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Spectroscopic Studies of the Copper Plasma Produced by the Laser Ablation

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Abstract: In the present work we report the spectroscopic studies of the copper plasma parameters produce by the fundamental mode of the a Nd:YAG laser at an atmospheric air pressure. The spatial characteristics of the optical emission of the copper plasma have recorded using the HR2000 spectrograph. The plasma parameter such as electron temperature was calculated using the Boltzmann Plot method. The following observed transitions at $3d^9 4s5s\ ^2D_{3/2} \rightarrow 3d^9 4s4p\ ^2F_{5/2}$ at 464.25 nm, $4p\ ^2P_{3/2} \rightarrow 3d^9 4s\ ^2D_{5/2}$ at 510.55 nm, $4d\ ^2D_{3/2} \rightarrow 4p\ ^2P_{1/2}$ at 515.32 nm $4d\ ^2D_{5/2} \rightarrow 4p\ ^2P_{3/2}$ at 521.82 nm and $4p\ ^2P_{3/2} \rightarrow 3d^9 4s\ ^2D_{3/2}$ at 570.02 nm have been used to calculate the plasma temperature at different positions along the direction of expansion of the plasma. The electron number density along the axial direction of the expansion of the plasma has been calculated using the Stark line broadening parameter. It has been observed that close to the surface of the target the electron temperature and the electron number density is found to be maximum whereas the distance from the surface increases the along the axial and lateral direction, these parameters decreases exponentially.

Keywords: LIBS, Copper plasma, Stark broadening, Boltzmann plot

1. INTRODUCTION

The Laser induced breakdown spectroscopy (LIBS) is useful technique for elemental analysis of the materials in the form of solids, liquids and gases, it has a variety of applications like materials analysis, environmental monitoring, determination of soil contamination, forensics and biomedical studies of teeth and bones, art restoration/conservation (pigments, precious/ancient metals), military and safety needs (explosive particles, chemical and biological warfare agents) (Caridi *et al.,* 2010; Samad *et al.,* 2010; Aryal *et al.,* 2012)

In this technique when a high intensity, focused laser beam strikes a solid or liquid target, material is evaporated and dense ionized hot plasma is produced. In this phenomenon the nanosecond laser beam interacts in the two ways (i) laser matter interaction (ii) laser plasma interactions. In this technique the quantitative analysis of the laser induced plasma depend on the laser parameters (laser wavelength, pulse duration and fluence), sample properties (specific heat, latent heat of vaporization etc) , ambient conditions (nature and pressure of the ambient gas) and the detection system (lenses combination, slits, grove density of the slits etc.)(Hoyer *et al.,* 2012; Cristoforetti *et al.,* 2010; Shaikh *et al.,*2006; Hafeez *et al.,*2008).

In the LIBS the radiations emitted from the plume of the laser induced plasma can be analyzed temporally and spatially using a spectrometer equipped with fast registering detectors to cover the entire visible part of the electromagnetic spectrum.

The LIBS technique is a versatile tool for the analysis of materials as the emitted radiation by the laser produced plasma mainly contains the identifiable transitions of the constituent elements.

The laser produced plasma generated on the copper (Cu) surface has been extensively studied using the excimer laser and Nd: YAG laser. (Dreyfus *et al.,*1991) studied the copper plasma using the Laser Induce Fluorescence LIF technique. (Kumar and Thareja 1990) studied the spectroscopic properties and the plasma properties of the Cu plasma in the presence of neon gas environment. Subsequently (Lee and Sawan 1992) used the ultraviolet laser wavelength of 193 nm excimer laser to study plasma parameter of the Cu in air at atmospheric pressure. (Hafiz *et al.,*2003) reported the plasma life time and electron number density of Cu plasma produced by 355 nm Nd: YAG Laser.

In the present work, we have reported the new results for the comparative study of the Cu plasma produced by the fundamental (1064 nm), Second Harmonic Generation (532 nm) and the Third Harmonic Generation (355 nm) of a Nd:YAG laser. We have studied the spatial variation of the transition lines and the electron temperature and the electron number density of the Cu plasma. The electron temperature have calculated using Boltzmann plot method and the electron number density have been estimated using

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Stark broadened profile of the transition lines of Cu. For the first time we have studies the CuO molecules belongs to the $A^2\Sigma \rightarrow X^2\pi$ systems generated by the 1064 nm of Nd: YAG laser.

2. EXPERIMENTAL

A schematic experimental setup is given in the **(Fig. 1).**

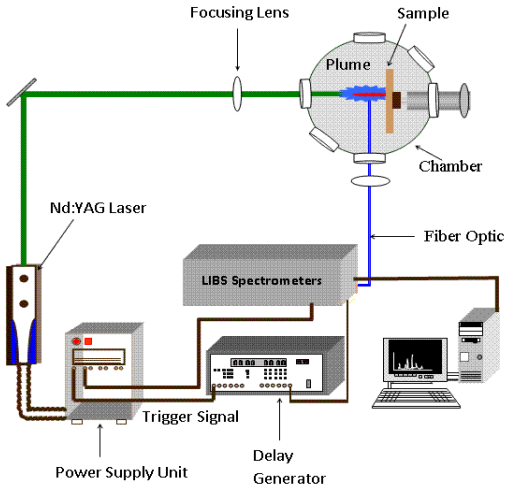


Fig. 1 (Color on line) Experimental setup

The laser source was a Nd:YAG (Quantel Brilliant B) used in the fundamental, SHG and THG modes with a pulse repetition rate of 10 Hz and pulse width of 5nsec. The laser beam diameter was about 8 mm in all the three modes. The output laser beam was focused by a convex lens of 10cm focal length onto a copper target mounted on a rotating table. For each spectrum, the copper sample was rotated and a new portion of the sample was exposed for the next laser shot. The data was obtained using a high-resolution fiber optic spectrometer (HR 2000, Ocean optics) equipped with a Sony ILX511 linear silicon CCD array detector having 2K pixels. Each pixel has a size of 14μm x 200μm. This detector has a 12 bit A/D resolution and a corrected linearity range ≥ 99.8%. The spectrometer has a detectable range from 270 nm to 720 nm with a H3 type grating having 600 groves/mm groove density. This detection system has the option to be triggered externally that makes it possible to start acquiring the data at a certain instant of time. For that reason, the three channels programmable pulse/delay generator (HP 8160 A) triggered the spectrometer, whereas the generator itself was triggered by the Q-Switch synchronization output of the laser system. By such arrangements, we synchronized the entire experimental setup and minimized any time delay among the occurring events such as firing of the laser beam, production of the plasma and the detection of the emitted radiation from the plasma. The output data was averaged for 10 shots with an integration time of 50 msec. The detector was mounted on a micrometer linear platform with the help of which, the detector could be moved along the direction of the expansion of the plasma to study the characteristics of the laser-generated plasma plume.

3. RESULTS AND DISCUSSION

In the laser induced breakdown spectroscopy LIBS, the spectroscopic analysis of the transition line gives the whole information of the composition of the sample. The determination of the plasma parameters, electron temperature and electron number density are two fundamental parameters of the laser generated plasma studies. The plasma is generated for a very short interval of time and it expands due to the shock wave generated at the surface of the target material (Song and Alexender 1994). In the laser ablation process the plasma typically expands with supersonic velocity (Allmen and Blatter 1998).

In the first set of experiments we have studied the copper plasma using the 355 nm laser wavelength, the similar experiment have repeated using the 1064 nm and 532 nm laser. The calculated values of energy irradiance for 1064 nm, 532nm and 355nm are $4.5x10^{10}$ W/cm^2, $2.2x10^{10}$ W/cm^2 and $6.3x10^{10}$ W/cm^2 respectively.

In this set of experiment we have studied the spatial variation of the plasma plume along the axial direction. A portion of the recorded emission spectrum at a distance of 2.5 mm from the target surface covering the region between 453 – 600 nm is shown in **(Fig.2a).**

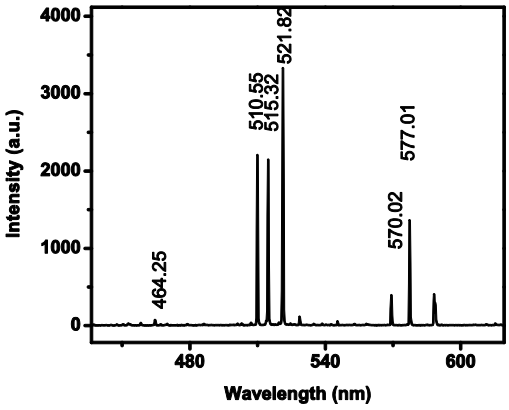


Fig.2a (Color on line)Emission spectrum of copper plasma generated by the 355 nm laser.

The spectrum clearly shows strong lines of neutral copper at 510.55 nm ($4p\ ^2P_{3/2} \rightarrow 3d^9 4s\ ^2D_{5/2}$), 515.32 nm ($4d\ ^2D_{3/2} \rightarrow 4p\ ^2P_{1/2}$), 521.82 nm ($4d\ ^2D_{5/2} \rightarrow$

4p $^2P_{3/2}$), 522 nm, 570.02 nm (4p $^2P_{3/2} \rightarrow 3d^9 4s\ ^2D_{3/2}$) , 577.01 nm and a weak line at 464.25 nm ($3d^9 4s5s\ ^2D_{3/2} \rightarrow 3d^9 4s4p\ ^2F_{5/2}$). We have also detected three very week lines around 503 nm, 504 nm and 507 nm attributed to Cu II emission. In addition, there is a line at 648.18 nm that we believe is due to the presence of iron as impurities in the sample that is listed by (Payling and Larkins 2000).

We have compared the intensities of three lines at 577.01 nm, 570.02 nm and 510.55 nm are attached to the 4p $^2P_{3/2,1/2} \rightarrow 3d^9 4s^2\ ^2D_{3/2,5/2}$ transitions according to the LS-coupling intensity rules, the intensity ratio of the three lines at 577.01nm, 570.02 nm and 510.55 nm should be 1:9:14. However, experimentally, it is noticed that the intensity ration of the 570.02 nm and 510.55 nm lines are 3:14. Similarly, the other multiplet structure lie at 521.82 nm, 522 nm and 515.32 nm attached to the 4d $^2D_{3/2,5/2} \rightarrow$ 4p $^2P_{1/2,3/2}$ transitions. The relative intensities of the above stated levels are also expected to be in the ratio 14:1:9 respectively. Experimentally, the 522 nm line is too weak to be detected, whereas the intensity ratio of the other two lines lying at 521.82nm and 515.32nm is 14:9.

The spectrum of the 532 nm laser produced Cu plasma is shown in **(Fig. 2b)** that shows all the transitions that have been observed in the case of 355 nm laser wavelength.

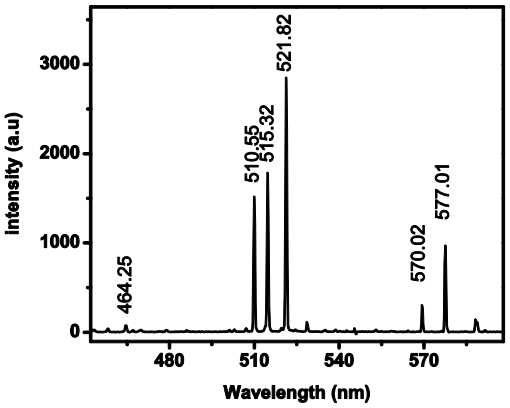


Fig.2b (Color on line) Emission spectrum of copper plasma generated by the 532 nm laser.

This spectrum has the similar trend as we have observed for the 355 nm laser generated plasma. The ratio of the spectral lines intensities at 570.02 nm and 510.55 nm is found to be 3:17, which is close to that found in the previous experiment. The intensity ratio of the other two lines at 521.82nm and 515.32 nm remains 14:9, that is exactly the same as observed in the previous experiment.

The plasma produced by the 1064 nm laser beam is shown in Fig. 2c covering a range from 315 nm to 675 nm. To our knowledge, it is for the first time that laser produced plasma by the fundamental of a Nd:AG laser has been used to study the copper plasma. In addition to the well documented spectral lines of atomic copper, we have observed molecular bands marked by an arrow in **(Fig. 2c).** These bands belong to the $A^2\Sigma \rightarrow X^2\pi$ systems of CuO molecules.

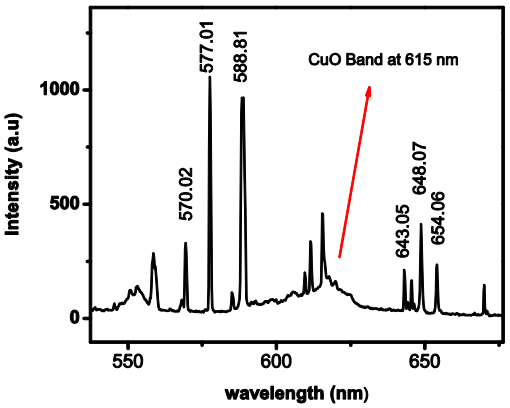


Fig.2c (Color on line) Emission spectrum of copper plasma generated by the 1064 nm laser.

The spatial variation of the transition lines of the Cu plasma produced by the 355 nm laser is shown in **(Fig. 3).** The similar trend in spatial variation of the transition lines of the Cu plasma generated by 1064 nm and 532 nm have been observed. In the case of the 355 nm laser we have observed the strongest transient lines due to the maximum coupling of the laser with sample and have smaller critical density compare to the 532 nm and 1064 nm lasers.

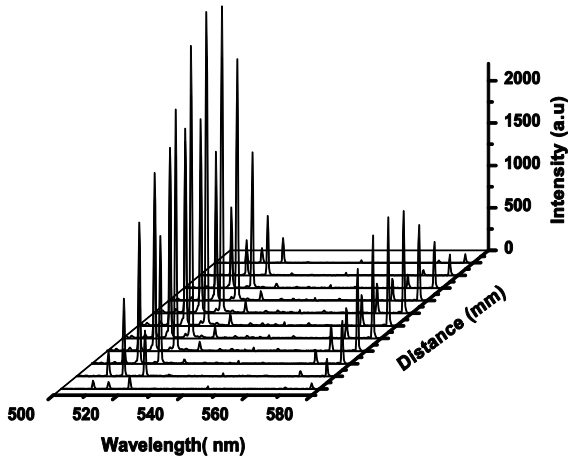


Fig. 3 (Color on line) Spatial variations in the spectral line intensities generated by the 355 nm laser.

From the spectroscopic analysis of these transition lines of the Cu plasma we have calculated the electron temperature using the Boltzmann plot method under the assumption of the local Thermodynamic Equilibrium (LTE). However, this condition is valid if the collision process is dominant then the radiative process of recombination. For that reason it is very important to check the validity of the LTE condition of the plasma (Griem 1964; Hoyer *et al.*, 2012; Farid *et al.*, 2013; Shaikh *et al.*,2006).

$$\ln\left(\frac{\lambda_{ji} I_{ji}}{hcA_{ji} g_j}\right) = \ln\left(\frac{N(T)}{Q(T)}\right) - \left(\frac{E_j}{kT}\right). \quad (1)$$

In order to determine the plasma temperature from equation (1), we plot ln $(\lambda_{ji} I_{ji} / hcg_j A_{ji})$ versus E_j for the observed spectral lines that yields a straight line and its slope is *-1/kT*. The temperature can therefore be obtained without having to know the total density of atoms or the partition function. We used the atomic copper emission lines at 464.25nm, 510.55 nm, 515.32 nm 521.82 nm and 570.02 nm. The spectroscopic constants of these parameters used in the calculation of the Boltzmann plot method is shown in **(Table 1)**. The electron number density of the Cu plsam has been calculated using the Stark broadened lie profile of the Cu transition line. The width of the Stark broadened lines (FWHM) $\Delta\lambda_{1/2}$ can be calculated using the relation (Griem 1965)

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

Where ω represents the electron impact width parameter and A reflects the ion broadening parameter. Therefore, the above equation reduces to a much simpler form that has been adopted to calculate the electron number density of the laser-induced plasma.

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

The value of ω corresponding to different plasma temperature is taken form the reference data tabulated by (Konjevic and Wiese 1990) The observed Full Width at Half Maximum (FWHM) of the transition lines at 464 nm, 509.9 nm, 514.69 nm, 521.21 nm and 569.23 nm are listed below in the **(table 2).**

Table 2. Full Width at Half Maximum of different transitions of Copper

Wavelength (nm)	FWHM (nm)
464	0.52
509.6	0.42
514.69	0.43
521.21	0.51
569.23	0.40

In the case of spatial variation of the Cu plasma plume produced by 355 nm , 532 nm and 1064 nm lasers, the electron temperature varies as (1200 – 6050) K, (10500 – 6000) K and (9500 - 5066) K respectively. Whereas the electron number densities varies as $(1.0 \times 10^{16} - 1.2 \times 10^{15})$ cm^{-3}, $(1.3 \times 10^{16} - 1.2 \times 10^{15})cm^{-3}$ and $(1.5 \times 10^{16} - 2.3 \times 10^{15})cm^{-3}$ respectively.

4 CONCLUSION

The Laser induced breakdown spectroscopy technique has been used to determine the Cu plasma parameters from the spectroscopic analysis of the transition lines of Cu.

In the comparative study of the laser wavelength effect we have observe the strong and enhanced signal in the case of 355 nm laser as compare to the 1064 nm laser wavelength. Both plasma parameters electron temperature and number density is found to be maximum in the case of 355 nm laser, may be because of the lower critical density and maximum reflection of 1064 nm laser. In the case of 1064 nm laser we have observed the CuO molecules belong to the $A^2\Sigma \rightarrow X^2\pi$ systems.

Table 1. Spectroscopic constants of neutral copper lines used in the calculation of electron temperature.

Wavelength (nm)	Transitions	Statistical weight (g)	Excitation energy (cm^{-1}) (E)	Transition probability (s^{-1}) (A)
464.25	$3d^9 4s5s\ ^2D_{3/2} \rightarrow 3d^9 4s4p\ ^2F_{5/2}$	4	65260.1	0.074×10^8
510.55	$4p\ ^2P_{3/2} \rightarrow 3d^9 4s\ ^2D_{5/2}$	4	30783.69	0.02×10^8
515.32	$4d\ ^2D_{3/2} \rightarrow 4p\ ^2P_{1/2}$	4	49935.20	0.6×10^8
521.82	$4d\ ^2D_{5/2} \rightarrow 4p\ ^2P_{3/2}$	6	49942	0.75×10^8
570.02	$4p\ ^2P_{3/2} \rightarrow 3d^9 4s\ ^2D_{3/2}$	4	30783	0.0028×10^8

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