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H-D analysis employing energy transfer from He metastable excited state in double pulse LIBS at low pressure He gas

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ABSTRACT

The laser induced breakdown spectroscopy (LIBS) experiment with a unique double pulse setup and operational procedure in low pressure (3 kPa) He ambient gas is performed for the study on the detection of light elements such as hydrogen (H) and deuterium (D) as well as elements of high excitation energies such as fluorine (F) and chlorine (Cl) which are usually difficult to be detected using ordinary LIBS technique. A nanosecond (ns) Nd:YAG laser operated in its fundamental wavelength with energy of 54 mJ is focused onto the Al target to generate the He plasma. Another picosecond (ps) Nd:YAG laser operated in its fundamental wavelength with energy of 2 mJ is focused onto the sample surface and activated 2 µs before the operation of ns laser. The application to polyvinylchloride (PVC) and polytetrafluoroethylene (PTFE) samples produces sharp and high intensity Cl and F emission lines. Meanwhile the sharp and well resolved H-D emission lines with merely 0.18 nm wavelength separation are also clearly detected from zircaloy sample. Further measurement of a set of zircaloy samples containing different concentrations of D yields a linear calibration curve with zero intercept. The detection limit of D is found to be about 10 ppm.

Keywords: double pulse low pressure LIBS, He metastable excited state, H-D analysis, F analysis, Cl analysis
Introduction

Since the discovery of LIBS in around 1980, it has found applications into many fields such as material analysis, fossil characterization, analysis of art and painting, biological study, food and drug analysis, industrial applications, surface mapping, environmental monitoring, isotopic analysis and a most remarkable application in the mega project of Mars exploration. Although LIBS has enjoyed its popularity as evidenced by its huge number of publications, it can still benefit from overcoming its disability to detect the very low mass atoms such as H and D which are important in nuclear engineering and the surveillance of nuclear terrorism. The detection of H and D in zircaloy is particularly important in both light and heavy reactor for early detection of crack in the tube. Besides D as one of the fuel components used in the thermo nuclear fusion reactor is readily bonded in solid as LiD. In gas phase, it is easily adsorbed by a certain metal and released via simple heating. Both compounds can be easily transported in disguise for dangerous abuses. Therefore the detection of D is important to prevent nuclear terrorism in the future.1-12

The failure of LIBS in detecting H and D is mainly due to the time mismatching effect. It was shown11-12 that in the case of low mass analyte atoms, the ablated atoms tend to move at higher speed, missing the formation of shock wave plasma responsible for the thermal excitation process which is formed by the heavier host elements. As a consequence of their premature passage, those atoms will largely miss the shock wave plasma induced thermal excitation, yielding only insignificant emission intensity. This effect is less severe at lower gas pressure. In a subsequent experiments,13-15 the low pressure ambient air and helium (He) gas were employed and this resulted in sharp H emission lines in both ambient gas with the H emission obtained in He gas exhibiting about 7 fold higher intensity, thanks to the contribution of He assisted excitation (HAE) mechanism.11-12 However low pressure condition is highly impractical to realize for H analysis of the zircaloy tube which is
immersed in the water tank of the nuclear reactor. For an insitu H analysis of zircaloy tube, an experiment was conducted using a double pulse technique and atmospheric pressure He gas in the sample chamber which is tightly attached to the zircaloy tube. The He gas plasma was generated by a nanosecond (ns) laser with the picosecond (ps) laser activated after a certain delay to ablate the sample from a perpendicular direction. The ablated atoms will then enter the cool He plasma and be excited by metastable excited He atoms when the plasma is practically free from the charge particles generated initially during the ablation process. Since there is no thermal excitation, the observed H emission line is very sharp and have a very low background. Using this technique, H and D emission lines which is only separated by 0.18 nm\textsuperscript{1,6,16,17} can be simultaneously detected. It should be noted that this double pulse technique is quite different with ordinary double pulse LIBS in which the first laser is used to ablate the material and after a certain delay, the second laser is fired to excite or re-excite the ablated atoms.\textsuperscript{18-25}

Despite the reasonable good spectral quality of H and D was obtained in that experiment, the He plasma which has typical orange color due to the He I 587.6 nm emission was found to suffer from the lack of the required long term stability when generated in atmospheric pressure ambient He gas.\textsuperscript{1,11-12,26-34} Based on the above cronology, we tried to generate He gas plasma under reduced pressure of around 3 kPa and we found that the emission of He I 587.6 nm is very stable. Then we used this low pressure He plasma as the source of the He metastable excited state which will excite the ablated target atoms induced by the second ps laser irradiation. In this stage of the experiment, we are able to detect Cl and F which is usually difficult to be detected in LIBS due to its high lying excitation energy. Finally, we also performed H-D analysis using zircaloy sample doped with hydrogen and deuterium.

Experimental Procedure
The experimental setup used in this study is presented schematically in Fig. 1. The chamber used in this work is a rectangular chamber of 20 x 11 x 17 cm$^3$ dimension. It is equipped with a number of large quartz plate to allow the detection of the plasma and for passing the laser irradiation. The chamber is connected with 2 servo motors to rotate the two perpendicularly positioned sample holders as shown in the figure. The chamber can be evacuated down to 1 Pa by a rotary vacuum pump and measured precisely using an analog Pirani gauge (Diavac Limited model PT-9P).

One of the laser systems used in this experiment is a ns Nd-YAG laser (Quanta Ray model LAB-130, 8 ns, maximum energy of 450 mJ) operated at its fundamental wavelength of 1,064 nm with 10 Hz repetition rate and a fixed energy output of 54 mJ. This laser system is focused using quartz lens of 150 mm focal length from the upper side of the chamber onto aluminum target to create the He gas plasma. The second laser is a picosecond (ps) Nd-YAG laser (Ekspla model PL2143, 20 ps, maximum energy of 30 mJ) operated in its fundamental wavelength of 1,064 nm with 10 Hz repetition rate and a fixed energy of 2 mJ. This laser is focused by a quartz lens of focal length 150 mm onto the sample to be analyzed.

The resulted plasma is examined by using detection system consisted of a spectrograph (McPherson, model 2061, f = 1000 mm, Czerny Turner configuration) and an gated intensified charge coupled device (ICCD, Andor 256x1024 pixels). The gate delay and gate width of the ICCD are fixed at 200 ns and 50 µs, respectively, in order to yield the most favorable emission spectra as shown in our previous works.$^{11-12}$ Digital delay generator (Stanford Research System, model SRS 535) is used to control the time delay between the operations of the two lasers system and the gated ICCD.

Several samples are used in this experiment. Copper plate (Rare Metallic, 5N, thickness 0.4 mm) is used to visualize the generated plasma. PTFE and PVC with 1 mm thickness are used to demonstrate the excellent emission spectra of F and Cl which have high excitation
energies and are usually difficult to detect in ordinary LIBS. Finally zircaloy plate containing 600 ppm of D and 50 ppm of H and another zircaloy plate containing 200 ppm and 1000 ppm of D is used to show the ability of this new technique for H-D analysis.

**Experimental Results and Discussion**

The first step of this study is taken to exhibit the different features of plasma generated by this unique double pulse technique. First, Cu plate is used in this experiment since Cu gives strong green color in contrast with orange color of He plasma. Fig. 2 (a) shows when only ns Nd:YAG laser of energy 54 mJ is focused onto Al target at surrounding He gas of 3 kPa. Hemispherical plasma of orange color associated with He I 587.6 nm and He I 667.9 nm emission lines is clearly observed. Instead of He emission, we also confirmed prominent Al emission lines of Al I 394.4 nm and Al I 396.1 nm. The use of Al is based on the selection of several kind of metals and organic sample in which we found that Al gives the maximum emission of He. This result will be reported shortly in a separate manuscript elsewhere. It should be emphasized that without introducing Al or other hard material, no plasma is generated even when the laser energy is increased up to 150 mJ (damage threshold for the optical system used in this study). This is quite different from the case when the ambient He gas is employed at atmospheric pressure.\(^{11-12}\) Fig. 2(b) shows when 2 mJ ps laser alone is focused onto Cu target in the same He ambient gas of 3 kPa, a hemispherical green plasma is generated, featuring typical of shock wave plasma.\(^{11-12}\) The green color is the combined contributions of the Cu I 510.5 nm, Cu I 515.3 nm and Cu I 521.8 nm emission lines. Fig. 2(c) shows the result obtained when the two laser systems are activated with 2 µs time lag for the ns laser. The green color Cu emission appearing on the top of the He gas plasma has become more pronounced in this figure compared to that seen in Fig. 2(b). This visual observation clearly demonstrates the effective contribution of He assisted excitation (HAE) mechanism in the presence of the He plasma as also observed in the case of previously
reported result using double pulse atmospheric He plasma.\textsuperscript{11-12} It is also interesting to note that the appearance of the relatively extended area of Cu emission is compensated by the corresponding shrinkage of the He gas plasma. This may be explained as the result of a big portion of the metastable-excited He atoms release their energies for the excitation of the Cu atoms, instead of giving them up in the form of photo emission.

As we have explained in the introduction, the He plasma generated in low pressure He surrounding gas has a high emission stability. This is demonstrated in Fig. 3 which shows the He I 587.6 nm emission intensity as a function of laser shots by using the Al target to induce the He plasma. It is clearly seen that the emission intensity of He I 587.6 nm is very stable with the fluctuation of less than 3%. This stable He light source is very important since the excitation energy of the ablated target is provided by the He metastable excited state.

In order to find the optimum time delay between the two laser operations, PVC and PTFE samples which are difficult to be analyzed in LIBS, are used separately, since those compounds contain high concentration of Cl and F, respectively. This experiment is performed using 2 mJ ps laser alone in He ambient gas of 3 kPa. The plasma has a jet like shape instead of hemispherical shape and the emission intensity of Cl and F are both very weak. Fig. 4 shows the emission intensity of Cl I 837.5 nm, C I 247.8 nm and H I 656.2 nm (main constituent of PVC) as a function of time delay between the ns and ps laser operation. Positive values of time axis mean ns laser is operated before the ps laser and the reversed order of laser operations are denoted by negative values. It is clearly seen from the figure that the maximum emission intensity is obtained when the ps laser is operated around 2 $\mu$s before ns laser operation. Similar result is also obtained for PTFE sample as shown in Fig. 5 where the maximum emission intensity of F I 685.6 nm, F I 690.2 nm and H I 656.2 nm are obtained when the ps laser is operated around 2 $\mu$s before ns laser operation. This time delay will thus be used for the next ensuing experiment.
Fig. 6 and Fig. 7 shows the spectra of PVC and PTFE, respectively in ambient He gas of 3 kPa. The ns laser energy is fixed at 54 mJ and the ps laser energy is fixed at 2 mJ with the ps laser operated 2 µs before the ns laser. The gate delay and gate width of the ICCD are fixed at 200 ns and 50 µs, respectively after the ns laser operation. It is seen from both figures the strong appearance of Cl I 837.5 nm and F I 685.6 nm and F I 690.2 nm emission lines featuring almost negligible background in both spectra with almost 50x higher intensities, in clear contrast to the result obtained with 2 mJ ps laser alone.

We have proposed in our previous works,\textsuperscript{11-12} that the successful detection of high lying excitation energy elements such as Cl (12.5 eV) and F (14.5 eV) which are usually difficult to be detected in LIBS is due to the role of energy transfer from the metastable excited He atoms by means of Penning-like collision process as explained below:

\begin{equation}
\text{He}^* + X(\text{ground state}) \rightarrow \text{He} + (X^+ + e^-) \quad \text{Penning effect} \quad (1)
\end{equation}

\begin{equation}
X^+ + e^- \rightarrow X^{***} \quad \text{Recombination} \quad (2)
\end{equation}

\begin{equation}
X^{***} \rightarrow X^{**} \rightarrow X^* \quad \text{by the cascade transitions}
\end{equation}

\begin{equation}
X^* \rightarrow X + \nu \quad \text{Emission} \quad (3)
\end{equation}

The ablated atoms which collides with the He metastable atoms (He*) will be ionized, resulting a high energy free electron as shown in the Equation (1). The energy of the free electron is corresponding to the energy difference between the metastable excited state energy of He and the ionization energy of the ablated atom (X). The free electron released from X is expected to undergo multiple collisions with the He metastable atoms before recombining with X ion to produce the X atom at some higher energy level (X^{***}) as shown in Equation (2). This is followed by non radiation cascaded transitions until ending at some lower excitation state (X*) which will proceed the downward transition with atomic photo emission used as an analytical spectral line of the analyte atom X as shown in Equation (3). This unique excitation process is known to occur in the cool plasma when ions and electrons
have already recombine.\textsuperscript{11-12} Thus the resulted spectrum as shown in Fig. 6 and 7 have very low background and very sharp emission lines of around 0.04 nm line width, close to the limit of the spectrograph of 0.025 nm.

Encouraged by the above result, a H-D analysis in zircaloy sample which contains 50 ppm of H and 600 ppm of D is also performed under the same condition for getting Figs. 6 and 7 and the result is presented in Fig. 8. The strong and well resolved D I 656.1 nm and H I 656.2 nm emission lines are clearly observable. Since only limited D doped zircaloy sample is available for analytical measurement, another zircaloy plate containing 200 ppm and 1000 ppm of D is also measured and the resulted calibration curve for D I 656.1 nm which only consists of 3 points is presented in Fig. 9. The linear calibration line with zero intercept is obtained at this stage and using Fig. 8, the detection limit of D is estimated to be around 10 ppm which is much better than the needed requirement of several hundred ppm in nuclear power station.

**Conclusion**

Analysis of elements with high excitation energies such as Cl and F has been successfully performed using a special double pulse LIBS in low pressure (3 kPa) ambient He gas. Furthermore the successful detection of D and H in zircaloy plate with excellent resolution is also achieved with linear calibration line and zero intercept for D. These remarkable performances of the special experimental setup is explained as the results of employing the HAE mechanism to its full advantage which is realized by using double pulses with judicious choice of time delay between the two laser operations. The feasibility of developing its in situ implementation is being investigated and the result will be published elsewhere.
Acknowledgement

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References


Figure Captions

1. Complete schematic diagram of the experimental setup used in this study.

2. Plasma picture (a) when only 54 mJ ns laser is focusing to the aluminum target which is rotated at 3 rpm; (b) when only 2 mJ ps laser is focusing to the copper sample which is also rotated at 3 rpm; (c) when both lasers are operated with the ns laser operated 2 µs after the ps laser in He ambient gas of 3 kPa.

3. Emission intensity of He I 587.6 nm as a function of laser shots when 54 mJ ns laser is focused onto the aluminum target which is rotated at 3 rpm in He ambient gas of 3 kPa. The gate delay and gate width of the ICCD is fixed at 200 ns and 50 µs, respectively.

4. Emission intensity of Cl I 837.5 nm, C I 247.8 nm and H I 656.2 nm (main constituent of PVC) as a function of time delay between the ns and ps laser operation. Positive value means ns laser is operating preceding of the ps laser and vice versa. The 54 mJ ns laser is focused onto Al target and 2 mJ ps laser is focused onto PVC sample in 3 kPa ambient He gas. The gate delay and gate width of the ICCD is fixed at 200 ns and 50 µs, respectively.

5. Emission intensity of F I 685.6 nm, F I 690.2 nm and H I 656.2 nm (main constituent of PTFE) as a function of time delay between the ns and ps laser operation. Positive value means ns laser is operating preceding of the ps laser and vice versa. The 54 mJ ns laser is focused onto Al target and 2 mJ ps laser is focused onto PTFE sample in 3 kPa ambient He gas. The gate delay and gate width of the ICCD is fixed at 200 ns and 50 µs, respectively.

6. Emission spectra of PVC in (a) C wavelength region, (b) H wavelength region and (c) Cl wavelength region (main constituent of PVC). The 54 mJ ns laser is focused onto Al target and 2 mJ ps laser is focused onto PVC sample in 3 kPa ambient He gas. The gate delay and gate width of the ICCD is fixed at 200 ns and 50 µs, respectively.
7. Emission spectra of F I 685.6 nm, F I 690.2 nm and H I 656.2 nm (main constituent of PTFE). The 54 mJ ns laser is focused onto Al target and 2 mJ ps laser is focused onto PTFE sample in 3 kPa ambient He gas. The gate delay and gate width of the ICCD is fixed at 200 ns and 50 µs, respectively.

8. Emission spectra of D I 656.1 nm and H I 656.2 nm from zircaloy sample containing 600 ppm of deuterium and 50 ppm of hydrogen. The 54 mJ ns laser is focused onto Al target and 2 mJ ps laser is focused onto zircaloy sample in 3 kPa ambient He gas. The gate delay and gate width of the ICCD is fixed at 200 ns and 50 µs, respectively.

9. Emission intensity of D I 656.1 nm versus its concentration in zircaloy sample.
Fig. 1
Fig. 2

(a)

(b)

(c)
Fig. 3
Fig. 4

Intensity (arb. units)

ns - ps laser synchronization (µs)

-4 -3 -2 -1 0 1 2 3 4

19

Cl I 837.8 nm
C I 247.8 nm
H I 656.3 nm
Fig. 5

Intensity (arb. units)

F I 685.6 nm
F I 690.2 nm
H I 656.2 nm

ns - ps laser synchronization (μs)
Fig. 6

(a) CI 247.8 nm

(b) HI 656.2 nm

(c) CI 837.5 nm
Fig. 8
Fig. 9

D I 656.1 nm emission intensity (arb. units)

D concentration (ppm)