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Measurement of Stark broadening parameters of Fe II and Ni II spectral lines by laser induced breakdown spectroscopy using fused glass samples

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ABSTRACT

The Stark widths of 36 Fe II and 27 Ni II spectral lines are measured by laser induced breakdown spectroscopy (LIBS). The use of fused glass samples prepared by borate fusion is evaluated for Stark broadening measurements in LIBS experiments. The spectra of laser-induced plasmas generated from fused glass samples containing oxides show improved line-to-background ratios compared to those measured with alloys. The diagnostics of the fused glass laser induced plasmas shows that their characteristic parameters are not very different from those of alloy plasmas. The electron density in the experiment is in the range $(0.8–10) \times 10^{17}$ cm^{-3} and the temperature varies from 12000 K to 17600 K. These experimental Stark width data, most of which had not been measured previously, complete the data for Fe II and Ni II reported in earlier works, determined by LIBS using alloy samples.

1. Introduction

Stark widths are relevant parameters in plasma spectroscopy, essential for the diagnostics of the electron density in astrophysical and laboratory plasmas [1]. A continued research effort has been made in the past to provide Stark broadening data. Critical compilations of experimental data are published periodically [2,3], and references to articles in this topic are collected in the updated database [4]. Nevertheless, Stark width data are still scarce for many elements, probably due to the difficulty of conventional plasma sources for producing high density plasmas containing certain elements. In the last decade, laser induced breakdown spectroscopy (LIBS) has been used with increasing interest for the measurement of Stark widths, due to the ability of this technique to produce plasmas of high electron density from different types of materials. In most cases, laser induced plasmas have been generated from metals or metallic alloys [5–7]. Recently, experimental Stark broadening parameters for Mg I and Mg II lines have been determined from the spectra emitted by a laser-induced plasma generated using a pellet formed from the powder mixture of oxides and salts [8]. Metallic alloys and pellets are two of the most common laboratory-made samples used in LIBS. In a recent work [9], sample preparation as fused glass disks has been introduced, with the focus on the analysis by LIBS of rocks and minerals. For these samples, it is shown that the fused glass approach produces better results in terms of separability between different sample materials and analytical precision than does the more commonly used method of pressed powder pellets.

In previous works of our group [10–12], we have used LIBS to measure the Stark widths of several Fe II and Ni II lines. In these works, the laser induced plasmas were generated from Fe–Cu and Fe–Ni samples, for the measurement of Fe II lines,

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and Ni–Cu, Ni–Al samples in the study of Ni II lines. In all cases, some observed lines of the elements of interest could not be studied due to their overlapping with lines emitted by the matrix elements of the samples used. The aim of the present work is to evaluate the use of laser-induced plasmas generated from fused glass samples as spectroscopic sources for the measurement of Stark widths. As a test of this approach, the study will focus on Fe II and Ni II lines that could not be measured in previous works where the plasmas were generated from metallic alloys.

2. Experiment

The experimental setup is the same used previously [12], so it is only described briefly. A Nd:YAG laser (wavelength 1064 nm, pulse energy 300 mJ, pulse width 4.5 ns, and repetition rate 20 Hz) is used to generate the laser-induced plasmas. In the experiment, the pulse energy is reduced to 60 mJ using an optical attenuator. The laser beam is focused in vertical direction by a lens of 126 mm focal length placed at 122 mm from the sample surface. During the measurements, the sample is rotated at 100 rev min^{-1}. A system of plane and concave mirrors collects the plasma emission from the lateral direction, forming a 1:1 image onto the entrance slit of a spectrometer (Czerny-Turner, focal length 0.75 m, gratings of 1200 and 3600 lines mm^{-1}). With this configuration, the measured spectra are spatially-integrated along the line-of-sight and also along the plasma axis. The slit width and the grating are selected according to the required resolution in the experiment. The detector is an intensified charge-coupled device (ICCD, 1200 × 256 effective pixels). The spectra from 100 laser pulses are averaged in order to obtain spectra with good signal-to-noise ratio. The spectra have been measured at 11 time windows, centered at instants of the plasma lifetime ranging from 0.4 to 6 μs. The width of the time windows increased with the delay, from 0.04 to 2 μs.

The samples have been prepared by borate fusion of Fe_2O_3 and NiO oxides in powder form. The flux used has been a mixture of lithium tetraborate and lithium borate of 50/50 composition. The iron and nickel oxides are mixed separately with the flux. The fluxer allows simultaneous fusion of three samples using Pt–Au crucibles and molds. The masses of the oxides and flux have been selected to obtain samples with the desired concentrations of the element of interest. Using Fe_2O_3, five samples with Fe concentrations in the range 0.05–1.0 at% have been prepared, whereas in the case of NiO, the four samples obtained have concentrations from 0.1 to 0.8 at%.

3. Results and discussion

3.1. Characterization of the emission from laser induced plasmas generated from fused glass samples

In this subsection, we describe firstly the general features of the spectra obtained using fused glass samples and later the results of the diagnostics of the laser induced plasmas. When working with fused glass samples, the concentration of the solved material is small. Therefore,

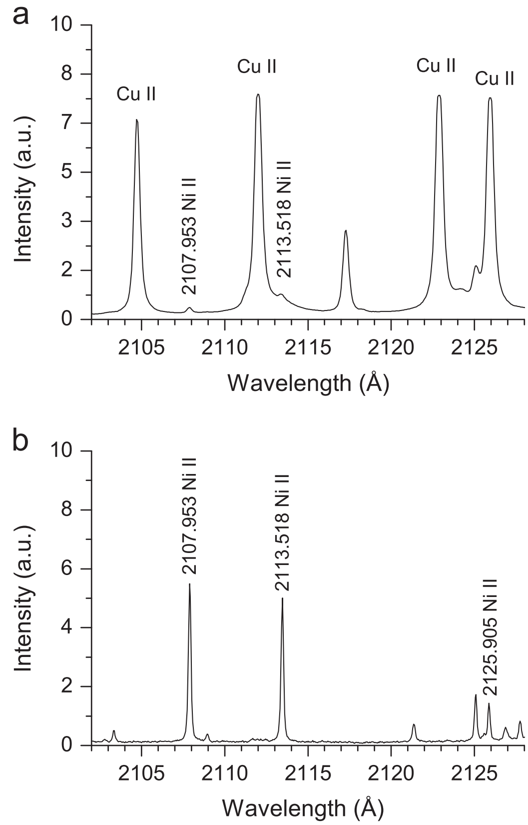

Fig. 1. Spectra containing three Ni II spectral lines of interest measured using a Ni–Cu alloy (a) and a fused glass sample prepared from NiO (b).

the borates used as solvents in fusion constitute the matrix of the samples obtained. The spectrum emitted by this glass matrix is very simple. In the spectral range studied, which goes from 2000 to 4000 Å, only a few intense B I lines and a weaker Li I line are observed. As an example, Fig. 1a shows the spectrum measured using a Ni–Cu alloy compared to the same spectral region obtained from a fused glass sample (Fig. 1b). The Ni content was similar in both samples: 1.0 at% for the Ni–Cu alloy and 0.8 at% for the fused glass. Three Ni II lines of interest, shown in the figures, are emitted in this spectral region. As can be seen, in the Ni–Cu spectrum of Fig. 1a, the Ni II lines are overlapped to strong Cu II lines resulting from the emission of the copper matrix. In contrast, in the fused glass spectrum of Fig. 1b, the Ni II lines are well resolved and show a high line-to-background ratio, which makes them more suitable for accurate line width measurements in the studied wavelength range. The example shown in Fig. 1b is typical of the spectrum obtained from fused glass samples, so the use of this approach for sample preparation has allowed us to measure the Stark widths of many lines that could not be included in previous works.

The characteristic parameters of the laser induced plasmas generated from fused glass samples have been obtained by the same techniques used in previous works [10–12]. The electron density is determined from the Stark broadening of the H_α line, which is observed in the LIBS spectrum due to the emission coming from the water