SYNTHESIS AND SPECTRA OF A GROUP OF HYDROXY FERRIC SULFATES RELEVANT TO MARS.

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Introduction: Mars carries a name of "Red Planet" because of its reddish appearance. The surficial color of Mars has been attributed to ferric-bearing phase in the regolith that was supported by mission observations[1]. Ferric sulfates have been found on Mars by observations of orbiters, lander, and rovers. The *Opportunity rover* revealed the existence of Jarosite [$KFe^{3+}(SO_4)_2(OH)_6$] in outcrops at Meridiani Planum (over hundreds kilometers) using Mössbauer spectroscopy[2]. Ferric hydroxysulfate [$Fe(SO_4)OH$] was suggested existing in the sedimentary deposits in Aram Chaos[3] using VNIR spectroscopy. The *Spirit rover* identified different kinds of ferric sulfates within the subsurface regolith at Gusev crater[8, 9]. A VNIR spectral analysis using Pancam data of subsurface materials, excavated by the *Spirit rover* in Gusev crater at three different locations, implied the presence of a mixture of basic, neutral, and acidic ferric sulfates with various degrees of hydration, including ferricopiapite [$Fe^{2+}{}_{2/3}Fe^{3+}{}_4(SO_4)_6(OH)_2{\cdot}20(H_2O)$], hydronium jarosite [$(H_3O)Fe^{3+}{}_3(SO_4)_2(OH)_6$], fibroferrite [$Fe^{3+}(SO_4)(OH){\cdot}5(H_2O)$], rhomboclase [$HFe^{3+}(SO_4)_2{\cdot}4(H_2O)$] and paracoquimbite [$Fe^{3+}{}_2(SO_4){\cdot}9(H_2O)$] [10]. It is nevertheless hard to make definitive identification of these hydrated ferric sulfates due to the heavily overlapped VNIR spectral bands, as well as the lacking of laboratory spectral studies of a wide variety of hydrated ferric sulfates. More importantly, yellowish soil at Tyrone site in Gusev crater has shown a Pancam spectral changes after being exposed to current Martian surface atmosphere for 175 sols, determined to be caused by the dehydration of hydrous ferric sulfates[11]. This finding demonstrated not only the huge different environmental conditions at surface and within the subsurface of Mars, but also the needing of knowledge on the pathway of phase transition among ferric sulfates.

The difficulty in these mission data interpretations calls for a deeper understanding of fundamental properties of ferric sulfates. Up to now, eight hydrous ferric sulfates [12], four mixed cation ferric sulfates [13], and a set of Na, K, H_3O-jarosite solid solutions [14, 15] have been synthesized in laboratory, and their spectral characteristics studied. This study reports our effort to synthesize the hydroxy ferric sulfates in fibroferrite-group, $Fe(SO_4)(OH){\cdot}xH_2O$ (x=0, 2, 5), and the spectral characterizations.

Synthesis of Ferric Hydroxy Sulfates: We chose melanterite, a mineral form of hydrous iron(II) sulfate $FeSO_4{\cdot}7H_2O$, as the starting phase for the synthesis. 20 g melanterite was grinded with an agate mortar, then was held by a crucible with a cap. $Fe(SO_4)OH$ is synthesized by heating this sample at 240 °C for 24hrs in a muffle furnace. In order to synthesize butlerite $Fe(SO_4)(OH){\cdot}2H_2O$ and fibroferrite $Fe(SO_4)(OH){\cdot}5H_2O$, Relative Humidity (RH) buffer solutions were employed for $Fe(SO_4)OH$ to rehydrate under controlled temperature (T) and RH. The LiBr, LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaBr, KI, NaCl, KCl, KNO_3 saturated aqueous solutions and pure water can provide 6-100% RH between 5 and 80 °C [14, 16,17]. We found that butlerite $Fe(SO_4)OH{\cdot}2H_2O$ can be synthesized in a RH range of 30-80% between 5 and 80 °C. It would take 15 days to form butlerite when the small bottle which contained $Fe(SO_4)OH$ sample was held in NaCl saturated aqueous solution at 80 °C. Up to now, we synthesized two salts in fibroferrite-group, $Fe(SO_4)OH$ and butlerite, successfully. Then we employed Raman, MIR and VNIR spectroscopic methods to study their spectral characteristics related to crystal structures.

Molecular Spectral Characterizations: As shown in Fig.1, In the principal H_2O/OH Raman spectral region, $Fe(SO_4)OH$ has a single narrow peak at 3452 cm^{-1}. Butlerite has two wide overlapped peaks (3453 and 3294 cm^{-1}) contributed by its structural H_2O. SO_4 usually shows four fundamental vibrational modes. ν_1 symmetric and ν_3 antisymmetric stretching modes occur > 900 cm^{-1}. ν_2 symmetric and ν_4 antisymmetric bending modes occur around 400 and 600 cm^{-1}. The ν_1 mode was observed at 1098 cm^{-1}

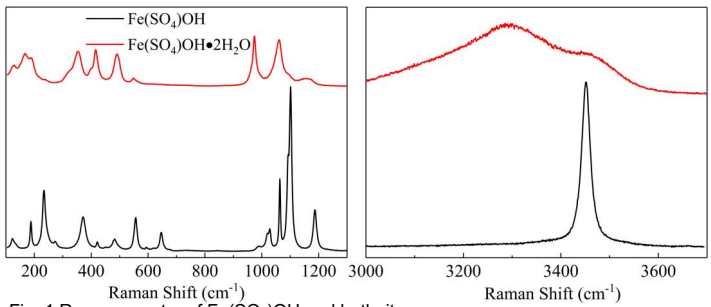

Fig. 1 Raman spectra of $Fe(SO_4)OH$ and butlerite

in the spectrum of $Fe(SO_4)OH$ and 1024 cm^{-1} in butlerite, with ν_3 modes at 1186, 1101, and 1062 cm^{-1} for $Fe(SO_4)OH$, and at 1109 and 1224 cm^{-1} for butlerite. Raman peaks of butlerite at 405 and 468 cm^{-1}, and shoulders at 373 and 450 cm^{-1} are assigned to $\nu_2(SO_4)^{2-}$ symmetric bending vibrations [18]. The 645 cm^{-1} peak in $Fe(SO_4)OH$ and 601 and 542 cm^{-1}in butlerite are assigned to their $\nu_4(SO_4)^{2-}$ asymmetric bending mode. Raman peaks appeared between 300 and 150 cm^{-1} are assigned to the Fe-O and Fe-OH stretching and lattice vibration modes, e.g., 186 and 232 cm^{-1} in $Fe(SO_4)OH$ and 184, 221 and 242 cm^{-1} in butlerite.

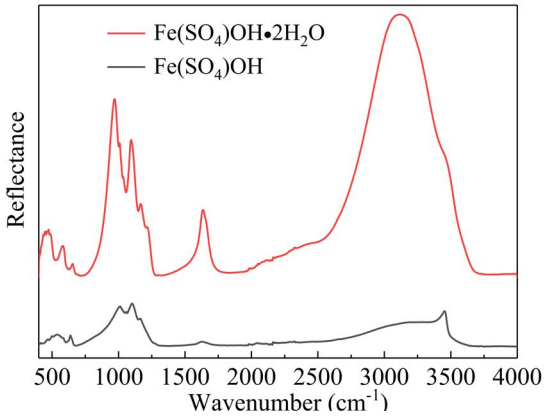

Fig. 2 Infrared spectra of $Fe(SO_4)OH$ and butlerite

The strong and wide Mid-IR band (3126 cm^{-1}) and shoulder (3455 cm^{-1}) of butlerite in H_2O/OH spectral region were assigned to the vibrations of its structural H2O molecules[18]. $Fe(SO_4)OH$ has a narrow single OH peak (3455 cm^{-1}), connected to a broad shoulder due to the absorbed H_2O in the sample. Butlerite has a strong H_2O bending mode at 1636 cm^{-1}. $\nu_3(SO_4)^{2-}$ (triple degenerated) band consists five sub-peaks at 1035, 1097, 1124, and 1218 cm^{-1} in butlerite, and 1054, 1100, and 1164 cm^{-1} in $Fe(SO_4)OH$. The $\nu_1(SO_4)^{2-}$ feature occurs at 1005 and 969 cm^{-1} in $Fe(SO_4)OH$ and in butlerite respectively. The $\nu_4(SO_4)^{2-}$ mode could be seen at 652 and 579 cm^{-1} in butlerite and 636 cm^{-1} in $Fe(SO_4)OH$.

The VNIR spectra of $Fe(SO_4)OH$ and butlerite [$Fe(SO_4)OH{\cdot}2H_2O$] are normally contributed by overtones, combinational modes of H_2O & OH groups, and the Metal-OH stretching (Fig. 3). For $Fe(SO_4)OH$, the absorptions at 1489, 1833, 2237, and 2384 nm are very narrow, matching well with the narrow OH fundamental stretching mode seen in Raman and MIR spectra (3452 cm^{-1}). The spectral band centered at 428 and 954 nm are attributed to Fe^{3+} electronic transitions[20]. For butlerite, the feature at 2241 nm is assigned to OH combination stretching plus bending vibration mode. The H_2O stretching overtone and combination band of butlerite are at 1476 and 1502 nm, and at 1960 and 2026 nm[20].

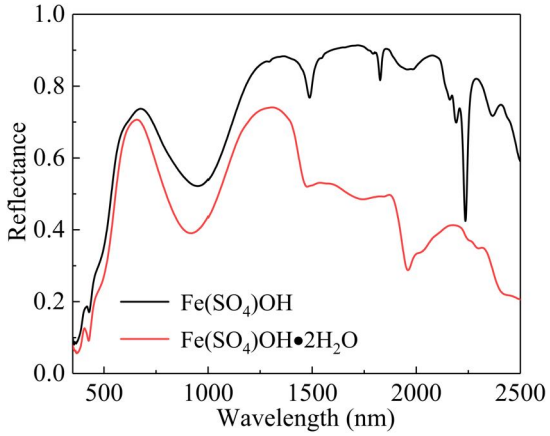

Fig. 3 VNIR spectra of $Fe(SO_4)OH$ and butlerite

Further work: We are going to keep working on the synthesis of fibroferrite-group and to characterize them with Raman, Mid-IR and VNIR. The investigations on the phase transformation pathways of fibroferrite-group will provide some assistance for interpreting the future Mars mission observations

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