Study of Hydrogen and Oxygen and Its Reaction With Host Elements in Sandstone by Laser-Induced Breakdown Spectroscopy (LIBS)

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Abstract. A study of hydrogen and oxygen and its reaction with host elements in a sandstone has been done by laser-induced breakdown spectroscopy (LIBS). The sandstone was irradiated by Nd-YAG laser (1064 nm, 7 ns) with varied energy of 60 mJ till 140 mJ in surrounding air gas pressure of 1 atm and produced plasma. The emission intensities of hydrogen H I 656.2 nm and oxygen O I 777.2 nm in the plasma were captured by HR 2500+ spectrometer and displayed in intensity as a function of wavelength. The data show that the emission intensities of hydrogen and oxygen increase with increasing laser energy at a gradient of 5.4 and 11.8 respectively every increasing laser energy of 20 mJ. To characterize the reaction process between hydrogen and oxygen with the host elements of the sandstone, a 0.2 ml demineralized water was dropped on the sandstone surface and was analyzed as a function of delay time reaction and temperature. The data show that the oxidation reaction between host elements and oxygen occurred after 25 minutes that the oxygen emission intensity increases and the hydrogen emission intensity decreases. Another data also show that the increasing temperature of sandstone until 80°C increased intermolecular bond between oxygen and host element and dehydrogenation took place after reaching this temperature.

1. Introduction

Laser induced breakdown spectroscopy (LIBS) has become an analytical tool in detection of major, minor elements, as well as, light element such as hydrogen presents in solid, liquid and gases. But rare report was found in case of studying reaction hydrogen and oxygen with the host elements. This mainly due to hydrogen is very light and fast-moving atom, as well as, easily reacts to other atoms. As a result, it is very difficult to know the hydrogen as host element or as impurity, and also a weak intensity observed in the emission.

Many researchers had done different methods to improve the detection of Hydrogen element. D.A. Cremers et al., using the delay time detection method, the background intensity reduce and atomic intensity increase. Kurniawan et al., using low-pressure (5 torr) ambient helium had demonstrated the detection of the sharp H I 656.2 nm and D I 656.1 nm emission lines from the zircaloy sample. Z.S. Lie et al., study excitation mechanism using TEA Co2 laser. Hery et al., using an orthogonal double-pulse laser-induced breakdown spectroscopy (LIBS) technique. It was
demonstrated, specifically, that a strong and sharp D emission line was detected with a time difference ($\tau = -1$) $\mu$s and free from the interfering H I 656.2 nm spectral line. Based on evidences above, this research focused on the characteristics of hydrogen and oxygen in a sandstone sample and its reaction to other host elements called oxidation and reduction processes.

2. Material and Method

2.1 Sample Preparation

In order to understand the characteristics or the reaction process of hydrogen and oxygen in the sandstone, three treatments were conducted in this experiment: first, without added demineralized water to sandstone. This sample used to characterize hydrogen and oxygen as host elements in the sandstone. Second without heating the sandstone but varying the delay time reaction before laser irradiation. In this treatment 0.2 ml demineralized water was dropped onto the surface of sandstone and time lag of 5, 15, 25, 35 and 45 minutes before laser irradiation; third, by varying the heating temperature (45, 65, 75, 80 and 90°C) after certain time of optimum delay time reaction process in the second treatment.

2.2 Experimental Setup

The experimental setup used in this study is illustrated in Figure 1. The commercial LIBS system consists of Ocean Optics HR 2500’ spectrometer, a sample chamber, Nd:YAG laser (model CRF 200, 1,064 nm, 7 ns) and OOILOBS software. For this experiment, the Nd-YAG laser was operated at 10 Hz repetition rate with energy of 60 - 140 mJ. Using 150 magnifier included commercial LIBS, the laser irradiation was guided and focused through 10 cm focal length biconvex lens onto a sand on sandstone sample surface and the resulted emission radiation was analyzed by optical multichannel analyzer containing 14,336 CCD pixels in the wavelength region of 200 – 980 nm with resolution of 0.1 nm. All the experiments were conducted in surrounding gas of air at 760 Torr (1 atm) pressure.

3. Results and Discussion

When a pulse laser is focused on surface sample of a sand on sandstone, the leading edge of the pulse rapidly heats, melts and vaporizes a small amount of material sample into a layer just above the surface. This material, then moves fast and compresses a surrounding gas to produce shockwave. The energy of shockwave is used to excite electrons in the atom. These electrons will decay to ground state and emit a photon with a specific wavelength. The emissions are captured by spectrometer and displayed in intensity as a function of wavelength as shown in figure 2.

![Figure 2. A Spectrum of Hydrogen in a various laser energy.](link)

Figure 2 shows that the emission intensity of Hydrogen increases with the increasing laser energy. The lower laser energy, the lower energy of shockwave deposited in the gas behind it and a consequence a small amount of hydrogen atoms excited. The higher energy laser, the energy of shockwave is strong enough and a result a lot of hydrogen atoms excited. Hence, the emission intensity of Hydrogen increases.

Figure 2 is part of spectrum emission of sandstone in hydrogen region. Actually, the sandstone contains some emission lines of elements such as Si, Na, H, K, Ca, O, N, Fe, Al, Ba, and Mg. To understand the characteristics of Hydrogen and Oxygen elements, first, it is plotted the emission intensity of Hydrogen and Oxygen as host elements in the sandstone as a function of laser energy displayed in Figure 3.
Figure 3. The emission intensities of Hydrogen and oxygen in various laser energy.

Figure 3, shows a linear relationship between emission intensity and laser energy. The data state that the intensity of both hydrogen and oxygen increase with increasing laser energy with a slope of 5.4 and 11.8 respectively, every increasing laser energy of 20 mJ.

To characterize the reaction process between hydrogen and oxygen with other host elements in the sandstone, a 0.2 ml demineralized water was dropped on the sandstone surface and was analyzed as a function of delay-time reaction and temperature as shown in Figure 4 and 5.

Figure 4. Emission Intensities of Hydrogen and Oxygen as a function of delay-time reaction process radiated with laser energy of 120 mJ.

\[
2X + 2H_2O \rightarrow 2XOH + H_2(gas) \quad (1a)
\]

\[
2XO + H_2 \quad (1b)
\]

Data in Figure 4 state that in early time 5 – 15 minutes, the emission intensity of Hydrogen increases about twice compare to hydrogen as host element in figure 3 at the same laser energy of 120 mJ. To explain this phenomenon, it is better to show a redox reaction as shown in equation 1. The reaction in equation 1a is illustration to explain redox reaction between H_2O with host element (X) and produce base (XOH) and H_2 gas. Before leaving the sandstone, the H_2 gas was irradiated by laser and as result the emission intensity of hydrogen rises. However, after 25 minutes, this emission intensity reduces that can be caused by releasing of this gas and after 45 minutes the intensity of hydrogen is the same as in host element.

On the other hand, in the time of 5 till 25 minutes, the emission intensity of Oxygen decreases about three fourth compare to oxygen in host element in figure 3 in the same laser energy. This can be caused by the wet condition of the sandstone that it has weaker intermolecular bond and it also absorbs laser energy. But this intensity increases after 25 minutes and it is caused by increasing intermolecular bond of the base. To understand more detail the Hydrogen and Oxygen characteristics, a 0.2 ml demineralized water was dropped on sandstone surface and after 15 minutes this stone was heated 5 minutes with varied the temperature of 45 °C till 90 °C and the result is in figure 5.
Figure 5. Emission intensities of Hydrogen and oxygen as a function of temperature, radiated with laser energy of 120 mJ.

Data in figure 5 show that in the early temperature 45 °C, the emission intensity of both hydrogen and oxygen decrease compare to the condition 15 minutes in data figure 4 but nearly the same value with condition in 25 minutes in the same figure. The reason is some Hydrogen gas was released from the sandstone and also the intermolecular bond in the base was not strong enough to react with laser. At the temperature of 65 °C, the emission intensity of both hydrogen and oxygen increase but reversed phenomena with the figure 4 after 25 minutes delay time reaction. This phenomena can be explained that emission intensity of hydrogen in figure 4 only comes from H₂ gas resulted from redox reaction (eq. 1a), however, in figure 5, hydrogen emission is also from H₂ gas from dehydrogenation (eq. 1b). When the stone was heated up until 80 °C, the emission of hydrogen decreased as hydrogen gas in the stone was released. In other hand, the same reason in the figure 4, the emission intensity of oxygen in the figure 5 continue increasing, but it’s value is higher than in the case of delay time reaction. At higher temperature of 80 °C, the oxygen and hydrogen dissociated and come out from stone before irradiating laser. As a result the emission intensity of these elements decreased.

4. Conclusion and Future Work

Based on data, it can be concluded that the redox reaction process can be studied using LIBS method. Redox phenomenon was analyzed with variables of delay time detection and temperature of sample. The data show that the oxidation reaction between host elements and oxygen occurred after 25 minutes that the oxygen emission intensity increases and the hydrogen emission intensity decreases. Another data also show that the increasing temperature of sandstone until 80 °C increased intermolecular bond between oxygen and host element and dehydrogenation took place after reaching this temperature.

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