

INTEGRATED REMOTE RAMAN AND LIBS INSTRUMENT WITH 532 NM LASER EXCITATION FOR CHARACTERIZING MINERALS AT 9 M . S. K. Sharma¹, A. K. Misra¹, P. G. Lucey¹ and R. C. F. Lentz¹, ¹Hawaii Institute of Geophysics and Planetology, University of Hawaii, 2525 Correa Rd., Honolulu, HI 96822 (sksharma@soest.hawaii.edu).

Introduction: Raman Spectroscopy and LIBS, Laser-Induced Breakdown Spectroscopy, are highly complimentary techniques being developed to remotely probe the surface of geological samples. Raman spectroscopy uses either a CW or a pulse visible laser of modest average power (100-700 mW/cm²) to identify the molecular fingerprints of the sample from its Raman spectrum [1]. For the CW-laser based remote Raman system, there are two significant issues: interference of the high ambient light background during the day, and long-lived fluorescence with the Raman spectra of the sample [2]. However, utilizing a pulsed laser system and gated receiver overcomes those limitations. Pulsed Raman spectroscopy offers two important benefits: the ability to discriminate against (a) unwanted ambient light, and (b) long-lived fluorescence emission from the sample. In the past, pulsed Raman spectroscopy has been used for measuring high quality Raman spectra of minerals at high temperatures and for investigating phase transitions at high temperature and anharmonicity of various vibrational modes [3]. In general, LIBS uses a pulsed 1064 nm laser of high peak power (>1 GW/cm²) for ablating material from the surface of the sample to probe the elemental composition [4,5]. For space applications, we previously demonstrated a combined remote Raman and LIBS system. This system used a single pulsed laser operating at dual wavelengths of 1064 nm and 532 nm for exciting both the Raman and LIBS spectra of minerals by adjusting the laser power electronically [6]. In this work, we have developed an integrated remote Raman and LIBS system for measuring both the Raman and LIBS spectra with a single 532 nm laser line of 35 mJ/pulse and 20 Hz. The system can also be reconfigured to perform micro-Raman and micro LIBS analysis which have applications in trace/residue analysis and can analyze very small samples in nano gram amounts.

Experimental Setup: Figure 1 depicts a schematic diagram of a combined Raman spectroscopy and LIBS system. The integrated remote Raman and LIBS systems use the following common components: (i) a telescope (Meade LX200R Advanced Ritchey-Chrétien, 203 mm clear aperture, f/10); (ii) a frequency doubled mini Nd:YAG laser source (Model ULTRA CFR, Big Sky Laser, 532 nm, 20 Hz) (iii) a 10x beam expander (iv) an intensified CCD detector (Princeton Instruments, PI-MAX); and (v) Kaiser spectrograph.

The 532 nm pulsed laser beam was focused to a 300 μ m diameter spot on the target 9 m away with a 10x beam expander. For Raman measurements the laser power at 532 nm was electronically adjusted to 25 mJ/pulse, and for combined LIBS and Raman measurements the laser power was increased to 35 mJ/pulse.

For the combined Raman and LIBS measurements,

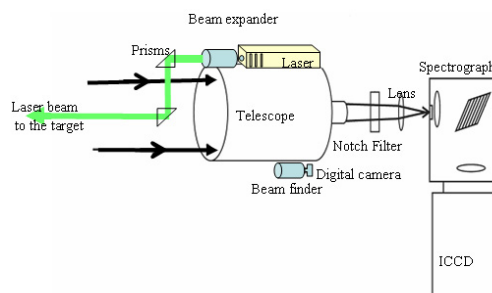


Fig. 1. Experimental set-up used for measuring remote LIBS and Raman spectra of minerals. Laser: 532 nm frequency doubled Nd:YAG, 35 mJ/pulse, 20 Hz; Kaiser HoloSpec spectrograph; ICCD: Intensified CCD detector.

the signals excited by the Big Sky laser were collected with a 203-mm diameter reflecting telescope in 180-degree geometry, coupled directly to a Kaiser F/1.8 HoloSpec transmission-grating spectroscope through a 100- μ m slit after passing through a 532-nm holographic super-notch filter (NF) to remove the reflected and Rayleigh-scattered laser light from the sample. The HoloSpec spectrometer measured the Raman spectra from 70 cm⁻¹ to 4500 cm⁻¹ when excited with a 532 nm laser. The grating covered the spectral region between 534 nm to 699 nm, which was sufficient for identifying some of the major atomic emission lines of measured samples from their LIBS spectra.

Results: Figure 2 shows the Raman spectra and the combined Raman and LIBS spectra of calcite (CaCO₃) and of gypsum (CaSO₄·2H₂O) at 9 m in air in the 534-615 nm wavelength range. The Raman spectra of these samples were excited with 25 mJ/pulse of the 532 nm laser and accumulated for 1 sec in the gated mode with 2 μ s gate. The lattice modes of calcite at 155 and 282 cm⁻¹ are clearly visible, along with internal modes of carbonate ions at 711 (ν_4), 1085 (ν_1), and 1434 (ν_3) cm⁻¹. In addition, a combination mode of carbonate ions at 1748 cm⁻¹ and the symmetric

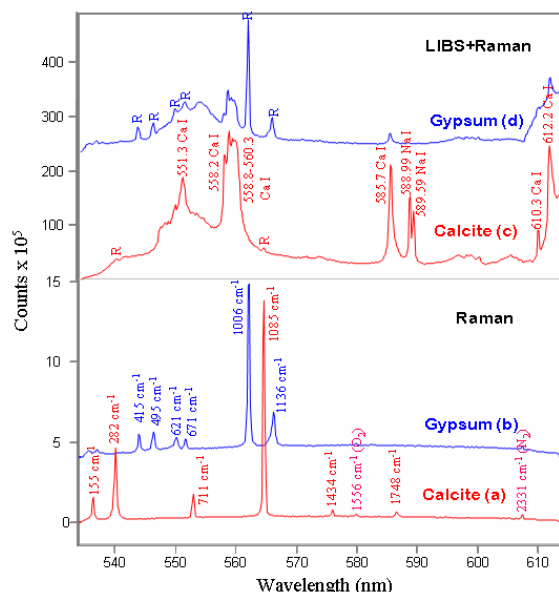


Fig. 2. Remote Raman spectra of calcite (curve a), and gypsum (curve b) at 9 m excited with 532 nm and 25 mJ/pulse, and combined LIBS and Raman spectra calcite (curve c), and gypsum (curve d) excited with 532 nm and 35 mJ/pulse.

stretching modes of atmospheric O_2 and N_2 , respectively at 1556 and 2331 cm^{-1} are also detected.

In the Raman spectrum of gypsum (Fig. 2, curve b), the strongest Raman peaks observed at 1006 cm^{-1} originate from the symmetric stretching vibrations of the SO_4^{2-} ion, $\nu_1(SO_4)$, and its position depends on degree of hydration. The other internal mode of vibration of sulfate ions appear at 1136 (ν_3), 415 and 495 (ν_2), and 621 and 671 (ν_4) are clearly visible [7].

In the combined LIBS and Raman spectra of calcite (Fig. 2, curve c) and of gypsum (Fig. 2, curve d) the Raman lines are marked with letter "R". In the spectrum of calcite, the 1085 cm^{-1} Raman line of carbonate appears only as a weak line. In the combined LIBS and Raman spectra of gypsum, most of the prominent Raman lines of sulfate are clearly visible indicating that the LIBS spectrum is produced only by a few hot spots in the focused laser beam. As both calcite and gypsum contain Ca cations, the LIBS lines in Fig. 2 (spectra (c) and (d)) originate from Ca I excited states. In the combined LIBS Raman spectrum of calcite the LIBS lines at 588.99 and 589.59 nm indicate presence of trace amount of Na ion in the calcite sample.

Figure 3 shows the remote LIBS spectra of minerals magnetite (Fe_3O_4), hematite (Fe_2O_3), α -quartz ($\alpha\text{-SiO}_2$, Qz) and forsterite (Mg_2SiO_4 , Fo) in the $540\text{--}690\text{ nm}$ spectral range at 9 m excited with 532 nm laser pulses of 35 mJ/pulse . The LIBS spectra of magnetite and hematite are dominated by the Fe I emission lines. Both of these iron oxides contain a few ppm of

Na as indicated by the presence of Na I emission lines at 589.0 and 589.6 nm (Fig. 3).

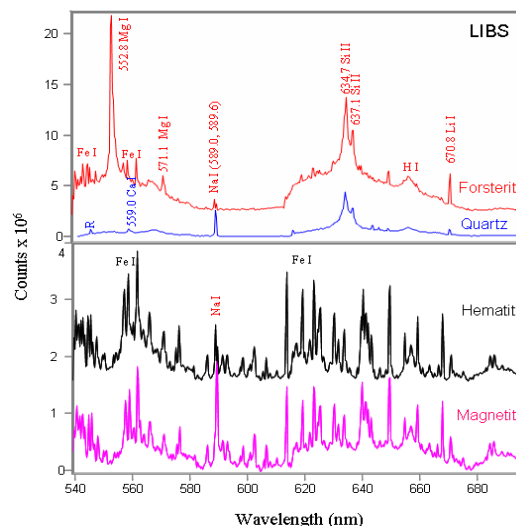


Fig. 3. Remote LIBS spectra of magnetite, hematite, α -quartz, and forsterite at 9 m excited with 532 nm laser pulses of 35 mJ/pulse .

The remote LIBS spectra of Fo and Qz show strong emission lines of Si at 634.7 and 637.1 nm (Fig. 3), and weak emission lines of Na and Li indicate the presence of these elements in trace amounts. The Fo LIBS spectrum contains strong emission lines of Mg at 552.8 nm and a weak line at 571.1 nm . A number of weak Fe emission lines are also observed in the LIBS spectrum of Fo indicating that this sample is indeed Mg-rich olivine (Fo 92) containing $\sim 8\%$ of iron [3].

Conclusion: We have developed an integrated instrument capable of performing simultaneous LIBS and Raman spectroscopy with a single pulsed laser source radiating 532 nm pulses from a remote distance. This instrument will be a powerful active remote sensing tool for characterizing planetary surface mineralogy on future rover missions.

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References: [1] Knight, A. K. *et al.* (2000) *Appl. Spectrosc.* 54, 331-340. [2] Sharma, S. K. *et al.* (2003) *Spectrochim. Acta A*, 59, 2391-2407. [3] Sharma, S. K. (1989) *Vib. Spectra Struc.*, 17 B, 513-568 [4] Wiens, R. C. *et al.* (2000) *LPSC XXXI*, #1468. [5] Wiens, R. C. *et al.* (2005) *Spectrochim. Acta A*, 61, 2324-2334. [6] Sharma, S. K. *et al.* (2007) *Spectrochim. Acta A*, 68, 1036-1045. [7] Chio, C. H. *et al.* (2007) *J. Raman Spectrosc.*, 38, 87-99.