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Advancing the experimental design for simultaneous acquisition of laser induced plasma and Raman signals using a single pulse☆

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ABSTRACT

Simultaneous acquisition was performed of combined signals that show highly resolved and identifiable peaks of both LIBS and Raman signals. A LIBS-Raman combination using a single light source is a daunting task, because the energy required for Raman shift is relatively low, compared to the energy required for laser ablation. Here, we utilize an expanded-focused beam that allows simultaneous detection of the signals of laser induced plasma and Raman shift. A beam expander obtains the Raman signal with minimized interference from the plasma, and a focusing lens of small diameter generates strong laser induced plasma for LIBS. The position of the focusing lens can be adjusted to control the area of Raman scattering to ensure a strong Raman signal. In the proposed design, the key to minimized interference is to generate the Raman scattering apart from the plasma, which allows for sufficiently long gate width and wide area for Raman detection. Furthermore, axial relocation of the end of the optical fiber can easily optimize the Raman, LIBS, or combined Raman-LIBS signal.

1. Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) is a technique to analyze atomic composition by detecting plasma generated by laser ablation. A breakdown of the chemical bonds occurs when a high powered pulsed laser focuses on the sample surface. Then plasma is generated that contains electrons, atoms, and ions. Raman spectroscopy, on the other hand, uses the shifted emission light, which is unique for each molecule, for its composition analysis. When a monochromatic light source such as laser irradiates a sample surface, a very small amount of the scattered light shifts, which involves the energies of molecular vibrations.

Studies on a combined LIBS-Raman system have been performed for the noticeable advantages when the two are combined into a single unit. The two techniques are complementary to each other, in that the LIBS signal is sensitive to elemental composition, while Raman gives information on the mineral structure and polymorphs. Also, LIBS and Raman spectroscopy share various optical components for laser irradiation and detection, and thus the development of a compact system in theory is straightforward. The combined system is capable of depth profiling by laser ablation, which is not possible in Raman spectroscopy alone.

Combined LIBS and Raman spectroscopy has the potential to unveil geological structures in planetary science and geology [1–10]. In particular, its stand-off capability has been exploited to detect and categorize explosive materials [11,12]. Depth profiling analysis of multi-layered materials, such as metal alloy, polymer, fresco and terra-cotta, has also been carried out [13,14]. Furthermore, it has been used to classify pigments, inks, etc., by providing complementary information on both the molecular and elemental composition of samples [15,16].

However, most studies have used two laser pulses, even though a single laser has been used, as the energy required for Raman shift is relatively low compared to that required for laser ablation. Sharma et al. adjusted the energy and spot size for LIBS and Raman detection of calcite, gypsum, and barite minerals [4], and simultaneously acquired both signals. Giakoumaki et al. used the energy range of 0.01 to 10 mJ/pulse for LIBS [5], and employed a variable angle attenuator to reduce the laser energy for Raman detection. Dreyer et al. obtained LIBS and Raman signals using a diode pumped Nd:YLF laser operating at 523 nm [6], by adjusting the proper energy for LIBS or Raman detection by a change in the Q-switch repetition rate. Hoehse et al. employed a diode pumped solid state laser for LIBS-Raman study [8], and used output wavelengths of 1064 nm and 532 nm to obtain LIBS and Raman signals, respectively. Glaus et al. applied a fiber-coupled LIBS-Raman system to perform a depth profiling study [13], irradiating laser energy of 0.02 to 0.15 mJ, and 1.0 mJ, on the samples for Raman and LIBS detection, respectively.

Three experimental setups have been suggested for simultaneous detection of laser induced plasma and Raman shift. Moros et al. employed time-resolved study to carry out simultaneous detection of explosive at stand-off distance [11]. The Raman shift signal occurred immediately after laser irradiation. Therefore, they detected the Raman signal early with a very short integration time, and then obtained the LIBS signal. They used a holographic imaging spectrograph with a

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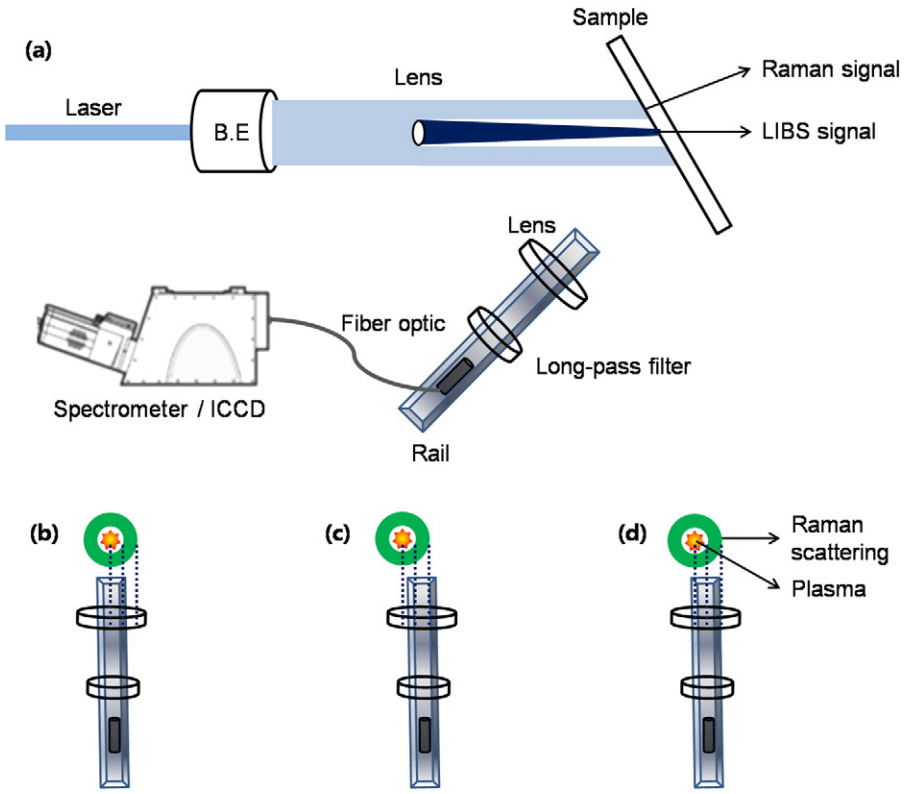

Fig. 1. (a) Schematic of the expanded-focused laser beam for simultaneous LIBS-Raman signals, and direction of the collection part for (b) LIBS, (c) Raman, and (d) simultaneous detection.

detector-intensified CCD for Raman detection, and employed a Czerny–Turner spectrograph with a detector-intensified CCD for LIBS data acquisition. Sharma et al. used a pulsed laser operating at dual wavelength of 1064 nm and 532 nm for simultaneous excitation of both LIBS and Raman spectra at stand-off distance [1]. When the laser beam passes the distance of 8.6 m, the 532 nm laser beam focuses in front of the 1064 nm beam, due to chromatic aberration in the beam expander. Consequently, the diameters of the concentric laser spots were 600 μm and 900 μm for 1064 nm and 532 nm beams, respectively so that simultaneous acquisition was possible. Matroodi et al. used a Glan-Taylor prism to divide a laser pulse into two beams [7]. A focused beam irradiated the sample surface to generate micro plasma for emission of the LIBS signal. The other beam directly irradiated the same point on the sample without focusing, for the Raman signal. The average laser energy for Raman and LIBS excitation was 35 and 5 mJ, with diameters of 5 mm and 0.1 mm, respectively. The Raman shift signal mixed with the plasma emission, and was detected in a single spectrum.

The present study suggests a combined LIBS-Raman system, and employs a beam expander to expand a laser beam to obtain the Raman signal without interference with the plasma. Also, we use a focusing lens of small diameter to generate the laser induced plasma for LIBS. The position of the focusing lens controls the area of Raman scattering. The proposed experimental design enables the simultaneous acquisition of laser induced plasma and Raman signals, with minimum interference between plasma and Raman scattering. Additionally, the LIBS, Raman, or combined LIBS-Raman signals can be independently obtained, by adjusting the axial location of the end of the optical fiber.

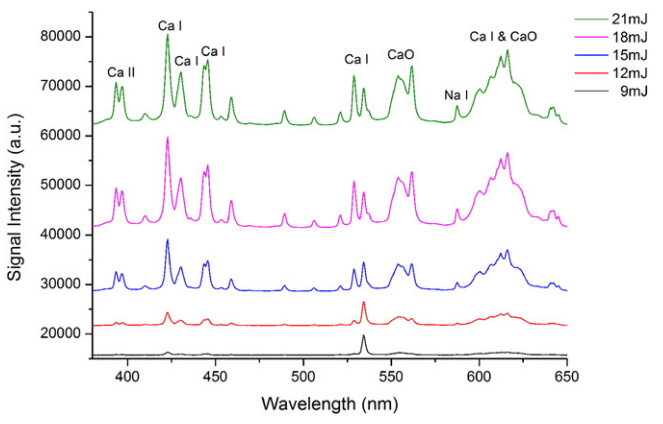

Fig. 2. LIBS spectra of aragonite sample versus energy change.

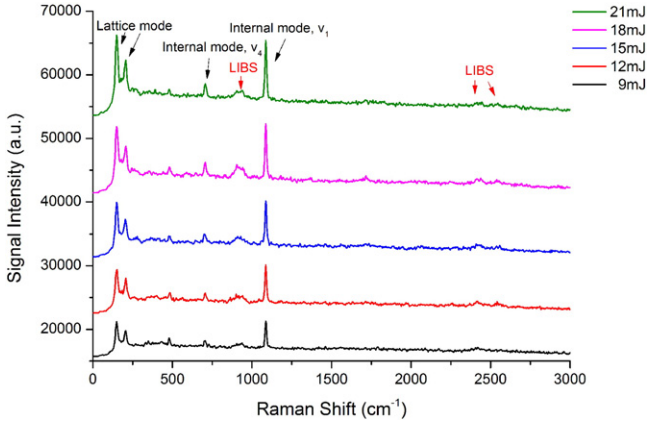

Fig. 3. Raman spectra of aragonite sample versus energy change.