

NEW MICROSCOPIC LASER-COUPLED SPECTROSCOPY INSTRUMENT COMBINING RAMAN, LIBS, AND FLUORESCENCE FOR PLANETARY SURFACE MINERALOGY. J. Blacksberg¹, Y. Maruyama³, M. Choukroun¹, E. Charbon³, G.R. Rossman², ¹Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, Jordana.blacksberg@jpl.nasa.gov, ²California Institute of Technology, Division of Geological and Planetary Sciences, Pasadena, California 91125, grr@gps.caltech.edu, ³Circuits and Systems, Delft University of Technology, Delft, The Netherlands, y.maruyama@tudelft.nl.

Introduction: *In situ* exploration of planetary surfaces requires multiple techniques that, when used together, allow us to form a more complete picture of their formation histories and evolution. In the past decade, laser spectroscopy techniques (LIBS, Raman) have been the subject of increasing attention and development [e.g., 1, 2, 3] because they can provide fast and non-destructive surface mapping of mineral structure and composition, without requiring any sampling or handling. We present a time-resolved laser spectroscopic technique that can collect microscopic Raman spectra as well as additional and complementary elemental information, all with the same instrument. Using a picosecond-scale pulsed laser and a fast time-resolved detector we can simultaneously collect spectra from Raman, Laser Induced Breakdown Spectroscopy (LIBS), and fluorescence emissions that are separated in time due to the unique decay times of each process. The use of a laser with high rep rate (40 KHz) and low pulse energy (1 μ J/pulse) allows us to rapidly collect high signal to noise Raman spectra while minimizing sample damage. Increasing the pulse energy by about an order of magnitude creates a microscopic plasma near the surface and enables the collection of LIBS spectra at an unusually high rep rate and low pulse energy. Simultaneously, broader fluorescence peaks can be detected with lifetimes varying from nanosecond to microsecond.

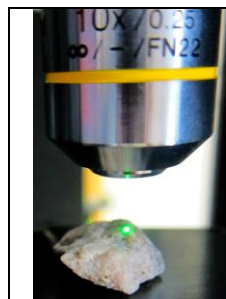


Figure 1. Image of our pulsed 532 nm microchip laser focused to $\sim 1 \mu\text{m}$ spot on a natural mineral sample with no prior sample preparation. The Raman, LIBS, and fluorescence spectra are collected and sent to the spectrometer through the same objective lens.

Application to Planetary Mineralogy: Raman spectroscopy is under consideration for a host of planetary surface missions (e.g. Mars, primitive bodies, Venus, the Moon). The versatility of this technique is due to the fact that nearly all crystalline minerals can be identified based upon the unique narrowband spectroscopic features in the Raman spectrum. Microscopic Raman,

which would be implemented close-range (e.g. on a rover arm), can be directed to a specific target within the context of its natural mineral setting. The laser spot can be focused down to a very small size ($\sim 1\text{-}5 \mu\text{m}$) comparable to mineralogical grains, which is the foundation for two dimensional Raman mapping. Using time-resolved Raman spectroscopy, we can realize all of these benefits, with additional advantages [4]. First, we can collect Raman spectra with high signal to noise even in the presence of large background fluorescence that is often associated with altered minerals (e.g. clays, sulfates, phosphates). This fluorescence is separated out in time providing further potentially useful information (e.g. fluorescence lifetime of the fluorophors). Finally, as we demonstrate here, we can use microscopic time-resolved laser spectroscopy in a

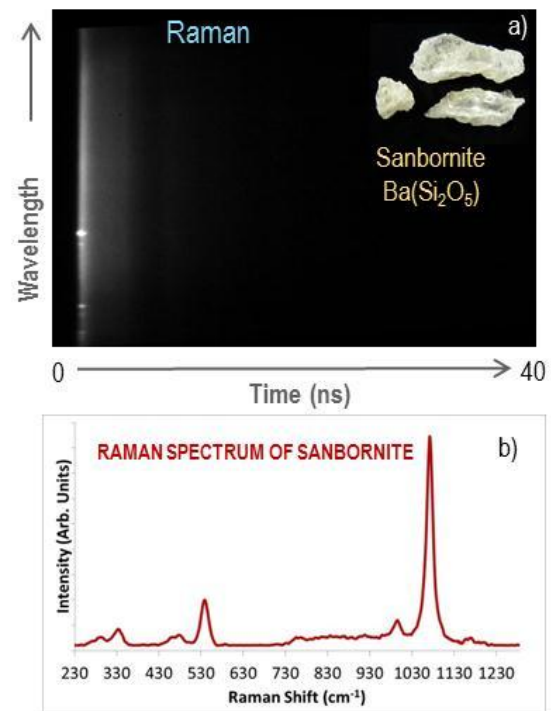


Figure 2. Raman spectrum of sanbornite. a) Streak camera image showing Raman spectrum on the left. The peaks are 500 ps wide corresponding to the laser pulse width. b) Spectrum averaged over the duration of the laser pulse (500 ps).

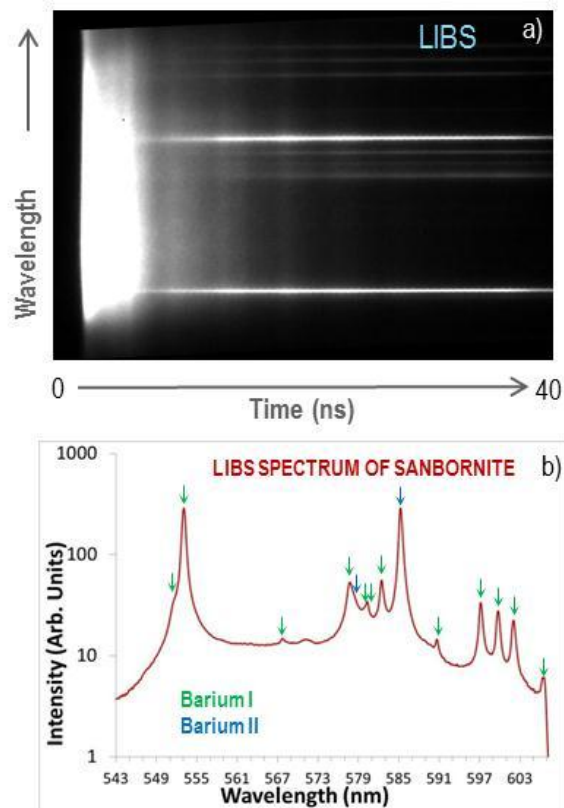


Figure 3. LIBS spectrum of sanbornite. a) Streak camera showing the bright plasma emission (first few ns) followed by the barium atomic emission lines from sanbornite. b) LIBS spectrum averaged over the last 20 ns of the time window, eliminating the plasma background.

new way: to obtain microscopic LIBS spectra along with the Raman spectra. This can be accomplished by small changes in the laser energy between scans.

Time-Resolved Laser Spectroscopy Instrument Development: We will present Raman, LIBS, and fluorescence spectra obtained on natural mineral samples. We demonstrate this technique using a photocathode-based streak camera as well as a newly-developed solid state Single-Photon Avalanche Diode (SPAD) sensor array based on Complementary Metal-Oxide Semiconductor (CMOS) technology [5]. Using this new SPAD array that is compact and similar in size to a standard uncooled CMOS or CCD image sensor, we have demonstrated that we can achieve equal or greater sensitivity to the streak camera. The use of a solid state time-resolved detector offers a significant reduction in size, weight, power, and overall complexity, putting it on par with instruments that do not have time resolution, while providing enhanced science return.

Combined microscopic Raman and LIBS spectra are shown in figures 2 and 3 for sanbornite, a barium silicate mineral. The Raman spectrum of sanbornite is obtained using the baseline laser energy. When the

laser energy is increased to overcome the LIBS threshold, barium atomic emission lines are visible. These spectra are typical for acquisition times of 3 sec (LIBS) and 30 sec (Raman) at a laser rep rate of 1 KHz.

We have previously demonstrated that we can detect Raman spectra with high fluorescence rejection using a SPAD array [5]. Here we demonstrate that complementary LIBS spectra can also be obtained using the SPAD array with high signal to noise ratio. Figure 4 illustrates the ability to eliminate the plasma background using an electronic delay on the SPAD array. This new phenomenon will be investigated further, and in particular the effects of the environment (e.g. gases present, pressure) and energy threshold on the LIBS and Raman spectra will be explored.

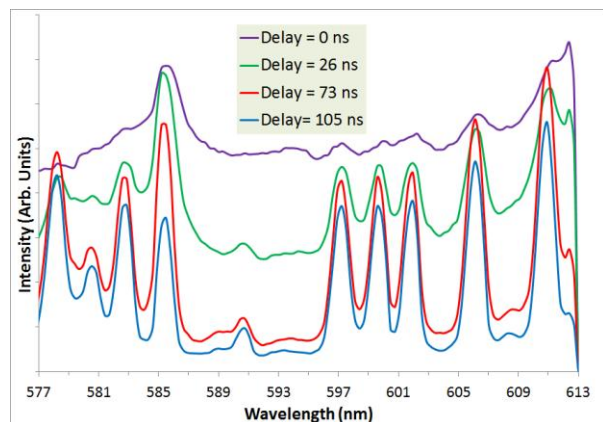


Figure 4. LIBS spectrum of barite showing barium emission lines using the 128x128 SPAD array. The data is averaged over a gate of width ~ 35 ns. The delay time is measured with respect to the start of the laser pulse. With increasing delay time, the plasma background is effectively eliminated.

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