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Spectroscopic study the plasma parameters for Pb doped CuO prepared by pulse Nd:YAG laser deposition

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Abstract

In this work, plasma parameters such as, the electron temperature (T_e), electron density n_e, plasma frequency (f_p), Debye length (λ_D) and Debye number (N_D), have been studied using optical emission spectroscopy technique. The spectrum of plasma with different values of energy, Pb doped CuO at different percentage (X=0.6, 0.7, 0.8) were recorded. The spectroscopic study for these mixing under vacuum with pressure down to $P=2.5\times10^{-2}$ mbar. The results of electron temperature for X=0.6 range (1.072-1.166) eV, for X=0.7 the T_e range (1.024-0.855) eV and X=0.8 the T_e is (1.033-0.921) eV. Optical properties of CuO:Pb thin films were determined through the optical transmission method using ultraviolet visible spectrophotometer within the range (190 – 1100) nm.

Key words
Laser Induced Plasma Spectroscopy (LIPS), Optical Emission Spectroscopy (OES), Lead (Pb), Cupper mono oxide (CuO).

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دراسة طيفية لمعلمات البلازما لاوكسيد النحاس المشوبة بالرصاص بأستخدام الترسيب لليزر النبضي Nd:YAG

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الخلاصة

في هذا البحث، تم دراسة معلمات البلازما من درجة حرارة الالكترون (T_e)، كثافة الالكترون (n_e)، تردد البلازما (f_p)، طول كرة ديباي (λ_D) وكذلك عدد الجسيمات في كرة ديباي (N_D) بأستخدام تقنية مطياف الانعباث البصري والذي يعمل على التقاط الطيف الناتج من البلازما عند طاقات مختلفة باستخدام مزيج من احادي اوكسيد النحاس CuO المشوب بالرصاص Pb بنسب مختلفة (X=0.6, 0.7, 0.8) حيث تمت دراسة الطيف الناتج تحت ظروف الفراغ اي بضغط يصل بحدود 2.5×10^{-2} mbar حيث حساب درجة حرارة الالكترون عند X=0.6 وكانت قيم درجة حرارة الالكترون هي (1.072-1.166) الكترون-فولت، X=0.7 فان درجة الحرارة هي (1.024-0.855) الكترون-فولت وكذلك بالنسبة X=0.8 ان الدرجة الحرارة بحدود (1.033-0.921) الكترون فولت. حيث تمت عملية حساب الخصائص البصرية للغشاء CuO:Pb بأستخدام المطياف بمدى طول موجي يتراوح (190 nm-1100 nm).

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 [1], The ablation process using long pulse duration lasers (> 1 ns) is divided into three stages. In the first stage, the laser light interacts with the solid resulting in rapid ionization of the target surface into plasma on a time scale short compared with the pulse duration. In the second stage, the laser light is efficiently absorbed by the plasma which expands isothermally. In the third stage, after the end of the laser pulse, the resultant plasma plume expands quasi-adiabatically in a medium, which can include vacuum or a background gas, with or without applied fields [2], Sample types can be wide ranging because optical absorption processes initiate LIBS sampling, thus, allowing analysis of solids, liquids, and gases [3], once the energy from the laser pulse heats, ablates, atomizes, and ionizes the sample material, a plasma is formed.

The plasma plume is then spectrally resolved and detected by a spectrograph and a detector. Both quantitative and qualitative information, such as elemental composition, can be deduced from the resulting plasma spectrum. Emission line properties such as widths, shapes, and shifts can provide information on plasma temperature and electron density [4]. Plasma temperature is an important thermodynamic property due to its ability to describe and predict other plasma characteristics such as the relative populations of energy levels and the speed distribution of particles. The method used in this laboratory experiment is the Ratio Method using two lines of Hydrogen, which assumes that local thermodynamic equilibrium (LTE) is met within the plasma. Under vacuum with pressure tell to $2.5*10^{-2}$ mbar, it has been shown through approximations that LTE is usually met after a couple hundred nanoseconds after plasma formation using LIBS with irradiances greater than 10^8 W/cm^2. The Ratio Method is a common way of reporting plasma temperature can be calculated through the intensity ratio of a pair of spectral lines of atom or ion of same ionization stage [5]. In LTE, The plasma temperature (T) is calculate from the equation [5]:

$$T = \frac{(E_2 - E_1)}{k\, ln\left(\frac{I_1 \lambda_1 A_2 g_2}{I_2 \lambda_2 A_1 g_1}\right)} \qquad (1)$$

where I is the intensity, g is the statistical weight, A is the transition probability, λ is the wavelength, E is the energy of excited state in eV and k is Boltzmann constant.

Electron density describes the number of free electrons per unit volume. There are several credible techniques used to determine electron density, including plasma spectroscopy, microwave and laser inter ferometry, and Thomson scattering. The determination of electron density by linear Stark broadening of spectral lines, as used in this lab, is a well established technique. Line broadening in LIBS plasmas is caused primarily by Doppler width and the Stark effect. Doppler width is dependent only on the temperature and atomic mass of the emitting species; this type of broadening is disregarded in this experiment as the Doppler width of the hydrogen line used is usually between 0.04 and 0.07 nm. The Stark effect is considered a type of pressure broadening that involves interactions of radiators and neighboring particles. In plasmas, these interactions are caused by collisions of ions and to lesser extent electrons. The Stark effect is mainly responsible for the line broadening of the hydrogen line used in this experiment [4, 6].

Saha-Boltzmann equation utilizes spectral lines of the same element and successive ionization stages. the Saha-Boltzmann equation is given as [5]:

$$n_e = \frac{I_1}{I_2^*} 6.04 \times 10^{21} (T)^{3/2} e^{\frac{(E_1 - E_2 - X_Z)}{kT}} \ cm^{-3} \qquad (2)$$

where

$$I_2^* = \frac{I_2 \lambda_2}{g_2 A_2} \qquad (3)$$

X_Z is the ionization energy of the species in ionization stage z in eV, I_z is the line intensity for transition from upper level-2 to lower level-1, $\lambda_2$is the corresponding wavelength of transition from level-2 to level-1, g_2 is the statistical weight of transition from level-2, $A_2$is the transition probability from level-2 to level-1 and T is the electron temperature The subscript z denotes the ionization stage of the species for the referred.

While the plasma frequency is calculate from the equation [7]:

$$f_p \approx 8.98\sqrt{n_e}\ \text{(Hz)} \qquad (4)$$

This frequency which depends only on the plasma density, is one of the fundamental parameters of plasma. Because of the smallness of *m*, the plasma frequency is usually very high [7].

The response of charged particles to reduce the effect of local electric fields is called *Debye shielding* (λ_D) and the shielding gives the plasma its quasi-neutrality characteristic. a distance λ_D, called the *Debye length* which defined by[8] :

$$\lambda_D = \left(\frac{\varepsilon_o k T_e}{n_e e^2}\right)^{1/2} = 743 * (T_e / n_e)^{½} \qquad (5)$$

Debye length should be very small when compared with the system dimension this first condition for plasma existence [9] $\lambda_D <<< L$, where: λ_D: is the Debye length (cm), L: is the system dimension (cm), n_e: is the density of the electron $\left(m^{-3}\right)$, T_e: is the electron Temperature (K) , e: is the electron charge (C) and N_D also known as the number of particles in the Debye sphere which is dependent on electron density and electron temperature this Second condition for plasma existence $N_D >>> 1$ as follows[10]:

$$N_D = \frac{4\pi}{3} n_e \lambda_D^3 \qquad (6)$$

Experimental setup

The diameter of laser spot can be changed by changing the distance between the laser lens and the target. Pulse duration (9 ns) with 6 Hz repetition frequency and the wavelength is 1064nm. The exactly distance during the measurements for system accuracy and precision. In this work, the focal length of lens is 10 cm. A shorter focal length lens can produce a small beam waist, and therefore, stronger breakdown, but it also has a smaller depth of focus, Fig. 1 shows a schematic diagram for the LIBS setup.

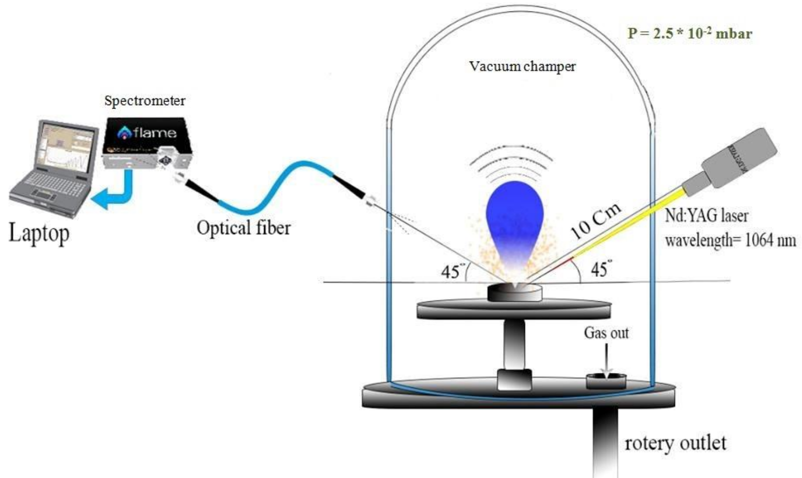


Fig. 1: Laser Induced Plasma Spectroscopy (LIPS) System configuration.

The spectrometer analysis was done using the light emitted from sample bombarded by the pulsed laser. The spectrometer with short response time from Ocean Optics (HR 4000 CG-UV-NIR) was used in the setup to analyze emitted light.

The light produced by the ablated plasma was collected by the optical fiber which was set at angle of about 45 degree to axes of the laser beam to avoid splashing and then guided to the entrance slit of the spectrometer. The spectrometer has a high resolution depending on grating used in it, and responds to a wavelength between 200-900 nm with 3648 pixels. Nd:YAG laser at wavelength 1064 nm is tightly focused on the target to produce plasma plume.

In order to insure exposing a fresh surface after every train of shots the target surface was rotated rate. The spectrum of plasma with different value of energies, by prepare Mixing between Pb with CuO at different percentage (X=0.6, 0.7, 0.8) with the laser pulse energy was varied from 500 to 1000 mJ, each spectrum was obtained over a wavelength range of (300-800) nm.

Finally the results were analyzed and compared with National Institute of Standards and Technology data (NIST) [11] and evaluate the plasma parameters such as electron density (n_e), electron temperature (T_e), and then the plasma characteristics will be calculated.

Results and discussion

Figs. 2, 3 and 4 respectively show the emission spectra of laser induced on CuO:Pb component at X=0.6, 0.7 and 0.8 percentage target plasma which confined in vacuum in the spectral range 300-800 nm with E=(500, 600, 700, 800, 900, 1000) mJ. The optical emission spectra of CuO:Pb component at X=0.6, 0.7 and 0.8 percentage target plasma which confined in vacuum was recorded using OES technique.

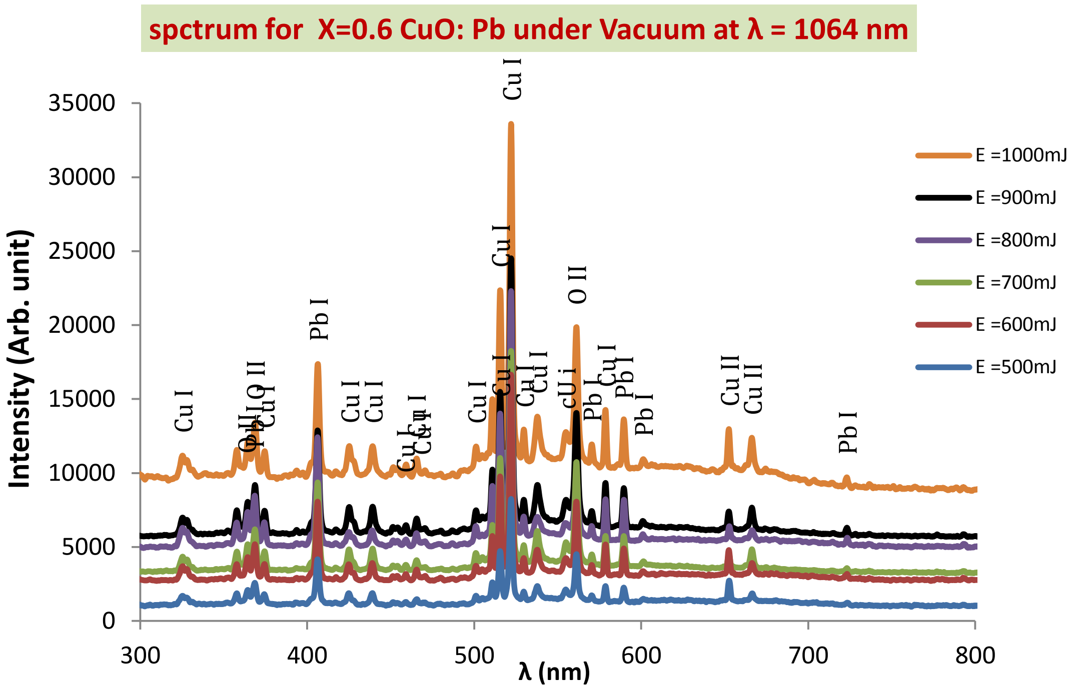


Fig. 2: Emission spectra of laser induced on CuO:Pb component at X=0.6 target in vacuum with different laser energies.

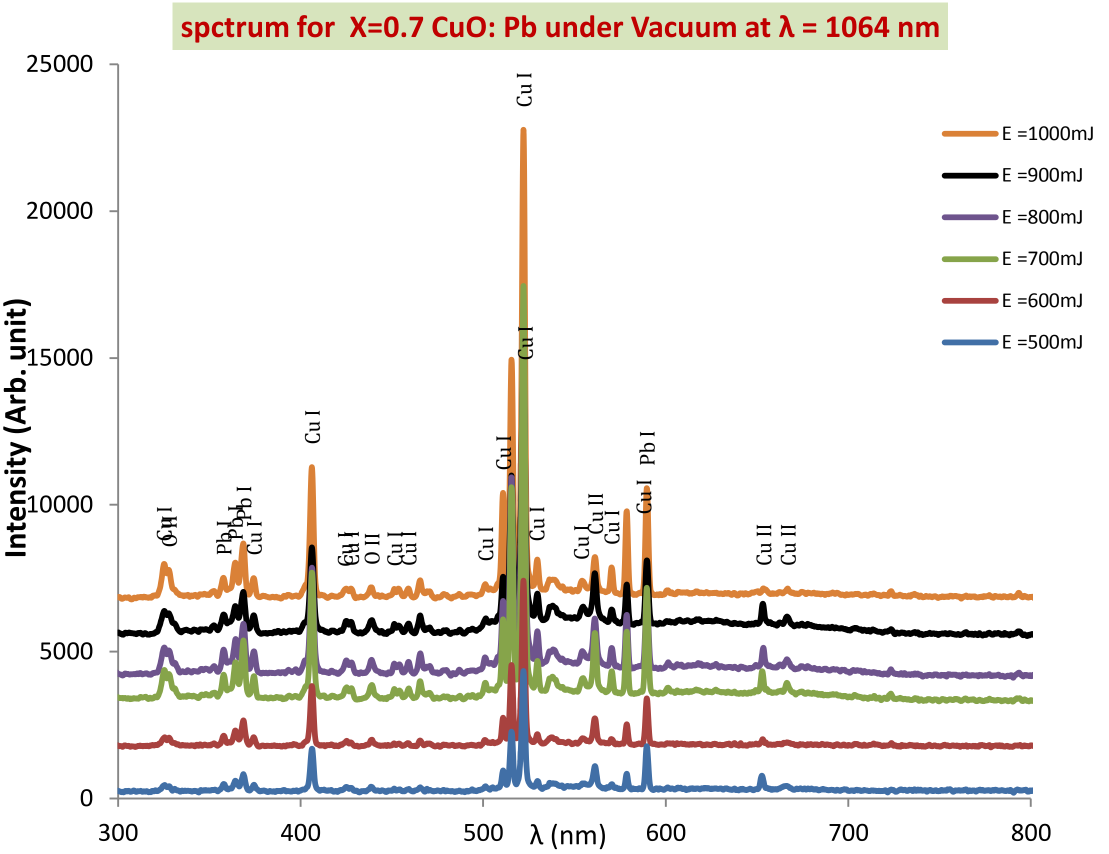


Fig. 3: Emission spectra of laser induced on CuO:Pb component at X=0.7 target in vacuum with different laser energies.

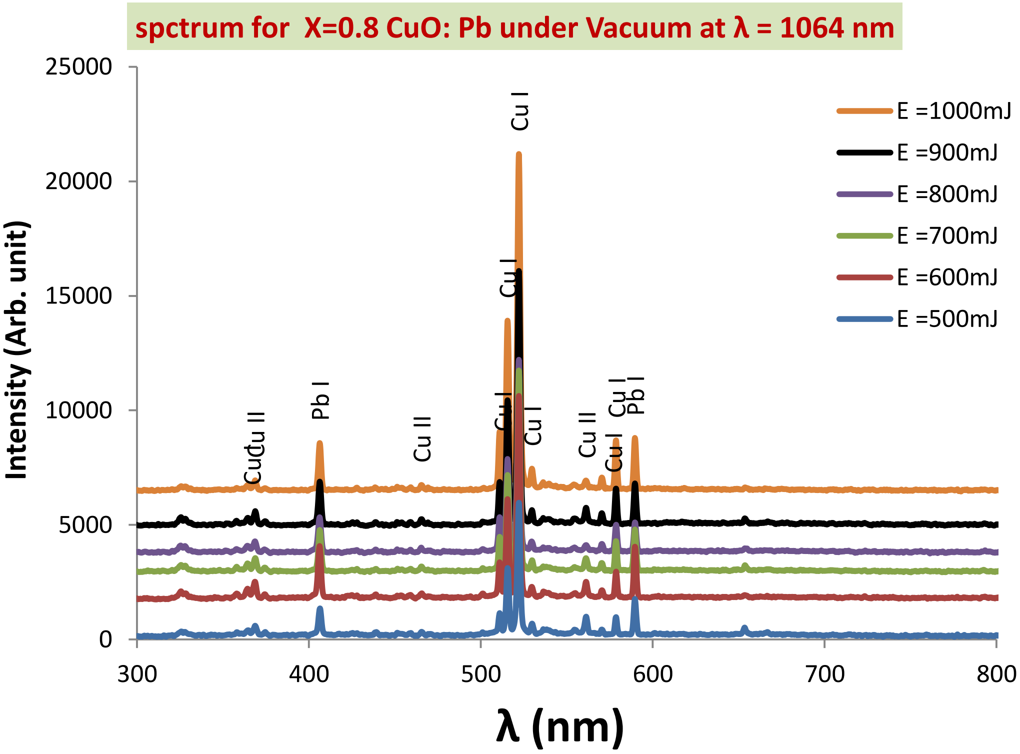
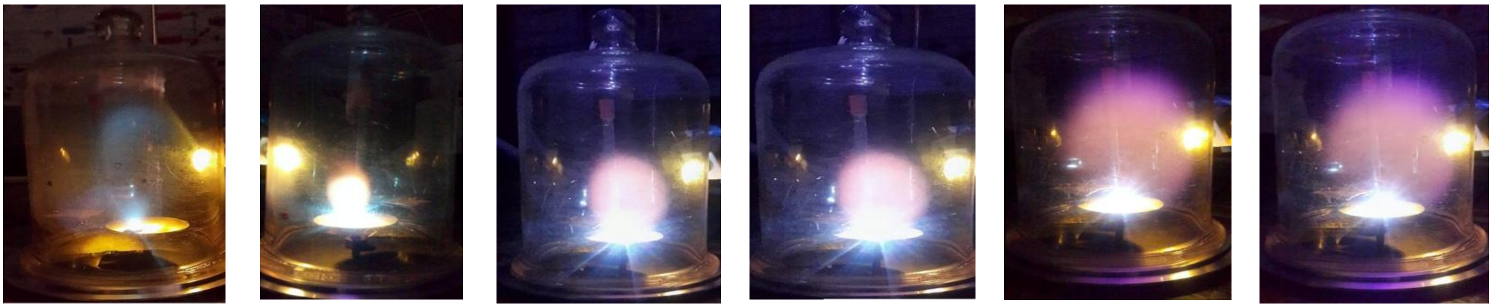


Fig. 4: Emission spectra of laser induced on CuO:Pb component at X=0.8 target in vacuum with different laser energies.



a) Energy =500 mJ b) Energy =600mJ c) Energy =700 mJ d) Energy =800 mJ e) Energy =900 mJ f) Energy =1000 mJ

Fig. 5: Plume plasma for CuO:Pb component At X=0.6 target in vacuum with different laser energies.

From the above figures one can note that when the Pb doped CuO increase the emission lines of Cu are more than lines of Pb.

Tables 1, 2 and 3 display the calculated electron density (n_e), electron temperature (T_e), plasma frequency (f_p), Debye length (λ_D) and Debye number (N_D) for CuO:Pb at X=0.6, 0.7 and 0.8 targets at different laser pulse energies by the ratio method can be calculated through the intensity ratio of a pair of spectral lines of atom or ion of same ionization stage. All calculated plasma parameters (λ_D, f_p and N_D) were satisfied the criteria for the plasma. It shows that f_p decrease with laser energy because it is proportional with ne, while λ_D and N_D increase with it such as in (Hussain and Al-Razzaq) [12].

Table 1: Plasma parameters for CuO:Pb at X=0.6 in Vacuum with different laser energy.

Laser energy (mJ)	**Te (eV)**	**n_e (cm^{-3})**	**f_p (Hz)**	**λ_D (cm)**	**N_d**
1000	1.148	1.85E+17	3.9E+12	1.7E-04	3.9E+06
900	1.139	1.73E+17	3.7E+12	1.8E-04	4.0E+06
800	1.130	1.63E+17	3.6E+12	1.8E-04	4.1E+06
700	1.096	1.27E+17	3.2E+12	2.0E-04	4.4E+06
600	1.060	9.56E+16	2.8E+12	2.3E-04	4.9E+06
500	1.010	6.31E+16	2.3E+12	2.8E-04	5.6E+06

Table 2: Plasma parameters for CuO:Pb at X=0.7 in Vacuum with different laser energy.

Laser energy (mJ)	**Te (eV)**	**n_e (cm^{-3})**	**f_p (Hz)**	**λ_D (cm)**	**N_d**
1000	1.024	8.12E+16	2.6E+12	2.5E-04	5.0E+06
900	0.999	6.52E+16	2.3E+12	2.7E-04	5.4E+06
800	0.997	6.41E+16	2.3E+12	2.7E-04	5.4E+06
700	0.990	6.04E+16	2.2E+12	2.8E-04	5.5E+06
600	0.961	4.61E+16	1.9E+12	3.2E-04	6.0E+06
500	0.855	1.48E+16	1.1E+12	5.3E-04	9.0E+06

Table 3: Plasma parameters for CuO:Pb at X=0.8 in Vacuum with different laser energy.

Laser energy (mJ)	Te (eV)	n_e (cm^{-3})	f_p (Hz)	λ_D (cm)	N_d
1000	1.033	8.73E+16	2.7E+12	2.4E-04	4.9E+06
900	0.990	6.03E+16	2.2E+12	2.8E-04	5.5E+06
800	0.945	3.94E+16	1.8E+12	3.4E-04	6.4E+06
700	0.936	3.60E+16	1.7E+12	3.5E-04	6.6E+06
600	0.934	3.51E+16	1.7E+12	3.6E-04	6.6E+06
500	0.921	3.08E+16	1.6E+12	3.8E-04	6.9E+06

The variation of (T_e) and (n_e) was determining the Ratio Method using two lines of Cupper (Cu I in this part) for CuO:Pb at X=0.6, 0.7 and 0.8.is shown in Figs. 6-8 for different laser energies.

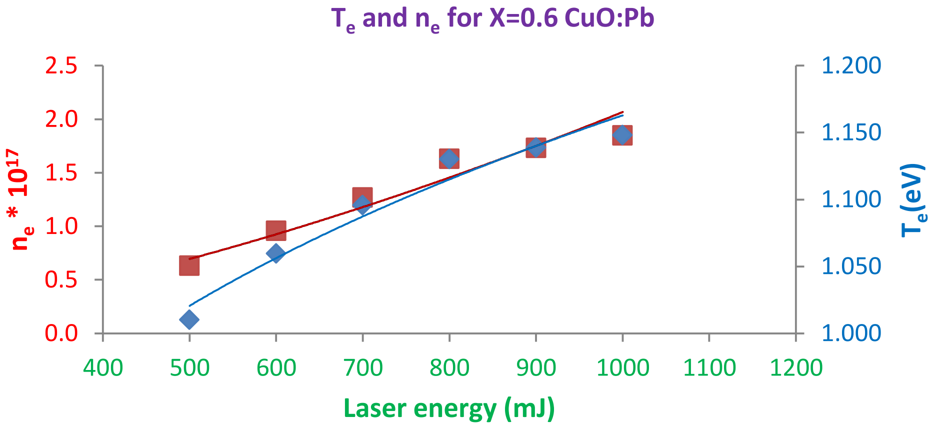


Fig. 6: The variation of (T_e) and (n_e) versus the laser energy for CuO:Pb at X=0.6 in Vacuum.

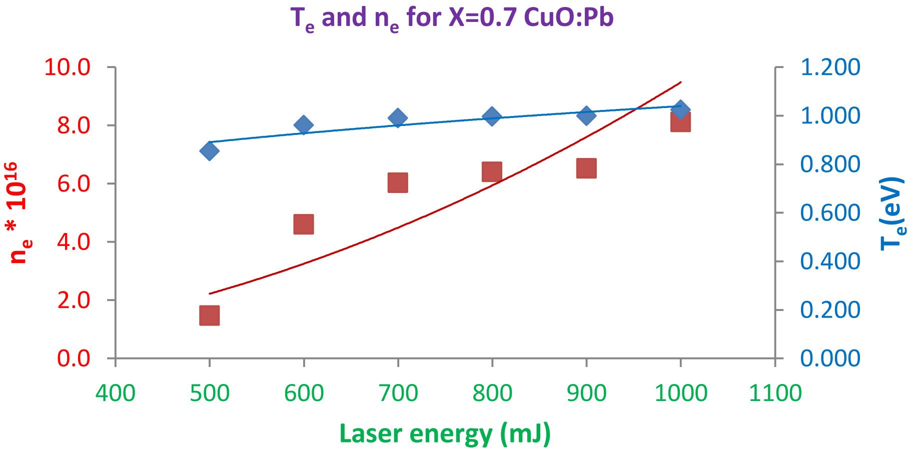


Fig. 7: The variation of (T_e) and (n_e) versus the laser energy for CuO:Pb at X=0.7 in Vacuum.

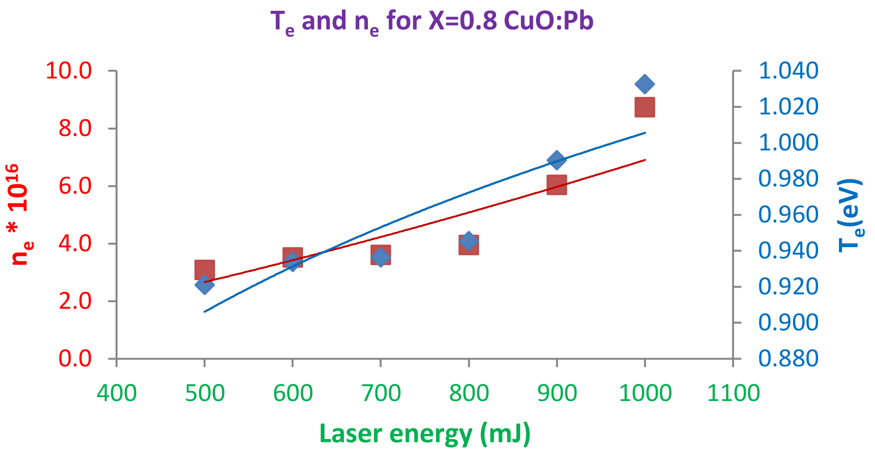


Fig.8: The variation of (T_e) and (n_e) versus the laser energy for CuO:Pb at X=0.8 in Vacuum.

The values of Te were obtained from the Ratio method, as shown in Figs. 6-8, from the analysis of recorded Cu I peaks for plasma induced on CuO:Pb component under Vacuum using 1064 nm laser, with different laser energies 500, 600, 700, 800, 900 and 1000 mJ. The values of Te are calculated through the intensity ratio of a pair of spectral lines of atom or ion of same ionization stage.

The same behavior for plasma temperature (Te), Te increase with laser energy and electron density (ne) in 1064 nm and at different laser peak powers in Figs. 6-8 but with higher values in 532 nm because the high kinetic energy gained to ejected electrons from higher photons energies. ne increase reaching maximum values at 1000 mJ laser energy, then decrease with lower laser energy this agree (Ali. A-K. Hussain and A. A. Al-razzaq) [12].

Conclusions

The spectral lines intensities of the laser induced plasma emission exhibited a strong dependence on pulsed laser energy. It is found that the intensities at different laser peak powers increase with increasing laser peak power and then decreases when the power continues to increase. The values of Te, N_D and λ_D were increased in case of laser induced plasma in vacuum environment while the values of n_e and f_p were decreased in the same operating conditions. We note that when doping increases (i.e. CuO increase, Pb decrease) from the mixed the emission lines of Cu are more than lines of Pb.

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