Diagnostics of liquid-phase laser ablation plasmas by spectroscopic methods

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Abstract. We adopted spectroscopic diagnostics for investigating plasmas produced by laser ablation of a graphite target in water. By taking pictures of optical emissions at various delay times after the irradiation of the ablation laser pulse, we examined the size, the lifetime, and the transient expansion of the plasma. The spectrum of the optical emission was also measured at various delay times. No line emissions were observed in the spectrum. The blackbody temperature of the plasma was evaluated by fitting the continuum spectrum with the Plank equation. In addition, we examined the propagations of compressional waves in water by shadowgraphy.

1. Introduction
Recently, laser ablation in liquids attracts much attention as a novel method for synthesizing new materials [1, 2, 3]. For example, clusters of ZnO with a unique structure have been obtained by ablating a Zn target in water with a surfactant [4, 5]. Although the synthesis mechanism of the unique clusters has not been understood well, it is suggested that the highly nonequilibrium condition with high temperature and high pressure may have positive influence for the synthesis of such new materials. In addition, the laser-ablation technique in liquids has several advantages from the engineering point of view. The most important advantage is the simple synthesis apparatus. Since this method requires no vacuum equipments, the change of the target and the collection of clusters can be done by an easier way than conventional laser ablation techniques using vacuum environments. In spite of the usefulness of laser ablation in liquids, the behavior of the plasma produced by liquid-phase laser ablation has not been examined well. In this work, we investigated the laser-ablation plasma produced in water using three spectroscopic diagnostics.

2. Experimental
The experimental apparatus for shadowgraphy is schematically shown in Fig. 1. A quartz glass cell with a length 40 mm and a width of 20 mm was filled with distilled water. A graphite target installed in the quartz cell was irradiated by Nd:YAG laser pulses at a wavelength of 1.06 μm from the normal direction. We moved the target together with the quartz cell up and down to disperse the ablation point. The duration and the repetition rate of the YAG laser pulse were 6 ns and 10 Hz, respectively. The YAG laser beam was focused using a lens, and the fluence on the target surface was estimated to be 28 J/cm². In the shadowgraphy measurement, the
ablation space was illuminated by an expanded He-Ne laser beam as shown in Fig. 1. The
He-Ne laser beam passed through the ablation space was projected on a screen, and the image
of the He-Ne laser beam on the screen was taken using a gated CCD camera with an image
intensifier (ICCD camera). An interference filter with the transmission at the wavelength of
the He-Ne laser (632.8 nm) was placed in front of the camera. By changing the delay time \( t_D \)
between the irradiation of the YAG laser pulse and the trigger to the gate of the ICCD camera,
we obtained the temporal variation of the image of compressional waves in water. The same
ICCD camera was used for measuring the image of the optical emission from the plasma by
removing the He-Ne laser and the screen from Fig 1. An interference filter with a transmission
wavelength of 560±5 nm was used for measuring the optical emission image. For measuring the
optical emission spectrum from the plasma, we used a monochromator combined with a gated
ICCD camera. A quartz optical fiber was used for guiding the optical emission to the entrance
slit of the monochromator.

3. Results and discussion
3.1. Intensity and size of optical emission
We took optical emission images at various delay times \( t_D \) after the irradiation of the YAG laser
pulse with a gate width of 2 ns. The peak position of the intensity was roughly stationary, and
was located at approximately 0.3 mm from the target surface. Figure 2 shows the cross section
of the optical emission intensity across the peak along the direction perpendicular to the YAG
laser beam. As shown in the figure, the size of the plasma was less than 1 mm. The emission
intensity decreased with \( t_D \), while we observed the expansion of the plasma. Figure 3 shows the
temporal variation of the peak intensity and the size of the optical emission image defined by full
width at half the maximum (FWHM). The temporal variation of the optical emission intensity
had a fast spike at the beginning. The duration of the spike (FWHM) was approximately 10
ns, and the waveform of the spike roughly followed the waveform of the YAG laser pulse. The
size of the optical emission expanded rapidly during the YAG laser pulse. The initial expansion
speed of the optical emission was approximately \( 2.4 \times 10^7 \) mm/s. This expansion speed is slower
than the initial expansion speed of a laser-ablation plasma produced in a gas [6], suggesting
the tight confinement of the plasma by the ambient water. It should be emphasized that the
temporal variation of the optical emission intensity had a long tail component, and we observed
the optical emission at \( t_D = 1 \) \( \mu \)s. At \( t_D \geq 10 \) ns, the volume of the optical emission region

Figure 1. Experimental apparatus for shadowgraphy.
continued expanding with a slower speed of $5 \times 10^6$ mm/s as shown in Fig. 3.

### 3.2. Emission spectrum and blackbody temperature

In the measurement of the optical emission spectrum, we lengthened the gate width to 50 ns to obtain sufficient signal intensities. The spectra observed at $t_D = 25 \pm 25$, $125 \pm 25$, and $1025 \pm 25$ ns are shown in Fig. 4. We observed no line emissions in the spectrum, and it was occupied by continuum emission completely. This result is different from that reported in a reference [7]. We evaluated the blackbody temperature of the plasma by fitting the spectrum with the Plank equation. In Fig. 4, the plots represent the spectra observed experimentally, and the curves show the results of fitting using the Plank equation. As indicated in Fig. 4, the blackbody temperature immediately after the irradiation of the YAG laser pulse ($t_D = 25 \pm 25$ ns) was approximately 4300 K. The temperature decreased with $t_D$, and the temperature at $t_D = 125 \pm 25$ ns was approximately 3000 K. The continuum optical emission was also observed at $t_D = 1025 \pm 25$ ns, and the temperature was still as high as 2500 K. The observation of the continuum optical emission that can be fitted with the Plank equation indicates the plasma produced in water is very dense. In addition, the temperature of the plasma is higher than 2500 K at $t_D \leq 1 \mu s$. This high-density, high-temperature condition may have a positive influence on the synthesis of new materials. In addition, the high-density, high-temperature environment is surrounded by water at room temperature. This highly nonequilibrium condition may also be a positive factor in the synthesis of new materials by laser ablation in liquids.

### 3.3. Observation of compressional waves by shadowgraphy

Figure 5 shows an image of shadowgraphy taken at $t_D = 2 \mu s$. We detected two types of compressional wave. One had a spherical wave front, which may be originated from the excitation of a shock wave due to the expansion of the plasma. The front of the other wave was parallel to the target surface. The parallel wave was excited in several times with a frequency of 740 kHz. The parallel wave may be owing to the vibration of the target, which may be induced by the
Figure 4. Optical emission spectra (plots) observed at various delay times after the irradiation of the YAG laser pulse. The curves represent the fittings by the Plank equation.

Figure 5. Image of shadowgraphy observed at 2 μs after the irradiation of the YAG laser pulse.

laser irradiation. The propagation speeds of both the wave fronts were \((1.4 - 1.5) \times 10^6\) mm/s, which is roughly consistent with the sound velocity in water.

4. Conclusions
In this work, we investigated laser ablation of a graphite target in water using spectroscopic diagnostics. The laser-ablation plasma produced in water was smaller than 1 mm. The temporal variation of the optical emission intensity roughly followed the waveform of the YAG laser pulse. However, it was also found that the tail component of the optical emission intensity survived beyond 1 μs. The spectrum from the plasma had a blackbody distribution, and the temperature deduced from the spectrum was higher than 4000 K immediately after the irradiation of the YAG laser pulse. Compressional waves were excited in water by the expansion of the plasma. According to these experimental results, it has been revealed that the laser-ablation plasma produced in water is very dense due to the confinement effect of the ambient water, and has a high temperature and a high pressure. In addition, the laser-ablation plasma in water is highly transient and nonequilibrium. Because of these unique conditions, laser ablation in liquids is a useful technique for synthesizing new materials.

5. References
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