Laser-induced plasma emission enhanced by microwaves in argon gas for potential application of nuclear fuel material analysis

Ali Khumaeni1*, Motonobu Tampo2, Masabumi Miyabe3, Katsuaki Akaoka3, and Ikuo Wakaida3

1Department of Physics, Faculty of Science and Mathematics, Diponegoro University, Tembalang, Semarang 50275, Indonesia
2Institute of Materials Structure Science, KEK, Tokaimura, Ibaraki 319-1195, Japan
3Fuel Debris Analysis Group, Collaborative Laboratories for Advanced Decommissioning Science, Japan Atomic Energy Agency, Tokaimura, Ibaraki 319-1195, Japan

*E-mail: khumaeni@fisika.undip.ac.id

Abstract. To perform quantitative analysis of nuclear fuel materials by using laser-induced breakdown spectroscopy (LIBS), emission spectral lines of atoms should be clearly identified, which is far from other atomic and molecular disturbances, low background emission, and optimum emission intensity. To this end, intensified microwaves were introduced into the laser-induced plasma in LIBS. Gadolinium oxide (Gd₂O₃) was employed for the simulation of nuclear fuel material. Enhancement of laser plasma was obtained when the microwave was introduced into the laser plasma. Total emission intensity of Gd significantly increased for the case of microwave-assisted laser plasma, which revealed that the microwave can effectively be employed to increase the sensitivity. Furthermore, the analytical lines of Gd can be clearly identified, which are far from the molecular bands disturbance and have high emission intensity with low background intensity. The enhancement factors for neutral Gd I at 470.9 nm and ionic Gd II at 458.3 nm were 40 and 45 times for the LIBS with microwaves case. The plasma temperatures were 9500 K and 4800 K for the LIBS with and without microwaves, respectively. The microwave-assisted laser-induced plasma in Ar gas has high potential for the analysis of impurity in nuclear fuel materials.

1. Introduction

Recently, laser-induced breakdown spectroscopy (LIBS) has become well known method for the rapid and direct qualitative and quantitative elements in various samples in science and industries [1-2]. In this conventional method, a pulsed neodymium-doped yttrium aluminium garnet (Nd:YAG) laser is focused onto a sample target to induce a small luminous plasma just above the sample. Elemental composition of the target can be obtained by analyzing the atomic emission from the plasma [3-4]. Compared to other conventional analytical methods such as inductively coupled plasma optical emission spectroscopy (ICP-OES) and atomic absorption spectroscopy (AAS), the LIBS has several advantages including simple sample preparation and rapid and multi-
elemental detection [5]. One of the LIBS applications is monitoring of uranium and plutonium in the fuel production process [6]. However, the LIBS has weak points including low sensitivity to perform the analysis of impurity elements in the materials, which have complex spectral lines, such as nuclear fuel elements.

Several methods have been developed to improve the sensitivity including double pulse LIBS [7], combination between LIBS and laser-induced fluorescence (LIF) [8], and resonant and LIBS [9]. However the methods are costly because the other laser system is required. The other method used to improve the sensitivity is microwave-assisted laser-induced breakdown spectroscopy (MA-LIBS) [10]. The use of MA-LIBS has advantages including low-cost instrument and that the sensitivity of analytical measurement can be effectively enhanced. In this method, the microwave-assisted laser-induced plasma was induced in air for nuclear fuel analysis. However, it was found that the molecular bands coming from air clearly appeared disturbing the analytical lines.

In this study, an enhancement of laser-induced plasma emission assisted by microwaves in argon (Ar) gas was performed for the detection of Gd lines in gadolinium oxide (Gd$_2$O$_3$) pellet as a simulation of nuclear fuel material. By using Ar gas as a replacement of air, the molecular bands from air such OH bands and N$_2$ molecules can significantly be suppressed, increasing the signal to noise ratio (S/N) of the analytical lines coming from the analyte. The results certified that the emission lines of Gd can be clearly and separately detected. This method has high prospect to analysis of impurity in materials, which have complex spectral lines such as nuclear fuel materials.

2. Experimental Procedure

The basic experimental setup used in this study is shown in Fig. 1. A second-order harmonic of Q-switched Nd:YAG laser (Quanta-Ray, Spectra Physics, 532 nm, 8 ns) was directly focused onto a sample surface through a quartz window using quartz lens with a focal length of 200 mm. During the experiment, the laser energy was 5 mJ. The laser plasma was enhanced by intensified microwave field induced with an antenna; the antenna was circular shaped with a diameter of 3 and 9 mm. Microwave was generated by using a magnetron at a frequency of 2.45 GHz (Muegge MG0500D-215TC, 0-1 ms). The power of the magnetron was 400 W. The Nd:YAG laser and microwave were operated in the synchronization mode with a delay time of 10 μs for the Nd:YAG laser bombardment relative to the microwave generation.

![Fig. 1 Experimental setup in this work](image)

The sample used in the experiments was gadolinium oxide (Gd$_2$O$_3$) pellet as a simulation of nuclear fuel of uranium oxide (U$_2$O$_3$). The Gd$_2$O$_3$ has similar physical and chemical characteristics...
with \( \text{U}_2\text{O}_3 \) and it is not harmful for human being; if the analysis is made by using real nuclear fuel of \( \text{U}_2\text{O}_3 \), special treatment of sample preparation and its experiment should be carried out. The sample was 1 mm thick and 10 mm in diameter. The sample was made by compressing \( \text{Gd}_2\text{O}_3 \) powder of 1 g by the pressure of 1.5 MPa. During the experiment, the sample was placed in a metal chamber equipped by windows, on which the fine gold mesh (lattice constant of 100 μm and wire diameter of 30 μm) was attached. The chamber functioned to block the microwave radiation. The pressure of the surrounding gas in the chamber was set at 0.67 kPa. During the experiment, the Ar gas (purity 99.999%) was flowed.

The emission spectrum was obtained by using an ICCD camera (Andor, iStar) through a high-resolution echelle spectrometer (ARYELLE) with the resolution of 50 pm at the wavelength of 360-460 nm. The light emission of the laser plasma was collected by using an optical fiber, which fed into the spectrometer. The plasma radiation at 2-5 mm from the sample surface was imaged in a ratio of 1:1 onto one end of the fiber by using a quartz lens (f= 100 mm).

### 3. Results and Discussion

First, the generation of luminous plasma from the \( \text{Gd}_2\text{O}_3 \) sample has been carried out by using different method of standard LIBS and MA-LIBS in Ar gas at 0.67 kPa. Figure 2 shows the photographs of plasma emission in (a) standard LIBS, and (b) MA-LIBS coupled by antenna. In this experiment, the laser energy was 5 mJ and the microwave power was 400 W.

![Photographs of plasma emission taken from the \( \text{Gd}_2\text{O}_3 \) sample by using (a) LIBS, and (b) MA-LIBS](image)

It is clearly seen that bright white color plasma with a diameter of around 3 mm was produced by using LIBS method [Fig. 2(a)]. When a microwave was introduced into the LIBS plasma region via a loop antenna, the plasma diameter was enlarged of around 10 mm and the plasma emission was much brighter [Fig. 2(b)] compared the case of LIBS plasma. This revealed that the microwave can effectively enhance the plasma emission induced by the LIBS method. The mechanism of plasma enhancement by microwave is assumed as follows: when the microwave is radiated into the LIBS plasma, the electrons are accelerated, increasing the kinetic energy. Together with the increment of kinetic energy, the number of collisions between electrons and constituents increase, which affect the plasma temperature and the densities of electrons, ions, and neutral atoms in the plasma, allowing the enhancement of plasma emission.

To ensure that the antenna is never ablated and disturbed the analytical spectrum during the experiment, the emission spectra from the \( \text{Gd}_2\text{O}_3 \) sample in Ar gas were obtained by using only microwave without laser irradiation (Fig. 3). It should be noted that the antenna for transmitting the microwaves from magnetron was made of Cu coaxial cable. It is seen in Fig. 3(a) that completely no neutral Cu lines at 324.7 nm and 327.4 nm were observed, which means that no ablation of antenna material takes place during the microwave irradiation. Thus, the antenna used in this study
never disturbs the analytical lines. Furthermore, completely no Gd lines occurred in the spectrum by using microwaves. This certified that microwave irradiation cannot ablate and vaporize the Gd$_2$O$_3$ sample and thus, it cannot be employed to perform analysis by using microwave only.

![Emission spectra obtained from the Gd$_2$O$_3$ sample by using only microwave radiation at wavelength region (a) 300-450 nm, and (b) 700-850 nm](image1)

Figure 3 (b) shows the emission spectrum obtained from the Gd$_2$O$_3$ sample at wavelength region of 700-850 nm by using microwave only. Completely no Gd lines occurred in the spectrum. However, many neutral argon (Ar) lines clearly appear with high emission intensity such as Ar I at 706.7 nm, 738.3 nm, and 763.5 nm. From this result, we concluded that the microwave irradiation can excite Ar gas used as an ambient gas, but cannot vaporize and excite the Gd in the Gd$_2$O$_3$ sample target. This result certified that the microwave only cannot be employed to perform analysis of Gd because it is not able to ablate the sample target and therefore no atomization and excitation of elements from the sample target take place.

![Emission spectra of Gd obtained from the Gd$_2$O$_3$ sample at wavelength region 450-600 nm by using LIBS and MA-LIBS](image2)

Fig. 4 Emission spectra of Gd obtained from the Gd$_2$O$_3$ sample at wavelength region 450-600 nm by using LIBS and MA-LIBS

To examine the effect of the microwave on the enhancement of emission spectrum for nuclear material analysis, the MA-LIBS was then employed to detect the Gd emission obtained from the Gd$_2$O$_3$ sample target, as a simulation material of nuclear fuel material. Figure 4 shows the emission spectrum taken from the Gd$_2$O$_3$ sample by using LIBS (red line) and MA-LIBS (blue line) at 450-
600 nm. The argon gas was used as an ambient gas at 0.67 kPa. The laser energy was 5 mJ and the laser was irradiated at 10 Hz irradiation. The power of microwaves was 400 W. Many Gd lines clearly appear in the spectrum of LIBS and MA-LIBS; Gd has complex spectral lines as well as nuclear fuel material such as uranium. Based on NIST database, neutral and ionic Gd has 821 lines from 200 to 800 nm [11]. The emission intensities of Gd lines significantly increased when the microwaves were employed (blue line). Total emission intensity enhancement is approximately 30 times higher for the case of MA-LIBS. From this spectrum, we also obtained the enhancement factor of neutral and ionic Gd lines. The enhancement factors for the neutral Gd I at 470.9 nm and ionic Gd II at 458.3 nm were approximately 40 and 45 times as shown in Fig. 5(a) and 5(b), respectively for the case of MA-LIBS. It should also be noted that the hydroxyl (OH) bands and N\(_2\) molecular lines appeared in MA-LIBS method in air [10] completely disappeared. This result indicates that the microwave-assisted laser-induced plasma in Ar gas can be used to clearly and separately detect adjacent analytical lines, which are very complex in nuclear fuel materials.

![Emission spectra of the Gd obtained from the Gd\(_2\)O\(_3\) sample at wavelength region (a) 462-474 nm and (b) 450-460 nm by using LIBS and MA-LIBS](image)

Based on our previous experiment [12], it is assumed that the enhancement of laser-induced plasma emission by microwaves is due to the increment of plasma temperature when the microwaves are introduced in the laser plasma. In order to estimate the plasma temperature in LIBS and MA-LIBS a Boltzmann plot method was employed. For the calculation of plasma temperature, selected lines and their spectroscopic data obtained from Kurucz database were used as shown in Table 1 [13].

| Elements | Wavelength (nm) | Upper level energy (eV) | Upper level degeneracy | Transition probability (s\(^{-1}\)) |
|----------|-----------------|-------------------------|------------------------|-----------------------------------|
| Gd II    | 454.01          | 5.055                   | 10                     | 8.58 x 10\(^7\)                  |
| Gd II    | 458.24          | 3.956                   | 8                      | 3.17 x 10\(^6\)                  |
| Gd II    | 460.11          | 3.251                   | 10                     | 5.15 x 10\(^6\)                  |
| Gd II    | 501.08          | 3.531                   | 16                     | 1.03 x 10\(^6\)                  |
| Gd II    | 510.01          | 4.028                   | 14                     | 4.08 x 10\(^6\)                  |
| Gd II    | 515.67          | 3.973                   | 10                     | 7.28 x 10\(^6\)                  |
| Gd II    | 561.62          | 3.267                   | 14                     | 3.12 x 10\(^6\)                  |
| Gd II    | 585.52          | 3.711                   | 8                      | 3.06 x 10\(^6\)                  |
It is assumed that local termodynamic equilibrium (LTE) is achieved in the plasma LIBS and MA-LIBS. The Boltzmann plot equation in LTE condition is as follows,

\[ \ln \left( \frac{I}{g_k A_k} \right) = -\frac{1}{k_B T} E_k + C \]  

(1)

Where \( I \) is the integrated intensity of spectral lines occurring between the upper energy level \( k \) and lower energy level \( i \), \( \lambda \) is the transition line wavelength, \( g_k \) is the degeneracy of the upper energy level, \( A_k \) is the transition probability, \( k_B \), \( T \), and \( E_k \) are Boltzmann constant, the plasma temperature, and energy of the upper energy level, respectively, \( C \) is a constant for a given atomic species. Using the Boltzmann plot equation (Eq. 1) and measurements of spectral lines (Table 1) using LIBS and MA-LIBS, Boltzmann plot was made as shown in Fig. 6.

Fig. 6 Boltzmann plot from the analysis of ionic Gd II lines

The slope of the curve results in plasma temperature of approximately 4800 K and 9500 K in LIBS and MA-LIBS, respectively. It is assumed that the increment of the plasma temperature in MA-LIBS is due to the reheating of plasma by microwave as in the case of double pulse LIBS (DP-LIBS) [14]. As is known the plasma temperature is contributed by electron collision in the plasma region. When the microwaves are introduced in the plasma region, the electrons are accelerated and multiple collisions of electrons increase, which affects the plasma temperature and the densities of electrons, ions, and neutral atoms in the plasma, resulting in the improvement of emission intensity. The enhanced plasma temperature in MA-LIBS can effectively increase the intensities of analytical lines, resulting in high signal to intensity (S/N) ratio of Gd lines.

4. Conclusions

Enhancement of laser-induced plasma was carried out using antenna-coupled microwaves in the Gd2O3 pellet. In this study, the MWs was generated by magnetron and transferred into the laser-induced plasma via coaxial cable to enhance the plasma emission. The results revealed that the laser plasma emission was enhanced indicated by enlarge in diameter. The analytical lines can clearly be identified with high emission intensity and low background emission and is far from the molecular disturbance. Total emission intensity of Gd significantly increased for the case of MA-LIBS (approximately 30 times) compared to the case of LIBS emission. The enhancement factors for neutral Gd I at 470.9 nm and ionic Gd II at 458.3 nm were approximately 40 and 45 times, respectively, for the MA-LIBS case. The plasma temperature for MA-LIBS is 9500 K and it is
4800 K for LIBS case. The MA-LIBS method has high potential to be employed for the sensitive detection of impurity in nuclear fuel materials, which is very difficult to be made using standard LIBS and conventional analytical methods. In this study, the experiment was made at low pressure environment because the MWs power has limitation at 400 W. This is a challenge to study at atmospheric pressure by using higher power of MWs in order to realize in-situ analysis, which is generally carried out at 1 atmosphere.

References
1. Tognoni E, Palleschi V, Corsi M, Cristoforetti G 2002 Spectrochim. Acta part B 57 1115
2. Rusak D A, Castle B C, Smith B W, Winefordner J D 1998 Trends in Analyt. Chemist. 17 453
3. Cremers D A, Barefield J E II, Koskelo A C 1995 Appl. Spectrosc. 49 857
4. Radziemski L J 2002 Spectrochim. Acta Part B 57 1109
5. Cremers D A, Radziemski L J 2006 Handbook of Laser-Induced Breakdown Spectroscopy (John Wiley and Sons, Chichester)
6. Cremers D A, Beddingfield A, Smithwick R, Chinni R C, Jones C R, Beardsley B, Karch L 2012 Appl. Spectrosc. 66 250
7. Babushok V I, DeLucia F C Jr., Gottfried J L, Munson C A, Miziole A W 2006 Spectrochim. Acta Part B 61 999
8. Telle H H, Beddows D C S, Morris G W, Samek O 2001 Spectrochim. Acta Part B 56 947
9. Goueguel B, Laville S, Vidal F, Sabsabi M, Chaker M 2010 J. Anal. At. Spectrom. 25 635
10. Khumaeni A, Motonobu T, Katsuaki A, Ikuo W 2013 Optics Express 21 29755
11. Kramida A, Ralchenko Y, Reader J, and NIST ASD Team 2015 NIST Atomic Spectra Database (ver.5.3), [Online]. Available:http://physics.nist.gov/PhysRefData/ASD/lines_form.html [2016, October 11]. National Institute of Standards and Technology, Gaithersburg, MD.
12. Khumaeni A, Akoka K, Miyabe M, Wakaia I 2016 Front. of Phys. 11 114209
13. Smith P L, Heise C, Esmond J R, Kurucz R L, 2016 Atomic Spectral Line Database. Available: http://www.pmp.uni-hannover.de/cgi-bin/ssi/test/kurucz/sekur.html [2016, October 11]
14. Giacomo A D, Aglio M D, Bruno D, Gaudiuso R, Pascale O D 2008 Spectrochim. Acta Part B 63 805