MIR, NIR AND RAMAN SPECTRA OF MAGNESIUM CHLORIDES WITH SIX HYDRATION DEGREES -- IMPLICATION FOR MARS AND EUROPA. Erbin Shi\textsuperscript{1,2}, Zongcheng Ling\textsuperscript{1}, Alian Wang\textsuperscript{2}, \textsuperscript{1}Institute of Space Sciences and Shandong Provincial Key Laboratory of Optical Astronomy & Solar-Terrestrial Environment, Shandong University, Weihai, 264209, China; \textsuperscript{2}Department of Earth & Planetary Sciences and McDonnell Center for the Space Sciences, Washington University in St. Louis, MO, 63130 (irvingshi@epsc.wustl.edu).

Introduction: Hydrous chlorides and perchlorates have been identified on Mars using MIR and VNIR data from orbital remote sensing [1, 2]. The deliquescence of these Cl-bearing salts within Martian subsurface salty layers may occur under the conditions of current obliquity period [3]. In this sense, the studies on the stability of hydrous chlorides and perchlorates at Mars-relevant environmental conditions are critical to understand their formation, preservation, and phase transformations on Mars, thus important for evaluating their potential contribution to Martian water reservoir.

Laboratory study [4] has suggested that calcium and magnesium would be the major cations in the chlorides and perchlorates found at the Phoenix site. The standard MIR, NIR and Raman spectra of calcium chlorides with various hydration degrees are available in the literature [5], but those of hydrous magnesium chlorides are still incomplete. In this study, we report a systematic study of MIR, NIR and Raman spectroscopic features of magnesium chlorides with all six hydration degrees, with the goal to support future orbital remote sensing and in-situ detection of them on Mars and on other planetary bodies, i.e. Europa [4].

Synthesis of MgCl\textsubscript{2}·nH\textsubscript{2}O (n=1, 2, 4, 6, 8, 12): Analytical reagent grade MgCl\textsubscript{2}·6H\textsubscript{2}O were purchased from Sinopharm Chemical reagent co. LTD (ShangHai) and recrystallization was then performed. MgCl\textsubscript{2}·4H\textsubscript{2}O were obtained from heating MgCl\textsubscript{2}·6H\textsubscript{2}O at 353 K in a vacuumed oven for 48 hrs. MgCl\textsubscript{2}·2H\textsubscript{2}O was prepared by heating MgCl\textsubscript{2}·4H\textsubscript{2}O at 373 K in the same vacuumed oven for 48 hrs. MgCl\textsubscript{2}·H\textsubscript{2}O was synthesized by heating MgCl\textsubscript{2}·2H\textsubscript{2}O at 393 K in the same vacuumed oven for 48 hrs. MgCl\textsubscript{2}·8H\textsubscript{2}O was synthesized from MgCl\textsubscript{2}·6H\textsubscript{2}O under a fixed relative humidity that was controlled by saturated lithium chloride solution at 253 K for 48 days. MgCl\textsubscript{2}·12H\textsubscript{2}O was synthesized from a saturated aqueous solution of MgCl\textsubscript{2} at 194.5 K controlled by dry ice [4, 6].

XRD identification of synthesized MgCl\textsubscript{2} hydrates: The XRD analyses were made using a Bruker D8 diffractometer at ambient laboratory conditions. MgCl\textsubscript{2}·6H\textsubscript{2}O is the stable phase in laboratory, whose XRD pattern matches very well with the one in PDF++2018 database. For other unstable MgCl\textsubscript{2}·nH\textsubscript{2}O (n=1, 2, 4, 6), fast (in 2 minutes) and slow (in 30 minutes) XRD measurements were made. The XRD patterns from fast measurements have the major lines but normally at quite low SNR. The XRD patterns from slow measurements have all the lines of targeting phase, but also have additional lines. For example, a few additional lines of MgCl\textsubscript{2}·6H\textsubscript{2}O was seen in the XRD patterns of MgCl\textsubscript{2}·4H\textsubscript{2}O and MgCl\textsubscript{2}·2H\textsubscript{2}O, and a few additional lines of MgCl\textsubscript{2}·2H\textsubscript{2}O in the XRD pattern of MgCl\textsubscript{2}·12H\textsubscript{2}O. We did not make the XRD analyses of MgCl\textsubscript{2}·8H\textsubscript{2}O and MgCl\textsubscript{2}·12H\textsubscript{2}O, which changed into liquid at room temperature. Their phase ID were made by comparing with the spectral data in literature [4, 6].

Raman and MIR spectral features of six magnesium chlorides (Fig. 1, 2): Raman and MIR spectroscopy both reveal the fundamental vibrational modes. The crystal structure of MgCl\textsubscript{2}·nH\textsubscript{2}O (n=1, 2, 4, 6, 8, 12) all consisting of Mg(H\textsubscript{2}O)\textsubscript{6}Cl\textsubscript{6} (x=1, 2 and 6) octahedra in unit cell. For Mg(H\textsubscript{2}O)\textsubscript{6}Cl\textsubscript{6} octahedra in different hydrates, Mg coordinates less with Cl but more with H\textsubscript{2}O when hydration degree increases. [7-8]. This fact affects the MIR, VNIR, and Raman spectral features of six MgCl\textsubscript{2} hydrates.

Both the Raman and MIR spectra of these MgCl\textsubscript{2}·nH\textsubscript{2}O (n=1, 2, 4, 6, 8, 12) consist the peaks from the fundamental vibrations of structural H\textsubscript{2}O and the lattice vibrations of MgCl\textsubscript{2}. The vibrational modes of H\textsubscript{2}O in these chlorides are both Raman and IR active: the peaks near the 1600 cm\textsuperscript{-1} are due to H\textsubscript{2}O bending mode vibration (\nu) [9]; the peaks in range of 2900-3800 cm\textsuperscript{-1} are contributed by the symmetric and asymmetric stretching mode (\nu\textsubscript{1}&\nu\textsubscript{2}), and the first overtone of the bending mode (2\nu) of H\textsubscript{2}O [3, 4, 9]. These peaks are different in peak position, numbers of sub-peaks, and peak widths among different MgCl\textsubscript{2}·nH\textsubscript{2}O (n=1, 2, 4, 6, 8, 12), as
well as different between the Raman and MIR spectra of the same MgCl₂·nH₂O.

Lattice vibration modes of Mg-O/Mg-Cl bonds appear in Raman and MIR spectra below 500 cm⁻¹, contributed by the vibrations of the bonds of Mg-Cl or of Mg-O (of H₂O). The number of Raman peaks in this range is higher than that of MIR peaks. The Raman and all MIR/NIR spectra were collected by using a inVia Raman spectrometer and Nicolet Nexus 670 (Thermo Fisher) FTIR Nexus spectrometer, respectively. MgCl₂·6H₂O is a stable phase at lab-conditions, whose standard Raman and IR spectra were readily obtained. For MgCl₂·nH₂O (n=1, 2, 4), the samples were sealed in bottles immediately after removal from oven, and the Raman spectra were taken through the wall of sample bottles. MIR spectra of these samples were measured in open-air but in very short time (140 s), no apparent rehydration was noticed in the spectra. For MgCl₂·8H₂O and MgCl₂·12H₂O, Raman and MIR spectra were taken at dry-ice temperature (Tdryice).

Since we could not obtain XRD patterns of MgCl₂·8H₂O and MgCl₂·12H₂O at Troom, the phase ID of MgCl₂·12H₂O was confirmed by the matching of obtained Raman spectrum with those in literature [6]. The phase ID of MgCl₂·8H₂O was confirmed by our gravimetric measurement results (before and after the three runs of baking), and by the similarity in obtained NIR peaks with published literature data [4].

**NIR spectral features of six magnesium chlorides:** NIR spectra were obtained using the Crikect accessory of Nexus 670, which was cooled to Tdryice beforehand. The Tmean during NIR measurements was -56.2°C and the measurements were completed within 35 s. There are several diagnostic absorption features in the reflectance spectrum of MgCl₂·nH₂O (n=1, 2, 4, 6, 8, 12), caused by the combinations of vibrational overtones of hydroxyl, H₂O and metal-hydroxylic, which can be described in four regions [9]. The bands in first region (λ≤1.35 μm) are attributed to high order overtones and combination modes of H₂O. The bands of 1.35<λ≤1.65 μm are ascribed to the first overtone of the fundamental stretching modes of H₂O. Spectra in the 1.65<λ≤2.70 μm region belongs to the combination modes of the stretching, bending and translation modes of H₂O. The bands in fourth region (λ≥2.65 μm) are attributed to stretching fundamentals ν₁ and ν₃ and first overtone of bending 2ν₂ of H₂O similar to those in MIR and Raman spectra. As display in Fig. 3, every MgCl₂·nH₂O (n=1, 2, 4, 6, 8, 12) has a unique NIR spectra profile, especially the bands near 1.2, 1.4, 1.9 and 2.4 μm. For instance, the MgCl₂·nH₂O (n=1, 2, 4), have triple bands near 1.4 μm but their band positions are different in positions and shapes. In contrast, MgCl₂·6H₂O appeared double bands and others appeared single band near 1.4 μm.

**Implications for Mars and Europa:** Magnesium chloride with different hydration states are potentially distributed widely at the surface and in subsurface of Europa and Mars. However, the spectra of magnesium chlorides, especially in VNIR spectral range, are frequently covered by the bands of other minerals thus difficult to be distinguished in remote sensing and in situ detection on Mars [1, 3, 4]. The lack of standard spectra through systematic laboratory studies is another reason for this difficulty. The spectral data of this study fill a gap in current spectral libraries and would help to distinguish the chlorides from others hydrated salts.

**Conclusion:** We have successfully synthesized six magnesium chlorides with all possible hydration degrees and carried out gravimetric, XRD, MIR, NIR, VNIR, and Raman measurements. The spectra obtained here will serve to fill a gap in current spectral libraries and can be used to interpretation of spectra features in the missions to Mars and Europa.

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