Poster

Crystal structure and phase transition in orthorhombic $FeSO_4OH$

G. Giester[1], D. Talla[1], J.M. Meusburger[2], J.L. Bishop[3], M. Wildner[1]

[1]*Institut für Mineralogie und Kristallographie, Universität Wien, Josef-Holaubek-Platz 2, A-1090 Wien, Austria*

[2]*NASA Ames Research Center, P.O. Box 1 Moffett Field, CA 94035-1000, USA*

[3]*SETI Institute, 339 Bernardo Ave, Suite 200, Mountain View, CA 94043, USA*

gerald.giester@univie.ac.at

The presence of hydrated sulfate phases on the surface of Mars has been firmly established after their discovery in Martian soils by the Viking landers in the 1980's. Since then, much has been understood about their role, such as their influence on the water budget at equatorial latitudes of Mars. Their ability to repeatedly rehydrate and dehydrate – based on the surrounding humidity and temperature levels – enables temporary H_2O storage [1]. Recently, iron hydroxysulfates have been attributed to unusual spectral features near 2.23 and 2.4 µm observed in CRISM spectra of small outcrops in sulfate-rich regions of Juventae Chasma, Capri Chasma and Aram Chaos [2-4]. These correspond to bands present in vibrational spectra of the basic sulfate of ferric iron.

$Fe^{3+}SO_4OH$, obtained by hydrothermal reaction at 200 °C, had been described [5] to crystallize in the orthorhombic space group *Pnma*. Later, a dehydration product of metahohmannite, $Fe^{3+}{}_2(H_2O)_4O(SO_4)_2$, was examined by synchrotron powder diffraction [6], indicating an OD-polytype of $FeSO_4OH$ with monoclinic space group $P2_1/c$. Recently, the symmetry was revised to $C2/c$ evaluating new X-ray and neutron powder diffraction data [7,8]. The present single-crystal X-ray diffraction study was done on needle-shaped crystals (Fig. 1a) synthesized at conditions similar to those reported by [5]. Data were collected at room temperature, 200 and 100 K, each proving orthorhombic symmetry with unit cell parameters close to 7.3, 6.4 and 7.1 Å. The RT data are consistent with the *Pnma* structure model [5]. However, upon cooling the symmetry is reduced to space group $P2_12_12_1$, coupled by inversion twinning with roughly equal proportions of components. The loss of the mirror plane allows the coordination polyhedra to tilt slightly, probably triggered by the hydrogen bonding system. While at room temperature a symmetric bifurcated H-bond is present with O···O=3.077 Å (2×), it splits to 2.984/3.162 Å and 2.953/3.176 Å at 200 and 100 K, respectively (Fig. 1b,c). Refinement of the LT data in $P2_12_12_1$ significantly improves the *R*-indices (e.g. *R*1 at 100 K from 0.095 to 0.013) and reduces residual electron densities (from 6.7 to 0.4 e Å^{-3}) compared to solutions in *Pnma*, despite only moderate changes in the structure. Band splittings in low-temperature FTIR spectra indicate a *Pnma*→$P2_12_12_1$ transition temperature of 216 K, i.e. well within the diurnal cycle in the equatorial region of Mars.

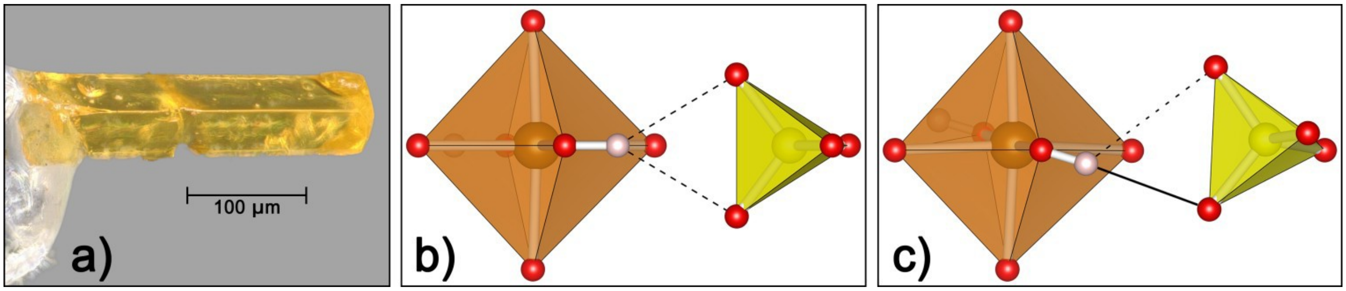

Figure 1. **a)** Crystal of $FeSO_4OH$; Structure detail **b)** at room temperature, space group *Pnma*; **c)** at 100 K, space group $P2_12_12_1$.

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This work was supported by the Austrian Science Fund (FWF) grant-in-aid number P34227-N.