

**THE RAMAN SPECTRA OF FERRIC CHLORIDES AND FERROUS CHLORIDES.** Yongxv Li<sup>1</sup>, Erbin Shi<sup>1</sup>, Zongcheng Ling, <sup>1</sup>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. (202100830049@mail.sdu.edu.cn)

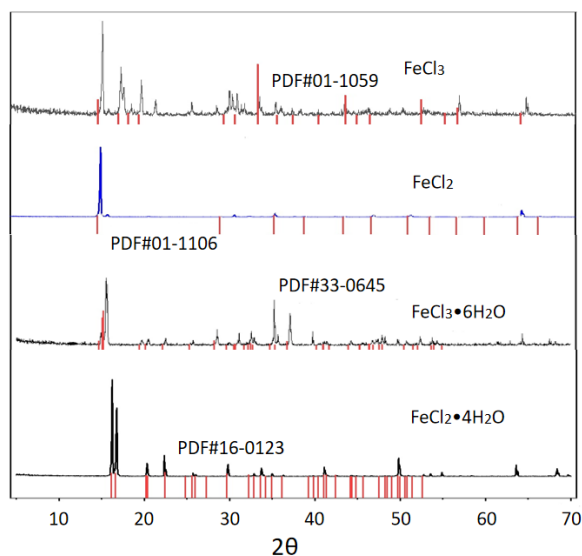
**Introduction:** Using orbital remote sensing data from the Mars Odyssey Thermal Launch Imaging System, chlorine-containing materials have been found on Mars. These minerals are found mainly in the southern highlands.<sup>[1,2]</sup> Chlorine salts (such as chlorides, chlorates, and perchlorates) are an important factor affecting the stability of water on the surface of planetary bodies. In order to study their effect on the stability of water on the planet's surface, we need to first locate where these chloride salts exist. This is usually done through remote sensing. To date, only anhydrous chlorides have been remotely detected, mainly due to the lack of hydrating chloride salts in the spectral library used to identify the features.<sup>[3]</sup> Simulations suggest that the perchlorate detected at the Phoenix landing site may be related to iron, which indicated that the ferrous/ferric chlorides may also occur on Mars due to the perchlorate ions being well oxidative.<sup>[4]</sup> The goal of this study is to acquire the Raman spectra and other spectroscopies of ferric chlorides and ferrous chlorides to enrich the spectrum library of chlorine salts and explore the possibility of chlorine ferric salts and chlorine ferrous salts on Mars to pave the way.

**Samples and Experiments:** We prepared/bought four ferric and ferrous chlorides first, including  $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$  ( $n = 0, 4$ ),  $\text{FeCl}_3 \cdot n\text{H}_2\text{O}$  ( $n = 0, 6$ ), other phases will be prepared in future. The crystalline structures of ferric chlorides and ferrous chlorides were confirmed by powder XRD measurements (Rigaku Ultima IV) using a radiation ( $\lambda = 1.54052 \text{ \AA}$ ) at 40 kV and 40 mA and a  $0.02^\circ$  step size from the  $2\theta$  range of  $10^\circ$  to  $70^\circ$ . The Raman spectra of the synthesized ferric chlorides and ferrous chlorides were collected with an inVia Raman imaging system (Renishaw Company). The 532 - nm line of a DPSS laser was used for excitation, and a long - working - distance  $50\times$  objective ( $\text{NA} = 0.75$ ) for signal collection. The Raman spectra from 100 to  $4,000 \text{ cm}^{-1}$  were collected that covering both the fundamental and lattice vibrational modes of molecules. The inVia system has a spectral resolution better than  $1 \text{ cm}^{-1}$  and a spectral repeatability of  $\pm 0.2 \text{ cm}^{-1}$ . All instruments and measurements were employed at Shandong University, Weihai.

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  is the stable phase of ferrous chlorides and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  is the stable phase of ferric chlorides in a temperature range of  $5^\circ\text{C}$  to  $50^\circ\text{C}$  at laboratory conditions, whose standard XRD and Raman spectra

were readily obtained at ambient conditions in the laboratory. For the Raman measurements, the unstable samples of  $\text{FeCl}_2$  and  $\text{FeCl}_3$  were rehydration immediately after they remove from the sealed bottles.

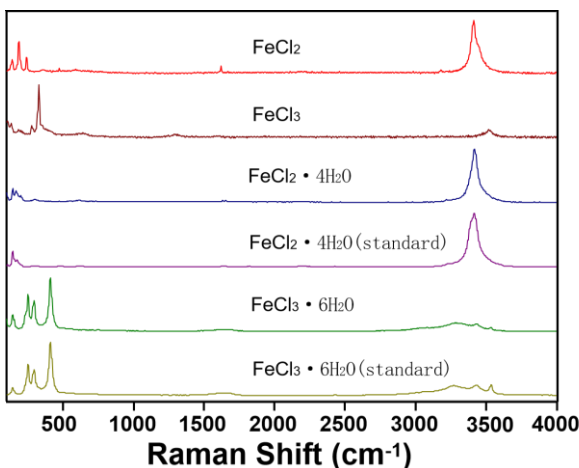
**Results and Discussion:** The XRD patterns collected from the prepared ferric chlorides and ferrous chlorides are shown in Figure 1. The diffraction patterns of two hydrated iron chlorides are overall matched with those of the PDF+2004 database by evaluating the positions of all apparent peaks, indicating that highly crystalline ferric chlorides were formed. However, for two anhydrous iron chlorides, there are many additional peaks due to their rehydrated. The color of two anhydrous iron chlorides was changed from light yellow to dark yellow within one minute and became liquid entirely ten minutes later when they were exposed to the atmosphere. Thus, a new method needs to be developed to keep the two anhydrous. This phenomenon also occurred in Raman measurements. The best method to keep the two anhydrous iron chloride is to seal them in transparent bottles when running the Raman measurements and run fast XRD measurements.



**Figure 1.** XRD patterns of prepared ferric chlorides and ferrous chlorides with different hydration states ( $\text{FeCl}_2$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ). The PDF files of the same phases are shown for comparison.

The Raman patterns collected from the prepared ferric chlorides and ferrous chlorides are shown in Figure 2. The Raman spectroscopies reveal the

fundamental vibrational modes of molecules. The measured Raman spectra of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  are identical to standard Raman spectra, this results indicated the prepared two hydrated iron phases are successful. Moreover, all samples were measured more than ten times at different locations, and all obtained spectra are identical. For two hydrated iron chlorides, the peaks that appeared  $<500 \text{ cm}^{-1}$  can be attributed to the lattice vibration of Fe-O. The peaks around  $1600 \text{ cm}^{-1}$  can be assigned to water bending vibration. The features in  $2800\text{--}4000 \text{ cm}^{-1}$  are contributed by the water stretching vibration. On the other hand, the peaks  $<500 \text{ cm}^{-1}$  in the anhydrous  $\text{FeCl}_2$  and  $\text{FeCl}_3$  Raman spectra are also due to the lattice vibration of Fe-O. The water features in the spectra are because of their rehydration in the air. These two anhydrous iron chlorides are easy to rehydration and may be significant to indicate the occurred Recurring slope lineae (RSL) in the summer on Mars, the details will be discussed in the future study.



**Figure 2.** The Raman spectra of ferric chlorides and ferrous chlorides with different hydration states ( $\text{FeCl}_2$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) in the range of  $100 - 4,000 \text{ cm}^{-1}$ .

**In future work:** In this study, four iron chlorides were prepared and bought. The obtained Raman spectra of two hydrated ferric chlorides will be helped to interpret the Recurring slope lineae on Mars and to the benefit of our knowing the habitability of Mars. In the future, more iron chlorides, chlorate, and perchlorate will be synthesized and all of them will be employed different spectroscopies to obtain their spectra features, such as MIR, VINR, LIBS, etc.

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**References:** [1] Osterloo, M. M. et al. (2008), *Science*, 319, 1651–1654. [2] Osterloo, M. M. et al. (2010), *JGR Planets*, 115, E10. [3] Hanley, J. et al. (2013), *Diss.* [4] Glavin, D. P. et al. (2013), *JGR Planets*, 118, 1960–1961.