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Experimental and theoretical studies of laser-induced breakdown spectroscopy emission from iron oxide: Studies of atmospheric effects

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ABSTRACT

We report on a comprehensive study of the emission spectra from laser-induced breakdown spectroscopy (LIBS) measurements on iron oxide. Measurements have been made of the emission from Fe_2O_3 under atmospheres of air, He, and Ar, and at different atmospheric pressures. The effect of varying the time delay of the measurement is also explored. Theoretical calculations were performed to analyze the plasma conditions and find that a reasonably consistent picture of the change in plasma temperature and density for different atmospheric conditions can be reached. We also investigate the sensitivity of the O I 777 nm emission lines to the plasma conditions, something that has not been explored in detail in the previous work. Finally, we also show that LIBS can be used to differentiate between FeO and Fe_2O_3 by examining the ratio of the intensities of selected Fe emission to O emission lines.

1. Introduction

The ubiquity of laser-induced breakdown spectroscopy (LIBS) as an easy-to-use and reliable tool for rapid species identification has been well established now for several decades [1–4]. The application of LIBS for a wide variety of industrial applications, especially in the recycling, manufacturing and oil exploration industries, has been discussed extensively in the literature (for example, see the book of Noll [5]), and LIBS is also increasingly being used for such applications as cultural artifact preservation [6], magnetic fusion diagnostics [7], and geologic sampling. A flagship example of the use of LIBS in a geologic and planetary exploration manner is the ChemCam instrument on the Mars Science Laboratory rover *Curiosity* [8], which has allowed analysis of a wide variety of rocks on Mars [9]. LIBS is also useful for nuclear forensic applications [10, 11].

Concurrently, many investigations of the basic properties of LIBS plasmas have been reported, with usually a stated aim of providing quantitative analysis tools such as calibration-free LIBS [12, 13]. Several studies have been reported of the effect of atmospheres on the generation of a LIBS plasma and the resulting emission intensity, and a recent review by Effenberger and Scott [14] provides a comprehensive summary of such work. The early study of Iida [15] examined the change in emission intensities of spectral lines from a LIBS plasma under different atmospheres. The work of Yalcin et al. [16] also explored the effects of the reduction in pressure of the ambient gas, and Aguilera and Aragón [17] explored the temporal evolution of the temperatures and densities of LIBS plasmas under different atmospheres. On the theoretical front, a detailed fluid dynamic model developed by Shabanov and Gornushkin [18] provides very useful insight into the effects of the ambient gas on LIBS plasmas, along with other interesting findings.

While many studies of LIBS explore the complex emission spectra of Fe arising from iron oxide targets (for example [19]) in various atmospheres, we have found very few studies of the corresponding emission spectra arising from O from similar targets. In this work we aim to make a detailed investigation of both the Fe and O emission spectra, under differing atmospheric conditions. Study of the emission spectra arising from two plasma components allows us to assess the importance of matrix effects, since the atomic state populations and resulting emission from each component are related (via the plasma electron density) to the population and emission from all other components. Following [15, 17], we study the properties of LIBS plasmas in atmospheres of helium, air, and argon, and under differing pressures. We compare the measured and theoretical predictions of the LIBS emission in spectral windows where Fe emission dominates, and where O emission dominates, and show how the O emission is quite sensitive to the temperature of the LIBS plasma. Finally, we also explore the difference in emission spectra from Fe_2O_3 targets compared with FeO targets, and show how comparing ratios

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of emission lines from Fe and O may be used to distinguish between the two oxides. Our study is complementary to a similar study by Nasrazadani and Namduri [20].

The paper is organized as follows. Section 2 provides a brief discussion of the measurements used to generate the emission spectra presented in this paper. Section 3 provides a short description of our theoretical approach to the modeling of LIBS plasmas from iron oxides in various atmospheres. In Section 4 we present a detailed comparison of the LIBS measurements with our theoretical calculations and discuss the implications of our comparisons. We end with a short summary and outlook for future work.

2. Experimental set-up

The laser excitation source used in these experiments was a Big Sky Ultra 100 pulsed Nd:YAG laser operating at 1064 nm with 8 ns pulse width and a variable attenuator producing pulse energies up to 100 mJ at 20 Hz. A laser pulse energy of approximately 33 mJ at 10 Hz was used for all experiments. A 2.5 cm diameter plano-convex focusing lens with a focal length of 10 cm was used to focus the laser pulses onto the sample, perpendicular to the surface of the sample. The focal spot size had a diameter of approximately 300 μm. A two lens system was used to collect the plasma light from the sample consisting of a 25 cm diameter focusing lens (FL 12.5 cm) combined with a 25 cm diameter collimating lens separated by a distance of 12.5 cm. The output from this collection lens system was directed to the entrance end of a broadband UV/VIS/NIR 1 meter fiber optic cable with a 400 μm inner core diameter. The fiber optic cable collected the plasma emission and transferred the light to the spectrometer. A medium resolving power echelle spectrometer from Catalina Scientific (EMU65) was used to collect LIBS spectral data between 200–1000 nm. The resolving power of the spectrometer system is approximately 10,000 in its current mode of operation. The detector used is a Raptor Photonics EMCCD. The delay time and gate width used in most of the experiments presented here were 500 ns and 1 μs, respectively, apart from one study in which the delay time was systematically varied, as discussed in Section 4. Each spectrum presented here is the average of 100 laser shots (individual spectra). The spectra presented here have been corrected with the instrument response function, which was generated by using calibrated light sources and measuring the response of the system (including the grating and the detector.)

LIBS spectral data was collected from this system under helium, argon, and air conditions at different pressures. The gases used in this work were acquired from AirGas. The argon gas was ultra-high purity and the helium gas was standard grade. The FeO (purity 99.9%) and Fe_2O_3 (purity 99.8%) samples were purchased from Aldrich. The samples were pressed at 35,000 psi for five minutes to form 25 cm diameter pellets. The sample chamber was an in-house designed cube (approximately 25 cm on each side) equipped with 5 cm UV grade optical windows. The pressure in this system was monitored with a MKS pressure gauge combined with a mechanical pump to adjust pressures between 1–1000 Torr.

3. Theoretical modeling

Our calculations of the LIBS spectra from iron oxide use similar atomic models to those used in our previous studies [21, 22]. We use the Los Alamos suite of codes (for an overview, see [23]). Our atomic structure calculations begin with the Los Alamos CATS code [24, 25], where we adjust the computed energy levels to their NIST values [26] as discussed in detail previously [21]. We perform atomic structure and collision calculations for neutral and singly ionized Fe, O, He, Ar, and N, and use the Los Alamos GIPPER code [27] to calculate ionization cross sections. Our plasma modeling calculations then proceed using the ATOMIC code [28, 29]. In this paper, we report only calculations that have been performed in local thermodynamic equilibrium (LTE), which was previously shown [21] to be an adequate approximation for the temperatures and densities generally found in LIBS plasmas. We make use of the electron collisional line broadening models of Dimitrijevic and Konjevic [30], as recently discussed in some detail [31]. In efforts to properly include matrix effects, which we define here as the influence of the global electron density on all plasma constituents [22], we take special care to include within the plasma the constituent elements at the same mass ratios as in the sample. Our calculations are iterated until self-consistency is established between the global electron density and mass densities of all the plasma components [32]. We also make the implicit assumption that the LIBS generated plasma will have the same ratios of component masses as the sample. The atmosphere within which the measurement is performed is also clearly an important factor in modeling the spectra from LIBS plasmas. A portion of the atmosphere may become a plasma constituent, and the atmospheric mass and pressure can influence the plasma evolution, as discussed recently in detail [18], and as we explore in this work.

To estimate the amount of atmospheric gas in the LIBS plasma, we performed test calculations for the Fe_2O_3 in argon case, and adjusted the mass of argon present so that the 772.4 nm Ar I emission line intensity is in reasonable agreement with the measurement. This mass density of argon was then converted into an atom number density, and this number density value was subsequently assumed to be the amount of atmosphere coupled into the LIBS plasma. This number density value then fixes the number of atoms of helium or air used in the ATOMIC calculations for the iron oxides in the helium and air atmospheres. We include only N or O atoms for the air calculations (i.e. we ignore the minor constituents of air), and in all calculations we assume that all molecules are fully dissociated. Finally, test calculations, performed in the manner of Colgan et al. [22], showed that the plasmas under investigation here were optically thin under the conditions of interest and so we do not consider any effects due to radiation transport in this study.

4. Results and discussion

In Figs. 1 and 2 we present measurements of the spectrum from Fe_2O_3 in atmospheres of helium, air, and argon, all at a pressure of 595 Torr (atmospheric pressure in Los Alamos). Each spectrum shown is the average of 100 shots that all used a time delay of 500 ns and a gate width of 1μs. Fig. 1 shows a sample (524–545 nm) of the line-rich spectrum from Fe and Fig. 2 shows the prominent triplet of O I emission lines around 777 nm. We also observe a strong Ar I line at 772.4 nm in the lower panel of Fig. 2. The intensity of the measured spectra increases significantly from helium to air to argon (note the change in scale of the y-axes of Figs. 1 and 2), a result that agrees with the conclusions of an earlier study [18]. We note also the better signal-to-noise ratio found in the measurements performed in Ar compared to those in He. The observed increase in intensity is probably due to the increased confinement of the LIBS plasma produced by the heavier atmospheres of air and argon compared to helium, as discussed in detail in previous work [18]. The results reported by Iida [15] indicated, however, that the emission intensity was largest in a helium atmosphere (compared to Ar or air). However, the Iida measurements were performed at pressures of 760 Torr (slightly higher than the pressure of the measurements presented in Figs. 1 and 2) and other measurements reported by Iida [15] showed that, at lower pressures, the emission intensities under He atmosphere were lower than the intensities under Ar atmosphere. Furthermore, the experiments of Iida used a very long gate width of 1 ms, much longer than the width of 1 μs used in the present measurements. A heavier ambient gas inhibits the plasma expansion, resulting in a plasma