

HYDRATION STATES OF FERRIC SULFATES IDENTIFIED BY LASER INDUCED BREAKDOWN SPECTROSCOPY. Erbin Shi¹, Changqing Liu¹, Zongcheng Ling^{*1}, ¹Shandong 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; erbinshi@sdu.edu.cn).

Introduction: Several ferric sulfates have been identified or suggested to exist on Mars by remote sensing and in situ detections, such as ferricopiapite, paracoquimbite, $\text{Fe}(\text{OH})\text{SO}_4$, etc.^[1-4] These phases/minerals are products of evaporation and diagenetic process^[1-3]. Thus, the ferric sulfates provide mineralogical evidence clues for past water activity on Mars and have attracted the attention of planetary geochemists. The hydration status of the ferric sulfates is very easily changed due to minor variations in climate parameters, such as air, humidity, temperature, and pH.^[3] A typical example on Mars is the phase transformation of subsurface ferric sulfates that occurred after they were excavated by the Spirit rover wheel from the subsurface and then being exposed to present-day atmospheric conditions at the Martian surface.^[4] Therefore, ferric sulfates maybe can be used to trace paleoclimate on Mars. However, it is because of the very sensitivity to environmental conditions, the detection of hydration status or clear phases of the ferric sulfates on Mars still has enormous challenges.

As a powerful spectroscopic technology for chemical composition analysis, laser induced breakdown spectroscopy (LIBS) has been applied on Mars detections and helped to understand the chemical compositions of the rocks, minerals, and soils on Mars. Especially, the LIBS payload named ChemCam onboard the Curiosity rover has quantified the hydrogen content in veins and fractures at Gale Crater and helped to identify the undefined calcium sulfates as bassanite.^[5]

The goal of this study is to use the advantage of LIBS to fulfill the hydration states determination of ferric sulfates in the laboratory and then provide a good reference for ferric sulfates detection on Mars.

Experiment setup and Instruments: Five ferric sulfates were synthesized in this work. The rhomboclase

was synthesized by the 10 mL saturated ferric sulfates solution added 0.6 g concentrated sulfuric acid at 50 °C for 1 day. The pentahydrate ferric sulfate was prepared using the hydrothermal method.^[6] The 1.52 mL deionized water and 0.48 mL concentrated sulfuric acid was used to solve the 1.98 g ferric sulfate powder. Then the solution was transferred to an autoclave at 90 °C for one week. The kornelite was synthesized using $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ powder under 95°C in KI- H_2O saturated solutions (RH% = 59.92%) for 24 h in an oven^[6]. The paracoquimbite was synthesized at

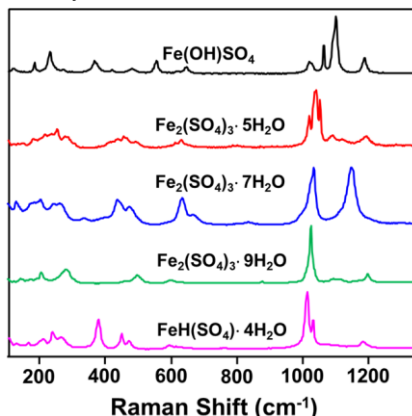


Figure 1. The Raman spectra of synthetic five ferric sulfates.

25°C in NaBr- H_2O saturated solutions (RH%=57.58%) using the synthesized ferricopiapite as the starting material for three weeks. The ferricopiapite was synthesized using the ferric iron sulfate saturated solution at 25°C and the RH% range from 20% to 60% in the atmosphere for one week until the liquid solutions were all converted to solid entirely. The $\text{Fe}(\text{OH})\text{SO}_4$ was synthesized by heating the melanterite for three days at 180°C.^[1]

An inVia Raman imaging system (Renishaw Company) was used, which uses a 532-nm line of a DPSS laser for excitation, a long working distance 50 × objectives (NA = 0.75) for signal collection. The Raman spectra from 100 to 1400 cm^{-1} were collected (Figure

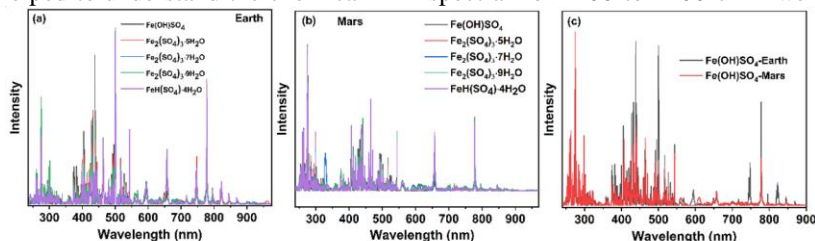


Figure 2. The LIBS spectra of five ferric sulfates were obtained from (a) the Earth environment and (b) Mars-like conditions. (c) The LIBS spectra of $\text{Fe}(\text{OH})\text{SO}_4$ were acquired from Earth and Mars conditions, respectively, to evaluate the effects of the environment.

1). LIBS measurements were performed in a vacuum chamber with the simulated atmospheric environment of Mars (700 Pa CO_2) and Earth environment, respectively. The system has been equipped with a Q-switched pulsed Nd: YAG laser with a power of 200 mJ and a wavelength of 1064 nm. Six spectra were collected at different locations for each sample and every spectrum of them is acquired by an accumulation of ten shots. All instruments and measurements were employed at Shandong University, Weihai.

Results and discussion: The phase identification of five synthesized samples was made by laser Raman spectroscopy (Figure 1). For each sample, Raman data of more than 100 points were collected from a flattened powder sample. All measured Raman spectra of five ferric sulfates are identical to the standard Raman spectra and no other phases were detected, indicating that these samples are homogeneous (detailed description and Raman peak assignments of these ferric sulfates are in Ling and Wang (2010)).^[6] Therefore, the synthesized five ferric sulfates can be used to quantify the hydrogen content by LIBS technology in the next step.

The LIBS spectra of five ferric sulfates in the three spectral regions under the earth and simulated Mars environment are shown in figures 2 a and b, respectively. The Fe emission lines dominate in the UV and VIS-NIR spectral regions. The hydrogen emission line is produced from the dissociation of the water molecules and hydroxyl appears at 656.7 nm. The oxygen lines around 778 nm can be attributed to oxygen in sulphate ions (SO_4^{2-}), water molecules, and hydroxyl (OH^-) in crystallized ferric sulfates. However, no matter what is measured under the Earth's environment and Martian conditions, all ferric sulfates LIBS spectra are not produced S lines. This is because the detection limit of the sulfur element is higher than other elements and the LIBS system's performance is not well. The LIBS spectra of the same samples under Earth and Mars-like environments are different. In the UV region (238-400 nm), the intensity of LIBS signal under the earth environment is weaker than in Mars-like environments. Oppositely, in the VIS-NIR region, the peak intensity of LIBS under the earth environment is higher under simulated Mars conditions (Figure 2c). Moreover, the ratio of signal to noise is higher and the peaks width of iron, hydrogen, and oxygen emission lines are narrow under the Mars-like environment (Figures 3a and b). These results may be caused by the interaction between plasma and surrounding atmosphere.

A number of experimental parameters affect the standoff LIBS signal. They are related to laser irradiance (laser energy, focus, and distance to target), atmosphere (total pressure/density and composition), and target properties (different chemical/physical

matrices and mixtures).^[7] However, those results do not affect quantifying the hydrogen content using the LIBS outputs in this study. Consequently, we normalize the signals to compensate as much as possible for the undesired effects of these parameters. All LIBS spectra used to quantify the hydrogen content were carried out through total spectrum intensity normalization. The peak intensity of the analyzed H emission lines ($\text{H}\alpha$ at 657.0 nm) increases monotonously with the increasing number of water molecules over iron atoms in the ferric sulfate samples (Figures 3c and d). In Mars

conditions, the linear regression equation is $y = 0.0681x + 0.0293$ with $R^2 = 0.98$. In Earth's environment, the linear regression equation is $y = 0.0575x + 0.0462$ with $R^2 = 0.997$. These results demonstrated that the hydration state of the ferric sulfates can be extracted from their LIBS spectra. This capability will be significant when encountering ferric sulfates in a sampling spot on Mars and Earth.

Conclusion: In this study, a new method was used to identify the hydration states of ferric sulfates under Mars-like environment and Earth environment. The results should help identify the ferric sulfates on Mars surface using the LIBS hydrogen emission lines, and explore the corresponding geological implications. In the future, more technologies or spectroscopies will be developed to help to determine the hydration states of ferric sulfates and other hydrated minerals, such as the MIR and VNIR, etc.

Acknowledgments: This study was supported by the National Natural Science Foundation of China (U1931211, 41972322, 11941001), the Pre-research project on Civil Aerospace Technologies No. D020102 funded by China National Space Administration (CNSA), the China Postdoctoral Science Foundation (2022M721916).

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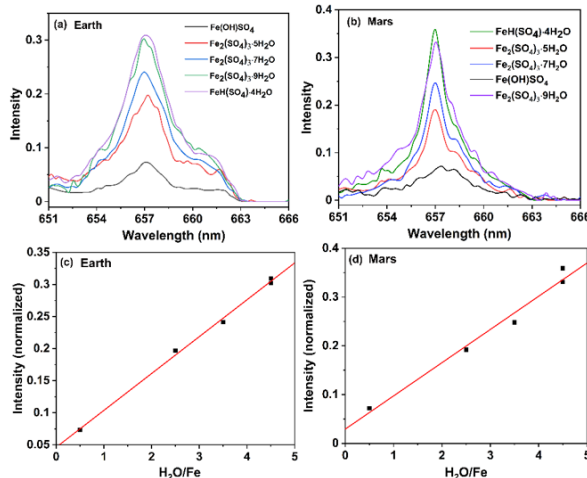


Figure 3. The $\text{H}\alpha$ emission lines in five ferric sulfates LIBS spectra were measured under (a) Earth and (b) Mars conditions, respectively. From the (a) and (b) can be concluded that the H peak intensity increased with the ratio of water molecules over iron atoms. Moreover, the $\text{H}\alpha$ peak width under Mars conditions is narrower than Earth environment. (c) and (d) is the dependency of $\text{H}\alpha$ emission lines intensity on water molecules over iron atoms in Earth and Mars-like environments, respectively. All of them showed a good linear relationship.