

Polarised absorption spectra of wulfenite in the OH vibrational and UV-Vis spectral regions

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Infrared spectroscopy has become the most widely used method for detecting traces of hydrogen bonded to oxygen. Polarised IR spectroscopy provides an excellent method for the characterisation of structurally incorporated OH or H₂O defects; on the other hand this method presents a very useful tool for the identification of extremely fine-grained (submicroscopic) included hydrous mineral phases. The polarised IR absorption spectra in the high-energetic OH fundamental region of varicoloured wulfenite (PbMoO₄) crystals from different localities are characterised by a relatively sharp band at 3380 cm⁻¹, that is strongly polarised perpendicular to the *c*-axis, and by a broad band centred at around 3150 cm⁻¹, weakly polarised with slightly stronger absorption parallel to the *c*-axis. In different samples the intensity ratio of these two bands differs widely.

Heating experiments performed on crystal slabs show a decrease of the 3380 and 3150 cm⁻¹ band intensities with increasing temperature. Heating to 500 °C causes both bands to disappear. A very weak band at 2345 cm⁻¹, assigned to the presence of CO₂, intensifies to a dominant absorption band after heating to 500 °C. Deuteration experiments performed at 300 °C produce OD absorption bands at 2500 and 2330 cm⁻¹ which are related to the 3380 and 3150 cm⁻¹ bands by the usual OH/OD wavenumber factor of 1.35.

Optical absorption spectra of wulfenite crystal slabs are dominated by a polarised absorption edge. Perpendicular to the *c*-axis, the apparent onset of this edge is found around 25000 cm⁻¹ in colourless samples, and gradually shifts into the visible spectral region in brownish-yellow, yellow, orange, and orange-red crystals, in the latter case with an onset at around 17000 cm⁻¹. Parallel to the *c*-axis, the respective edges occur at higher energies by roughly 1000 cm⁻¹, thus resulting in a distinct pleochroic behaviour of coloured wulfenite crystals. Additional minor spectral features are related to samples from specific localities, *e.g.* absorption bands due to Nd³⁺ in wulfenite from the Red Cloud Mine, Arizona, or a weak broad band at ~14000 cm⁻¹ in some samples from Mežica, Slovenia.

Preliminary measurements on very thin platelets (~10 µm) of orange-red samples show, however, that the above-mentioned “absorption edge” is actually caused by a broad pre-edge band centred around 23000 (⊥*c*) and 23800 cm⁻¹ (//*c*), probably related to small contents of Cr⁶⁺ replacing Mo in tetrahedral coordination.

In some crystal parts, scanning electron microscopy reveals a porous structured surface and extremely fine-grained inclusions only rich in Fe or in Zn. The appearance of the CO₂ band argues for the presence of siderite and smithsonite as included carbonate phases. Low but strongly varying amounts of S, As and P, detectable by electron microprobe, could be indicative of the presence of included submicroscopic hydrous sulphate, arsenate and/or phosphate phases which determine the absorption behaviour of wulfenite in the OH stretching vibrational region. Minerals of the alunite-beudantite-crandallite family, crystallising in the trigonal system, are promising candidates. Especially (plumbo)jarosite shows great similarities in its OH powder spectrum with the OH spectrum of wulfenite single-crystals. The pleochroism of the band at 3380 cm⁻¹ could be indicative of an oriented intergrowth of this mineral phase with wulfenite, resulting in a common *c*-axis direction. This assignment suggests the presence of (plumbo)jarosite as a very minor but specific component of wulfenite, occurring in samples from different localities and paragenesis. However, besides an assignment to oriented included hydrous phases, the low-energetic pleochroic absorption band around 3150 cm⁻¹, requires a discussion of the presence of ‘intrinsic’ OH defects, inherent to the crystal structure of wulfenite.