

Spectroscopic, structural and computational study of guyanaite, β -CrOOH

Sandro Jahn¹, Bernd Wunder¹, Monika Koch-Müller¹, Anke Watenphul², Michael N. Taran³

¹Deutsches GeoForschungsZentrum GFZ, Section 3.3, Potsdam, Germany

²Deutsches Elektronen-Synchrotron, HASYLAB, Hamburg, Germany

³Institute of Geochemistry, Mineralogy and Ore Formation, National Academy of Science of Ukraine, Kyiv, Ukraine

Guyanaite, β -CrOOH, is a chromium oxyhydroxide with a structure similar to the high pressure δ -AlOOH or ϵ -FeOOH phases. Christensen (1966) performed the first structure refinement of β -CrOOH from x-ray powder diffraction data and suggested an orthorhombic space group $Pnmm$ with cell-dimensions $a = 4.861 \text{ \AA}$, $b = 4.292 \text{ \AA}$, $c = 2.960 \text{ \AA}$. The structure is based on a near-ideal hexagonal closest packing of oxygen atoms parallel to (101). Edge-sharing CrO_6 -octahedra form chains along the direction [001], which are connected via oxygen-corners, thus forming layers of octahedra parallel to (101). To resolve the hydrogen positions in the structure, neutron powder diffraction experiments were performed by Christensen et al. (1976) and Fujihara et al. (2002). From these studies, three hydrogen-bonding models were derived: (1) a fully disordered hydrogen bond model (space group $Pnmm$), (2) a symmetric hydrogen bond model (space group $Pnmm$) and (3) an asymmetric hydrogen bond model (space group $P2_1nm$). For all three models, extremely short O...H.....O distances of about 2.472 \AA are obtained (Fujihara et al. 2002). Taken the correlation of O-H stretching frequencies and hydrogen bond lengths in minerals (Libowitzky, 1999), the frequency of the corresponding O-H stretching band would be between 1300 and 1400 cm^{-1} .

Here, we use spectroscopic techniques in combination with first-principles simulation methods to further investigate the structure and the nature of hydrogen bonding in β -CrOOH. Single-phase samples were synthesized in piston-cylinder and multi-anvil press experiments at conditions ranging from 4.0 GPa at 600°C to $13.5 \text{ GPa}/1100^\circ\text{C}$. Rietveld refinement of the x-ray powder diffraction data yielded structural parameters consistent with earlier studies. The diffuse optical reflectance spectra of the synthesized β -CrOOH samples in the visible and NIR ranges, ca. $5000 - 30000 \text{ cm}^{-1}$ are rather typical of Cr^{3+} -bearing minerals and compounds. FTIR spectra, taken in the range of $4000 - 450 \text{ cm}^{-1}$ show as the highest-energy absorption feature a broad and intense mountain-like band complex from about 1800 down to 800 cm^{-1} with a sharp peak at 1421 cm^{-1} followed by a relatively sharp band around 580 cm^{-1} . The absence of absorption features above about 2000 cm^{-1} confirms the strong hydrogen bonding with almost symmetrized O-H-O bonds. First principles DFT simulations confirm these observations. At $T=0 \text{ K}$, β -CrOOH is found to be antiferromagnetic. Both LDA and GGA exchange-correlation functionals predict almost identical total energies for models (2) and (3) using the experimental unit cell volume. The calculations suggest almost complete hydrogen bond symmetrization already close to room pressure. This is in contrast to δ -AlOOH, where hydrogen bond symmetrization is predicted at much higher pressures (Tsuchiya et al., 2008; Sano-Furukawa et al., 2009). Finally, we use frequency spectra obtained from first-principles molecular dynamics simulations to interpret bands in the FTIR absorption spectra.

References:

Christensen A.N. (1966), *Inorganic Chemistry*, 5, 1452-1453.

Christensen A.N. et al. (1976), *Journal of Solid State Chemistry*, 19, 299-304.

Fujihara T. et al. (2002), *Journal of Physics and Chemistry of Solids*, 63, 309-315.

Libowitzky E. (1999), *Monatshefte für Chemie*, 130, 1047 – 1059.

Sano-Furukawa A. et al. (2009), *American Mineralogist*, 94, 1255-1261.

Tsuchiya J., Tsuchiya T., Wentzcovitch R.M. (2008), *American Mineralogist*, 93, 477-482.