SPECTROSCOPIC ANALYSIS OF CA-SR SULFATE SOLID SOLUTIONS FOR IN-SITU OBSERVATIONS ON MARS. Erbin Shi, Xiaojia Zeng, Jian Chen, Enming Ju, Zongcheng Ling* (Shandong 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: For the in situ APXS and ChemCam detections of calcium sulfate veins by Curiosity rover, the calculated mole ratio of Ca$^{2+}$ and SO$_4^{2-}$ is not equal to $^1$. This strongly indicates that other metal sulfates or solid solutions of calcium sulfates may exist$^3$. For example, the high Sr abundance (~320-360 ppm) has been detected for the Selwyn outcrop located between the Sheepbed member and Gillespie member in Gale crater$^1$. Such mobilized Sr$^{2+}$ can replace Ca$^{2+}$ in the sulfate mineral$^{1,2}$. For the Perseverance rover in Jezero crater, the recently discovered light-toned veins are also interpreted as cations-mixed calcium sulfate$^5$. Based on these in situ observations, it is reasonable to suggest that Sr is expected within calcium sulfate to form new solid solutions on Mars$^3$.

To reveal the composition of sulfate solid solutions and their geological implications on Mars, this work performs the spectroscopic analysis of Ca-Sr sulfate solid solutions in the laboratory. The relationship between spectral features (XRD, Raman, MIR, and VNIR) and chemical components in synthesized solid solutions has been analyzed. Moreover, the quantitative method of cations in solid solutions was developed to quantify the Ca$^{2+}$ and Sr$^{2+}$ contents in solid solutions to help reveal the behavior of Ca$^{2+}$ and Sr$^{2+}$ in sulfate solid solutions on Mars.

Synthesis of Ca-Sr sulfate solid solutions: The Ca$_{3-x}$Sr$_x$SO$_4$:0.5H$_2$O was synthesized by adding 40 mL of Na$_2$SO$_4$ solution to 60 mL of mixed-solution of CaCl$_2$ and SrCl$_2$ with stirring at ambient temperature. The cation and anion concentrations in the reaction solution are both 0.1 mol/L, with the mole ratio of Ca$^{2+}$/(Ca$^{2+}$+Sr$^{2+}$) in the mixed solution varying from 0% to 100%. The previous and present studies have shown that the products will be converted to SrSO$_4$ and CaSO$_4$:2H$_2$O, respectively, when the reaction time is more than 10 minutes. Therefore, the whole synthesis process of Ca$_{3-x}$Sr$_x$SO$_4$:0.5H$_2$O was precisely controlled within 10 minutes$^7$. The products were centrifuged and cleaned at least three times with anhydrous ethanol to fix them. Lastly, the synthesized samples were dried at 50°C for 24 hours. In addition, as the mole ratio of Ca$^{2+}$ in the mix-solution increased, a new phase appeared in products. Therefore, the reaction was employed under a boiling solution in the case of a mix-solution with Ca$^{2+}$/(Ca$^{2+}$+Sr$^{2+}$) from 60 to 100%. The chemical formula of synthesized samples was calculated by the mole contents of cations (Ca$^{2+}$ and Sr$^{2+}$) and SO$_4^{2-}$-added in the reaction solution. The Ca$_{3-x}$Sr$_x$SO$_4$:0.5H$_2$O (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) solid solutions were synthesized in this study.

Results: XRD pattern of synthesized SrSO$_4$:0.5H$_2$O was well matched with bassanite and the results reported in Takahashi et al. (1993), indicating that SrSO$_4$:0.5H$_2$O is successfully synthesized in this study (Figure 1). However, there are minor differences in the XRD pattern between the synthesized SrSO$_4$:0.5H$_2$O and Takahashi’s sample. Compared with Takahashi’s result, the XRD pattern of SrSO$_4$:0.5H$_2$O in this study exhibits few extra peaks and lower intensity. This may be due to the SrSO$_4$:0.5H$_2$O being a metastable phase and very sen-

![Figure 1](image1.png)

**Figure 1.** XRD patterns of Ca$_{3-x}$Sr$_x$SO$_4$:0.5H$_2$O (x = 0, 0.2, 0.4, 0.6, 0.8, and 1). 2

![Figure 2](image2.png)

**Figure 2.** Raman spectra of Ca$_{3-x}$Sr$_x$SO$_4$:0.5H$_2$O (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) and SrSO$_4$. 2

![Figure 3](image3.png)

**Figure 3.** MIR spectra of Ca$_{3-x}$Sr$_x$SO$_4$:0.5H$_2$O (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) and SrSO$_4$. 2

![Figure 4](image4.png)

**Figure 4.** MIR spectra of Ca$_{3-x}$Sr$_x$SO$_4$:0.5H$_2$O (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) and SrSO$_4$. 2
sitive to environmental conditions. The XRD measurement conditions and instrument resolution may also affect the results. For the XRD patterns of Ca, Sr, SO₄·0.5H₂O series (x = 0, 0.2, 0.4, 0.6, 0.8, and 1), with the increase of Ca²⁺ mole ratio, the 2 theta peaks at 14.5° and 2θ shift towards the larger angles. Based on the results of XRD, we found that when x < 0.6, the structure of the synthesized samples is similar to SrSO₄·0.5H₂O, and when x ≥ 0.6, the structure of the synthesized samples is similar to CaSO₄·0.5H₂O.

Their Raman and MIR spectra can be divided into three regions (Figures 2 and 3)¹. The first region is 100–1300 cm⁻¹, in which the features originated from SO₄²⁻ tetrahedron. The features in the 400–600 cm⁻¹ are attributed to the SO₄²⁻ tetrahedron symmetric bending (v₁) modes. The features in the range of 600–900 cm⁻¹ can be assigned to asymmetric bending (v₄) modes. In the range of 900–1100 cm⁻¹, the features are attributed to asymmetric stretching (v₃) modes and the features in the range of 1100–1300 cm⁻¹ are due to the SO₄²⁻ tetrahedron symmetric stretching vibration (v₂). The second and third regions are 1500–1800 cm⁻¹ and 2600–3700 cm⁻¹, respectively. In these two regions, all Raman features are from OH and H₂O vibrations in the sample’s structure. The feature around 1630 cm⁻¹ is due to the H₂O bending modes. Note that when the mole ratio of Ca²⁺/(Ca²⁺+Sr²⁺) is more than 40% in the synthesized samples, they did not show H₂O bending features around 1630 cm⁻¹. This result also indicates that the structures of Ca₉Sr₄SO₄·0.5H₂O and Ca₉Sr₄SO₄·0.5H₂O are similar to bassanite. In the third region, the Raman spectral features are due to the H₂O symmetric stretching modes. The additional peaks from 2000 cm⁻¹ to 2200 cm⁻¹ in MIR spectra of SrSO₄ are due to the SO₄²⁻ tetrahedron overtones/combinations and other peaks may originate from the adsorbed H₂O molecules and CO₂ in the atmosphere⁵.

With the increase of Ca²⁺ mole ratio, the main features around 1000 cm⁻¹ systematically shift towards larger wavenumbers. A positive relationship between the mole ratio of Ca²⁺ and its main feature of SO₄²⁻ tetrahedron (v₁) was derived by linear fitting (Figure 4).

The linear fitting result shows that they have a good linear relationship with an R² = 0.994 and the linear regression equation is: M = 0.0678P - 67.763, where P is the peak position (v₁ of SO₄²⁻ tetrahedron) around 1000 cm⁻¹, M is the mole ratio of Ca²⁺.

The V NIR spectra of Ca, Sr, SO₄·0.5H₂O (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) and SrSO₄ were acquired from 350–2500 nm (Figure 5). The features around 1.17 μm, 1.43 μm, and 1.92 μm can be used to distinguish them. In general, the VNIR reflectance spectroscopy reveals the overtones and combinational modes of fundamental vibrational modes of hydroxyl. The observed VNIR spectral features can also be subdivided into four regions. The features that appeared in the first region (λ ≤ 1.05 μm) are attributed to the overtone modes of H₂O (3v₁w or 3v₂w), the subscript w means the vibration modes originated from water). The second region (1.09 ≤ λ ≤ 1.26 μm) is due to the combination modes of H₂O (v₁w + v₂w + v₃w). The features located in the range of 1.33 ≤ λ ≤ 1.48 μm are ascribed to the first overtone of the fundamental stretching modes of H₂O (2v₁w or 2v₁w). The spectra in the 1.69 ≤ λ ≤ 2.3 μm region belong to the combination modes of the H₂O, such as v₁w (v₁w) + v₂w + v₃w (LT means the translation modes of H₂O) and v₁w (v₁w) + v₂w, as well as the combination modes of H₂O and SO₄ tetrahedron, e.g. v₁w (v₁w) + 3v₁SO₄.

**Conclusions:** A series of Ca–Sr sulfate solid solutions were synthesized for spectroscopic analysis. Specifically, we systematically investigated the XRD patterns, Raman, MIR, and VNIR spectral features of these solid solutions. The results show that the main Raman and XRD features varied with the cations content. Especially, the main Raman spectral features (v₁ of SO₄²⁻ tetrahedron) and XRD features varying with the cation content, can be used to aid the mineral phase identifications in calcium sulfate veins on Mars.