

# Combined Remote LIBS and Raman System for Identifying the Composition of Minerals

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**Abstract**—The authors have developed an integrated remote laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy system for measuring both LIBS and Raman spectra. The system has been used for analyzing both Raman and LIBS spectra of minerals in air. These experiments demonstrate that by focusing a 532nm Nd:YAG pulsed laser beam with a 5× beam expander to a 1.5 mm diameter spot on a sample surface located at 15 meters away, it is possible to identify the compositions of the sample by using this remote LIBS and Raman spectrum detection system.

**Keywords**—stand-off detection; combined LIBS and Raman spectroscopy; minerals compositions analysis

## I. INTRODUCTION

Both laser induced breakdown spectroscopy (LIBS) and Raman spectroscopy are widely used analytical techniques for the determination of the elemental composition of materials<sup>[1,2]</sup>. The main features of LIBS and Raman are listed as follows: no sample preparation, remote sensing capability, fast detection and on line measurement. Both techniques have remarkably wide applications, such as planet surface detection, mineral prospection, steel furnace monitoring, automobile exhaust monitoring. In Raman spectroscopy, the rotational and vibrational transitions in molecules are recorded<sup>[3]</sup>. Raman spectrum could also show lattice vibrational modes. Therefore, Raman spectrum of allotrope such as rutile and anatase could be distinguished.<sup>[2]</sup> This is a shortcoming in elementary composition analysis. By combining LIBS and Raman spectroscopy, both molecular structural information and elemental compositions of the sample could be obtained simultaneously<sup>[2,4]</sup>.

## II. EXPERIMENTAL SETUP

The combined remote LIBS and Raman spectrometer system uses a high power Nd:YAG laser (Sol Instruments, @532 nm, 10 Hz, 120 mJ per pulse, 10 ns pulse width) as the excitation source. The laser beam is guided with four mirrors into a beam expander and focused onto the distant target. The focused laser spot size is 1.5 mm at a distance of 15 meters and the theoretical irradiance value is up to 0.53GW cm<sup>-2</sup>.

The produced plasma is collected by a Cassegrain telescope (Celestron, C6-A-XLT-CG-5) which is coaxial with the laser emission optical path, mounted on a equatorial instrument, thus enabling the inspection of a well-defined area. The plasma image is guided to a spectrometer (Sol Instruments, MS3504i) using a 2 m long optical fiber. The spectrometer is fitted with a 600/1800 grooves mm<sup>-1</sup>, 500 nm blazed grating, providing a spectral window that ranges from 360 nm to 800 nm. Dispersed light is recorded using an ICCD (Andor iStar DH320T-18U-03). The timing parameters used for Raman detection mode are: 0 μs as the delay time from the input of a 532 nm Rayleigh Scattering signal (considered as zero time) and 30 ns as the integration time. The timing parameters used for LIBS detection mode are: 1.5 μs as the delay time from the input of a 532 nm Rayleigh Scattering signal (considered as zero time) and 1.5 μs as the integration time.

To switch from LIBS detection mode to Raman detection mode, the beam expander is adjusted by changing the distance between two optical lenses and defocusing the beam in order to produce a larger spot size on the target. In this study, the laser spot size is defocused to 10 mm in diameter at a distance of 15 meters<sup>[5]</sup>. The whole switching process is completed within 1 minute.

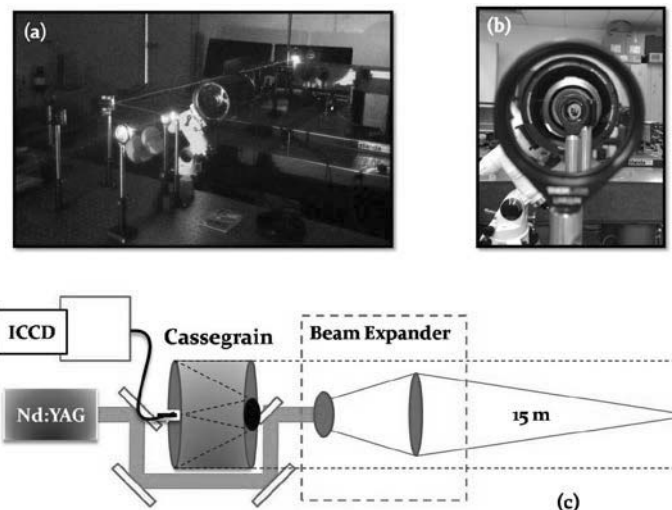


Fig.1 Coaxial Remote Detection System: (a) The coaxial remote detection system is operated in a laboratory environment. (b) The front view of the

coaxial remote detection system. (c) The schematic diagram of the coaxial remote detection system.

### III. RESULTS AND DISCUSSION

With the purpose of identifying the chemical composition of the materials, an integrated Raman spectroscopy and LIBS detection was carried out using the above combined remote LIBS and Raman system. The following results have shown both the Raman spectral data and the LIBS data.

Firstly, it is essential to identify the kinetic difference between Raman process and LIBS. After the laser induction, three processes happen at the same time, including Raman emission, continuum emission, and atomic emission. They all have different lifetime (shown in Fig. 2(a)). As the experimental section described, the time window for Raman spectral signal is 0-10 ns and for LIBS signal is 1.5-3  $\mu$ s.

Dolomite is used as an example to illustrate the detection process. Raman spectral presents the molecular stretching signal, which includes Mg-O symmetric stretching and CO<sub>3</sub><sup>2-</sup> symmetric stretching (shown in Fig.2(c)). LIBS presents the atomic emission spectral, which includes Ca, Mg, Na. Combining Raman and LIBS spectra, all compositions of dolomite are successfully identified.

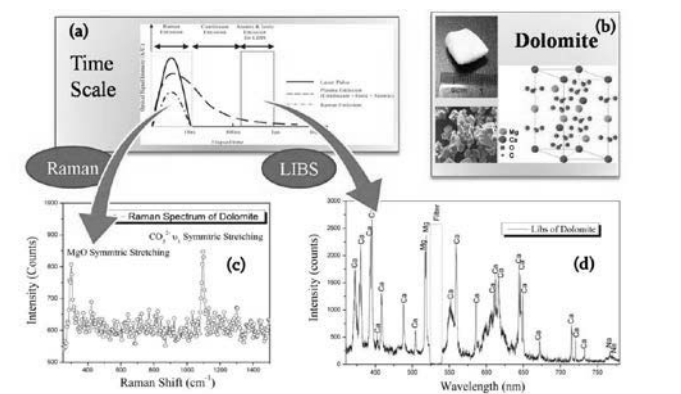


Fig.2 (a) Time scale of the kinetic process after the 532 nm laser beam is irradiated on sample. (b) Molecular model of dolomite and the photo of the dolomite used in the experiment. (c) Raman spectrum of dolomite, timing parameters are 0 ns as the delay time from the input of a 532 nm Rayleigh Scattering signal and 30 ns as the integration time. (d) LIBS of dolomite, timing parameters are 1.5  $\mu$ s as the delay time from the input of a 532 nm Rayleigh Scattering signal and 2  $\mu$ s as the integration time.

In the following experiments, a series of minerals are measured by the remote detection system. Raman shift peaks shown in Fig.3 reveal the molecular stretching of the minerals, including C-O, S-O, and Si-O symmetric stretching. Raman peaks of calcite and dolomite are located at 1073.4 and 1081.3  $\text{cm}^{-1}$  which belongs to symmetric stretching of CO<sub>3</sub> group<sup>[4]</sup>. Raman peaks of gypsum and barite are located at 1002.3 and 970.6  $\text{cm}^{-1}$ , respectively, corresponding to symmetric stretching of SO<sub>4</sub> tetrahedral<sup>[4]</sup>. Therefore, calcite and dolomite are classified as carbonate, gypsum and barite is classified as sulphate. Moreover, quartz and plagioclase are classified as silicate (shown as in Table 1).

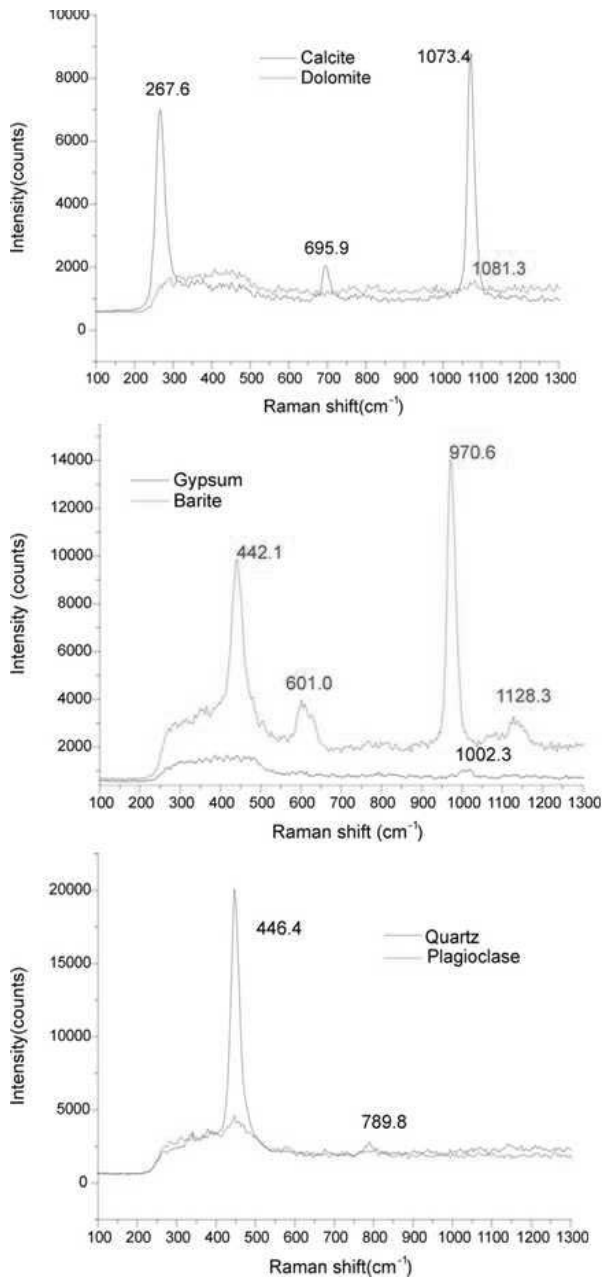


Fig. 3 Raman spectra of calcite, dolomite, gypsum, barite, quartz, and plagioclase.

Table 1 Raman shifts of minerals and their molecular stretching classification.

	C-O symmetric stretching	S-O symmetric stretching	Si-O symmetric stretching	
Calcite	1073.4			Carbonate
Dolomite	1081.3			
Gypsum		1002.3		Sulphate
Barite		970.6		
Quartz			446.4	Silicate
Plagioclase			445	

LIBS data of the above minerals are shown in Fig.4. All the identified atomic spectral are listed in Table 2. Combined

Raman spectral and LIBS provides more comprehensive information (shown as in Table 2).

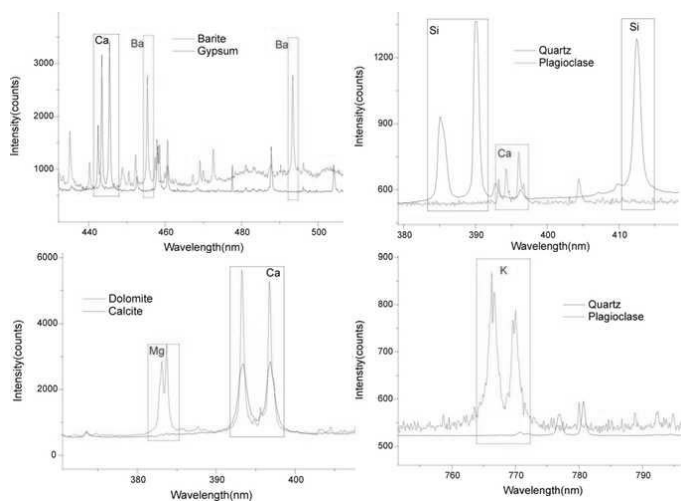


Fig. 4 LIBS of minerals, including calcite, dolomite, gypsum, barite, quartz, and plagioclase.

Table 2 Compositions of minerals identified by LIBS and Raman

Minerals	LIBS	Raman
Calcite	Ca	C, O
Dolomite	Ca, Mg	Mg, C, O
Gypsum	Ca	S, O
Barite	Ba	S, O
Quartz	Si	Si, O
Plagioclase	Si, Ca, K	Si, O

#### IV. CONCLUSIONS

A combined remote LIBS and Raman spectroscopy

detection system is built up, which has been used to examine a series of minerals. According to Raman spectrum data, calcite and dolomite are classified as carbonate, gypsum, barite and plagioclase is classified as silicate. Moreover, LIBS has been used to identify the information of element composition of the minerals. To achieve this, two steps are applied into the stand-off detection system. Firstly, Raman spectrum measure reveals the molecular bond of minerals and then LIBS is used to obtain the atomic emission spectrum. In general, it has been approved to identify the composition of the minerals by using the remote LIBS and Raman system simultaneously, at a stand-off distance of 15 meters.

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