of $(34.7 \times 10^{18} - 50.5 \times 10^{18})$ cm$^{-3}$, rose by the factor of 1.45 along with the rise in the laser energy from 400 to 1000 mj. Along with the rise in laser irradiance, the temperature as well as the number density were found to rise to a level of 1000 mj.

REFERENCES


