

MIR, NIR AND RAMAN SPECTRA OF MAGNESIUM CHLORIDES WITH SIX HYDRATION DEGREES -- IMPLICATION FOR MARS AND EUROPA.

Erbin Shi^{1,2}, Zongcheng Ling¹, Alian Wang²,
¹Institute of Space Sciences and Shandong Provincial Key Laboratory of Optical Astronomy & Solar-Terrestrial Environment, Shandong University, Weihai, 264209, China; ²Department 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 can occur under the conditions of current obliquity period [3]. These deliquescence would generate transient liquid water, i.e., brines, which might support the occurrence of RSL (recurring slope lineae) [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 H₂O 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 MgCl₂·nH₂O (n=1, 2, 4, 6, 8, 12): Analytical reagent grade MgCl₂·6H₂O were purchased from Sinopharm chemical reagent co. LTD (Shanghai) and recrystallization was then performed. MgCl₂·4H₂O were obtained from heating MgCl₂·6H₂O at 353 K in a vacuumed oven for 48 hrs. MgCl₂·2H₂O was prepared by heating MgCl₂·4H₂O at 373 K in the same vacuumed oven for 48 hrs. MgCl₂·H₂O was synthesized by heating MgCl₂·2H₂O at 393 K in the same vacuumed oven for 48 hrs. MgCl₂·8H₂O was synthesized from MgCl₂·6H₂O under a fixed relative humidity that was controlled by saturated lithium chloride solution at 253 K for 48 days. MgCl₂·12H₂O was synthesized from a saturated aqueous solution of MgCl₂ at 194.5 K controlled by dry ice [4, 6].

XRD identification of synthesized MgCl₂ hydrates: The XRD analyses were made using a Bruker D8 diffractometer at ambient laboratory conditions. MgCl₂·6H₂O is the stable phase in laboratory, whose XRD pattern matches very well with the one in PDF++2018 database. For other unstable MgCl₂·nH₂O (n=1, 2, 4), 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 MgCl₂·6H₂O was seen in the XRD patterns of MgCl₂·4H₂O and MgCl₂·2H₂O, and a few additional lines of MgCl₂·2H₂O in the XRD pattern of MgCl₂·H₂O. We did not make the XRD analyses of MgCl₂·8H₂O and MgCl₂·12H₂O, 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 MgCl₂·nH₂O (n=1, 2, 4, 6, 8, 12) all consisting of Mg(H₂O)_xCl_{6-x} (x=1, 2 and 6) octahedra in unit cell. For Mg(H₂O)_xCl_{6-x} octahedra in different hydrates, Mg coordinates less with Cl but more with H₂O when hydration degree increases. [7-8]. This fact affects the MIR, VNIR, and Raman spectral features of six MgCl₂ hydrates.

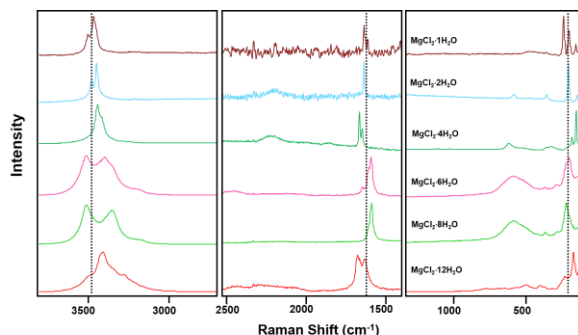


Figure 1. The Raman spectral of magnesium chlorides in the range of 100-3800 cm⁻¹.

Both the Raman and MIR spectra of these MgCl₂·nH₂O (n=1, 2, 4, 6,

8, 12) consist the peaks from the fundamental vibrations of structural H₂O and the lattice vibrations of MgCl₂. The vibrational modes of H₂O in these chlorides are both Raman and IR active: the peaks near the 1600 cm⁻¹ are due to H₂O bending mode vibration (ν_2) [9]; the peaks in range of 2900-3800 cm⁻¹ are contributed by the symmetric and asymmetric stretching mode (ν_1 & ν_3), and the first overtone of the bending mode ($2\nu_2$) of H₂O [3, 4, 9]. These peaks are different in peak position, numbers of sub-peaks, and peak widths among different MgCl₂·nH₂O (n=1, 2, 4, 6, 8, 12), as

well as different between the Raman and MIR spectra of the same $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$.

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 H_2O). 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 spectrometer, respectively. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is a stable phase at lab-conditions, whose standard Raman and IR spectra were readily obtained. For $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ ($n=1, 2, 4$), 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 $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, Raman and MIR spectra were taken at dry-ice temperature (T_{dryice}).

Since we could not obtain XRD patterns of $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ at T_{room} , the phase ID of $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ was confirmed by the matching of obtained Raman spectrum with those in literature [6]. The phase ID of $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ 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 T_{dryice} beforehand. The T_{mean} 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 $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ ($n=1, 2, 4, 6, 8, 12$), caused by the combinations of vibrational overtones of hydroxyl, H_2O and metal-hydroxyl, which can be described in four regions [9]. The bands in first region ($\lambda \leq 1.35\text{ }\mu\text{m}$) are attributed to high order overtones and combination modes of H_2O . The bands of $1.35 \leq \lambda \leq 1.65\text{ }\mu\text{m}$ are ascribed to the first overtone of the fundamental stretching modes of H_2O . Spectra in the $1.65 \leq \lambda \leq 2.70\text{ }\mu\text{m}$ region belongs to the combination modes of the stretching, bending and translation modes of H_2O . The bands in fourth region ($\lambda \geq 2.65\text{ }\mu\text{m}$) are attributed to stretching fundamentals ν_1 and ν_3

and first overtone of bending $2\nu_2$ of H_2O similar to those in MIR and Raman spectra. As display in **Fig. 3**, every $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ ($n=1, 2, 4, 6, 8, 12$) has a unique NIR spectra profile, especially the bands near 1.2, 1.4, 1.9 and 2.4 μm . For instance, the $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ ($n=1, 2, 4$), have triple bands near 1.4 μm but their band positions are different in positions and shapes. In contrast, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 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 difficult. 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.

Acknowledgements: EBS thanks the CSC. AW thanks the special fund from MCSS at WUSTL. ZCL thanks the supports from the NSFC (41473065), the NSF of Shandong Province (JQ201511), Qilu (Tang) Young Scholars Program of Shandong University, Weihai (2015WHWLJH14).

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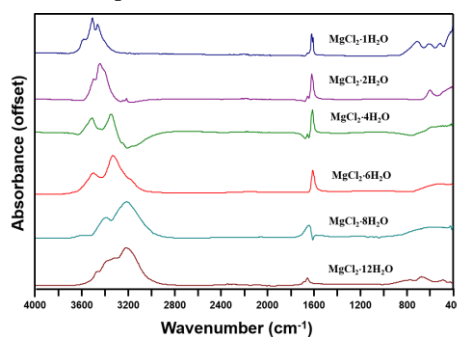


Figure 2. The MIR spectra of magnesium chlorides in the range of 400-4000 cm^{-1} .

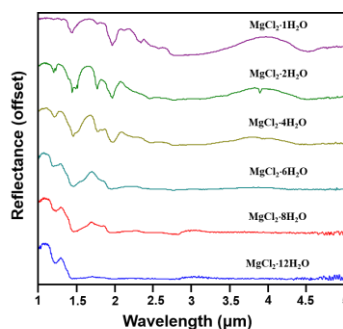


Figure 3. The NIR spectra of magnesium chlorides in the range of 1-5 μm .