$MgSO_4$•11H_2O – POWDER XRD, RAMAN AND VIS-NIR SPECTROSCOPIC CHARACTERIZATION

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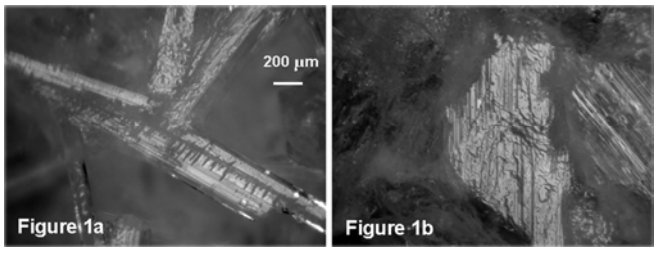
Why $MgSO_4$·11H_2O? Hydrous Mg-sulfate with 11 structural waters (11w hydrate), a new low temperature hydrated Mg-sulfate phase, was first reported in 2006 by Peterson & Wang [1]. They did a structural refinement using single-crystal XRD and suggested that the crystal molds in outcrops at Meridiani [2] could indicate melting and loss of the 11w hydrate. Chou et al. [3] proposed a phase boundary between epsomite ($MgSO_4$·7H_2O) and a highly hydrated Mg-sulfate (with 12 or 11 structural waters), and suggested this highly hydrated phase might be one of the forms of Mg-sulfates that could be stable at the current Mars surface and in its subsurface, especially in martian polar regions. Vaniman and Chipera [4] also observed the formation of this phase in their low temperature experiments.

We are interested in the ***spectral features*** of $MgSO_4$·11H_2O, including Raman and VIS-NIR spectroscopy [5,6,7,8]. The VIS-NIR spectral features would specifically help to interpret spectra obtained from OMEGA (Mars Express orbiter) and CRISM (MRO orbiter). Confirming the existence of $MgSO_4$·11H_2O on Mars would further our understanding of the hydrologic evolution of Mars.

Preparation of Crystals: $MgSO_4$·11H_2O samples were prepared from a solution of epsomite ($MgSO_4$·7H_2O, Sigma-Aldrich, SigmaUltra) in water using a 7:3 mass ratio. Epsomite was first ground to a particle size < 150 μm to ensure its total dissolution in water. The 7:3 mass ratio of epsomite to water yields a H_2O to $MgSO_4$ molar ratio of 12.9 to 1 -- higher than the needed 11 to setup a margin allowing a small amount of evaporative water loss observed during the preparation process. The solutions in petri dishes were put into two different freezers kept at -5˚C and -15˚C respectively and allowed to equilibrate. After a few days, a polycrystalline mat formed in petri dishes of all prepared samples (Fig.1). In addition, the mat climbs up along the wall of petri dishes, indicating a considerable volume increase compared to epsomite. Structural data suggests a 43% cell volume increase on conversion of epsomite to 11w hydrate. On the basis of the total consumption of water from the initial H_2O to $MgSO_4$ molar ratio (12.9:1) and the obvious volume increase, we conclude that a highly hydrated Mg-sulfate was formed at temperatures below 0˚C. When the H_2O to $MgSO_4$ molar ratio was much higher than 12.9 in the initial solution, a thin layer of water ice was formed beneath the polycrystalline mat.



XRD confirmation of $MgSO_4$·11H_2O: We built a special XRD sample mount to measure the diffraction pattern of powders at temperatures below 0˚C. The mount attaches to a small box holding powdered dry ice, and can keep the sample temperature below 0˚C either for ~ 24 minutes when thermally isolated, or for ~ 17 min when inserted into the sample chamber of XRD diffractometer. When analyzing the polycrystalline sample formed at low T with this mount, 3-4 repeated XRD scans from 10˚ to 40˚ 2θ using 0.1˚steps be made before the sample totally converts to epsomite.

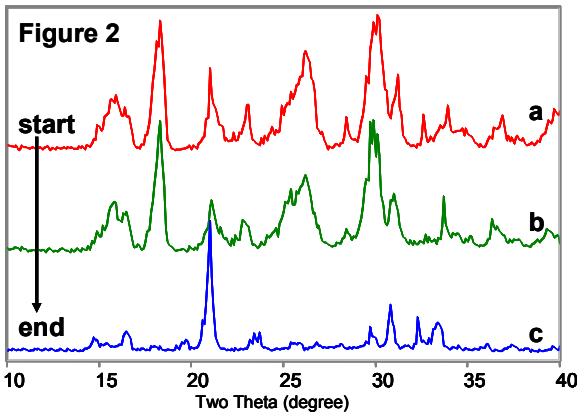
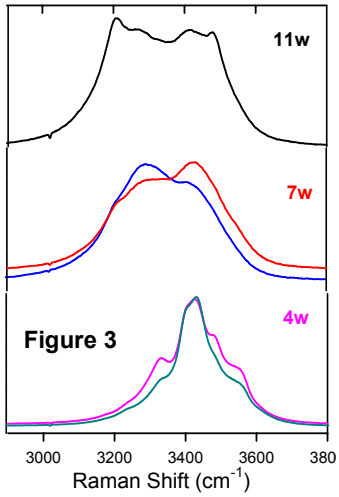


Figure 2 shows a set of XRD patterns obtained from a series of repeated scans. The XRD pattern of the end phase (Fig. 2c) is of epsomite. The starting phase (Fig. 2a) has a very different diffraction pattern, with the strongest lines occurring at 2θ values of 15.8˚, 18.1˚, 18.3˚, 26.2˚, 29.9˚, 30.1˚, 31.0˚, and 31.2˚. These positions are consistent (within experimental error) with the line positions of powder XRD pattern calculated by Ron Peterson [1] based on their single-crystal XRD refinement for $MgSO_4$·11H_2O.

Raman spectral characterization of $MgSO_4$·11H_2O: Multiple Raman spectra were taken from each of the three prepared 11w hydrate samples. The Raman measurements were made by inserting an optical-fiber-connected Raman probe into a thermally isolated box with the $MgSO_4$·11H_2O samples sitting on top of dry ice.

Compared to the spectra of epsomite and hexahy-

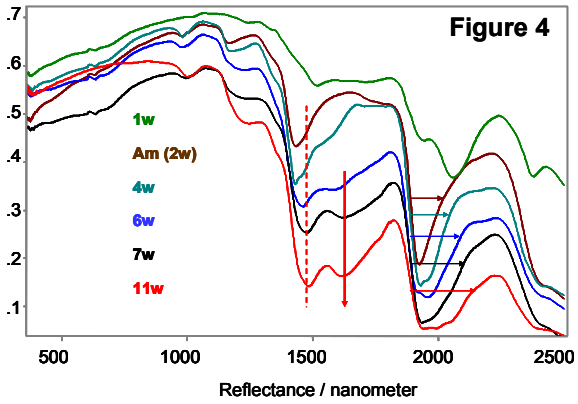
drite ($MgSO_4 \cdot 6H_2O$), the most distinct differences in the spectrum of $MgSO_4 \cdot 11H_2O$ are the Raman peak shape and sub-peak positions in the fundamental H-O-H stretching vibrational region. Figure 3 compares the "water peaks" of 11w hydrate with those of epsomite (7w) and starkeyite ($MgSO_4 \cdot 4H_2O$, 4w). Spectra from the lower two phases are shown with two different crystal orientations. This comparison confirms the specificity of the spectral peaks of 11w hydrate, not being an orientation effect. The distinct sub-peak feature suggests that all eleven water molecules have distinct crystallographic sites in the structure of 11w hydrate.



The ν_1 peak position (984.3 cm^{-1}) of the SO_4 tetrahedron in 11w hydrate is almost indistinguishable from that of epsomite (984.1 cm^{-1}) and only a little higher than the same peak of hexahydrite (983.5 cm^{-1}), while their minor peak positions of SO_4 fundamental peaks differ slightly [7]. Similarly, a very small ν_1 peak position difference (Δ=0.6 cm^{-1}) is noticed for hexahydrite and epsomite, which we have interpreted [7] to mean that the extra-water molecule in epsomite could not exert a strong enough hydrogen bonding effect on the ν_1 peak of SO_4 because it is not connected to any SO_4 and $Mg(OH_2)_6$ polyhedra. For the same reasons, we suggest that the very similar ν_1 peak positions of 11w hydrate and epsomite mean that the extra five structural water molecules in 11w hydrate are also not connected to either SO_4 or $Mg(OH_2)_6$. The structural hints given by this Raman spectral analysis are consistent with XRD structural refinement results of $MgSO_4 \cdot 11H_2O$ [1], i.e. the extra five water molecules occur in the spaces between the polyhedra.

VIS-NIR spectral features of $MgSO_4 \cdot 11H_2O$: For VIS-NIR reflectance measurements, we used a Analytical System Device that covers a 0.4 to 2.5 µm spectral range. Speculon™ was used for a 100% reflectance standard. This spectrometer has a optical-fiber-connected probe (coupled with a source) that can be directly deployed on the petri dish containing the $MgSO_4 \cdot 11H_2O$ sample. The sample was kept at the temperature of dry ice during the experiment except for the very quick spectra acquisitions of ~ 1 sec.

Figure 4 compares the VIS-NIR spectrum of $MgSO_4 \cdot 11H_2O$ with spectra from epsomite (7w), hexahydrite (6w), starkeyite (4w), kieserite ($MgSO_4 \cdot H_2O$, 1w), and an amorphous Mg-sulfate ($MgSO_4 \cdot 2H_2O$ by weight measurement, [Am (2w)]). Following an increase of the hydration state from Am (2w) to 11w hydrate, there are four major changes in the spectral range of 1.0 to 2.5 µm as follows: (1) The position of ~1.4 µm peak shows a systematic shift toward longer wavelengths (red dashed line in Fig. 4). (2) Starting from starkeyite, a shoulder at ~ 1.6 µm appears and its intensity increases when more water molecules are incorporated into the crystal structure (red solid arrow in Fig. 4). (3) The shapes of the ~ 1.9 µm band changes with the structural changes among different hydrous Mg-sulfate hydrates. Except for kieserite, these band shape variations would be difficult to discriminate in the spectra obtained by orbital remote sensing. (4) The bandwidth of the ~ 1.9 µm band, nevertheless, shows a systematic increase following the increase of hydration state (arrows in Fig. 4), and thus would be very useful for remote-sensing data analysis.



The information obtained in this study, XRD confirmation of synthesis of the 11w hydrate and its Raman & VIS-NIR spectral features, provides a basis for our next systematic study on the stability field and phase transition pathways of $MgSO_4 \cdot 11H_2O$ at two temperatures of -10˚C and -20˚C with controlled relative humidity. Raman spectral features will be used to conduct non-interruptive, *in situ* analysis at intermediate and final equilibrated stages.

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References: [1] Peterson & Wang (2006) *Geology,* 957-960. [2] Squyres et al (2004) *Science,*1709-1714. [3] Chou et al. (2005) *GSA & personal communications.* [4] Vaniman & Chipera (2006) *LPI Contribution No 1331,* p73. [5] Wang et al., (2006) *37th LPSC,* abs#2168. [6] Wang et al., (2006) *37th LPSC*, abs#2191. [7] Wang et al. (2006) *GCA,* 6118-6135. [8]. Wang et al. (2006) *LPI Contribution No 1331,* p75.