RAMAN, MIR, AND NIR SPECTROSCOPIC STUDY OF CALCIUM SULFATES: GYPSUM, BASSANITE, AND ANHYDRITE.
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Introduction: Gypsum ($CaSO_4.2H_2O$) and bassanite ($CaSO_4.0.5H_2O$) were identified on Mars by OMEGA on Mars Express and CRISM on MRO [1, 2, 3]. Anhydrite ($CaSO_4$) is non-active in the spectral range of OMEGA and CRISM, but may also exist [4]. Ca-sulfate was inferred from compositional correlations revealed by APXS on Mars Exploration Rovers [5, 6, 7], but no definitive identification, as well as its hydration state, was made because of the lack of an *in situ* mineral identification tool (e.g. Raman or XRD).

Compared to Mg-sulfates and Fe-sulfates, Ca-sulfates are more stable under Mars conditions and contain a limited range of H_2O content, 2w, 0.5w, 0w per SO_4 [8], thus they may not play an important role in the water cycle on Mars. However when Ca-sulfates were mixed with others, e.g. Mg-sulfates, Ca-sulfates can affect the hydration and dehydration pathways of the latters [9]. In addition, although Ca does not form solid solution in sulfates with Mg or Fe, but it does form (Ca, Na)- or (Ca, K)-sulfates as solid solutions. Furthermore, the natural occurrence of three Ca-sulfates does not always follow the predictions of thermadynamics or phase boundaries. Therefore, it is very important to establish a good understanding of the spectroscopic characters of pure Ca-sulfates, in order to make definitive identification of many different types of sulfates, as well as other salts.

In this abstract, we report a comprehensive spectroscopic study of gypsum, bassanite, and anhydrite. Raman and Mid-IR spectra were acquired. Their peaks were assigned to the fundamental vibrational modes of $(SO_4)^{2-}$ and H_2O in three structures. These knowledge was then used to assign the overtone and combinational modes in their NIR spectra. This set of spectral peak assignments will help the interpretation of NIR spectral data from current orbital missions (OMEGA and CRISM), and for the future mission to Mars, i.e. Raman on ExoMars.

Samples and measurements: Pure chemicals were used for this study, which produce the identical spectra as those from natural minerals. They are gypsum (Sigma Aldrich 255548-100G) with 98% purity, bassanite (Sigma_Aldrich 307661_25G) with 98% purity, and gamma-anhydrite (Aldrich 237132-100G) with 99% purity. We used an infrared spectrometer (Thermo Nicolet Nexus 670) to record the attenuated total reflectance (ATR) Mid-IR spectra ($400 – 4000$ cm^{-1}) and diffuse reflectance NIR spectra ($1.0 – 5.0$ μm) of three samples. Their Raman spectra were recorded using a Raman spectrometer (Kaiser HoloLab5000-532nm, $100 - 4000$ cm^{-1}). The obtained spectra are shown in Figure 1, 2, and 3 respectively.

Peak assignments in Raman and MIR: The fundamental vibrational modes of gypsum, bassanite, and anhydrite were assigned to the peaks in Raman and Mid-IR spectra. Our assignments for most peaks are consistent with those in previous literature [10, 11, 12]. In Raman spectra of gypsum, bassanite, and anhydrite, the strongest peaks were found at 1008, 1015, and 1017 cm^{-1} respectively, up-shifted following the decrease of the hydration degree. These are υ_1 symmetric stretch vibration modes of SO_4 tetrahedra. Variations in the structure of covalent bonded ionic group and its chemical environment are the general cause for the variations in Raman spectral patterns and for the systematic shift of Raman peaks. In addition, hydrogen bonding affects the coordinating oxygen of SO_4 tetrahedra. Gypsum, bassanite, and anhydrite all exhibit doublet for υ_2 symmetric bending of SO_4 tetrahedra, as (415, 439 cm^{-1}), (427, 489 cm^{-1}) and (416, 499 cm^{-1}) respectively. The other peaks of SO_4 tetrahedra are much weaker. The peaks at 1135 cm^{-1} in gypsum, 1128 cm^{-1} in bassanite, and 1110, 1128, 1159 cm^{-1} in anhydrite are υ_3 antisymmetric stretch vibration modes, and peaks at 620 and 670 cm^{-1} in gypsum, 628 and 668 cm^{-1} in bassanite, and 612, 629, and 676 cm^{-1} in anhydrite are υ_4 antisymmetric bending vibration modes. In Mid-IR spectra, the strongest peaks were found at 1102, 1111, and 1094 cm^{-1}, for the three samples, respectively, which are υ_3 antisymmetric stretch vibration modes of SO_4 tetrahedra. The gypsum, bassanite, and anhydrite exhibit two (667, 595 cm^{-1}), two (659, 594 cm^{-1}) and three (672, 610, 591 cm^{-1}), antisymmetric bending vibrations, respectively, in the mid-IR spectra. The peaks at 595 cm^{-1} in gypsum and 594 cm^{-1} in bassanite split into two peaks (610 and 591 cm^{-1}) in anhydrite, which indicates a lowering of symmetry in anhydrite. The shift of frequency from 672 cm^{-1} in anhydrite to 659 cm^{-1} in bassanite indicates that the sulfate ions in bassanite are linked with water molecules by hydrogen bonding, because in general the hydrogen bonding will lower the frequency of the absorption band. In addition, there is a very weak peak at 1003 cm^{-1} in gypsum, 1007 cm^{-1} in bassanite, and 1015 cm^{-1} in anhydrite, which should be the υ_1 symmetric stretch vibration modes of SO_4 tetrahedra. Because of the selection rules, these peaks are very weak in the infrared spectra, but very strong in Raman spectra. The presence of water in the gypsum and bassanite can be detected and characterized by peaks in spectral region

near 3500 cm^{-1} and 1600 cm^{-1}. In the high frequency Raman spectra, the peaks around 3500 cm^{-1} in the gypsum and bassanite are caused by stretch vibration modes of water, and no peaks for υ_2 bending vibration modes of water were observed in the three samples. In Mid-IR spectra, the peaks at 3395 cm^{-1} in gypsum and 3553 cm^{-1} in bassanite are υ_1 symmetric stretch vibration modes of water, and the peaks at 3489 cm^{-1} in gypsum and 3605 cm^{-1} in bassanite are υ_3 antisymmetric stretch vibration modes of water. There are two IR peaks for O-H bending vibration modes (1682, 1619 cm^{-1}) in the gypsum spectrum, one peak (1617 cm^{-1}) in bassanite, and no peaks in anhydrite. The presence of two peaks in gypsum indicates that there are two crystallographic distinct types of water. One type of water is linked with sulfate ions by hydrogen bonding, and the corresponding peak has lower frequency (also due to the hydrogen bonding) and high intensity. The other one is directly linked to calcium ions.
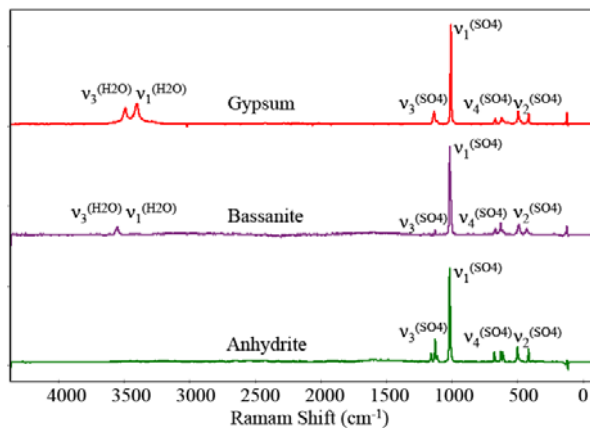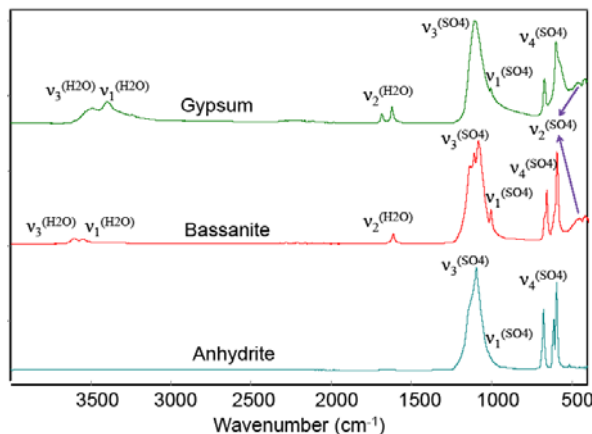

Figure 1 Raman Spectra

Figure 2 MIR Spectra

Peak assignments in NIR: The assignments for overtone and combinational modes in NIR spectral range were shown in Fig. 3. All three samples have strong absorption bands in the range of 4 - 5 μm, caused by combination modes of the fundamental stretch vibrations of SO$_4$ tetrahedra. A broad absorption band near

3 μm is present in all spectra and is due to the fundamental vibrational modes (υ_1, υ_3, and $2\upsilon_2$) of structural water in gypsum, bassanite, and adsorbed water in anhydrite. In addition, a prominent spectral feature around 1.9 μm is seen in the spectra of all three samples. The band in anhydrite spectrum is very wide and weak, caused by the combinational mode ($\upsilon_2 + \upsilon_3$) of the water adsorbed on the surface of anhydrite grains. In contrast, the bands in similar region of the spectra of hydrated Ca-sulfates, gypsum and bassanite, are much narrow and strong because they were produced by structural water molecules with distinct crystallographic sites. The similar phenomenon was observed for the bands near 1.4 μm and 1.1 μm, where gypsum and bassanite show more complicate band shapes. The combination modes of (SO$_4$)$^{2-}$ and H$_2$O vibrations were seen only in the spectra of gypsum and bassanite, in ranges of 1.7 - 1.8 μm, and 2.1 - 2.3 μm.
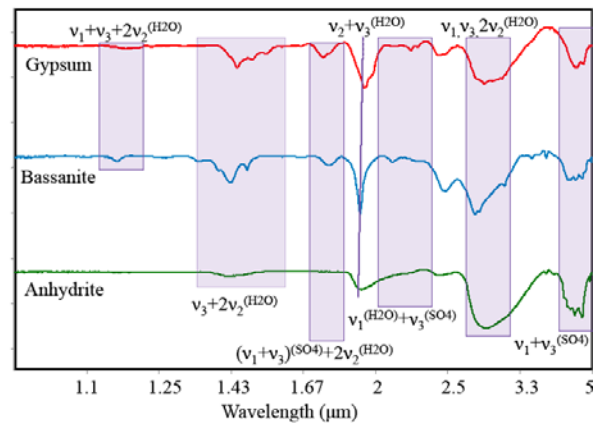

Figure 3 NIR Spectra

Conclusion: Ca-sulfates were found on Mars by various missions. In this study, the assignments of fundamental vibrational modes were made in Raman and Mid-IR spectra, and overtone and combinational modes in NIR spectral range. Our results can be used for the interpretation of the mission data from current and future exploration to Mars and to Venus.

References: [1] Gendrin et al. (2005), *Science, 307,* 1587-1591. [2] Langevin et al. (2005), *Science, 307,* 1584-1586. [3] Roach et al. (2007), *LPSC XXXVIII,* Abst #1970. [4] Bibring et al. (2005), *Science, 307,* 1576-1580. [5] Clark et al. (2005), *EPSL, 240,* 73-94. [6] Wang et al. (2006), *JGR, 111,* JE002513. [7] Ming et al. (2006), *JGR, 111,* JE002560. [8] Chou et al. (2007), *JGR, 112,* E11004. [9] Wang et al. (2008), *JGR, 113,* JE0003266. [10] Hass et al. (1956), *Pro Roy Soc London, 236,* 427-445. [11] Berenblut et al. (1971), *Spectrochimica, 27,* 1849-1863. [12] Takahashi et al. (1983), *Spectrochimica, 39,* 449-455.