SINGLE-CRYSTAL IR SPECTROSCOPY OF MeO(OH) MINERALS (Me = Al, Fe, Mn)

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Single-crystals of diaspore, AlO(OH), goethite, FeO(OH), and manganite, MnO(OH), as well as polycrystalline groutite, MnO(OH), were investigated by Fourier transform infrared spectroscopy (FTIR). Whereas goethite and groutite crystallize in the diaspore structure, manganite builds up a structure similar to that of rutile. The positions of the OH groups are, however, similar and facilitate direct comparison of the results. Measurements were performed on a Nicolet 60SX FTIR spectrometer, using polarized radiation and oriented sample sections. Extremely small sample fragments were investigated on a Nic-Plan FTIR microscope. Low-temperature data were collected in a commercial vacuum cryo-cell at 82°K. Because of the high water contents of the samples (10 to 15 wt-% H_2O), crystal sections had to be polished extremely thin. Using diamond films, sample thicknesses between 2 and 6 µm were obtained. Samples were glued to a carrier only during preparation. After the polishing process they were dissolved from the carrier and measured as unsupported platelets on a metal aperture.

The spectra (e.g. goethite, Fig. 1) show the following general features (the detailed peak positions are, of course, different in the various minerals). The OH stretching frequency is observed at ~ 3100 cm. According to the orientation of the OH vectors in the structure, the band is most intense parallel to *a*, and weaker parallel to *b*. The *c* direction only shows interference fringes from the extremely thin (2.5 µm), doubly polished platelet. Even though the sample is so thin, the band in the a spectrum is slightly truncated. The bending modes of the OH groups appear in the region between 800 and 1000 cm^{-1}. Components of the »in-plane« bending are observed parallel to *b*, and (very weak) parallel to *a*. The »out-of-plane« bending mode occurs in the *c* spectrum. The two weak bands at approximately 1650–1800 cm^{-1} are the first overtones of the OH deformation modes enhanced by resonance with the OH stretching modes. Whereas the spectra of the three diaspore-type minerals are very similar, the spectrum of manganite shows a stronger component of the »in-plane« bending mode parallel to *a*. This results also in the observation of three deformation bands in the powder spectrum.

Comparison of the spectra shows the following features. The frequencies of the OH stretching modes are in good agreement with the respective O-H···O distances of the hydrogen bonds (NOVAK, 1974). The O-H···O distances decrease from ~ 2.70 Å (goethite) via ~ 2.65 Å (diaspore) to ~ 1.58–1.60 Å (manganite and groutite) which correlates with a frequency shift from ~ 3100, via ~ 2950, to 2650–2700 cm^{-1}. The decrease of the stretching frequencies is also correlated with an increase of the frequencies of the deformation modes. This behavior is also confirmed at low temperatures. With decreasing temperatures the stretching frequencies are shifted to lower values, those of the bending modes to higher values. The intensities of the first overtones of the deformation modes deserve also some attention. Whereas they are weak in goethite, they increase up to manganite and groutite (where they are almost as strong as the stretching mode) with decreasing OH stretching frequency. This is explained by an increasing anharmonicity of the vibration with increasing strength of the hydrogen bond, which results in an increased resonance interaction between the bending overtone and the stretching vibration.

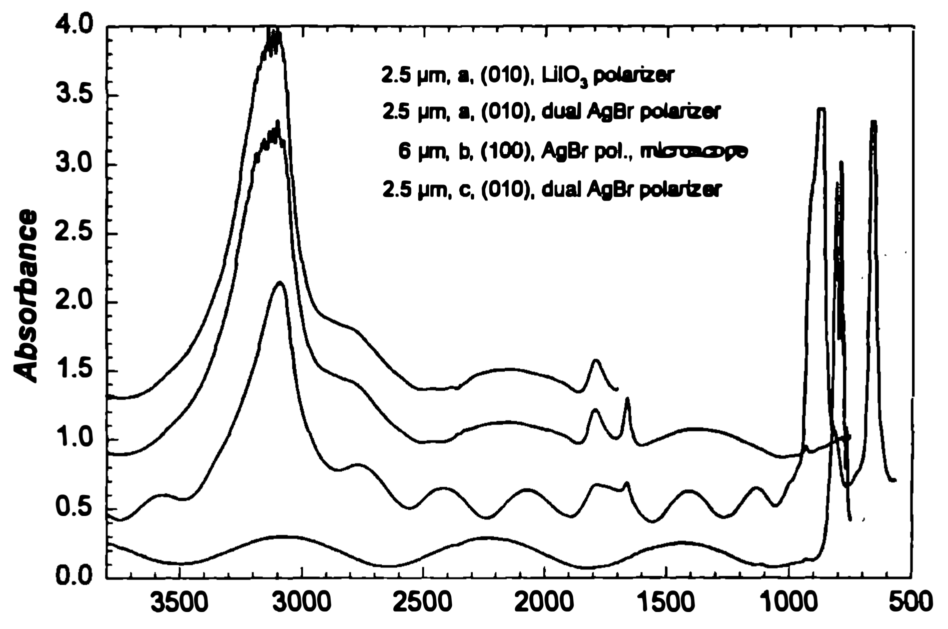

Fig. 1:
Polarized single-crystal IR spectra of goethite. Spectra are vertically offset.

NOVAK, A. (1974): Hydrogen bonding in solids. Correlation of spectroscopic and crystallographic data. - Struct. Bond., 18, 177–216.