

OH absorption coefficients of rutile and cassiterite deduced from nuclear reaction analysis and FTIR spectroscopy

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Summary

The OH content of four rutile and two cassiterite single-crystals was studied by nuclear reaction analysis (NRA) and by polarised FTIR microspectroscopy. The OH absorption bands of both minerals are centered around 3300 cm^{-1} with different absorption features. The analytical H_2O content determined by NRA ranges from 70 to 820 wt.ppm. The integrated molar absorption coefficients deduced from the total integrated OH absorbances are equal to $38000\text{ l}\cdot\text{mol}^{-1}\text{H}_2\text{O}\cdot\text{cm}^{-2}$ for rutile and $65000\text{ l}\cdot\text{mol}^{-1}\text{H}_2\text{O}\cdot\text{cm}^{-2}$ for cassiterite. For both minerals the absorption coefficients are significantly smaller than those expected from the linear calibration curves given by *Paterson* (1982) and by *Libowitzky* and *Rossmann* (1997).

Zusammenfassung

OH-Absorptionskoeffizienten von Rutil und Cassiterit ermittelt durch Kernreaktions-Analyse und FTIR Spektroskopie

Der OH-Gehalt von vier Rutil- und zwei Cassiterit-Einkristallen wurde mittels Kernreaktions-Analyse (NRA) und polarisierter FTIR Mikrospektroskopie untersucht. Die OH Absorptionsbanden beider Minerale sind um 3.300 cm^{-1} zentriert, mit unterschiedlichen Absorptionserscheinungen. Der analytische H_2O -Gehalt, der mit NRA bestimmt wurde, schwankt von 70 bis 820 Gew.ppm. Die integrierten molaren Absorptionskoeffizienten, die auf den gesamten integrierten OH-Absorptionen basieren, betragen etwa $38.000\text{ l}\cdot\text{mol}^{-1}\text{H}_2\text{O}\cdot\text{cm}^{-2}$ für Rutil and $65.000\text{ l}\cdot\text{mol}^{-1}\text{H}_2\text{O}\cdot\text{cm}^{-2}$ für Cassiterit. Für beide Minerale sind die Absorptionskoeffizienten signifikant kleiner als

die, die auf Grund der linearen Kalibrationskurven von *Paterson* (1982) und *Libowitzky* und *Rossmann* (1997) zu erwarten sind.

Introduction

Nominally anhydrous minerals (NAMs) are known to contain trace amounts of hydrogen, mostly in the form of hydroxyl groups. The physical and chemical properties of numerous NAM phases are influenced by trace amounts of hydrogen to an extent that is far out of proportion to its low concentration. These properties include melting behaviour, mechanical strength, and electrical conductivity (*Rossmann*, 1990).

The commonly used method for determining the H content of NAMs is IR spectroscopy which detects the absorptions caused by the stretching vibrations of OH groups. For converting the measured absorbance values (A) into absolute H₂O concentration values (c), the molar OH absorption coefficient (ϵ) for the mineral in question has to be known. The basis of the quantitative IR spectroscopic determination is the “Lambert-Beer’s law” in the form $c = A/\epsilon$, wherein the absorption coefficient $a = A/t$ (t is the thickness of the measured crystal plate). The determination of ϵ for calibrating IR spectroscopy requires a measurement of the absolute H (H₂O) content of at least one sample of the respective mineral ($\epsilon = a/c$).

In the past, thermal extraction methods have been mostly used for this purpose with the shortcoming of a relatively large amount of sample material which is needed to reduce the uncertainty of the extracted amount of water to an acceptable level. In many cases it is a difficult task to separate adequate amounts of sample material which is absolutely free of hydrous impurities. It may also be difficult to ascertain that all hydrogen has been extracted. As an alternative method, nuclear reaction analysis (NRA) has been employed (*Lanford*, 1992). Similar to thermal extraction, NRA is insensitive to the nature of chemical bonding and to matrix effects, provided that channeling is avoided, since just the concentration of protons is determined. An advantage of this method is that the amount of sample material may be much smaller than that for thermal extraction. Following an early application to garnets (*Rossmann et al.*, 1988), NRA was also applied to the determination of OH concentrations in natural titanite (*Hammer et al.*, 1996).

In the work reported here we used this method in combination with FTIR microspectroscopy for the determination of molar OH absorption coefficients for rutile, TiO₂, and cassiterite, SnO₂. Previously, a calibration for rutile has been obtained using thermal extraction by means of a moisture evolution analyser on a single sample (*Hammer and Beran*, 1991) and an earlier calibration was based on mass changes associated with H/D exchange affected by hydrothermal treatment (*Johnson et al.*, 1973). The ϵ values deduced from these two studies differ greatly so that a new calibration attempt seems desirable. For cassiterite which is isostructural to rutile, no previous determination of the molar OH absorption coefficient has been yet proposed.

Experimental

Samples

Rutile and cassiterite single-crystals of gem quality were used for the combined measurements. Rutile sample R5 originates from an unknown locality in Brazil,

Table 1. Analytical and spectroscopic data of OH-bearing rutile and cassiterite. The mean position of the OH absorption bands in rutile (R samples) and cassiterite (C samples) is 3300 cm^{-1} , t is the thickness of the crystal plates used for the measurements. All values are related to analytical H_2O : c concentration (standard deviations in round brackets), a_i integrated absorption coefficient ($a_i = A_i/t$), ε_i integrated molar absorption coefficient ($\varepsilon_i = a_i/c$)

Sample no.	t in cm	c in wt.ppm	c in $\text{mol} \cdot \text{l}^{-1}$	a_i in cm^{-2}	ε in $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-2}$
R5	0.0662	70(8)	0.017(2)	619	36000
R5a	0.0735	330(30)	0.078(7)	1810	23000
R6	0.0495	820(80)	0.190(20)	7300	38000
R7a	0.0639	270(30)	0.064(7)	2540	40000
CC	0.0486	170(20)	0.066(8)	4330	66000
CZ	0.0974	160(15)	0.062(6)	4060	65000

samples R5a and R6 come from the Brazilian localities Capao do Lana and Campo, respectively; sample R7a is from Millhollands Mill, Alexander Co., North Carolina. The cassiterite samples CC and CZ are from the famous localities of Cornwall and Zinnwald, respectively.

Sample preparation consisted of orienting isolated crystals or crystal fragments by morphology and optical methods, followed by preparing crystal slabs polished parallel to the c -axis. Mineral surfaces, free from internal cracks and solid impurities are required for NRA. For the IR spectroscopic measurements plane parallel, self-supporting crystal plates were prepared using a low-speed diamond saw. The accurate thicknesses of the crystal slabs, ranging from about 0.05 to 0.10 cm, are given in Table 1. Under the optical microscope the selected gem-quality samples proved to be free from inclusions and impurities. The maximum angular deviation of the polished slabs from the ideal orientation is estimated to be $\pm 2^\circ$.

NRA

The NRA method used here, as in previous investigations, is based on the resonant reaction $^1\text{H} (^{15}\text{N}, \alpha, \gamma) ^{12}\text{C}$. The sample is bombarded with a beam of high-energy ^{15}N ions and the presence of hydrogen is indicated by gamma-rays of energy 4.43 MeV emitted from the sample. The H concentration versus depth (hydrogen depth profile) in a sample is obtained by measuring the gamma-ray yield versus the ^{15}N beam energy which is increased stepwise beginning at the resonance energy of 6.385 MeV. Depths up to about $2\ \mu\text{m}$ can be probed, the limit depending on the sample material and density.

The ^{15}N beam was produced by the 7 MV Van-de-Graaff accelerator of the Institut für Kernphysik in Frankfurt am Main. The experimental set-up was an improved version of the set-up for high-sensitivity hydrogen detection described by *Endisch et al.* (1994). It is equipped with an ion gun for in-situ sample cleaning and with a modified sample holder which allows accurate positioning of the samples relative to the ion beam. Samples with a diameter down to about 1 mm can be

analysed. For the profiling measurements the samples were wrapped in Al foil except for an area somewhat larger than the diameter of the ion-beam spot. In this way charge build-up by the ion beam could be reduced to a level at which no sparking occurred and the measurement of the beam current was not affected. Previously to the start of a profiling measurement the sample was bombarded with ^{15}N ions, usually at 8 MeV, to an ion dose of $10^{15}/\text{cm}^2$. As observed in channeling experiments, after such a dose the crystalline structure is destroyed to a sufficient degree so that the gamma-ray yield in the subsequent profiling experiment will not be influenced by channeling effects.

As noted above, the NRA analysis probes only to a limited depth. Therefore, in order to ascertain that the result of a profiling measurement is representative for the bulk value, all samples were analysed a second time after polishing off about 20 μm , and the samples R5a, R6, and R7a were analysed a third time after a sputter treatment which resulted in a further removal of about 0.5 μm .

The gamma-ray yields from the profiling measurements were converted into H concentration values and H_2O weight fractions, respectively. The detection efficiency (η) of the experimental set-up needed for this conversion is generally determined by using a H containing reference material of well-defined composition. The material used was the polymer Kapton[®] ($\text{C}_{22}\text{H}_{10}\text{O}_5\text{N}_2$) in the form of a foil with a thickness of 100 μm . The ^{15}N ion energy was set to a value of 8 MeV so that the resonance energy was reached well below the surface. Since this material loses hydrogen under ^{15}N bombardment (about 2% per 10^{13} ions/ cm^2), for obtaining the true gamma-ray yield of the standard, repeated measurements with small ion doses were done and the measured yield curve was extrapolated to dose zero. The reproducibility of η determined in this way was better than 3%. The conversion of the gamma-ray yields also involves the stopping cross sections of ^{15}N ions in the reference material and in the sample material. Their errors, calculated on the basis of semi-empirical formulae (Ziegler, 1980), were about 5%. Thus, the conversion of the gamma-ray yields carries a systematic error of 8%, arising from (quadratically adding) the errors of the stopping cross sections and the error of η .

IR spectroscopy

Polarised single-crystal spectra were recorded from 4000 to 2500 cm^{-1} with a Perkin-Elmer FTIR spectrometer 1760X which was equipped with a CsI microfocus accessory, and a gold-wire grid polariser with an extinction ratio better than 1:100. Light intensities, emitted by a ceramic light source, were measured with a TGS detector. Background and sample spectra were obtained from 64 scans each in air and in the sample crystal, with 4 cm^{-1} resolution. Although the information depths of the two methods are quite different, the diameter of the circular measuring area was chosen according to the dimension of the NRA measuring field and amounts to 1 mm. The data handling was managed by the program IRDM.

Results

Typical hydrogen depth profiles measured on rutile and cassiterite samples are shown in Fig. 1 a and b, respectively. High-lying data points near zero depth arise

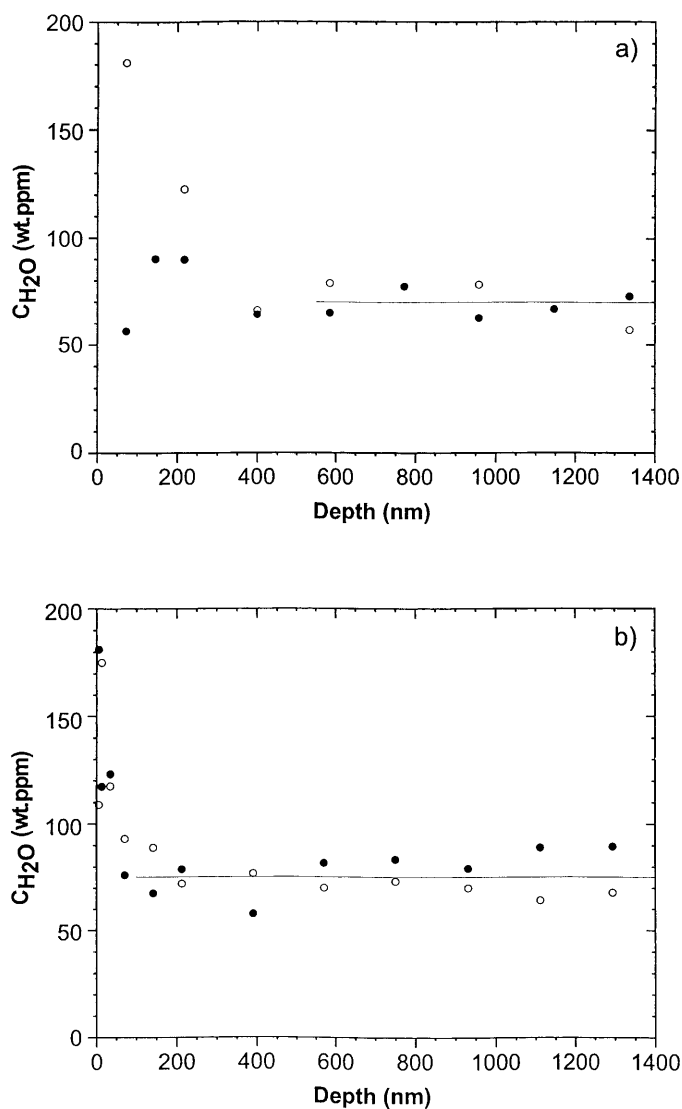


Fig. 1. Hydrogen depth profile of **a** rutile sample R5, **b** cassiterite sample CZ. The open and full circles denote data from the first and second profiling measurement, respectively. The line indicates the depth range that was used for averaging

from water adsorbed at and partly incorporated beneath the surface and were omitted from further evaluation. At larger depths the data points of a given profile indicate a uniform concentration, taking into account the statistical uncertainties. As demonstrated in Fig. 1 the profiles obtained in different measurements of a given sample agree rather well on average. Therefore, to deduce the H_2O concentration of a sample, all data points from the two (all samples) respective three profiling measurements (only samples R5a, R6, R7a) were averaged, thus reducing the statistical error. The concentration values obtained in this way are listed in Table 1 in units of wt.ppm H_2O and mole H_2O per liter. The listed errors were calculated by quadratically adding the systematic error of 8% described above and the statistical error for the respective sample (R5: 8%, R5a: 4%, R6: 6%, R7a: 8%, CC: 9%, CZ: 5%).

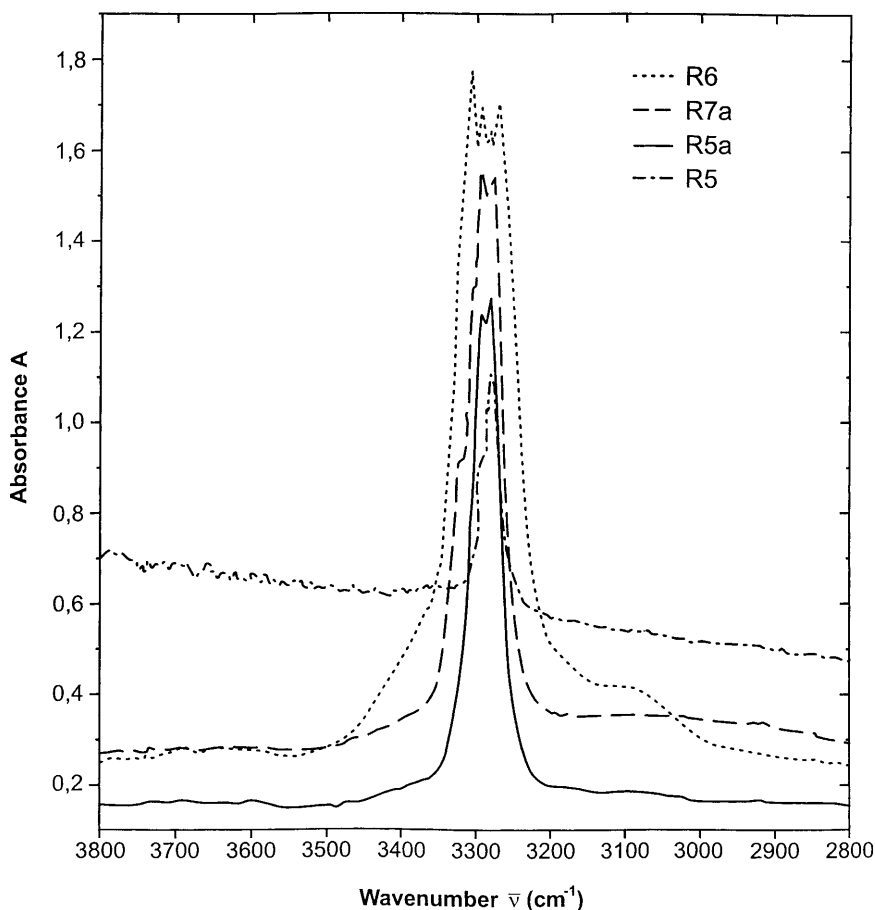


Fig. 2. Polarised single-crystal spectra in the OH stretching vibrational range of the rutile samples, with the electric vector of the polarised IR radiation vibrating perpendicular to the *c*-axis. The thicknesses of the measured crystal slabs are given in Table 1

The presence of OH in rutile and cassiterite from natural occurrences was established by *Beran and Zemmann* (1971) on the basis of IR spectroscopy. Rutiles are characterised by an absorption band centered in the 3300 cm^{-1} region, cassiterites reveal a doublet band with maxima at around 3250 and 3350 cm^{-1} . The OH absorption bands are strongly pleochroic. Maximum absorption occurs when the electric vector of the polarised IR radiation vibrates perpendicular to the tetragonal *c*-axis, thus indicating OH groups at the oxygen-site oriented approximately perpendicular to the plane of the three coordinating Ti-, and Sn-atoms, respectively (*Beran and Zemmann*, 1971; *Vlassopoulos et al.*, 1993).

The polarised OH absorption spectra of the rutile samples with the electric vector of the IR radiation vibrating perpendicular to the *c*-axis are represented in Fig. 2 and those of the cassiterite samples in Fig. 3. Integrated absorbance values (A_i in cm^{-1}) were obtained by integrating over the measured spectra, with baselines determined from the flat parts of the spectra. This results in a spectral region ranging from 3550 to 3050 cm^{-1} which defines the slope of the linear baseline. The

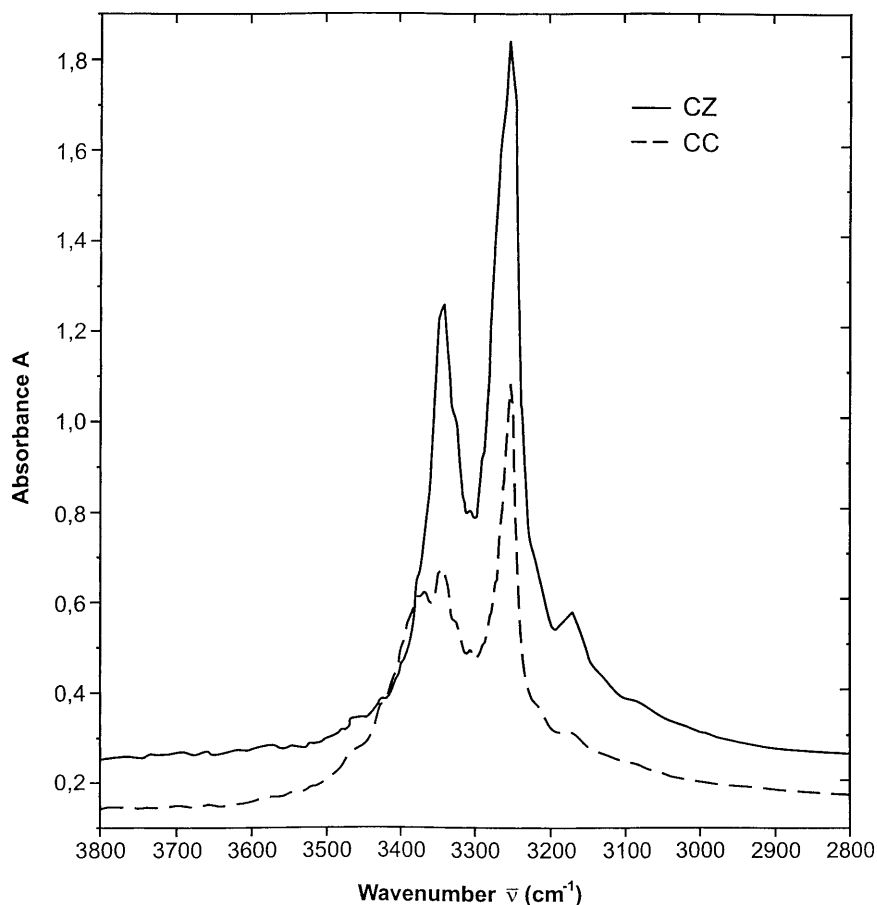


Fig. 3. Polarised single-crystal spectra in the OH stretching vibrational range of the cassiterite samples, with the electric vector of the polarised IR radiation vibrating perpendicular to the *c*-axis. The thicknesses of the measured crystal slabs are given in Table 1

integrated absorbance values measured parallel to the three orthogonal (tetragonal) axes were summed up to get the total integrated absorbance value which was used for the calculation of the integrated absorption coefficient a_i ($A_{i \text{ total}} = 2A_{i \text{ perpendicular to } c} + 1A_{i \text{ parallel to } c}$). Due to the strongly preferred orientation of the OH groups perpendicular to the *c*-axis, the integrated absorbances measured parallel to the *c*-axis were extremely small (practically zero) compared to those measured perpendicular to the *c*-axis. The integrated absorption coefficients a_i (in cm^{-2}) were calculated according to the relation $a_i = A_{i \text{ total}}/t$.

The integrated molar absorption coefficients $\varepsilon_i = a_i/c$ (in $1 \cdot \text{mol}^{-1} \text{H}_2\text{O} \cdot \text{cm}^{-2}$) calculated from the measured a_i and $c_{\text{H}_2\text{O}}$ values (see above) are given in Table 1. Their relative error is mainly determined by the error of the $c_{\text{H}_2\text{O}}$ values. There is a good agreement between three of the rutile samples, while sample R5a deviates significantly from the main trend; its ε_i value is not compatible with the others. This deviation of sample R5a is probably caused by OH inhomogeneities which

by chance led to increased $c_{\text{H}_2\text{O}}$ values in the NRA measurements. Under this assumption it is reasonable to omit this sample from further considerations. The ε_i values for the samples R5, R6, and R7a may be combined to calculate the integrated molar absorption coefficient for rutile, which gives $\varepsilon_i = 38000 + / -4000 \text{ l} \cdot \text{mol}^{-1}_{\text{H}_2\text{O}} \cdot \text{cm}^{-2}$.

The two cassiterite samples have nearly the same water content and also the integrated absorption coefficients are very similar. The ε_i values agree nicely, resulting by the same kind of calculation in an average value of $\varepsilon = 65000 + / -6000 \text{ l} \cdot \text{mol}^{-1}_{\text{H}_2\text{O}} \cdot \text{cm}^{-2}$.

Discussion

For a comparison with previously determined ε_i values for rutile, one must take into account that they have been obtained by using unpolarized IR radiation. In the study of *Hammer and Beran (1991)* a value of $6540 \text{ l} \cdot \text{mol}^{-1}_{\text{H}_2\text{O}} \cdot \text{cm}^{-2}$ was obtained on crystal plates cut parallel to the c-axis. Following the formula of *Paterson (1982)* this value must be divided by the orientation factor $\gamma = 1/4$ for normalisation, which results in $26200 \text{ l} \cdot \text{mol}^{-1}_{\text{H}_2\text{O}} \cdot \text{cm}^{-2}$ which is about 45% lower compared to the value of the present work. In a detailed study of the polarisation behaviour of IR absorption bands, *Libowitzky and Rossman (1996)* state that it is not possible (or only within a limited range) to determine correct absorbance values in anisotropic crystals by use of unpolarised IR radiation. Since four samples were used in the present work performed with polarised radiation, instead of one sample in *Hammer and Beran (1991)*, we consider the new value more reliable. In the study of *Johnson et al. (1973)*, the c-axis was oriented normal to the sample surface, so the orientation factor is $\gamma = 1/2$ (*Paterson, 1982*), and the normalised value is $60400 \text{ l} \cdot \text{mol}^{-1}_{\text{H}_2\text{O}} \cdot \text{cm}^{-2}$. This is about 60% higher than the new value.

It is interesting to note that the ε_i values obtained for rutile and for cassiterite are essentially lower than the values following from the IR absorption calibrations given by *Paterson (1982)* and *Libowitzky and Rossman (1997)* for water in minerals. The predicted values from these calibrations are around $150000 \text{ l} \cdot \text{mol}^{-1}_{\text{H}_2\text{O}} \cdot \text{cm}^{-2}$ (from *Paterson, 1982*) and $120000 \text{ l} \cdot \text{mol}^{-1}_{\text{H}_2\text{O}} \cdot \text{cm}^{-2}$ (from *Libowitzky and Rossman, 1997*), respectively for both, rutile and cassiterite, since the positions of the OH bands are practically the same. Thus, there are two more examples, in addition to that of the pyrope discussed in *Libowitzky and Rossman (1997)*, where the correlation between integrated absorbances and OH band position does not hold. The present values strengthen the supposition advanced by these authors that the spectroscopic properties of OH point defects in nominally anhydrous minerals may differ from those of stoichiometric components in hydrous minerals.

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