

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF A NEW FERRIC SULFATE, BILINITE?

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Introduction: The halotrichite group including many common hydrated sulfate minerals often shows an extensive solid solution series [1-4]. The normal formula can be written $AB_2(SO_4)_4 \cdot 22H_2O$, where A represents an atom of divalent ion such as Fe^{2+} , Mg^{2+} , Zn^{2+} or/and some combination of these cations and B represents an atom of trivalent metal ion such as Al^{3+} , Cr^{3+} or Fe^{3+} or even a combination of these cations [1-4]. On Earth, halotrichite minerals are often found in the environment as post-mining phases. Recent orbital spectral measurements by OMEGA aboard Mar Express have yielded evidence that indicating the presence of halotrichite on the Mars' surface [5]. The formation environment of the halotrichite group and others ferric sulfates have been identified or suggested on Martian surface can serve as mineralogical evidence for past water activity on Mars [6, 7]. Studying the fundamental spectral and structural properties of halotrichite group in laboratory will help to interpret the spectral from in-situ investigations and remote sensing on Mars and help to understand the hydrologic history of Mars.

Bilinite is one mineral member of halotrichite group, the difference from halotrichite is the trivalent metal ion replaced by Fe^{3+} ($Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 22H_2O$). As a representative mineral member of halotrichite group bilinite were widely distribution in mining area. But few studies on bilinite.

In this abstract, we report the first sythesisation of a new phase of hydrated ferric sulfate (HFS), probably a polymorph of bilinite ($Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 22H_2O$). And then conduct systematic X-ray diffraction and spectroscopic measurements on it with intent to further determine its phase and crystal structure.

Sample Synthesis: The primary goal of sample synthesis is to obtain the bilinite ($Fe^{2+}Fe_2^{3+}(SO_4)_4 \cdot 22H_2O$). The synthetic method followed the procedure of halotrichite. The saturated solution contained $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot xH_2O$ (V: V=1:1) were placed in a beaker, and a bag of each of the sulfate salts used to prepare the supersaturated solution was attached on opposite sides of the beaker. The beaker was covered with parafilm and left for a period of a two week in room temperature in order to make the new compound crystallize [3]. Crystals collected from the beaker were then washed with anhydrous ethanol and dried in room temperature. The HFS appears transparent in a green color (Figure 1).

Gravimetric Measurement: In order to determine the amounts of the components of a water in new crystal, the gravimetric measurement was performed. After placing the sample in the oven at $150^\circ C$ for 24 h, the mass changed before and after heating was calculated about 41.40%, closed to nominally complete water loss of bilinite (41.77%).



Figure 1. Optical picture of the HFS.

XRD Characterization: The phase identification of the HFS was conducted by X-ray powder diffraction (XRD). A Rigaku UltimaIV diffractometer with a $CuK\alpha$ radiation ($\lambda = 1.54052 \text{ \AA}$) was employed at acceleration voltage of 40 kV and current of 40 mA and scanned at 0.02° step from 5° to 90° . The XRD pattern of the new crystal cannot match with the simulated bilinite (Figure 2, refer to the Joint Commission on Powder Diffraction Standards database (JCPDS card no. 25-1153)) and other reference patterns of different kinds of ferric sulfates in PDF database 2004, indicated that the synthesized of HFS could have a new crystal structure, may be a polymorph of bilinite.

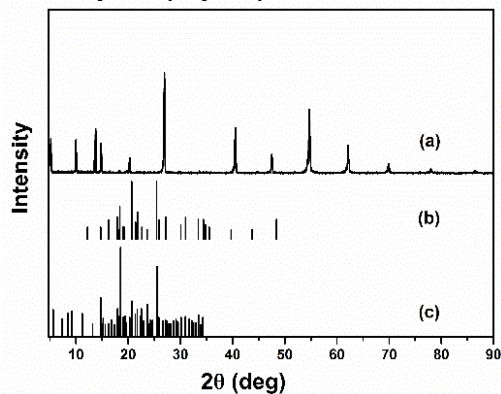


Figure 2. XRD pattern of (a) the synthetic HFS, (b) the simulated bilinite (JCPDS card no. 25-1153) and (c) the simulated halotrichite (JCPDS card no. 39-1387).

Spectroscopic Characterization: Raman, Mid-IR and VIS-NIR spectra of the newly-grown ferric sulfate

and halotrichite ($\text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$, the phase has been confirmed by XRD) were obtained by a Bruker vertex 70 Fourier Transform Infrared Spectrometer, and a Renishaw inVia[®] Laser Raman System, respectively. Among them, the peaks in Raman and IR spectra can provide information on the fundamental vibrational modes which are directly linked to its crystal structure.

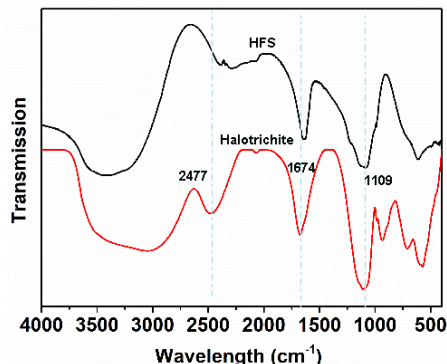


Figure 3. Mid-IR spectra of the synthetic HFS (black) and the halotrichite (red)

The Mid-IR spectra of HFS are shown in Figure 3. The spectral region between 3800 and 2700 cm^{-1} is ascribed to the water and OH stretching vibration. The bands in 1100–1200 cm^{-1} are also observed for HFS, assigning to ν_3 mode of SO_4^{2-} . The ν_1 symmetric stretching vibration of sulfate anions are observed between 900 and 1000 cm^{-1} . The band for HFS, observed at 988.5 cm^{-1} and 976.7 cm^{-1} is proposed to be due to sulfate anions associated with Fe^{3+} [3]. Moreover, the band at 615 cm^{-1} is attributed to ν_4 (SO_4^{2-}). The shape of the band profile for halotrichite in the higher wavenumber region (1000–3800 cm^{-1}) resembles that of HFS. This may suggest that the structure of new of ferric sulfate could be similar to halotrichite.

Raman spectra of the HFS and halotrichite are shown in Figure 4. The symmetric stretching vibrational (ν_1), bending modes (ν_2), and asymmetric stretching (ν_3) and bending modes (ν_4) of SO_4 tetrahedra in HFS is located at 977.9 cm^{-1} (ν_1), 991.0 cm^{-1} (ν_1), 1027.8 cm^{-1}

(ν_1), 451.2 cm^{-1} (ν_2), 482.2 cm^{-1} (ν_2), 1147.20 cm^{-1} (ν_3), 610.36 cm^{-1} (ν_4), respectively [8]. The Raman peaks in the 2800–3600 cm^{-1} spectral region is contributed to modes of structural water in HFS. The Raman peaks of HFS are very similar to halotrichite in term of peak positions and shapes. But the peak positions were not completely same, which can be attributed to different coordination environment and metal-oxygen bonds in halotrichite and HFS.

Conclusion: HFS has been successfully synthesized and characterized by Raman spectroscopy, MIR spectroscopy and gravimetric measurements method. Similar MIR and Raman spectral patterns indicate that HFS may have a similar structure to halotrichite. Moreover, the consistency of the amount of water calculated by the molecular formula of bilinite and gravimetric measurement, also supports that the HFS could be bilinite. For future work, we will determine the crystal structure of the HFS by various methods (e.g., single crystal XRD) to finally determine whether it is bilinite or not. And then we will conduct more other experiments (e.g., stability field) to better understand this new phase of ferric sulfate.

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Reference: [1] Frost, R.L. et al. (2010) *J Therm Anal Calorim.*, 99,501–507. [2] Menchetti, S. and Sabbelli, C. (1976) *Mineral Mag.*, 40, 599-608. [3] Palmer, S. J. et al. (2011). *Spectrochim Acta A.*, 79, 69-73. [4] Frost, R.L. et al. (2006) *J Near Infrared Spectrosc.*, 14, 167–178. [5] Gendrin, Al. et al. (2005) *Science*, 307, 1587-1591.[6] Xu, W. (2011) *Diss*, State University of New York at Stony Brook. [7] Liu, Y. et al. (2018) *Icarus*, 302, 62-79. [8] Ling, Z. C. and Wang, A. (2010) *Icarus*, 209, 422-433.

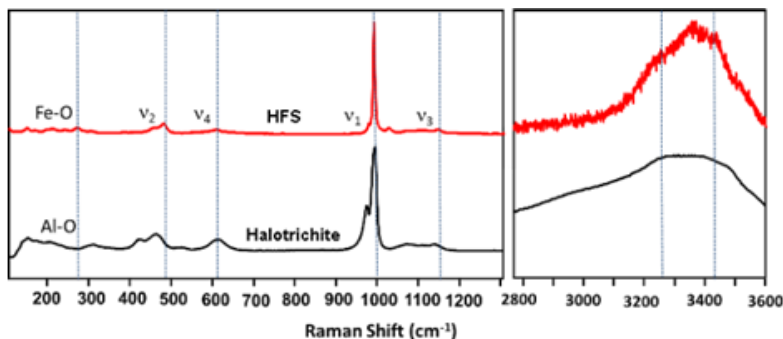


Figure 4. Raman spectra of the synthetic HFS (red) and the halotrichite (black).