

Picosecond Laser Induced Breakdown Spectroscopy (LIBS) with the Raydiance Discovery™ Platform

Nancy McMillan, Ph.D, New Mexico State University; Greg Spooner, Ph.D, Raydiance, Inc.

Abstract

High quality LIBS spectra and line structure were obtained using the Raydiance ultrashort pulse Discovery™ platform coupled with a high throughput spectrograph and a high sensitivity (non-gated) detector. With integration times of approximately 100 seconds, the resulting spectra had very good atomic line resolution and enabled positive identification of various elements in the gems. Real-time process control that approaches the high repetition rates and high average power of the Raydiance system will require shorter integration times, which in turn will require higher efficiency spectrographs, higher sensitivity detectors, or both.

Background

The Raydiance ultrashort pulse (USP) laser can be used to ablate material with high spatial precision. Individual ablation events are produced by the creation of a localized ionization event at the laser focus and the subsequent formation of a small volume of electron-ion plasma and transfer of the plasma energy into the surrounding material. In this process, the plasma emits optical radiation that can be analyzed to provide compositional information about the material of interest. This particular spectroscopic technique is referred to as laser induced breakdown spectroscopy (LIBS), and, potentially, could be used for analyzing or controlling USP laser ablation or other USP laser material processing.

In traditional LIBS, nanosecond pulses of millijoule energy (or greater) produce relatively large amounts of optical emission. The Raydiance Discovery™ system produces much shorter pulses (picosecond) with smaller pulse energies (microjoules). Picosecond and femtosecond laser LIBS, while rarely performed in practical applications, is generally associated with minimal laser damage to the sample, reduced thermal emission background and richer spectral line structure that has a more direct relationship to the actual material composition.¹ These advantages are a result of the fact that the plasmas are generated on time scales shorter than thermal diffusion or thermal equilibration processes operating in the material and because the plasma itself has minimal interactions with the laser pulse due to the short nature of the pulse.

The flexibility of Raydiance platform combined with spectroscopic techniques such as LIBS may enable real-time and continuous control of USP laser material processing, including biological materials and tissues.

An initial investigation was performed to determine the conditions required to produce LIBS spectra that demonstrated this potential.

Experimental Evaluation of LIBS Instrumentation with Raydiance Platform

The optical emission strength associated with LIB plasmas is dependent upon the pulse energy that creates the plasma. Because the Raydiance system operates at lower pulse energy than the longer pulse lasers used in traditional LIBS applications, high throughput spectrographs and sensitive detectors were used in this proof-of-concept work. However, it is likely that running the Raydiance system at high average power and repetition rates will obviate the need for the more sensitive detection equipment.

An evaluation was performed using a high throughput Echelle spectrograph (Catalina SE 200, with standard dispersion module, f/10 input, and 40 x 80 μm slit) and a back-illuminated CCD camera (Apogee Instruments U47.) The optical sensor was a multimode UV-transmissive fiber (0.22NA) in close proximity (<3 mm) from the ablation surface. Ablations were created at 500 kHz and 2.5 μJ on target. The sample was slowly translated with respect to the fixed position focusing lens (Mitutoyo NA M Plan APO NIR 0.40NA microscope objective) to minimize any laser damage to the surface. Gemstones with flat faces were chosen to allow for simple focusing onto a planar surface.

The detection instrument acquired plasma emission spectra in “open staring” mode, in which no time-gating of the detector array was performed.

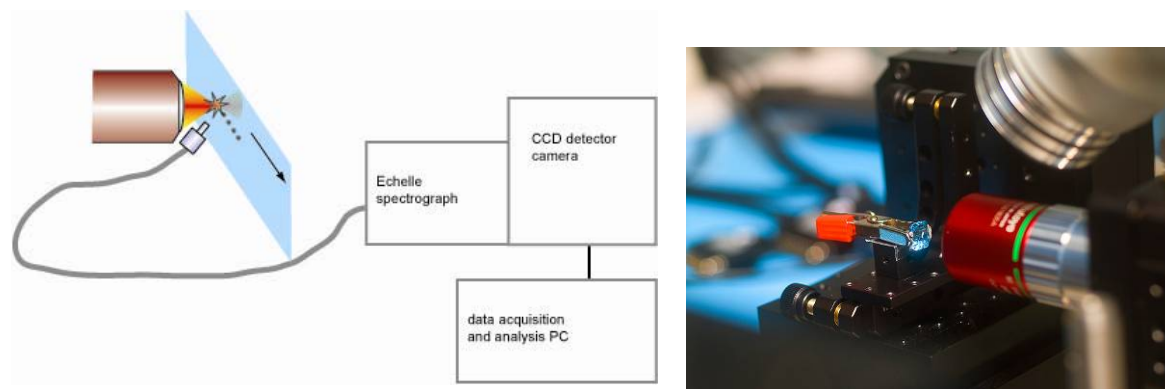


Figure 1: USP LIBS with Raydiance platform. Left image shows representation of LIBS experimental arrangement. Blue rectangle represents material being ablated and sampled by LIBS. The material is moved with respect to a fixed focus spot, with the plasma light being collected by a fiber in close proximity. Right image shows the ablation of a small gemstone. The white spot in the blue stone center is the plasma light (collection fiber not shown).

Results

High quality spectra were obtained with integration times of approximately 100 seconds, a sampling time consistent with the fact that the individual plasma emissions are relatively weak compared to conventional LIBS laser pulses. The resulting spectra had very good atomic line resolution and enabled positive identification of various elements in the gems (**Figure 2**).

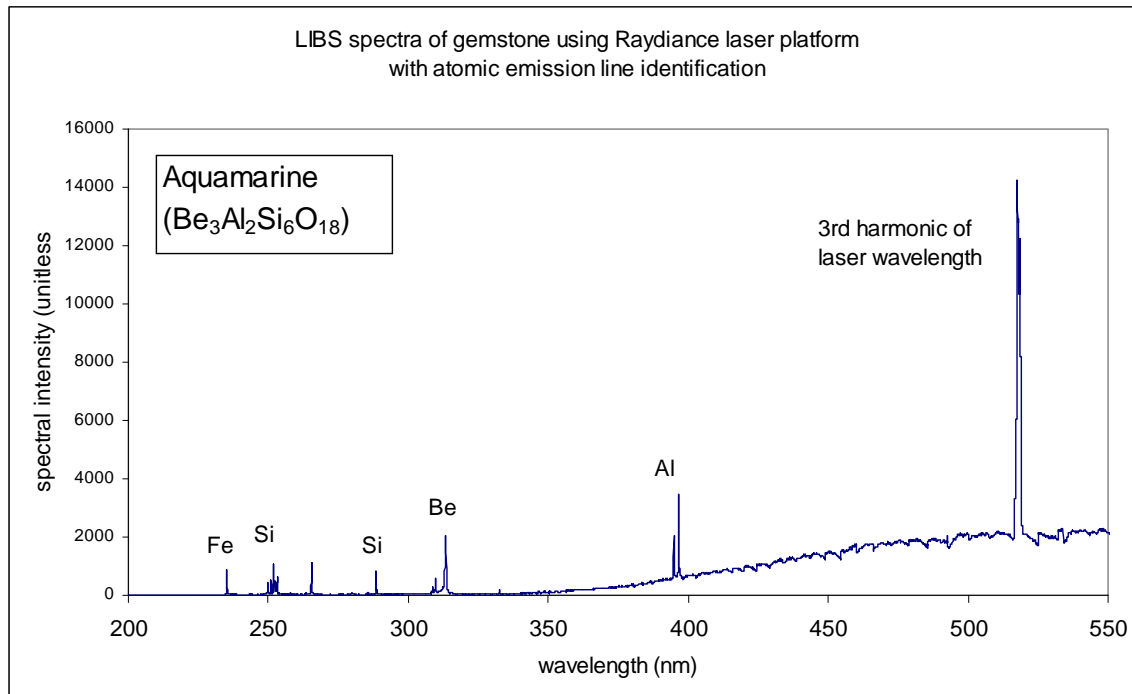


Figure 2: Representative spectra from evaluation of LIBS spectrometer with Raydiance USP laser platform. Some continuum is observed (smooth portion of spectrum). Elemental assignments are consistent with aquamarine gemstone composition, with trace iron signature. The 3rd harmonic of the 1552 nm laser wavelength is a dominant feature of the spectrum, as is a common feature of surface ablations with USP pulses.

As other workers have reported with ultrashort pulse LIBS, the thermal continuum contribution to the spectra was minimal, in contrast to what is commonly observed with nanosecond/higher energy pulses. This benefit of picosecond-LIBS suggests that non-time-gated spectral acquisition can be used for this application, which in turn means that high repetition rate laser ablation and long spectral integration times can be used without negative consequences on the quality of the spectra.

Conclusion

High quality LIBS spectra and line structure can be obtained with the Raydiance USP laser platform, provided a high throughput spectrograph and high sensitivity (non-gated) detector are used. The relatively small plasma optical emission strength requires relatively long integration times. Real-time process control that approaches the high repetition rates and high average power of the Raydiance system will require shorter integration times, which, in turn, will require higher efficiency spectrographs, higher sensitivity detectors, or both.

References

ⁱ Laser-Induced Breakdown Spectroscopy (LIBS) - Fundamentals and Applications. ed by Andrzej W. Miziolek, Vincenzo Palleschi, Israel Schechter, Cambridge University Press 2006, ISBN-13 978-0-521-85274-6. pp. 477-489.