Simulation study of a fluorine spectrums induced by laser sublimation

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Abstract

This paper aims to numerical study of the experimental spectrum, in the context of the diagnosis of solid materials by spectroscopy; the resulting spectrum of fluorine plasma has been analyzed. The plasma is generated after the sublimation of the solid sample the fluorine by Laser Induced Breakdown Spectroscopy (LIBS technique). The theoretical spectra and the electronic temperature of a obtained plasma have been calculated, this temperature (1.92 eV) is well matched to the laboratory plasma criteria. The main results also are showed that the resulting medium consisted of 96.63% Calcium and 3.36% Fluor.

1. Introduction

Spectroscopy is one of the most important modern methods in the diagnosis of material. The medium resulting from the analysis of the solid material is studied via different rays, and the resulting spectrum contains important and accurate information about the medium. There is a lot of research work that has been done on this subject [1–5]. Some is based on the study of the resulting spectral broadening (Doppler or Stark) in order to deduce the electron density or electron temperature of the medium [6–10], and many other works are based on spectral intensity by Boltzmann’s law and are often applied using its approximate plot. However, Boltzmann’s law requires that the resulting plasma be in thermodynamic equilibrium, even though laboratory plasma is often not in thermodynamic equilibrium. In this work, we will try to illustrate a new technical and numerical model that will allow us to deduce with precision the electron temperature and density of the medium.

LIBS technique is one of the most essential methods for gathering information of superior quality [11]. In this LIBS method, the analysis of laser spectral lines of many types of matter generated by plasma state, which results from an intensive laser–matter interaction [11–14]. Among the advantages of this technique, it is the detection of the lightest multi-elements through the micro dimension of the sample [15].

Using this (LIBS) method for the elemental analysis designation [16]. Fluorine is defined as a mineral composed of Fluor and Calcium, and it is naturally present in coal tar [17]. In this work, we will study exactly the experimental spectrum resulting from laser-generated plasma during fluorine sublimation using the LIBS technique (Laser Induced Breakdown Spectroscopy).

First of all, we present both our digital model and describe briefly the experience through which the experimental spectrum was recorded.

2. Experimental device

The principle of LIBS spectroscopy consists in focusing an energetic light pulse in the nanosecond range (commonly Nd:YAG at 1064-532-355 or 266 nm) on the surface of a solid sample (gas or liquid), and its spectral...
analysis of the light emission of the plasma produced by the ablation; using a light collecting device returning the latter in a spectrometer equipped by a CCD detector and a disc with multiple perforated blades (called a chopper) rotating at a frequency of 25 000 revolutions per minute.

The standard diagram of a laboratory LIBS experiment is shown in figure 1.

The studied experimental specters are registered from an experimental setup witch carried out by Dr Yann FOUCAUD et al. The experimental spectrum is presented in the figure 2.

In experimental work, the main used parameters are shown in table 1.

According the figure 2, a very high prevalence of vibration molecular bands from the CaF molecule in the fluorine spectrum around 530, 590, and 620 nm, which are the only spectral signatures capable of revealing the presence of fluorine in the interval spectral shown here (the measured data with a fluorine concentration of 9.53%).

3. Calculation of theoretical atomic

In order to study the experimental spectra resulting from the sublimation of the fluorine plasma, we have to redraw theoretically by an elaborate numerical program; it has been prepared by the FORTRAN language and is based on the following equations and laws of thermodynamic equilibrium [19]:

Table 1. The experimental parameters.

| Parameter       | Value                                         |
|-----------------|-----------------------------------------------|
| Fluencies       | 50 J.cm$^{-2}$ for pump laser                 |
| Pulse width     | a few tens of femtoseconds a few tens of nanoseconds |
| Delay number    | 400 ns                                        |

Figure 1. Schematic description of experimental setup.

Figure 2. Experimental spectrum resulting of the Fluorine.
The Maxwell-Boltzmann Distribution
The Boltzmann law
The Saha law
The Dalton law
The electric neutrality law
The law of conservation of matter

Our program considers all the broadening lines possible: Doppler, natural, effect Stark, Van der Waals collision, instrumental broadening and Voigt Profile. Spectroscopic methods are used in this program.

The recommended data are as follows:

- Minimal and the maximal wave lengths
- Number of the point representing the spectra
- Van der Waals Constant and atomic mass of etch element in the medium
- Experimental width: Gaussian or Lorentzian shape
- Input files of the atomic databases of each element

The database gives the concerned energy levels of each element with the statistical weights associated, the transition wavelengths and the radiated transition probabilities [20].

To calculate the theoretical spectra, the databases from atomic physics for all the elements that may exist in the medium have been set up (F, Ca and Ca +) along with possible impurities (O, H, N…).

The theoretical spectra calculated are presented in figure 3.

4. Results and discussion

4.1. Identification of the chemical elements responsible for spectral emission

The comparison between the theoretical spectra and the experimental spectrum (figure 2), allows identification some of the spectral lines are represented in the figure 4.

4.2. Calculation of the electronic temperature $T_e$

The spectral analysis was applied to the selection of the appropriate spectra, to calculate the average electronic temperature by using the Boltzmann method, which consists of calculating the intensity ratio between two transitions.

For the determination of the electronic temperature, we preferred to use the ratio of the intensity of two lines of the Fluor in the same stages. Therefore, the spectra recorded in table 2 were selected for our study. Atomic data for these transitions has been extracted from the NIST Atomic Spectra Database [21]. Experimental intensity values were taken from the experimental spectrum.

Let’s take: $\lambda_1$ and $\lambda_2$ two lines from population levels $N_m$ and $N_p$

The total intensity of each line is given by:

\[
I_1 = N_m A_1 hc / \lambda_1
\]

\[
I_2 = N_p A_2 hc / \lambda_2
\]

Where

$A_1$ and $A_2$ are the corresponding probabilities of spontaneous emission.

At the local thermodynamic equilibrium (LTE), the population of each level is given directly by the Boltzmann law according to the temperature of the medium [22]:

\[
N_m = (N_{1c} g_m / B_H(T)) \exp \left(-E_m / k_BT\right)
\]

Where,

$B_H(T)$ is the partition function of the Calcium

$R$ is the ratio between the intensities of peaks, from which:

\[
R = \frac{I_1(\text{exp})}{I_2(\text{exp})}
\]

\[
\frac{I_1}{I_2} = \frac{g_1 A_1 \lambda_1}{g_2 A_2 \lambda_2} \exp \left(\frac{E_2 - E_1}{k_BT}\right)
\]
After numerical application in the equation (7), the electronic temperatures 1.927 eV, this value is almost identical to the theoretical range between 02 and 05 eV [23, 24].

**4.3. Numerical calibrations and calculation of percentages**

The spectroscopic model used in calculating the percentages of chemical elements is based on the following steps:
Calculate the intensity ratio \( R_T \) for Calcium and Fluor theoretically, assuming that the same concentration (1 mol) for both those elements.

Calculate the intensity ratio \( R_E \) between Calcium and Fluor empirically from the experimental spectra.

In matching the ratios \( R_E \) and \( R_T \), the two factors \( y \) and \( x \) must be added. They represent the average number of moles for Calcium and Fluor, respectively.

Divide the experimental intensity of Calcium by \( x \) mol and the experimental intensity of Fluor by \( y \) mol. By matching them, it is possible to obtain the following relation:

\[
R_{EX} = R_T y
\]

From the previous data of table 1, for the Calcium element the spectrum (1) was chosen because of its probability and stability compared to the other spectra; however, the only identified spectrum (3) was chosen for the Fluor element.

We assume that all laser-induced atoms are excited; and also the numerical program gives the following theoretical intensities (see table 3):

Taking into account the distribution function for each element as follows: \( B(T) = 2g + 1 \)

According the experimental spectra, the following intensities were recorded and summarized in the table 4.

Using the intensities ratio method of two lines, we find that,

\[
R_T = \frac{I_{Ca}}{I_F} = 0.313
\]

\[
R_E = \frac{I_{Ca}}{I_F} = 9
\]
After compensation in equation (6), we obtain:

\[ 9x = 0.313y \Rightarrow x = 28.75 \]

As can be seen from our study, the 96.63% of the medium is the Calcium atoms and the remaining is 3.36% of Fluor atoms.

This is also clear, in the experimental spectrum; the most of identified radioactive elements are due to Calcium.

5. Conclusion

In this present study, a numerical model to analyze the spectra resulting from the laser sublimation plasma of fluorine was conducted; our model calculation were enabled to determine the radioactive elements in the medium, from the theoretical spectra calculations that are in good agreement with experimental spectra. We have also been able to calculate the electronic temperature of the medium (1.92 eV); this value is almost identical to the cold plasma classification of the laboratory. Our spectroscopic model also shows that our media consisted mainly of 96.63% Calcium and 3.36% Fluor.

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