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Comparison of zinc and cadmium plasma parameters produced by laser-ablation ☆

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Abstract

We report the measurement of the zinc and cadmium plasma parameters produced by the fundamental, second, and third harmonics of the neodymium-doped yttrium aluminium garnet laser. The excitation temperature has been determined from the Boltzmann plot method, whereas the electron number density is estimated from the Stark broadened profile of several spectral lines. The temporal evolution of the plasma has also been investigated. Besides, we present experimental relative transition probabilities of the Zn (4s5s $^3S_1 \rightarrow$ 4s4p $^3P_{0,1,2}$) and Cd (5s6s $^3S_1 \rightarrow$ 5s5p $^3P_{0,1,2}$) triplets and compare our data with that listed in the National Institute of Standards and Technology database. The experiments have been performed in air but also in He, Ne and Ar atmosphere to study the effects of ambient gas environment on the emission intensity of the atomic and ionic lines and on the plasma parameters.

Keywords: Laser produced plasma; Transition probabilities; Stark broadening; Zinc; Cadmium; Spectroscopy

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a useful technique for determining the elemental composition and plasma parameters of various solids, liquids and gases. LIBS use a low-energy pulsed laser (generally until a few hundreds of mJ) to generate the plasma which vaporizes a small amount of sample. Spectra emitted by the excited species, neutrals and ions, are used to develop the quantitative and qualitative analytical information. The plasma formation requires vaporization of the material surface and the vaporization of the sample occurs when the energy deposited on the target exceeds the latent heat of vaporization of the target. If the laser energy is very close to the breakdown threshold, the pulse-to-pulse fluctuation can cause the plasma condition to be unreproducible, which results in poor measurement precision. The two mechanisms responsible for electron generation and for growth in laser-induced breakdown are multiphoton absorption and collision-induced ionization [1]. The analytical performance of the LIBS technique depends strongly on the choice of the experimental conditions. There are mainly, the laser parameters (wavelength, energy, pulse duration, shot to shot power fluctuation, focusing spot size), the ambient conditions (gas, pressure), the physical properties of the sample and the acquisition delay and temporal window [2,3]. There are many experimental studies reported in the literature about the effect of the laser pulse duration on laser induced plasma emission, electron density and plume temperature [4,5]. Cabalin et al. [6] experimentally determined the laser induced breakdown thresholds of several metals (Zn, Al, Ag, Cu, Ni, Fe, Cr, Mo, and W) in air by using the fundamental, second and fourth harmonics of a Q-Switched Nd:YAG laser. Rieger et al. [7] studied the effect of the laser pulse duration (picosecond and nanosecond) on the laser produced silicon and aluminum plasmas using a KrF laser. Many theoretical models have been reported in the literature to understand the plume dynamics and to assess the plasma

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properties [8–12]. A number of researchers have experimentally investigated, the effect of the background gas and the laser wavelength on the mass ablation rate, the plasma temperature and electron number density. The effect of the laser wavelength on the plasma parameters was reported by Fabbro et al. [13] who used a Nd:glass laser that was frequency-doubled and quadrupled to give wavelengths of 1.06 μm, 0.53 μm, and 0.26 μm, respectively. Dittrich and Wennrich [14] also discussed that the mass ablation rate increases at shorter wavelengths. Barthe´lemy et al. [15] studied the effect of the laser wavelength on the axial and temporal behavior of the temperature and electron number density of an aluminum plasma, ablated by the 1064, 532 and 266 nm of the Nd:YAG laser with 6 ns pulse duration. Cristoforetti et al. [16] studied the variation of the emission line intensities of Cu(I) at 521.5 nm, Cu(II) at 224.7 nm and O(I) at 777.3 nm line with the ambient air pressure ranging from 0.1 torr to the atmospheric pressure. They observed that the emission intensity of the Cu(I) line at 521.5 nm increases with the pressure up to approximately 100 torr and then it slightly decreases up to the atmospheric pressure. However a different behavior of the O(I) line at 777.3 nm was reported. The effect of the ambient gas pressure on the spectral intensity of the zinc–aluminum alloy was studied by Kim et al. [17] using a Nd:YAG laser at 1064 nm. In the same paper they observed that the spectral intensity of the Al I line at 309.27 nm increases with the ambient pressure in air and argon, but it was more evident in the presence of argon than in air.

Iida [18] observed an appreciable effect of the ambient atmosphere (He, Ar and air) on sample vaporization, plasma emission intensity, excitation temperature and electron number density. Kumar and Thareja [19] studied the spatial and temporal behavior of the laser produced copper plasma in vacuum and in the presence of argon and neon gas. More over Jakckson and Gunther [20] compared the effect of He and Ar on the particle size distribution, for a Nd:YAG laser of 266 nm and an excimer laser of 193 nm, on pure copper sample. Extensive studies have been devoted to the plasma diagnostics and measurements of its parameters [21–25]. Mao et al. [26] studied the effect of the laser pulse duration on the ablation rate, using an excimer and a Nd:YAG laser and discussed the influence of the laser wavelength. Xu et al. [27] estimated the radiative lifetime and transition probabilities in Cd(I) and Cd(II). Recently Mayo et al. [28] determined the oscillator strength of Zn(II) lines and estimated the degree of ionization, using the fundamental mode of a Q-switched Nd:YAG laser.

The aim of the present work is to report the effect of the laser wavelength on the emission intensity and on the plasma parameters of pure zinc (99.99%) and cadmium (99.99%). The zinc and cadmium plasma have been generated by the fundamental (1064 nm), second (532 nm) and third (355 nm) harmonics of a Q-switched Nd:YAG laser. The excitation temperature and the electron number density have been determined from the Boltzmann plot method and Stark line broadening respectively. The relative transition probabilities of the Zn ($4s5s\ ^3S_1 \rightarrow 4s4p\ ^3P_{0,1,2}$) and Cd ($5s6s\ ^3S_1 \rightarrow 5s5p\ ^3P_{0,1,2}$) triplets have also been estimated using the temporal analysis of the emission lines. In addition, the effects of the ambient environment (Argon, Neon and Helium) on the emission intensity and on the plasma parameters have been studied.

2. Experimental setup

A schematic diagram of the experimental setup is similar as in our pervious work [29–31] as shown in Fig. 1. The laser used in our experiments was a Q-switched Nd:YAG (Quantel Brilliant) of 5 ns pulse duration and 10 Hz repetition rate. The laser beam was focused by a 10 cm quartz lens on the sample in a chamber. The estimated area of the laser spot on the target were 2.8×10^{-4} cm^2, 5.2×10^{-5} cm^2 and 2.3×10^{-5} cm^2 at 1064 nm, 532 nm and 355 nm, respectively. The target was mounted on the sample stage, which was rotated to provide a fresh surface after each laser pulse to avoid deep crater. The distance between the focusing lens and the sample was less than the focal length of the lens to prevent any breakdown of the ambient gas in front of the target. The emission from the plume was registered by the LIBS2000 (Ocean optics. Inc) detection system in conjunction with an optical fiber (high-OH, core diameter: 600 μm) having a collimating lens (0–45° field of view), placed at right angle to the direction of the plasma expansion. The optical emission of the plasma was observed through a 5 cm diameter fused silica window. The emission signal was corrected by subtracting the dark signal of the detector through the LIBS software. The LIBS2000 detection system is equipped with five spectrometers each having a slit width of 5 μm and covering the range between 200 and 720 nm. Each spectrometer has 2048 element linear CCD array and an optical resolution of ≈0.06 nm. The LIBS2000 detection system and the Q-switch of the Nd:YAG laser were synchronized. The LIBS2000 system triggered the Q-switch of the Nd:YAG laser and the flash lamp out of the Nd:YAG laser triggered the LIBS2000 detection system through a four-channel digital delay/Pulse generator (SRS DG 535). The output data were averaged for 10 laser shots. The system has been calibrated in wavelength by recording the well-known lines of neon, argon and mercury covering the wavelength range 200–720 nm. The uncertainties in the measurement are ≈0.02 nm. All the five spectrometers installed in the LIBS2000 are manufacturer calibrated in efficiency using the DH-2000-CAL standard light source. The data acquired simultaneously by all the five spectrometers were stored on a PC through the OOI LIBS software for subsequent analysis.

3. Results and discussion

In the first set of experiments the time-resolved diagnostic technique has been used to study the emission spectrum of Zn and Cd plasma produced by the 1064 nm of a Nd:YAG laser with 5×10^{10} W/cm^2 irradiance in air. At the initial state of the plasma (≈0 μs delay), it has been observed that an intense continuum emission of the cadmium plasma is instantaneously produced when the laser pulse reaches the target surface. The continuum quickly decreases with an increase in the delay time and the isolated lines of the excited Cd neutrals gradually emerge up to the time delay of 0.1 μs. The emission spectrum of the cadmium