Time-spatial resolved LIBS of atomic and molecular carbon in laser ablation plasma

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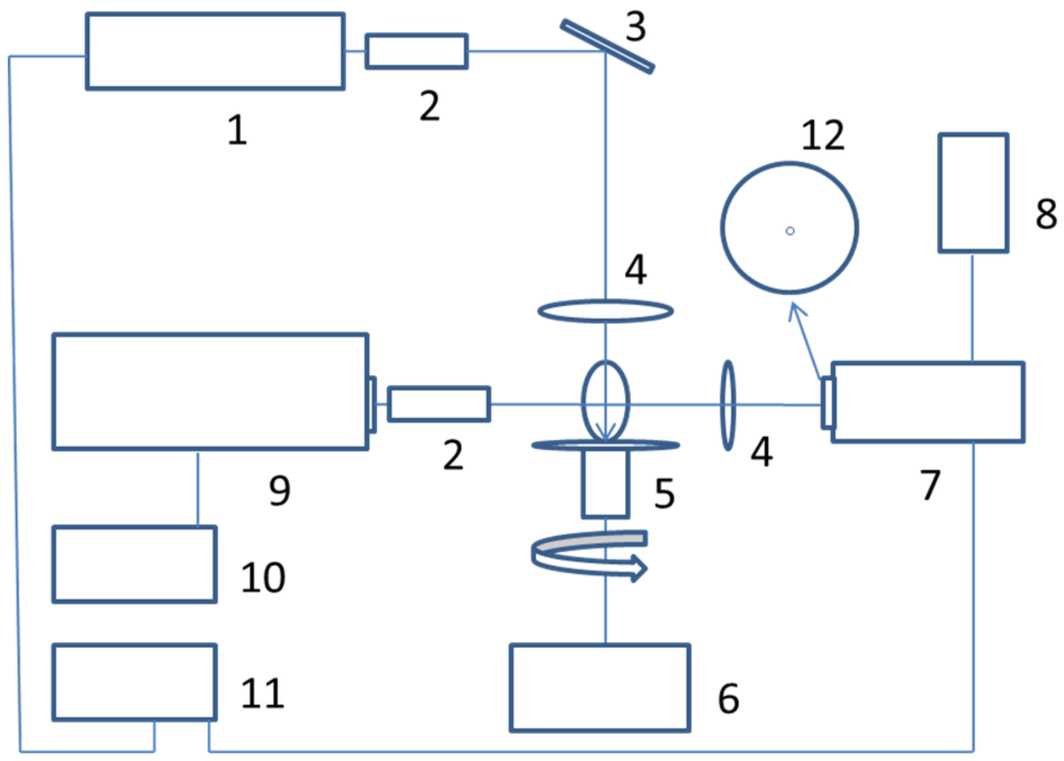
Introduction

LIBS is a well-proven method for analyzing atomic components of an unknown sample based on their characteristic emission spectra. LIBS combines the ability to analyze all types of materials in any phase state, to detect all elements (including light ones, which are difficult to analyze by other methods). LIBS has the ability to perform on-site analysis without preliminary sample preparation, as well as remote analysis. LIBS methods can be classified as practically non-destructive, since with laser excitation, nanograms or even picograms of the sample material are used for analysis. However, standard LIBS analysis, in terms of sensitivity and detection limit, is still behind traditional methods of spectrochemical analysis, in particular, using inductively coupled plasma. Therefore, improving LIBS analytical characteristics is highly relevant. A promising solution to the problem seems to be an additional analysis of the molecular emission bands arising in plasma cooling phase. The analysis can be carried out by observing radicals and diatomic molecules, strong molecular bands of which are often in the visible spectral region and can provide a higher detection sensitivity. In this work for elucidation a possibility to use molecular emission spectra in LIBS analysis of carbon containing materials time and space resolved spectra of laser ablation plasma from graphite were studied.

Experimental setup



1 - laser, 2 - telescope, 3 - rotating mirror, 4 - lens, 5 - graphite target, 6 - power supply for the motor with a reducer, 7 - photomultiplier, 8 - photomultiplier power supply, 9 - spectrograph, 10 - computer, 11 - digital oscilloscope,12 - an interference filter with a diaphragm

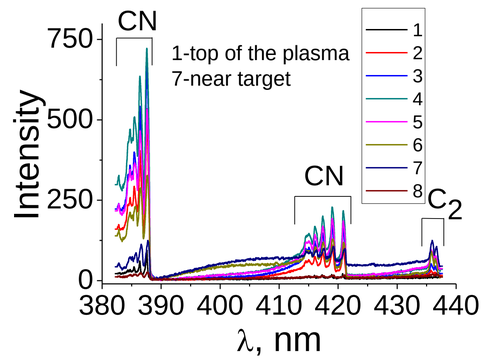
Laser plasma was formed when a graphite target was exposed to the radiation of a YAG: Nd^{3+} laser (Lotis TII LS2131D, Belarus). The wavelength of the generated radiation is 1064 nm, the pulse energy - see table, the pulse duration is 10 ns, the pulse repetition rate is 10 Hz. The diameter of the laser beam is 4 mm, the divergence is 1.5 mrad.
A laser beam passing through a telescope and a rotating mirror was focused with a lens (F = 280 mm) onto the surface of a graphite disk used as a target. To avoid the formation of a crater on the surface of the sample, and, consequently, to change in the linear dimensions of the erosion plume and, thus, distortion of the measured values, the disk was driven by a motor with a gearbox. Target rotation also made it possible to avoid its rapid destruction. A telescope was used to focus the plasma image onto the spectrograph slit. The selection of plasma emission was carried out at right angles to the incident laser beam. The analysis of radiation was carried out using a monochromator / spectrograph GSM-850 Lotis TII, made according to the Cherni-Turner scheme with a flat diffraction grating of 600 lines / mm. The size of the entrance slit was 50 μm. The emission spectra were recorded with a C10416 CCD detector (Hamamatsu). Spectral lines were recorded using a diaphragm with an aperture 0.5 mm in diameter in the center of the plasma formation.

Summary

The plasma electron concentration and electron temperature as well as vibrational temperature were determined in different zones of the expanding plasma and at different values of laser power densities ($2{,}2 \cdot 10^8 \div 3{,}7 \cdot 10^8$ W/cm^2) used in experiments. The electron temperature varied in the range 9700 – 10300 K, the electron concentration was estimated to be in the range from $0{,}8 \cdot 10^{18}$ cm^{-3} to $8{,}0 \cdot 10^{18}$ cm^{-3}, the vibrational temperature of the plasma was 4560 - 7350 K depending on the experimental conditions (laser power density, spatial zone of the plasma plume).

Results and Discussions

The temporal and spatial characteristics of the plasma spectra with special attention to molecular carbon including molecules CN and C_2 were analyzed. The atomic emission spectra of the plasma were used to estimate the concentration of electrons and the electron temperature of the plasma. The vibrational temperature of the carbon plasma was determined from the molecular spectrum of the radical CN ((Δv = 0, -1).



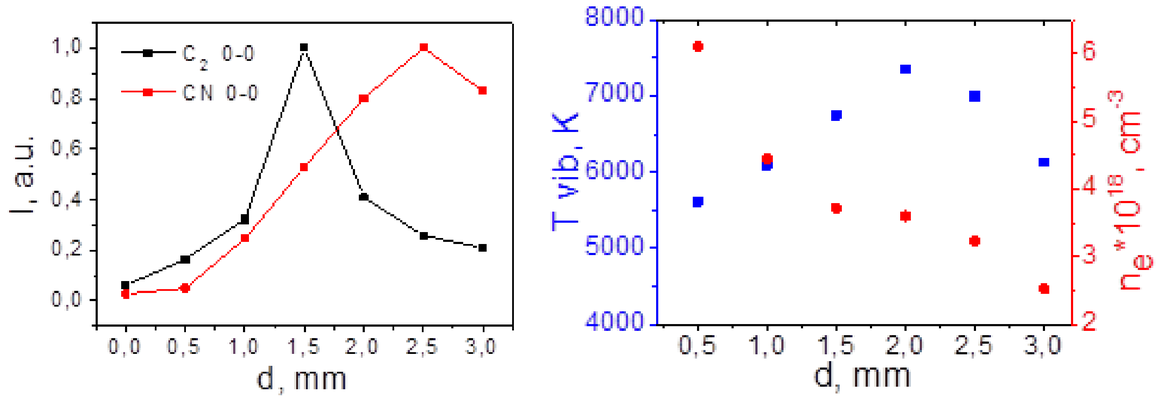


Figure 1 – The position of the intensity of the peak of the band, the concentration of electrons, and the vibrational temperature (determined from CN ((Δv = 0) depending on the distance from the target surface.

Table 1 - Estimation of the electron concentration and the electron temperature of the plasma at different power densities of laser radiation at 1.5 mm and 3.0 mm distance from the target surface.

W·10⁸, W/cm²	n_e ·10¹⁸, cm⁻³		T_e, K	
	d = 1.5 mm	d=3.0 mm	d = 1.5 mm	d=3.0 mm
2,25	6.94	4.16	10330	10140
3,14	3.72	2.52	10160	10040
3,53	1.94	1.34	9920	9784
3,71	1.84	1.08	9898	9706

It was found that the time range of dominance of the C2 and CN emission is related to the stage of the plasma decay (10–20 μs after the action of the laser pulse, depending on the plasma creating conditions.

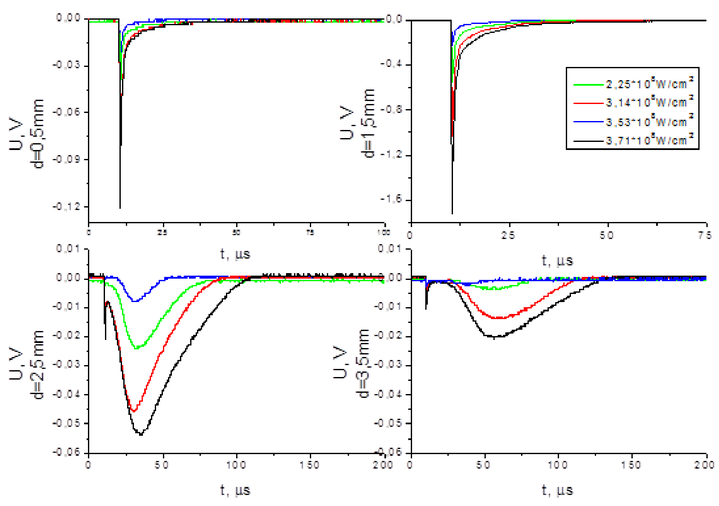


Figure 2 - Oscillograms of plasma emission decay recorded at the CN 421.16 nm line

Table 2 - Estimation of the vibration temperature from CN ((Δv = -1) on the different distances from the target surface at laser radiation power density of $3.14 \cdot 10^8$ W / cm ^{2}

d, mm	Tvib, K CN ((Δv = -1)
3	5880
2,5	5230
2	5050
1,5	5290
1	6800
0,5	7190
0	5460

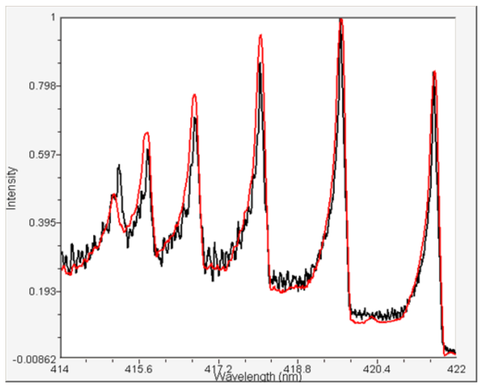


Figure 3 - Comparison of the calculated molecular spectrum CN (Δv = -1) (red curve) with the experimentally recorded one (black curve). Experiment parameters: d = 3 mm, laser radiation power density $3.14 \cdot 10^8$ W/cm^2. Model parameters: Te = 10000K, Tvib = 5880 K, Trot = 4500K.

Acknowledgements

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