

**LIBS, RAMAN AND VNIR SPECTROSCOPIC STUDIES OF HYDRATED MG-SULFATES RELEVANT TO MARS.** Ping Liu<sup>1</sup>, Changqing Liu<sup>1</sup>, Yanqing Xin<sup>1</sup>, Zongcheng Ling<sup>1\*</sup> <sup>1</sup>Shandong Provincial Key Laboratory of Optical Astronomy and Solar-Terrestrial Environment, School of Space Science and Physics, Institute of Space Sciences, Shandong University, Weihai, Shandong, 264209, China. (zcling@sdu.edu.cn).

**Introduction:** Hydrated sulfate minerals (e.g. Mg-sulfates, Ca-sulfates), products of the water-rock interactions, have been extensively found on Mars by various orbital and roving missions through visible and near infrared reflectance (VNIR) spectroscopy [1, 2]. Those hydrated mineral phases may provide clues of potentially habitable environments due to their association with ancient aqueous environments in which life might have thrived. Therefore, the identification of mineral types and their hydration states are keys to uncover the mysteries of Martian environment that will help to constrain current and past geologic processes that they experienced.

There are several methodologies to capture the information of mineralogy on Mars, e.g., VNIR is the traditional remote sensing methods that have been widely used for mineral identification on Mars (CRISM on MRO and OMEGA on Mars Express). Besides, laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy are two other complementary techniques that have been regarded as future superstars for chemical and mineralogical analysis for years. They show unique advantages such as little or no sample preparation, remote sensing and fast and in-suit analysis [3]. In recent years, the potentialities of LIBS and Raman have been demonstrated again in planetary exploration. For example, three LIBS instruments (ChemCam LIBS onboard Curiosity, SuperCam on Perseverance and Mars Surface Composition Detector (MarsCoDe) payload on Tianwen-1) and three Raman payloads (SuperCam, SHERLOC on Perseverance rover and RLS on ExoMars) are being or to be employed for Mars explorations.

In order to assess the potentials of using LIBS, Raman and VNIR to determine the chemistry, mineralogy and hydration states for Mars related salts, in this work, we choose Mg-sulfates with different hydration degrees as the targets and conduct a comprehensive spectroscopic study on them.

**Sample synthesis:** We firstly synthesized three hydration states of magnesium sulfate,  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$  ( $n=1, 4, 6$ ), from the starting phase of anhydrous Mg-sulfate and epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), which was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai).  $\text{MgSO}_4 \cdot 1\text{H}_2\text{O}$  was obtained by directing crystallization from anhydrous Mg-sulfate saturated solutions.  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  were synthesized by using the humidity-buffer technique at

fixed temperature and relative humidity, which was described in detail by Wang et al. [4].

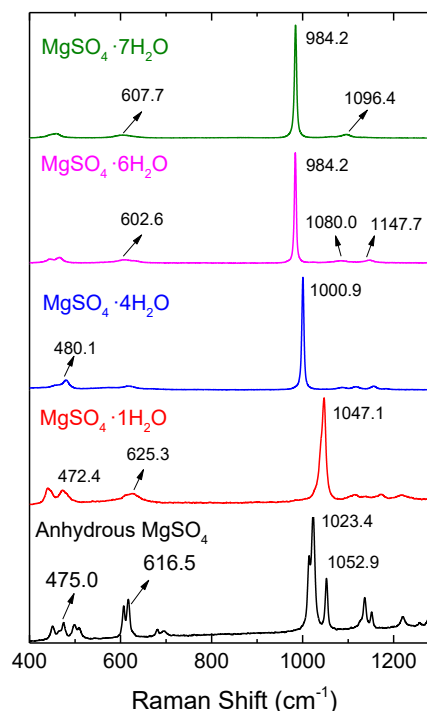


Fig. 1 Raman spectra of hydrated and anhydrous Mg-sulfate in the spectral region of  $\text{SO}_4$  fundamental vibrational modes.

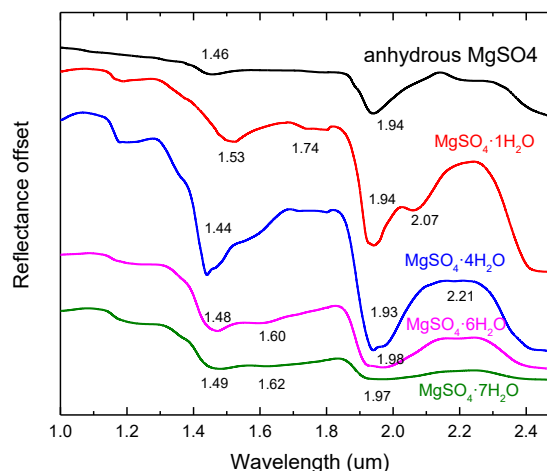


Fig. 2 VNIR spectra of anhydrous and various hydrated of Mg-sulfate.

**Raman and VNIR spectroscopic studies:** The Raman and VNIR spectroscopies of the synthesized

Mg-sulfate hydrates were recorded for characterizing the starting materials and synthetic products. The Raman and NIR spectra of these  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$  ( $n=0, 1, 4, 6, 7$ ) are shown in Fig. 1 and Fig. 2, which are good spectral references for their identification on Mars. The spectral characteristics are similar to the work of Wang et al. and Altheide et al. [4, 5], and the results indicate that each synthetic product is a single structure mineral. In addition, X-ray diffraction (XRD) measurements has also been used to further confirmed the crystalline structure of synthesized Mg-sulfate.

**LIBS measurements and data processing:** These pure Mg-sulfates are used as standard samples to obtained LIBS spectra under Mars atmospheric conditions. The laser source was a Q-switched Nd:YAG laser with wavelength of 1064 nm, which was operated at 1 Hz repetition with the laser output energy of 90 mJ. Samples were placed in a vacuum chamber with simulated Martian conditions ( $\text{CO}_2$ , 7 mbar). LIBS emission from laser ablation plasma was collected along the laser axis from 5 different points and 30 shots for each point.

After obtaining the LIBS signal, an automated routine was used to pre-process the LIBS series spectral data, which contains baseline removal, normalization, outlier discarding and averaging. Considering the spectral properties and sample characteristic, normalization each spectrum to the total emission intensity is a preferred approach

**Development of the calibration curves:** Figure 3 shows a pre-processing spectra of different hydrated Mg-sulfate. The peaks are identified by comparing to the NIST database. It is found that all the detected spectral lines are Mg I and Mg II lines expect H I (656.7 nm) and O I (777.9 nm). The signal of H I and O I increase as the rise of the number of  $\text{H}_2\text{O}$  in test targets. While, the Mg I and Mg II spectral intensities depict almost opposite trend, except the line of Mg II 448.2 nm.

Considering the different change trend between Mg I and Mg II spectral intensities, the sum of all peak area of Mg spectral lines are used to construct the calibration curve for Mg element. The calibration curve for Mg developed using five Mg-sulfate with different hydration states is depicted in Fig. 4(a). The nonlinear relation between element spectral intensity and element abundance in the various hydrated Mg-sulfate can be applied to build a LIBS quantitative database to detect hydration state of Mg-sulfate. In addition, the nice linear correlation between Mg element and H elements (Fig. 4(b)) in different hydrated Mg-sulfates presents that the ratio of detected Mg spectral intensity to H line can be used to identify the number of  $\text{H}_2\text{O}$  construct in Mg-sulfates. It also can detect the instability and phase

transitions of hydrated Mg-sulfates. In the next step, we will try to combine different spectroscopic dataset to fully evaluate the mineral information. Moreover, we will also use other hydrated states Mg-sulfates and different hydrated states Mg-chlorate to validate the quantitative method.

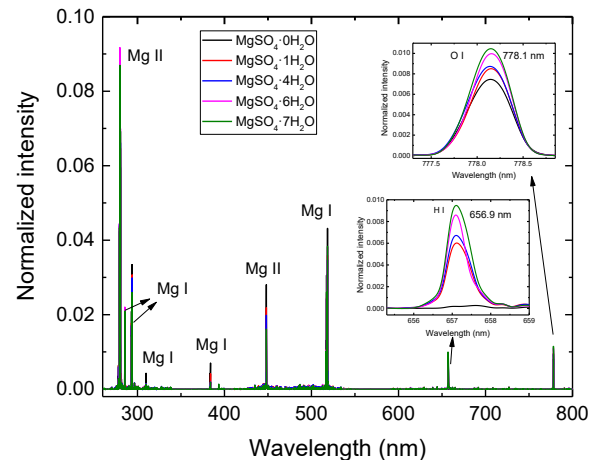


Fig. 3 Pre-processing spectra of various hydration states of Mg-sulfate.

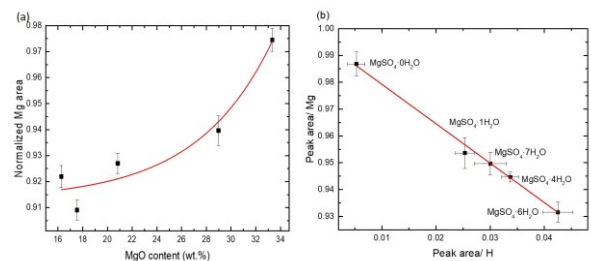


Fig. 4 (a) Calibration curve for Mg developed using five Mg-sulfate with different hydration states. (b) Correlation between Mg element and H elements in different hydrated Mg-sulfates.

**Acknowledgments:** We thank the fundings from the National Natural Science Foundation (U1931211, 11941001, 41972322), the Natural Science Foundation of Shandong Province (ZR2019MD008). This work is supported by the Pre-research project on Civil Aerospace Technologies No. D020102 funded by China National Space Administration (CNSA). This work is also supported by Physical-Chemical Materials Analytical & Testing Center of Shandong University at Weihai.

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