Spectroscopic Analysis of CdO$_{1-X}$: Sn$_X$ Plasma Produced by Nd:YAG Laser

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Abstract

In this work, the optical emission spectrum technique was used to analyze the spectrum resulting from the CdO:Sn plasma produced by laser Nd:YAG with a wavelength of (1064) nm, duration of (9) ns, and a focal length of (10) cm in the range of energy of 500-800 mJ. The electron temperature ($T_e$) was calculated using the in ratio line intensities method, while the electron density ($n_e$) was calculated using Saha-Boltzmann equation. Also, other plasma parameters were calculated, such as plasma ($f_p$), Debye length ($\lambda_D$) and Debye number (N$_D$). At mixing ratios of X=0.1, 0.3 and 0.5, the CdO$_{1-X}$:Sn$_X$ plasma spectrum was recorded for different energies. The changes in electron temperature and the densities were studied as a function of the laser energies. Outcome measure value of the electron temperature at the ratio of X = 0.1 was (1.079-1.054) eV, while at X=0.3 the $T_e$ range was (0.952-0.921) eV and at X=0.5 it was (0.928-0.906) eV.

Keywords: Laser Induced Plasma Spectroscopic (LIPS), Optical Emission Spectroscopic (OES), Cadmium oxide (CdO), Tin (Sn).

Keywords: تحليل طيفي للبلازما اوكسيد الكادميوم المشووع بالقصدير المنتجه بواسطة ليزر Nd:YAG

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في هذا البحث، تم استخدام تقنية طيف الأيونات البصري لتحليل الطيف الناتج من بلازما CdO:Sn بواسطة ليزر Nd:YAG ذو الطول الموجي (1064) نانومتر، وعده الزمنية (10) نانو ثانية، وطول بؤري ل (10) سنتيمتر، بينما تردد (6) هرتز في نطاق الطاقة (800-500) ملي جول. تم حساب درجة حرارة الإلكترونات ($T_e$) في طريقة شدة قطبيات طيفين، بينما تم حساب كثافة الإلكترونات ($n_e$) باستخدام معادلة ساها- بوتزمان، بالإضافة إلى حساب مح挽ات البلازما الأخرى مثل تردد البلازما ($f_p$)، وطول بعد ديبايز ($\lambda_D$) وعدد الجسيمات في كرة ديبايز ($N_0$), تم تسجيل الطيف الناتج من البلازما مع مختلف من الطاقة، لمكزك أوكسيد الكادميوم المشووع بالقصدير (CdO) في نسب متنوعة مختلفة (Sn) مختلفة من القيمة، وتم دراسة التغير في درجة حرارة غاز الإلكترونات وكثافات كدالة لقطات الليزر. مقاييس النتائج لدرجة حرارة غاز الإلكترونات عند نسبة X = 0.1 هي (1.079-1.054) كهروت كهرون

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Introduction

Laser-induced plasma spectroscopy (LIPS) is considered to be an established analytical technique used for the rapid determination of the elemental composition of samples. LIPS also can be defined as a type of analytical technique of atomic emission spectroscopy with which any type of matter, whether in liquid, solid or gaseous state can be analyzed [1]. In LIPS, a plasma is generated on the surface of a target by focusing a laser beam which excites and ionizes the target material. The plasma is emitted from the surface of the target material immediately after the laser beams photons reach that surface. Optical detection of certain atomic and molecular species is obtained by analyzing their emission spectra from laser induced plasma. The chosen experimental conditions strongly affect the analytical performance of LIPS. Parameters such as wavelength of laser light, laser pulse energy, pulse duration, observation time duration, ambient gas pressure, type and properties of the target, and the geometric setup of the optical instruments strongly influence the performance of LIPS [2]. Atomic components emit distinctive light that is received from optical fibers and transferred to the spectrometer for analysis [3]. Optical emission spectroscopy (OES) has recently gained a great deal of consideration for portrayal dependent on the LIPS. The ratio method is one of the most common techniques for the optical emission spectrum. It is used in calculating the electron temperature, while the Boltzmann plot method is one of the best methods for calculating the electron density [4]. In this experiment, the ratio method is used as a common method for calculating the electron temperature at which the intensity of a two of atomic or ion spectral lines at the same ionization stage can be calculated. In the local thermodynamic equilibrium (LTE), the plasma temperature is calculated by the following equation [5]:

\[ T = \frac{-(E_i-E_j)}{k \ln \left( \frac{I_1}{I_2} \right)} \]

where \( I_1 \) and \( I_2 \) refer to the intensity, \( g \) is the statistical weight, \( A \) is the transition probability, \( \lambda \) is the wavelength, \( E_i \) and \( E_j \) are the energy values of the excited state in eV, and \( k \) is the Boltzmann constant. Electron density describes the number of free electrons per unit volume. Saha-Boltzmann equation utilizes spectral lines of the same element and successive ionization stages. The Saha-Boltzmann equation is given as [6]

\[ n_e = \frac{I_1}{I_2} \times 10^{21} (T)^{3/2} e^{(E_i-E_j-X_e)/kT} \]

where:

\[ I_2^x = \frac{I_2}{g_2 A_2} \]

\( X_e \) is the ionization energy in eV, \( g_2 \) is the statistical weight of transition from level (2) to level (1), \( \omega_2 \) is the corresponding wavelength of transition from level (2) to level (1), and \( A_2 \) is a transition probability of transition from level (2) to level (1). While the plasma frequency is calculated from the equation [7]:

\[ f_p = \frac{e^2 \sqrt{n_e}}{m_e e^2} \]

This frequency depends only on the plasma density. The plasma frequency is one of the most important plasma parameters [7]. The Debye length is the fundamental characteristic of the behavior of plasma, as it represents the distance in which the individual particle affects another charged particle that carries a reverse charge inside the medium of the plasma. Debye length \( (\lambda_D) \) is directly proportional to the square root of the electron temperature and inversely to the electron density, according to [8]:

\[ \lambda_D = \frac{e^2 k_B T_e}{n_e q^2} \approx 7430 \times \left( \frac{T_e}{n_e} \right)^{1/2} \]

where \( n_e \) is the density of the electron, \( T_e \) is the electron temperature and \( e \) is the electron charge. The number of particles in the Debye sphere \( (N_D) \) is dependent on the electron density and electron temperature and it represents a second condition for plasma existence \( N_D \gg 1 \) as follows [9]:

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

In this experiment, plasma was generated using pulsed laser on solid target CdO:Sn. The experimental arrangement of laser induced plasma spectroscopy (LIPS) is shown in Figure-1.

![Figure 1-Schematic diagram of the experimental LIBS set-up](image)

The plasma was generated by a Q-switched pulsed laser Nd:YAG with a wavelength of (1604) nm and frequency of (6) Hz. The pulse laser energy was shifted utilizing streak light Q-switch delay through the laser controller and was estimated by energy meter. The laser beam was focused on the target, making an angle of 45° with it. The laser beam evaporates and ionizes the target material, creating a plasma plume above the target surface. Optical emission spectroscopy (OES) technique was used for the determination of electron temperatures, densities, and plasma frequency. The length of Debye and Debye number were determined mathematically. The spectrometer that is used must be fast with the same response time in every shot. Thus, Surwit (S3000-UV-NIR) spectrometer was used in the setup to determine emission wavelengths and has high efficiency goals, relying upon grinding utilized in it and reacting to a wavelength of 200-900 nm. The spectrum of plasma with different value of energies was prepared by mixing CdO with Sn at different percentages (X=0.1, 0.3, 0.5), while the laser pulse energy varied from 500 to 800 mJ. Each spectrum was obtained over a wavelength range of (300-700) nm. The results were discussed and compared with the National Institute of Standards and Technology data (NIST database). The plasma parameters were then evaluated [10].

Results and Discussion

The plasma resulting from the interaction of laser beams with the surface of the target material contains electrons and ions in an excited state, in addition to neutral atoms and radiation. The process of plasma analysis was performed by measuring the parameters of the electron temperature (T_e) and the electron density (n_e). The knowledge of the plasma temperature and density of the plasma species is important for understanding the atomic ionization and excitation processes occurring inside the plasma. The optical emission spectra of CdO:Sn plasma was recorded using an optical emission spectroscopy technique with 1064 nm Nd-YAG laser. Figures-(2, 3 and 4), respectively, show the spectroscopic patterns for laser induced on the CdO:Sn component at X=0.1, 0.3 and 0.5 percentages of target plasma, confined in the air in the spectral range of (300-700) nm with E=(500 - 800) mJ. These results agree with those of an earlier work [11].
Figure 2: Emission spectra induced by 1064 nm laser, with different laser energies for CdO:Sn at $X=0.1$ target in the air.

Figure 3: Emission spectra induced by 1064 nm laser, with different laser energies for CdO:Sn at $X=0.3$ target in the air.
Figure 4—Emission spectra induced by 1064 nm laser, with different laser energies for CdO:Sn at X=0.5 target in the air.

Tables (1, 2 and 3) show electron temperature (Te), electron density (ne), Debye length (\(\lambda_\text{D}\)), plasma frequency (\(f_\text{p}\)) and Debye number (\(N_\text{D}\)) for CdO:Sn at X=0.1, 0.3 and 0.5, respectively. 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. Criteria for the plasma were achieved through the results of the plasma parameters (\(\lambda_\text{D}\), \(f_\text{p}\) and \(N_\text{D}\)). It was shown that \(f_\text{p}\) is decreased with laser energy because it is proportional with \(n_\text{e}\), while \(\lambda_\text{D}\) and \(N_\text{D}\) increase with it.

### Table 1—Plasma parameters for CdO: Sn at X=0.1 with different laser energies.

| Laser energy (mJ) | Te (eV)   | n_e (cm\(^{-3}\)) | \(f_\text{p}\) (Hz) | \(\lambda_\text{D}\) (cm) | \(N_\text{D}\) |
|-------------------|-----------|--------------------|----------------------|--------------------------|--------------|
| 800               | 1.079     | 3.97E+17           | 5.7E+12              | 1.1E-04                  | 2.4E+06      |
| 700               | 1.070     | 3.70E+17           | 5.5E+12              | 1.2E-04                  | 2.5E+06      |
| 600               | 1.067     | 3.63E+17           | 5.4E+12              | 1.2E-04                  | 2.5E+06      |
| 500               | 1.054     | 3.25E+17           | 5.1E+12              | 1.2E-04                  | 2.6E+06      |

### Table 2—Plasma parameters for CdO: Sn at X=0.3 with different laser energies.

| Laser energy (mJ) | Te (eV)   | n_e (cm\(^{-3}\)) | \(f_\text{p}\) (Hz) | \(\lambda_\text{D}\) (cm) | \(N_\text{D}\) |
|-------------------|-----------|--------------------|----------------------|--------------------------|--------------|
| 800               | 0.952     | 1.44E+16           | 1.1E+12              | 5.6E-04                  | 1.1E+07      |
| 700               | 0.941     | 1.29E+16           | 1.0E+12              | 5.9E-04                  | 1.1E+07      |
| 600               | 0.923     | 1.08E+16           | 9.3E+11              | 6.4E-04                  | 1.2E+07      |
| 500               | 0.921     | 1.05E+16           | 9.2E+11              | 6.5E-04                  | 1.2E+07      |

### Table 3—Plasma parameters for CdO: Sn at X=0.5 with different laser energies.

| Laser energy (mJ) | Te (eV)   | n_e (cm\(^{-3}\)) | \(f_\text{p}\) (Hz) | \(\lambda_\text{D}\) (cm) | \(N_\text{D}\) |
|-------------------|-----------|--------------------|----------------------|--------------------------|--------------|
| 800               | 0.928     | 1.13E+16           | 9.6E+11              | 6.2E-04                  | 1.2E+07      |
| 700               | 0.924     | 1.08E+16           | 9.3E+11              | 6.4E-04                  | 1.2E+07      |
| 600               | 0.921     | 1.05E+16           | 9.2E+11              | 6.5E-04                  | 1.2E+07      |
| 500               | 0.906     | 9.85E+15           | 8.9E+11              | 6.7E-04                  | 1.3E+07      |
The variances of \( (\text{T}_e) \) and \( (\text{n}_e) \) as determined by the Ratio Method using two lines of cadmium (Cd I in this part) for CdO:Sn at X=0.1, 0.3 and 0.5 are shown in Figure 6 (a, b and c, respectively) for different laser energies.

**Figure 6 (a,b,c)** - The electron temperature \( (\text{T}_e) \) and electron density \( (\text{n}_e) \) change as a function of laser energy for CdO:Sn at different ratios.
The values of $T_e$ were obtained from the Ratio method as shown in Figure-6(a,b,c), via the analysis of the recorded Cd I peaks for plasma induced on CdO:Sn component in the air. A 1064 nm laser was used with different laser energies of 500, 600, 700 and 800 mJ. From the results, it can be noted that the electron density and the electron temperature were increased with the increase in laser energy. The reason for these increases is that the laser peak energy has a strong and important effect on the emission lines intensities, where the intensities of the spectral lines increase with increasing the laser peak energy because the mass ablation rate of the target also increases. The increase in laser energy will also increase its absorption in the plasma, resulting in more ablation, which leads to increasing the number of excited atoms and hence the peaks of spectral line intensities of plasma emission. This results agrees with that previously reported [12].

Conclusions

Plasma CdO:Sn was produced using a Q-switched Nd:YAG laser at a wavelength of (1064 nm) with different energies of 500 - 800 mJ. Optical emission spectroscopic studies were performed to determine the dependencies of plasma parameters, such as electron density and electron temperature. The plasma parameters were estimated in terms of their dependence on the laser energy. The results indicated that the values of $T_e$, $n_e$ and $f_e$ were increased with the increase of laser energy in the atmosphere, while the values of $N_0$ and $\lambda_0$ were decreased. We note that, when doping increases (i.e. CdO decreases and Sn increases) in the mixture, the intensity emission lines of both Sn and CdO were clearly increased as well as the peaks became sharper. All plasma parameters satisfied plasma conditions.

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