SYNTHESIS AND SPECTRAL STUDIES OF TWO CALCIUM SULFATE SOLID SOLUTIONS RELATED TO MARS. Enming Ju[1], Zongcheng Ling[1*], Yanqing Xin[1,2], Changqing Liu[1], and Erbin Shi[1] [1]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. [2]Key Laboratory of Lunar and Deep Space Exploration, CAS. (zcling@sdu.edu.cn).

Introduction: Ca-sulfate is an important salt on Mars, whose hydration states are important indicators for Mars environment and climate changes [1-2]. The Curiosity rover has analyzed abundant calcium sulfate veins occurring as fillings in the rock, which consists of gypsum and basanite in Yellowknife Bay, Gale crater [3]. Millimeter to centimeter-scale Ca-sulfates veins sometimes surround alteration halos, and Ca and mixed-cation sulfates may be introduced during aqueous fluids leaching parent materials [4]. Recognition of the sulfates is important for figuring out the water-rock interactions of the target, thus better understanding of the local environment evolution.

However, the discovery of Ca-sulfates is related to the occurrence, mineral species, spectroscopic datasets. Specifically, when Ca-sulfates were mixed with other sulfates, e.g. Mg-sulfates, which can affect their hydration and dehydration pathways. Furthermore, the calcium sulfates can form (Ca, Na)- or (Ca, K)-sulfates solid solutions and the natural occurrence of Ca-sulfates does not always follow the predictions of thermodynamics or phase boundaries. Calcium sulfate can form solid solutions with potassium and sodium on Earth [5]. Thus, it is very important to establish a solid understanding of the spectroscopic characterization of Ca-sulfate solid solutions, to make a definitive identification of different solid solutions of calcium sulfates, as well as other sulfates on Mars and Earth.

In this study, two solid solutions of Ca-sulfate were synthesized in the laboratory and reported their Raman spectroscopic properties. Calciolangbeinite ($K_2Ca_2(SO_4)_3$) and sodium calcium sulfate ($Na_4Ca(SO_4)_3$) were both synthesized by high temperature sintering, and their spectral data would support future in-situ detections of calcium sulfates on Mars by Raman payloads (e.g., SuperCam and SHERLOC aboard Perseverance rover).

Synthesis of $K_2Ca_2(SO_4)_3$ and $Na_4Ca(SO_4)_3$: Potassium sulfate and calcium sulfate powder were ground in a mortar, and then mixed according to the stoichiometric ratios of $K_2Ca_2(SO_4)_3$ (mol:mol = 1:2) and put into the crucible. The mixed powder was heated to 840℃ for 16 hours, and cooled slowly to room temperature. The synthesis method of $Na_4Ca(SO_4)_3$ is similar to $K_2Ca_2(SO_4)_3$. The mixed powder of sodium sulfate and calcium sulfate was heated to about 900℃ for 12 hours, and rapidly cooled to room temperature. Different from $K_2Ca_2(SO_4)_3$, the $Na_4Ca(SO_4)_3$ would not be synthesized when the crucible cooled slowly to room temperature.

XRD characterization: The phase identification of $K_2Ca_2(SO_4)_3$ and $Na_4Ca(SO_4)_3$ was conducted by X-ray powder diffraction (Rigaku UltimaIV, Japan) in Shandong University at Weihai. The samples were scanned at 0.02° step from 10° to 70° with a CuKα radiation (λ = 1.54052 Å) at 40 kV and 40 mA. As shown in figure 1, the XRD pattern of $K_2Ca_2(SO_4)_3$ is consistent with its PDF-2004 database (PDF#20-0867). The XRD pattern of $Na_4Ca(SO_4)_3$ shows a similar result as $K_2Ca_2(SO_4)_3$ which matched well with PDF#34-1238. These results indicated that the two samples were successfully synthesized.

Besides, the $K_2Ca_2(SO_4)_3$ and $Na_4Ca(SO_4)_3$ were stable at room temperature without hydration by repeated XRD measurements.

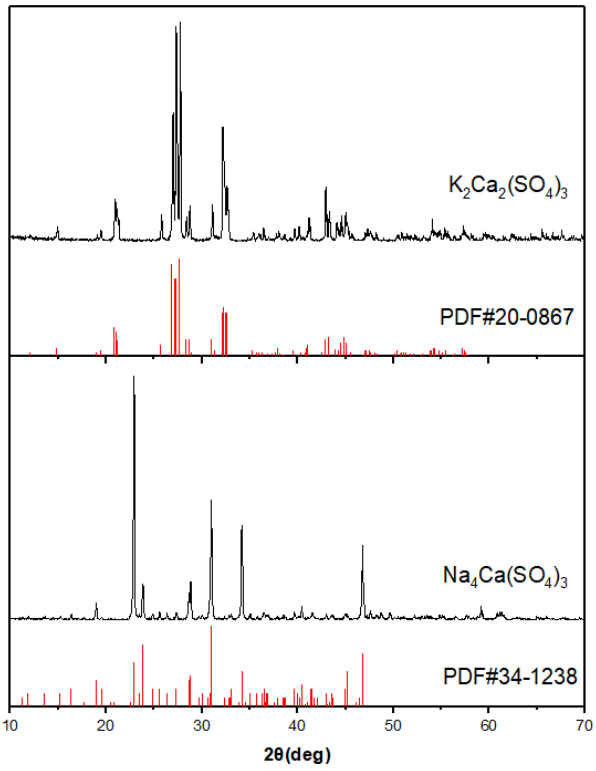

Figure 1. XRD pattern of the synthetic $K_2Ca_2(SO_4)_3$, the PDF#20-0867, the synthetic sodium calcium sulfate, the PDF#34-1238.

Raman spectral features of two solid solutions: Raman spectroscopy can reveal the fundamental vibra-

tional modes of $K_2Ca_2(SO_4)_3$ and $Na_4Ca(SO_4)_3$. Two samples of Raman spectral were acquired using the inVia® Raman System (Renishaw, UK) in Shandong University at Weihai. The fundamental vibrational modes from the SO_4 tetrahedra contribute Raman spectral features in region 150-1500cm^{-1}, including symmetric stretching modes (ν_1) located at 983 cm^{-1}, symmetric bending modes (ν_2) located at 450 cm^{-1}, asymmetric stretching modes (ν_3) located at 1105 cm^{-1}, asymmetric bending modes (ν_4) located at 611 cm^{-1} [6-7]. For $K_2Ca_2(SO_4)_3$, the symmetric stretching modes (ν_1) are the strongest diagnostic peaks, which split into three peaks located at 1004.5, 1018.7, and 1024.6 cm^{-1}, indicating a big distortion of the SO_4 tetrahedra in $K_2Ca_2(SO_4)_3$. The Raman spectra of $Na_4Ca(SO_4)_3$ (Figure 2) showed that the symmetric stretching modes (ν_1) split into 993.8 and 1011.6 cm^{-1}, indicated that $Na_4Ca(SO_4)_3$ may have smaller distortion of the SO_4 tetrahedra than that of $K_2Ca_2(SO_4)_3$.

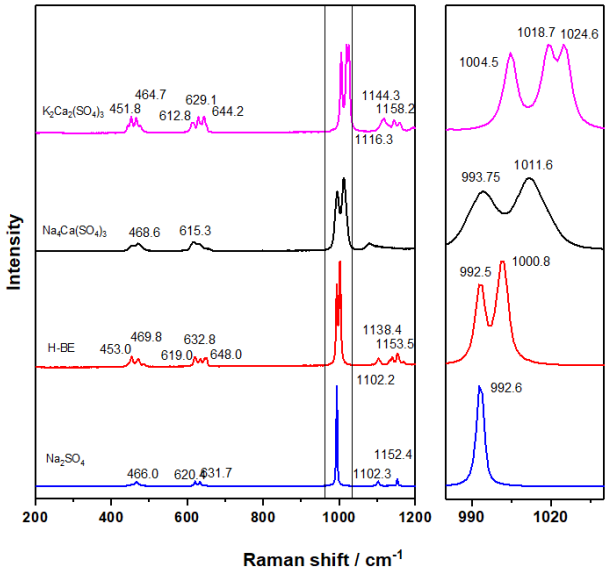

Figure 2. Raman spectra of $K_2Ca_2(SO_4)_3$, $Na_4Ca(SO_4)_3$, H-BE(humidity-buffer experiment) of $Na_4Ca(SO_4)_3$, and Na_2SO_4.

After that, a new experiment was set to study the $Na_4Ca(SO_4)_3$ stability and monitor whether a new phase appeared due to the H_2O into the structure using the humidity-buffer technique. Firstly, the sample was put into KCl saturated solution at 80℃ (~80% RH%). After 10 days, the Raman spectra and XRD patterns showed that $Na_4Ca(SO_4)_3$ gained structural water and decomposed. The Raman spectra of $Na_4Ca(SO_4)_3$ and reaction products from humidity-buffer experiment are shown in Figure 2, and 1000.8cm^{-1} contributes from $Na_2Ca(SO_4)_3$. Based on the previous report, our results reveal that the $Na_4Ca(SO_4)_3$ become $Na_4Ca(SO_4)_3{\cdot}2H_2O$ by getting structural water A 'labile salt' and the phase transition reactions can be divided into two steps [8]:

$$Na_4Ca(SO_4)_3 + 2H_2O(g) \rightarrow Na_4Ca(SO_4)_3{\cdot}2H_2O \quad (1)$$

$$Na_4Ca(SO_4)_3{\cdot}2H_2O \rightarrow Na_2Ca(SO_4)_3 + Na_2SO_4 + 2H_2O \quad (2)$$

Conclusion and future work: We have synthesized two solid solutions ($K_2Ca_2(SO_4)_3$, $Na_4Ca(SO_4)_3$), and obtained their XRD patterns and Raman spectra. These two solid solutions are stable in ambient conditions for a long time, which is different from the products synthesized using humidity-buffer technique that contains two H_2O molecules in the structure. In the future, more calcium sulfate solid solutions will be synthesized using multiple methods, and conduct a set of experiments to study the stability and spectra properties, such as the mid-IR and Vis-NIR spectra, which will be collected and used to help us to better interpret the orbital and in situ detection data.

Acknowledgments:

We thank the fundings from the National Natural Science Foundation (U1931211, 11941001, 41972322), and the Natural Science Foundation of Shandong Province (ZR2019MD008). This work is also supported by the Pre-research project on Civil Aerospace Technologies No. D020102 funded by China National Space Administration (CNSA) and Key Laboratory of Lunar and Deep Space Exploration (LDSE202002), CAS. This work is also supported by the Physical-Chemical Materials Analytical & Testing Center of Shandong University at Weihai.

References: [1] D. T. Vaniman. et al., (2018) *American Mineralogist, 103,* 1011-1020. [2] K. Robertson et al., (2013) *Icarus 223,* 407-417. [3] Nachon M. et al., (2014) *JGR, 119,* 1991-2016. [4] A.S. Yen et al., (2017) *Earth and Planetary Science Letters 471,* 186-198. [5] James K. et al., (1991) *JGR, 16,* 231-240. [6] Z.C. Ling. and A. Wang., (2010) *Icarus, 209,* 422-433. [7] K. Nakamoto, (1986), *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. Wiley, New York. [8] D. Freyer. et al., (1997) *Solid State Ionics, 96,* 29-33.