

LIBS – Raman Spectroscopy of Minerals Using Remote Surface Modification Techniques

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Overview: Laser Induced Breakdown Spectroscopy (LIBS) and Raman Spectroscopy are highly complementary techniques being developed to remotely probe the surface of geological samples. LIBS involves ablating material from the surface of the sample to probe the elemental composition. Raman spectroscopy uses the same laser to identify the molecular composition of the sample. For example, LIBS is used to determine that a sample contains calcium carbonate (CaCO_3) while Raman spectroscopy can determine if the CaCO_3 rock is calcite or aragonite.

Sharma *et al.* [1], Wiens *et al.* [2-3] and Thompson *et al.* [4] have demonstrated the feasibility and value of combining LIBS and Raman spectroscopy into an integrated system for Lunar and Planetary exploration. In this presentation, we will demonstrate that LIBS can be used to drill through the sample surface to remove dust or other coatings that will interfere with mineral analysis by Raman spectroscopy.

Experimental Setup: Figure 1 contains a diagram of the combined LIBS and Raman spectroscopy experimental setup. A detailed description of this combined system can be found in Wiens *et al.* [3] Both systems probed samples placed either in air or in a vacuum chamber filled with 7 Torr CO_2 to simulate the surface pressure on Mars. Previous experimental observations have demonstrated that LIBS benefits from the reduced pressure on Mars as the pressure affects the plasma generation.

The LIBS experiment employed a Surelite Continuum Nd:YAG laser, at 532 nm and 20 Hz, with a maximum power of 35 mJ. A 5x beam expander was used to focus the laser onto the sample 8.56 meters away. The laser creates an expanding plasma containing the electronically excited ions, atoms, and molecules from the surface of the sample. These electronically excited species emit light at frequencies indicative of the elements present. A 10.8 cm Newtonian reflecting telescope was used to collect some of this optical emission and direct the light into one of three Ocean Optics HR2000 Spectrometers with a 300 μm fiber. The three spectrometers were similar to those that will be used for ChemCam instrument, which includes the LIBS spectrometer, selected for the Mars Science

Laboratory (MSL) rover. These three spectrometers record the emission in three regions including 225-320 nm (“UV unit”) and 385-460 nm (“VIS unit”), and 500 – 930nm (“NIR unit”).

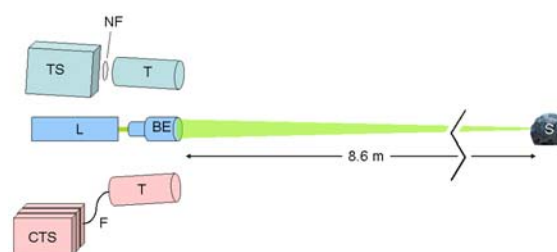


Fig. 1. Experimental set-up used for the LIBS and Raman spectra. TS = Raman transmission-grating spectrograph, NF = notch filter, T = telescope, L = laser, BE = beam expander, S = sample, F = fiber optic cable, CTS = Czerny-Turner spectrograph.

The Raman spectrometer employed a Big Sky Nd:YAG laser at 532 nm and 20 Hz. The Raman signal was collected with a 125 mm diameter Cassigranian reflecting telescope directly coupled to a Raman Holospec Spectrometer with a Princeton Instruments intensified CCD camera. The details of directly coupled remote Raman system are discussed elsewhere [5].

Samples: Anhydrite (CaSO_4) and the chocolate brown color calcite (CaCO_3) crystals with $\sim 10 \mu\text{m}$ hematite coatings were from Santa Eulalia, Mexico, and were purchased from Ward’s Natural Science Establishment, Inc., Rochester, New York. The powdered sample of Hawaiian basalt used for dusting the anhydrite sample was acquired from USGS.

Results: Figure 2 contains three pictures of the anhydrite sample before it was coated with the basalt dust, after the sample was coated and after some of the dust was removed with the LIBS laser. Figure 2 also contains three LIBS (left) and three Raman spectra (right) collected before dusting, after dusting and after the dust was removed.

Before the anhydrite sample (CaSO_4) was dusted, an abundance of calcium emission lines were observed from the LIBS spectrum as well as a signature due to strontium. The Raman spectrum depicts a strong line at 1017cm^{-1} which is a Raman fingerprint of the SO_4 symmetrical stretch. All of the remaining spectral features are from various internal modes of SO_4 .

The picture and spectra in the middle of Figure 2 were acquired after the anhydrite sample was coated with the dust. The Raman spectrum (right) no longer detects the spectral fingerprints from the anhydrite sample and only detects features from the room air, oxygen (1556cm^{-1}) and nitrogen (2331cm^{-1}). The LIBS spectrum was acquired as we began to remove some dust with the LIBS laser. The spectral features are much weaker than were observed before dusting, while most of the strong calcium emissions were still observed. Several new Fe and two strong Ti (453.32 and 453.48nm) LIBS emission lines were also observed from the basalt dust.

The bottom picture and spectra were obtained after the LIBS laser removed some of the dust with approximately 100 laser shots. Both LIBS and Raman spectra were nearly identical to the spectra obtained before the sample was dusted. The LIBS spectrum continues to record additional emission lines from the Fe and Ti in the basalt.

Similarly, after cleaning the hematite coating from a calcite crystal, we were able to record the Raman spectrum of the underlying carbonate material.

References:

[1] Sharma et al. [2003] *Spectrochimica Acta A*, 59, 2391-2407. [2] Wiens et al. (2000) *Lunar Planet. Sci. XXXI*, 1468-1469. [3] Wiens et al. (2005) *Spectrochimica Acta A*, 61, 2324-2334. [4] Thompson et al. (2005) *Lunar Planet. Sci. XXXVI*, 1517. [5] Misra et al. [2005] *Spectrochimica Acta A*, 61, 2281-2287.

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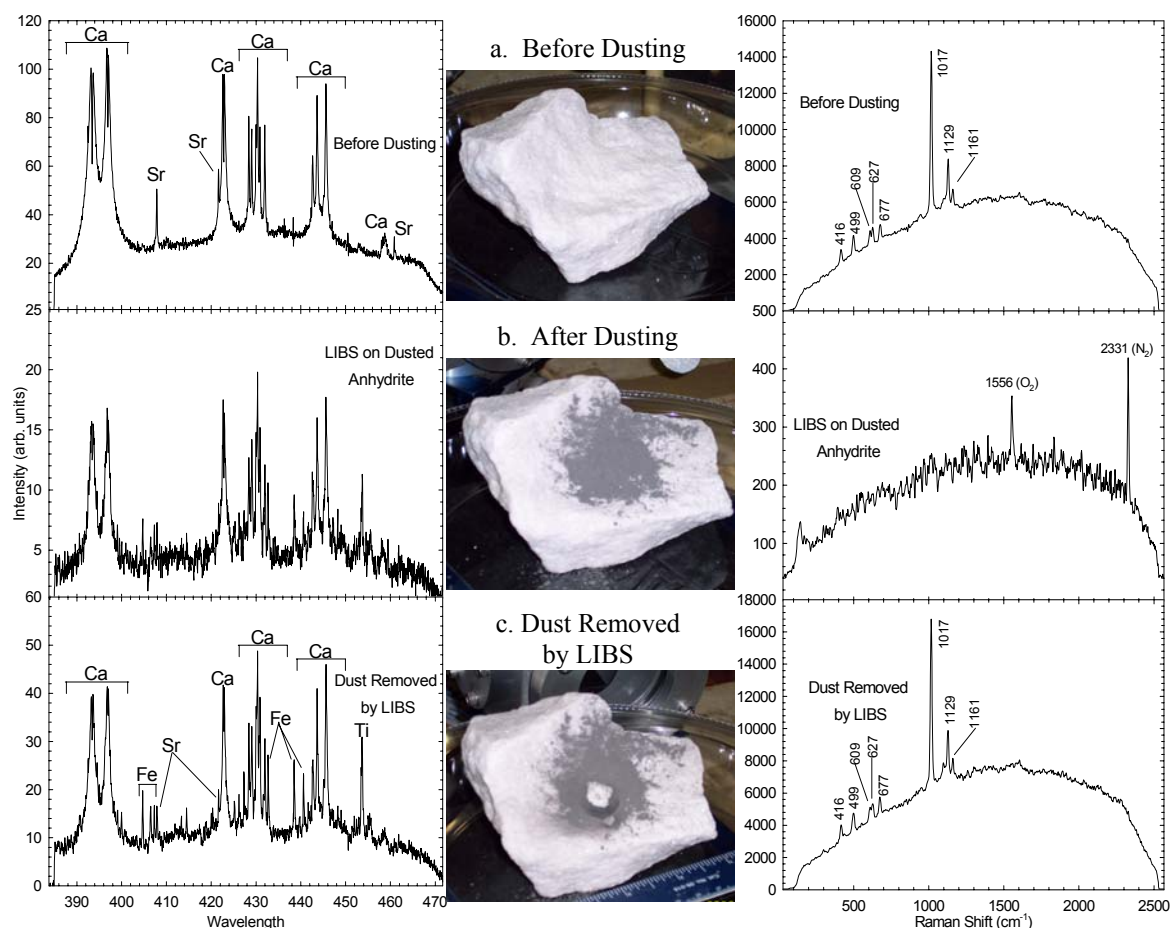


Fig 2. Left panel: LIBS of anhydrite samples figs. from top to bottom: before dusting anhydrite sample (see photograph (a) in the middle panel), after dusting the sample with Hawaiian volcano basalt powder (see photograph (b) in the middle panel), and after removing the dust by LIBS spark at the sample (see photograph (c) in the middle panel). The right hand panel shows the respective Raman spectra of the anhydrite samples to photographs (a), (b) and (c) in the middle panel.