Time-resolved plasma imaging in microwave-assisted laser-induced breakdown spectroscopy

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Abstract. To study the dynamics of luminous plasma induced by a pulse laser and microwaves (MWs), time resolved imaging of microwave-assisted laser-induced plasma was carried out. In this study, a luminous plasma was induced by a second harmonic Nd:YAG laser (532 nm, 8 ns, 5 J) on calcium oxide (CaO3) pellet at low pressure (5 Torr) of Ar gas. The luminous plasma was enhanced by intensified microwaves (MWs) generated from a magnetron. The image of plasma induced by laser has different features from the plasma induced by the laser with MWs. For the case of laser only, the plasma lifetime is approximately 50 μs, the plasma size at 5 μs is approximately 3 mm, and the neutral Ca emission is much brighter than the ionic Ca emission. When the MWs was introduced into the laser-induced plasma, the plasma emission was enhanced, namely the plasma lifetime was elongated of approximately 8 times, the plasma size at 5 μs was enlarged of approximately 3 times, and the ionic Ca emission is much brighter than the neutral Ca emission, which indicated that the plasma temperature is much higher than the case of laser only. Therefore, the plasma induced by the microwave-assisted laser can be effectively used for the analysis of elemental composition in materials with high sensitivity.

1. Introduction

Laser-induced plasma spectroscopy (LIPS), which is commonly known laser-induced breakdown spectroscopy (LIBS), has become a popular method for qualitative and quantitative elemental analysis in various kinds of materials including solids, liquids, and gases [1-4]. In standard LIBS, a pulse neodymium yttrium aluminum garnet (Nd:YAG) laser is commonly used as an optical source for generation of a luminous plasma on/in materials [5-6]. Compared to other atomic analytical methods such as X-ray fluorescence (XRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES), the LIBS is much superior due to less sample pretreatment, its capability for rapid and remote analysis, and much lower price of experimental devices. Recently, this method has been employed in various fields including environment [7-8], metal industries [9-10], and nuclear fields [11]. However, it is known that this method has less sensitivity for the quantitative analysis of materials.
Various methods have been suggested to improve the sensitivity of analytical detection. Some scientists used double pulse LIBS (DP-LIBS), in which two pulse lasers with interpulse delay in the range of nanosecond to microsecond are used to induce a luminous plasma [12-13]. Khumaeni et al. developed new method of microwave-assisted LIBS (MA-LIBS) coupled by antenna to enhance the laser plasma emission [14-15]. In this method, microwaves (MWs) generated by a magnetron were introduced into the laser-induced plasma. The results revealed that the MWs can be effectively used to increase the plasma temperature and extend the plasma lifetime, resulting in enhancement of laser-induced plasma emission. Enhancement factors of emission intensity from tens to hundreds were achieved.

In this study, time-resolved imaging of a luminous plasma induced by a pulse laser coupled with an intensified MWs was carried out. The microwave-assisted laser-induced plasma was induced on pelletized calcium oxide (CaO) used as a sample target. The results show that the plasma emission can be readily enhanced with enlarged plasma size, increased plasma temperature, and elongated plasma lifetime [15]. It should be noted the present study of time-resolved imaging of luminous plasma proved the assumption of mechanism of plasma enhancement generation by using MWs described in the previous report [15]. Furthermore, this study also displayed the dynamics of neutral and ionic atoms in the laser plasma with- and without MWs.

2. Experimental Procedure

The experimental arrangement in this research was shown in Fig. 1(a). The sample employed in this research was CaO pellet. The sample was placed into a circular metal chamber, on which the fine gold mesh (lattice constant of 80 μm and wire diameter of 30 μm) was attached in the inner chamber. During the experiment, Ar gas was flowed in the chamber at a reduced pressure (5 Torr).

![Experiment setup](image)

Fig. 1 (a) Experimental setup used in this research, (b) a loop antenna used to transfer the MWs from magnetron to laser plasma region.

A second-harmonic Nd:YAG laser (Quanta-Ray, Spectra Physics, 532 nm, 8 ns) was used as an optical source. To induce a luminous plasma, the laser was directly focused on a material target through a quartz window with a focal length of 200 nm. The laser plasma was enhanced by MWs generated by using a magnetron at a frequency of 2.45 GHz (MUEGGE, 400 W, 1 ms) via a loop antenna with a diameter of 3 mm [Fig. 1(b)], the Nd:YAG laser was operated 10 μs after the MWs generation. The luminous plasma emission was imaged by an intensified charge coupled device (ICCD) camera (Andor, iStar) through a quartz lens (f = 100 mm).
3. Results and Discussion

The effect of MWs in the enhancement of laser-induced plasma emission obtained from Ca$_2$O$_3$ pellet has been studied as reported in the previous work [15]. The plasma lifetime extended and the plasma temperature increased when the MWs was introduced into the laser plasma, resulting in enhancement of laser plasma emission and thus, increasing in signal to noise ratio (S/N) of ionic Ca (II) at 393.3 nm and 396.8 nm and neutral Ca (I) 422.6 nm emission intensities as shown in Fig. 3 in the previous paper [15].

In this study, the effect of the microwave to the enhancement of emission intensity was examined by studying the dynamics of plasma emission in Ca$_2$O$_3$ pellet using LIBS and MA-LIBS. To this end, time-resolved emission images of plasma induced by pulse laser without – (LIBS) and with MWs (MA-LIBS) in Ca$_2$O$_3$ pellet sample were recorded as shown in Figs. 2 and 3, respectively. Ionic Ca II at 393.3 nm and neutral Ca I at 422.6 nm emission lines were used as a representative of Ca emission spectra. Band-pass interference filters with center wavelengths of 394 nm for Ca ions (Ca II) and 420 nm for Ca neutral (Ca I) were used to study the dynamics of Ca ions (Ca II at 393.3 nm and 396.8 nm) and Ca neutral (Ca I 422.6 nm) in the plasma region, respectively. Both filters have bandwidth of 10 nm.

![Plasma emission images](image)

Fig. 2 Plasma emission images obtained from the Ca$_2$O$_3$ pellet sample using LIBS (a) without band-pass filter, (b) with band-pass filter of 394 nm, and (c) with band-pass filter of 420 nm.

Figure 2 represents the plasma emission images in LIBS without the use of band-pass filter [Fig. 2(a)], by using a 394 nm filter [Fig. 2(b)], and by using a 420 nm filter [Fig. 2(c)]. The lifetime of plasma emission was approximately 50 μs. Two black lines in the plasma image are loop antenna used to transfer the MWs from magnetron to the laser plasma region; the plasma emission most often occurred in the inner of loop antenna and therefore the wire of the antenna disturbs the image of the plasma to the ICCD. A laser plasma with a small diameter of approximately 3 mm was observed at 5 μs delay time. The brightest plasma emission clearly occurred at 5 μs. By increasing the delay time, the plasma expands away from the target surface and enlarges the diameter of
approximately 5 mm. It should be noticed that the plasma emission lifetime for the Ca ions [Fig. 2(b)] is much shorter (around 20 μs) than the case of Ca neutral of around 50 μs [Fig. 2(c)]. Furthermore, it can be observed that the Ca neutral emission is slightly brighter than the Ca ionic emission. These results indicate that the plasma temperature is not so high enough to ionize the Ca atoms as confirmed by the results shown in Fig. 5 of previous paper [15]. When the temperature is not so high enough, the atoms are excited to the excitation level of neutral atom and it is hard to be ionized due to lack of energy for excitation and ionization.

![Plasma emission images](image)

Fig. 3 Plasma emission images obtained from the Ca₂O₃ pellet sample using MA-LIBS (a) without band-pass filter, (b) with band-pass filter of 394 nm, and (c) with band-pass filter of 420 nm.

In contrary to the laser plasma in LIBS above, the luminous plasma induced by a pulse laser with MWs (MA-LIBS) shows different feature of plasma emission as displayed in Fig. 3. Very high-intense plasma emission with a diameter of approximately 8 mm at 5 μs delay time was clearly observed. With increasing the time, the plasma diameter was enlarged of approximately 15
mm at 200 μs delay time. The intensity of plasma emission slowly decreases with increasing the
delay time. It should be noticed that the plasma emission for the MA-LIBS without any filter as
shown in Fig. 3(a) was enlarged of approximately 3 times compared to the case of LIBS as
displayed in Fig. 2(a). This result revealed that the microwave plays an important role on the
enlargement of plasma diameter. It is assumed that in the case of microwave-assisted laser plasma,
the plasma consists of two regions, namely main plasma (inner layer) and outer layer plasma.
When the laser is focused on the sample target, main plasma with high electron density is induced.
Once the microwave is introduced into the laser plasma, the electromagnetic field induced by the
microwave is effectively absorbed by the laser plasma especially at outer layer of plasma region,
which has lower electron density. The microwave then accelerates the electron in the plasma,
increasing its kinetic energy. Along with the increment of kinetic energy, the number of collisions
between electrons and constituents increases, which affects the enlargement of plasma diameter
and the increase of the plasma temperature. It should be noticed that the plasma lifetime in MA-
LIBS extended very long lifetime (approximately 8 times longer than the LIBS case) due to long
MW duration.

It is also seen that from initial to later stages, the plasma emission of Ca ions [Fig. 3(b)] is much
stronger compared to the case of Ca neutral emission [Fig. 3(c)]. It should be pointed out that
stronger emission intensity of Ca ions indicates a high degree of ionization of calcium atoms in the
microwave-assisted LIBS. By observing the plasma images induced in LIBS with and without
microwave, it can be revealed that the microwave plays an important role on the enlargement of
plasma diameter, the extension of plasma lifetime and the increment of plasma temperature, which
means that the excitation process of atoms can effectively take place in the plasma region both in
the inner and outer layers of microwave-assisted laser plasma region, allowing to the improvement
of emission intensity in MA-LIBS. However, the experiment on this study was conducted at low
pressure environment, which is due to the limitation of the MWs power at 400 W. By higher power
of the MWs, the experiment has high possibility to be carried out at atmospheric pressure, which
enables one to study rapid and in-situ analysis of materials.

4. Conclusions

Time-resolved imaging of luminous plasma induced on Ca,O, pellet by laser without (LIBS)
and with MWs (MA-LIBS) has been conducted. The plasma characteristics are different between
LIBS and MA-LIBS. In case of LIBS, the plasma lifetime is approximately 50 μs, the plasma size
at 5 μs is approximately 3 mm, and the neutral Ca emission is much brighter than the ionic Ca
emission. This indicated that the plasma temperature in LIBS is quiet low because the degree of
ionization is low, which is shown by brighter emission of neutral Ca, and therefore, the atomization
and excitation of atoms cannot effectively take place. When the MWs were introduced into the
laser plasma (MA-LIBS), the plasma lifetime was extended of approximately 8 times, the plasma
size was enlarged 3 times longer at 5 μs than the case laser plasma without MWs (LIBS). Also, the
ionic Ca emission is much brighter than the neutral Ca emission. The stronger emission intensity of
Ca ions indicates a high degree of ionization of calcium atoms in the microwave-assisted LIBS.

The results certified that MWs have significant effect in the enhancement of plasma emission.
Therefore, LIBS assisted by MWs (MA-LIBS) can be employed to perform analysis of elemental
composition in materials with high sensitivity. Furthermore improvement of present method by
using higher power of MWs will be made in the near future in order to realize the analysis at
atmospheric pressure, which is enable one to conduct rapid and in-situ analysis of materials.

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