

## OH in naturally occurring corundum

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**Abstract:** Hydroxide bands arising from intrinsic hydrous defects have been observed in the infrared spectra of 159 corundum crystals from worldwide localities. The OH defects are most prominent in blue sapphire crystals, suggesting an association of OH with redox reactions involving iron. Using a calibration for OH in kyanite, the absolute concentrations for OH in corundum are found to be generally 0.5 wt.ppm or lower. The linear OH absorption coefficient for the most intense band centered at 3310  $\text{cm}^{-1}$  never exceeds 0.5  $\text{cm}^{-1}$ . In addition to the intrinsic OH defects, a number of previously identified hydrous inclusions often contribute to absorptions in the OH stretching region of the corundum infrared spectrum.

**Key-words:** corundum, OH defects, nominally anhydrous minerals, infrared spectroscopy.

### Introduction

While it is now established that trace amounts of OH commonly occur in nominally anhydrous silicate minerals, there have been comparatively few studies of OH in the common oxide minerals. Significant amounts of OH can occur in rutile (Hammer & Beran, 1991; Vlassopoulos *et al.*, 1993; Maldener *et al.*, 2001) and isolated instances of small amounts of OH have been reported in anatase, brookite, cassiterite (Beran & Zemann, 1971; Maldener *et al.*, 2001; Libowitzky & Beran, 2004; Losos & Beran, 2004), and manganese oxides (Potter & Rossman, 1979). Recognizing that there have been several reports of OH in synthetic corundum and occasional reports of OH in natural corundum, we studied naturally occurring corundum representing different varieties and geographic localities to ascertain if OH is a common component of this mineral and to determine the actual amount.

Colored varieties of corundum give us two of our most important gemstones: red rubies and sapphires in a variety of different colors. Large, synthetic single-crystals are grown for a variety of technological applications because, among other reasons, of their superior hardness and optical transmission. Consequently, a variety of studies addressed the infrared (IR) transmission of corundum. In synthetic corundum, OH groups are recognized both as a component of included phases and as a trace component of corundum itself. Belt (1967) described broad absorption bands

combined with several narrow bands in the OH region (3100-3600  $\text{cm}^{-1}$ ) of the IR spectrum of hydrothermally grown ruby and attributed two sharp bands at 3230 and 3180  $\text{cm}^{-1}$  to the presence of monohydrate phases (boehmite, diaspore). Eigenmann *et al.* (1972) described OH bands in Verneuil sapphires at 3310, 3230, 3180 and 3025  $\text{cm}^{-1}$  and Volynets *et al.* (1972) observed OH absorptions in the spectra of Verneuil-grown corundums with sharp bands at 3420, 3310, 3275, 3225 and 3160  $\text{cm}^{-1}$ . Polarized measurements of the sharp bands, now attributed to OH groups incorporated in the corundum structure, indicated that the OH groups causing them are aligned perpendicular to the *c*-axis.

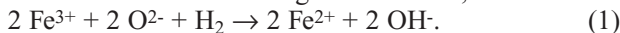
A polarized IR-spectroscopic study of a suite of 22 Verneuil-grown corundums (Beran, 1991) found that variously colored samples show a distinct variability in the region of the OH fundamental vibration. Narrow, strongly polarized OH bands are centered at 3310, 3230 and 3185  $\text{cm}^{-1}$  and are correlated to cation vacancies. Regarding this band as a triplet, two types of spectra are discernible; the type I spectrum is defined by a strong absorption band at 3230  $\text{cm}^{-1}$  whereas the band at 3310  $\text{cm}^{-1}$  is most prominent in type II spectrum. Additional weak bands at 3290  $\text{cm}^{-1}$  occur in (V, Cr, Fe, Ti)-doped "alexandrite" sapphires, weak bands at 3280 and 3160  $\text{cm}^{-1}$  were observed in colorless and light rose corundum. Moon & Phillips (1991) described strong OH bands centered at 3309, 3232 and 3187  $\text{cm}^{-1}$ , and additional weak bands at

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3367 and 3295  $\text{cm}^{-1}$ . The OH defects appear to be correlated to vacant Al sites and to the presence of tetravalent Ti (Moon & Phillips, 1994). Two distinct types of OH absorption bands were reported for hydrothermally treated synthetic sapphires by Kronenberg *et al.* (2000). The first type of bands is characterized by narrow bandwidths and strong polarizations with maximum absorbance measured perpendicular to the *c*-axis. Bands were observed at 3308, 3293, 3278, 3231, 3208, 3183, and 3163  $\text{cm}^{-1}$ . The second type of OH absorption consists of a broad isotropic band centered at 3400  $\text{cm}^{-1}$ , resembling closely the OH bands of hydrothermally grown quartz (Kronenberg, 1994).

A plausible model of OH incorporation, based on polarized measurements, was developed under the assumption of an incomplete occupancy of the cation positions. Assuming vacancies ( $V_{\text{Al}}$ ) in the Al lattice, in a model developed by Beran (1991), the OH dipole oriented perpendicular to the *c*-axis is coordinated to two Al atoms forming groups of face-sharing  $\text{Al}_2(\text{OH})\text{O}_8$ -double octahedra. In this model, the splitting of the triplet band with maxima at 3310, 3230 and 3185  $\text{cm}^{-1}$  is mainly controlled by vacancies and not by coloring cations. This model is reinforced by the study of Moon & Phillips (1991) who investigated the thermal behavior of the OH triplet band in a series of heating experiments on synthetic corundum and assigned the OH absorptions to different types of  $(\text{Ti}_{\text{Al}}V_{\text{Al}}\text{OH}_O)$  defect clusters.

There are also suggestions that OH may occur in natural corundum. Beran (1991) observed extremely weak OH absorptions at 3310, 3230 and 3185  $\text{cm}^{-1}$  in the spectra of a ruby from Sri Lanka and a blue sapphire from Montana. Because the samples used in this study were faceted gemstones, it was not ascertained if these corundums were in their natural state or if they had been subjected to high-temperature heat treatment, likely under reducing conditions. Such treatment is a common practice in the manufacture of the corundum gemstones that can introduce hydroxide in corundum through the reaction,



Hydroxide (OH) introduced this way has a spectrum with features at the same wavenumbers. This treatment is commonly applied to sapphires (Emmett *et al.*, 2003). Such concerns are justified in view of the observations of Smith (1995) and Peretti *et al.* (1995) of comparable sharp OH bands in heat treated ruby, but not in untreated natural samples. Further confirmation of OH in natural corundum is presented by Smith *et al.* (1995) who stated that OH bands are observed in the IR spectra of blue sapphires from basaltic sources in southern Vietnam, and Emmett *et al.* (2003) who reported OH bands at 3367, 3310, 3233, and 3185  $\text{cm}^{-1}$  in a pink sapphire from Vietnam. The present study represents an extension of the initial examination of natural corundums with many samples with better controlled histories.

## Sample description and experimental methods

A collection of 159 corundum crystals, summarized in Table 1, was obtained from private collectors and museum

collections with the objective of obtaining untreated crystals. Many of these represented old collections believed to have been collected before the practice of heat treating corundum became commonplace. Furthermore, many of these crystals have internal flaws that would render them unsuitable for gemstone purposes, but have sufficient clear regions to be studied with our techniques. To clarify the question of the presence of OH in naturally occurring corundum, samples from a variety of different localities were studied.

The samples were carefully cleaned in water but most were not ground and polished. Practically all crystals show rounded faces and most of them were elongated parallel to the *c*-axis. Thicknesses were generally in the range from 0.25 to 0.65 cm. The crystals were examined through different areas which varied from 100 to 600  $\mu\text{m}$  in diameter. We examined samples ranging from gem quality to turbid or altered. Generally, the morphology of the crystal made it possible to locate the *c*-axis and to use an orientation that placed the *c*-axis normal to the direction of the propagation of the infrared beam, but this was not accomplished with all samples. Unpolarized IR spectra were recorded from 4000 to 2400  $\text{cm}^{-1}$  on a Nicolet 60SX FTIR spectrometer operating at 2  $\text{cm}^{-1}$  resolution. A ceramic SiC light source, and a  $\text{LN}_2$  cooled MCT detector were used. Background and sample spectra were respectively obtained from 128 scans in air and through the sample crystal. For polarized measurements, a  $\text{LiIO}_3$  crystal polarizer was used with a Nicolet Magna 860 FTIR spectrometer with other details the same as for the unpolarized measurements. The linear absorption coefficient,  $\alpha$  (in  $\text{cm}^{-1}$ ), defined by  $\alpha = A/d$ , where  $A$  is the linear absorbance ( $\log[I_0/I]$ ) of the most intense and significant OH absorption band at 3310  $\text{cm}^{-1}$  and  $d$  the thickness of the crystal measured in cm, is presented in Table 1 for unpolarized spectra.

## Results and discussion

The presence of significant absorption at 3310  $\text{cm}^{-1}$  in the spectra of approximately one fifth of all studied samples proves that OH occurs in natural samples (Table 1). When the 3310  $\text{cm}^{-1}$  absorption is strong, additional weak bands at 3233 and 3185  $\text{cm}^{-1}$  are observed that are identical to the type II spectra of the synthetic corundums (light blue to blue sapphire, "amethyst"-colored sapphire) reported by Beran (1991). In the spectra of samples with the greatest intensity, additional weak bands are observed at 3395 and 3367  $\text{cm}^{-1}$ .

A significant correlation exists between the color and the OH-band intensities. Blue to dark blue sapphires generally show the highest amount of OH; the OH content of light blue sapphires is usually significantly lower. This is especially evident in crystals from Laos, showing varying colors from dark blue to bluish-gray. In general, blue corundums are from igneous sources and are the ones that contain the highest OH concentrations. Smith (1995) also observed the greatest OH concentrations in blue sapphires from basaltic rocks such as those from Australia. All corundums with the higher absorption coefficients have blue

Table 1. Localities, color, wavenumber positions and OH absorption coefficients for corundum.

Sample	Locality	Number of Samples and Color	Absorption coefficient per cm at 3310 cm <sup>-1</sup> (unpolarized)
LA 1386	Yogo Gulch, Judith Basin Co., Montana	2 yellowish-grey 1 greenish-grey 1 greyish-yellow 1 greenish-yellow 2 yellow 1 yellow/greenish-blue	bdl <sup>a</sup> bdl 0.006 bdl bdl bdl
LA 18947	Yogo Gulch, Judith Basin Co., Montana	1 light greenish-blue 1 blue/greenish-grey	bdl bdl 0.006
LA 16700	Yogo Sapphire Mine, Judith Basin Co., Montana	2 light blue 3 blue	bdl, 0.008 bdl
LA 16699	Dry Cottonwood Gulch, Silver Bow Co., Montana	1 colorless/yellow 2 light greyish-blue 4 greyish-blue	0.006 bdl, 0.003 0.01 - 0.012
LA 18946	El Dorado Bar, Lewis & Clark Co., Montana	2 greyish-blue 3 bluish-grey 1 greenish-blue 2 light blue 2 yellow 1 rose	0.01 - 0.016 bdl 0.01 0.01 bdl bdl
GRR 849	Rock Creek, Montana	2 colorless 2 light blue 1 greenish-blue 2 light yellow 2 rose	bdl bdl 0.007 bdl bdl
GRR 675	Near Coal Creek, Montana	1 colorless 1 yellow	bdl bdl
GRR 836	Montana	5 light blue 1 light greyish-blue 3 light greenish-blue	bdl bdl bdl - 0.05
LA 12229	Macon Co., North Carolina	1 dark blue 1 dark blue	0.12 0.16
LA 12230	Macon Co., North Carolina	2 greenish-grey 1 bluish-grey 1 greenish-blue	bdl 0.085 bdl
GRR 1054	Queensland, Australia	4 greenish-blue	0.03-0.17
GRR 1020	Australia(?)	1 blue 2 dark blue	0.15 0.1, 0.16 <sup>b</sup>
GRR 1047	Australia	1 blue	0.17
LA 6908	Australia	1 bluish-grey/yellow 1 greenish-blue/yellow 1 blue	bdl 0.01 0.49
GRR 1334	Malacheta, Brazil	1 blue (faceted)	0.33
GRR 1335	Goiaz, Brazil	1 light blue (faceted)	0.24
GRR 1021	Cambodia	1 brown/yellow	bdl
GRR 1065	Greenland	2 red	bdl
GRR 2236	Shandong, China	1 dark blue	0.184
GRR 906	Kenya	1 violet 1 rose 2 red	0.06 bdl bdl
GRR 1870	Ban Houayxay, Laos	4 greenish-blue 1 bluish-grey 3 blue 1 dark blue 1 green 1 brownish-green 1 brownish-yellow (zoned crystals)	bdl - 0.025 0.01 0.01 - 0.023 0.15 bdl bdl 0.01
GRR 788	Nigeria	1 dark blue/light blue (zoned)	0.14

Table 1. continued.

Sample	Locality	Number of Samples and Color	Absorption coefficient per cm at 3310 cm <sup>-1</sup> (unpolarized)
GRR 662	SE Asia	1 colorless	bdl
		2 greyish-blue	0.01, 0.10
GRR 1382	SE Asia	1 colorless	bdl
GRR 1045	Ratnapura, Sri Lanka	1 colorless	bdl
GRR 2239	Rwanda	1 dark blue	0.009
GRR 540	Sri Lanka	1 rose	0.003
GRR 673	Sri Lanka	3 yellow	bdl
GRR 674	Sri Lanka	1 colorless/yellow	bdl
		1 bluish-grey/yellow	bdl
		1 light grey/red	bdl
LA 19734	Sri Lanka	3 colorless	bdl
		1 colorless/yellow	bdl
		1 light blue	0.006
LA 19750	Sri Lanka	3 colorless	bdl
		2 greyish-blue	bdl, 0.01
		2 yellow	bdl
LA 6906	Sri Lanka	3 colorless/yellow	bdl
		1 light yellow	bdl
		1 grey	bdl
GRR 890	Umba Valley, Tanzania	2 violet	bdl, 0.015
		1 light blue	0.015
		1 blue	0.028
		1 bluish-green	bdl
		1 yellow	bdl
		1 red	bdl
GRR 730	Tanzania	1 violet	0.015
		1 blue	0.025
		1 yellow	bdl
		1 rose	0.01
		2 red	bdl, 0.025
GRR 838	Tanzania	1 colorless	bdl
		2 light violet	0.015
		1 violet	0.015
		2 violet/grey	0.02, 0.03
		1 light violet/yellow	0.015
		2 yellow/light blue	0.02, 0.027
		1 yellow	0.03
GRR 736	Chantaburi, Thailand	1 bluish-grey	bdl
		1 blue	0.048
		1 red	bdl

The absorption coefficient  $\alpha$  is defined by the absorbance,  $A = \log[I_0/I]$ , divided by the thickness of the crystal,  $d$ , measured in cm ( $\alpha = A/d$ ).

<sup>a</sup> bdl means at or below detection limit of about 0.002.

<sup>b</sup> GRR 1020; absorption coefficient per cm at 3310 cm<sup>-1</sup> (polarized E<sub>⊥</sub>c) = 0.42 - 0.71.

hues (Table 1). The highest absorption coefficient value of 0.49 cm<sup>-1</sup> was observed for a blue Australian sapphire and blue, faceted sapphires (that may have been heat-treated). Also some greenish-blue and violet sapphires show relatively strong absorption bands. Only one ruby sample yielded a very weak absorption at 3310 cm<sup>-1</sup>.

Of the large number of samples from Montana mines (Brownlow & Komorowski, 1988; Mychaluk, 1995), most sapphires from Dry Cottonwood Gulch show significant absorptions due to OH. Sapphires from the gemstone mines in Australia (Guo *et al.*, 1995) reveal the most intense absorption bands. Sapphires from Sri Lanka show very limited amounts of OH, and sapphires from Laos are

characterized by OH zoning. Absorption coefficients of sapphires relatively rich in OH are concentrated at around 0.15 cm<sup>-1</sup>.

Sapphires from Montana have been commercially heat-treated in a reducing atmosphere since the 1970's (Emmett & Douthit, 1993) with the consequent introduction of OH in the process (Emmett *et al.*, 2003). Comparison of the OH content of our suite of Montana samples to published results of heat-treated material makes it evident that the absorption bands of heat-treated dark blue sapphires are more intense than the bands of the corresponding untreated material. This supports previous suggestions that hydrogen enters mineral structures in a redox reaction, given by

equation (1), in which  $\text{Fe}^{3+}$  is reduced by hydrogen producing an OH group in its immediate vicinity (Skogby & Rossman, 1989; Redhammer *et al.*, 1993).

## Amount of OH

Measurements with polarized radiation on natural crystals confirm that the orientation of the OH dipole is perpendicular to [0001] as previously determined on synthetic material (Eigenmann *et al.*, 1972; Volynets *et al.*, 1972; Beran, 1991; Moon & Phillips, 1991). All OH bands show maximum absorptions when the electric vector of the polarized radiation vibrates perpendicular to the *c*-axis (Fig. 1). The absolute amount of OH can be determined from the total integrated areas of the OH bands by using the expression

$$\text{Abs}_{\text{tot}} = I \times d \times \text{concentration} \quad (2)$$

where  $\text{Abs}_{\text{tot}}$  is the total integrated intensity of the OH bands (as discussed in Bell *et al.*, 2003); *d* is the thickness in cm, concentration is in moles<sub>H<sub>2</sub>O</sub>/liter and *I* is the experimentally determined integral molar absorption coefficient. Note that the concentration of all hydrous species is reported as H<sub>2</sub>O.

The hydrogen concentration can only be accurately determined if the matrix specific integral molar absorption coefficient, *I* in equation (2), is known. By comparing the OH absorbance intensity of the natural sapphires with those of synthetic samples reported by Beran (1991), it is evident that the OH content of most of the natural material is in the same order of magnitude as most of the synthetic samples. The absolute amount of OH absorption in the IR spectrum is so low that it appears that an absolute measurement of the OH in corundum will not be possible with current absolute calibration methods at our disposal. Instead, we must indirectly determine the OH content through calibration of the OH band intensity with other standards which we will assume will reasonably represent the behavior of OH in corundum.

Engstrom *et al.* (1980) reported an approximate estimate for the OH content of a synthetic corundum based on the oscillator strength for the OH ion in TiO<sub>2</sub> from Johnson *et al.* (1973). The result was in the 0.1 wt.ppm range. Beran (1991) subsequently proposed a calibration of the OH content of sapphire using kyanite with small hydrogen contents, determined by conductometry, as a standard mineral (Beran & Göttinger, 1987). More similar to corundum than TiO<sub>2</sub>, kyanite is an aluminosilicate whose structure contains oxygen atoms arranged in a slightly distorted close-packed cubic array and whose IR spectrum shows comparatively sharp OH absorptions at around 3385 and 3270 cm<sup>-1</sup> centered in an energy region similar to that observed in corundum (Wieczorek *et al.*, 2004). The hydrogen concentrations thus calculated using the Beran & Göttinger (1991) kyanite standard for the synthetic sapphires varied from around 10 to 30 wt.ppm (expressed as H<sub>2</sub>O).

Subsequently, the accuracy of the kyanite calibration of Beran (1991) was questioned by Bell *et al.* (2004) who re-analyzed kyanite by nuclear reaction analysis (NRA) and

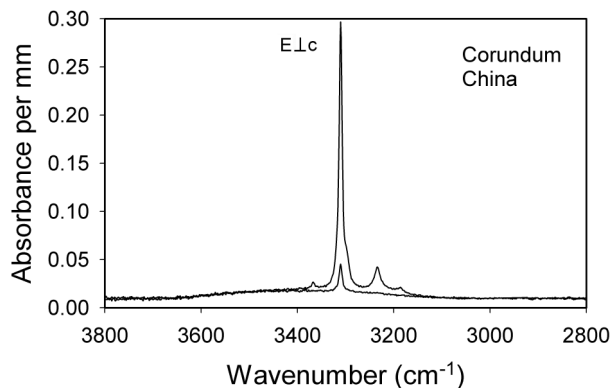


Fig. 1. Polarized single-crystal spectra in the frequency range of the OH stretching vibrations of a 0.973 mm thick, blue sapphire, GRR 2236, from Shandong Province, China (Guo *et al.*, 1992), plotted as 1.0 mm thick, with the electric vector of the polarized radiation vibrating perpendicular and parallel to the *c*-axis. This spectrum is representative of the sharp OH bands in all natural corundums, but of greater intensity than most. Underlying the sharp OH bands is a broad, unpolarized band centered near 3420 cm<sup>-1</sup> characteristic of liquid water and found in the spectra of many samples.

obtained a different calibration constant which indicated that the earlier work overestimated the OH content in kyanite by a factor of about 18. The integral molar absorption coefficient, *I*, derived by Bell *et al.* (2004) for kyanite is  $I = 32900 \text{ L} \times \text{mol}^{-1} \times \text{cm}^{-2}$ . This is between the corresponding values for olivine ( $I = 28450$ ) and clinopyroxene ( $I = 38300$ ) (Bell *et al.*, 2003, 1995).

The most OH-rich corundum in Table 1 that is not likely to have been artificially heat-treated is sample GRR 2236 from the Shandong Province, China. From Fig. 1, the  $\text{Abs}_{\text{tot}}$  (defined as  $\text{Abs}_{\parallel c} + 2 \times \text{Abs}_{\perp c}$ ) is 72.90. The weak broad band centered near 3420 cm<sup>-1</sup> that underlies the sharp OH bands was removed through a baseline correction before integration. The amount of H<sub>2</sub>O bound in the corundum is determined from the concentration,  $72.90 / 32900 = 0.00222$  moles H<sub>2</sub>O per liter (4000 g) of corundum. That corresponds to  $0.00222 \times 18 = 0.0399$  grams H<sub>2</sub>O per 4000 grams corundum, which corresponds to 10 wt.ppm. This is the highest observed hydrogen concentration in our natural (not heat-treated) corundum crystals. For most crystals values are 0.5 wt.ppm H<sub>2</sub>O or less. These values exclude the contribution of hydrous components that are present as inclusions of hydrous phases.

Approximations such as proposed by Paterson (1982) and modified by Libowitzky & Rossman (1997) provide an alternative way to estimate the integral molar absorption coefficients based on the energy of the absorption. For example, Paterson's (1982) relationship was used by Kronenberg *et al.* (2000) for the evaluation of the OH defect concentration in their hydrothermally treated corundums. The revised calibration of Libowitzky & Rossman (1997) leads to an estimate of the H<sub>2</sub>O in corundum GRR 2236 of about 3 wt.ppm H<sub>2</sub>O using the  $\text{Abs}_{\text{tot}}$  derived in the previous paragraph. While this is only an estimate of the amount of OH in corundum, it does serve to confirm the sub-ppm concentrations of OH we generally find in this

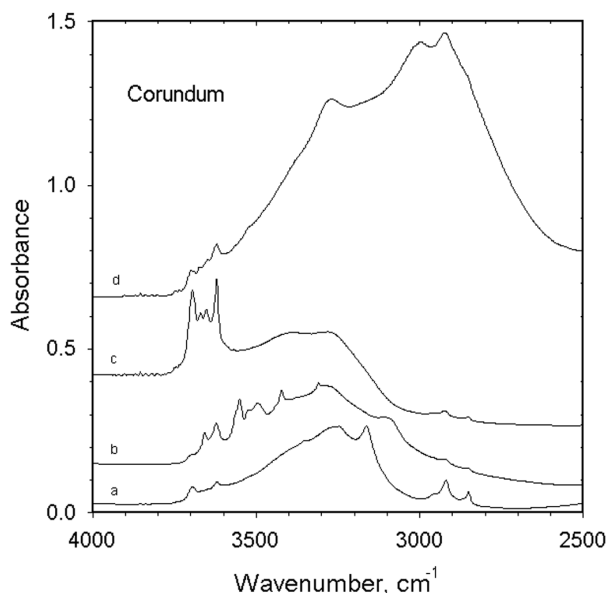


Fig. 2. Unpolarized spectra of corundum in the OH stretching region, taken through turbid crystal parts. (a) OH absorption features of goethite - GRR 673, (b) chlorite group minerals - GRR 838, (c) kaolinite group minerals - LA 16699, and (d) diaspore (plus weak kaolinite features) - GRR 730. Weak C-H stretching vibrations occur in the 2850-2950  $\text{cm}^{-1}$  region.

phase. It is interesting to note that the  $I$  values obtained on the basis of the NRA kyanite calibration are lower, by a factor of about three, than the values obtained from the IR calibration trend given by Libowitzky & Rossman (1997) and that a similar factor was reported by Maldener *et al.* (2001) for rutile and cassiterite, for olivine in Bell *et al.* (2003) and for pyrope in Libowitzky & Rossman (1997). The origin of the large differences between the kyanite calibration of Beran & Götzinger (1987) and the one by Bell *et al.* (2004) may be explained by the nature of the samples analyzed. The 1987 conductometric analysis required 300 mg of extremely pure kyanite. In retrospect, it is highly probable that the high hydrogen content that resulted in the calculation of a low  $I$  value was due to the presence of then undetected, submicroscopic inclusions of hydrous alteration products and strongly absorbed water located in incipient cleavages on fractured ends of grains.

As an alternative to using the total integrated intensities, it is possible to estimate the concentration of  $\text{H}_2\text{O}$  from the intensity of the 3310  $\text{cm}^{-1}$  OH absorption bands (A). This is related to the concentration of the OH groups (c) by the molar absorption coefficient ( $\epsilon$ ) and the thickness of the samples (d). This relation is expressed by Beer's law

$$A = \epsilon_{\perp c} \times d \times c \quad (3)$$

where  $\epsilon_{\perp c}$  is determined to be 1077 from the  $\mathbf{E}_{\perp c}$  spectrum of Fig. 1 (sample GRR 2236 from China). Because the spectrum of OH in corundum is generally similar from sample to sample, and because the intensity is primarily in the  $\mathbf{E}_{\perp c}$  direction, the OH content can be estimated from a single spectrum obtained in the  $\mathbf{E}_{\perp c}$  direction using the kyanite calibration discussed above. The calibration

derived above could be used as the basis for a less accurate calibration based on an unpolarized spectrum taken on a (0001) slab of corundum.

The calibration for unpolarized spectra taken on slabs cut parallel to the  $c$ -axis is different from that obtained with polarized spectra. In this case,  $\epsilon_{\text{unpol}}$ , obtained from the unpolarized spectrum of sample GRR 1020 (corundum from Australia), is 247. Use of  $\epsilon_{\text{unpol}}$  should be considered less accurate because of partial polarization effects in most IR spectrophotometers, even when used without polarizers. In the case of our instrument, rotating the sample 90 degrees about the axis of the light path resulted in a 30% reduction in the absorbance of the 3310  $\text{cm}^{-1}$  band in the unpolarized spectrum. Also noteworthy is the fact that the intensity of an unpolarized spectrum from a sample can vary by a factor of four depending on its crystallographic orientation.

## Hydrous mineral inclusions

All of the calibrations above do not include hydrous inclusions, yet such inclusions are abundant in many samples of corundum. Guo *et al.* (1995), Smith (1995) and references therein describe mineral inclusions in gem-quality sapphires mainly from Australian and Asian occurrences. Inclusions of hydrous minerals frequently occur in corundum and contribute to its IR spectrum. We observed the spectroscopic features of many of the hydrous minerals reported by Smith (1995) in gem rubies. Features of kaolinite, chlorite, diaspore, boehmite and goethite are the ones we most commonly encountered. We find no correlation between the intensity of the OH absorptions and the optical clarity of the crystals. Spectra taken through turbid portions of crystals show distinct groups of absorption bands centered at different wavenumbers within the OH fundamental region. Typical examples are shown in Fig. 2. The significant absorption peak of spectrum a) is due to the presence of fine-grained goethite dispersed along fracture surfaces in the crystal which causes the yellow color of a corundum sample from Sri Lanka. The absorptions of chlorite group minerals are frequently observed in sapphires from Montana and Tanzania (Fig. 2 b). The characteristic absorptions of diaspore with a maximum centered at around 2900  $\text{cm}^{-1}$  indicate the source of turbidity in rubies from Tanzania (Fig. 2 d). The most common phases identified from the spectrum of turbid parts of corundum crystals are kaolinite group minerals (Fig. 2c) which show how IR spectroscopy is a very useful method for the identification and characterization of very small amounts of extremely fine-grained contaminating mineral phases.

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## References

- Bell, D.R., Ihinger, P.D., Rossman, G.R. (1995): Quantitative analysis of hydroxyl in garnet and pyroxene. *Am. Mineral.*, **80**, 465-474.
- Bell, D.R., Rossman, G.R., Maldener, J., Endisch, D., Rauch, F. (2003): Hydroxide in olivine: A quantitative determination of the absolute amount and calibration of the IR spectrum. *J. Geophys. Res.*, **108(B2)**, 2105-2113.
- Bell, D.R., Rossman, G.R., Maldener, J., Endisch, E., Rauch, F. (2004): Hydroxide in kyanite: A quantitative determination of the absolute amount and calibration of the IR spectrum. *Am. Mineral.*, **89**, 998-1003.
- Belt, F.R. (1967): Hydrothermal ruby: Infrared spectra and X-ray topography. *J. Appl. Phys.*, **38**, 2688-2689.
- Beran, A. (1991): Trace hydrogen in Verneuil-grown corundum and its colour varieties - an IR spectroscopic study. *Eur. J. Mineral.*, **3**, 971-975.
- Beran, A. & Götzinger, M.A. (1987): The quantitative IR spectroscopic determination of structural OH groups in kyanites. *Mineral. Petrol.*, **36**, 41-49.
- Beran, A. & Zemmann, J. (1971): Messung des Ultrarot-Pleochroismus von Mineralen. XI. Der Pleochroismus der OH-Streckfrequenz in Rutil, Anatas, Brookit und Cassiterit. *Tschermaks Mineral. Petrogr. Mitt.*, **15**, 71-80.
- Brownlow, A.H. & Komorowski, J.-C. (1988): Geology and origin of the Yogo sapphire deposit, Montana. *Econ. Geol.*, **83**, 875-880.
- Eigenmann, K., Kurtz, K., Günthard, H.H. (1972): Solid state reactions and defects in doped Verneuil sapphire. *Helvet. Physica Acta*, **45**, 452-480.
- Emmett, J.L. & Douthit, T.R. (1993): Heat treating the sapphires of Rock Creek, Montana. *Gems Gemology*, **29**, 250-272.
- Emmett, J.L., Scarratt, K., McClure, S.F., Moses, T., Douthit, T.R., Hughes, R., Novak, S., Shigley, J.E., Wang, W., Bordelon, O., Kan, R.E. (2003): Beryllium diffusion of ruby and sapphire. *Gems Gemology*, **39**, 84-135.
- Engstrom, H., Bates, J.B., Wang, J.C., Abraham, M.M. (1980): Infrared spectra of hydrogen isotopes in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. *Phys. Rev. B*, **21**, 1520-1526.
- Guo, J., Wang F., Yakoumelos, G. (1992): Sapphires from Changle in Shandong Province, China. *Gems Gemology*, **28**, 255-260.
- Guo, J., O'Reilly, S.Y., Griffin, W.L. (1995): Corundum from basaltic terrains: a mineral inclusion approach to the enigma. *Contrib. Mineral. Petrol.*, **122**, 368-386.
- Hammer, V.M.F. & Beran, A. (1991): Variations in the OH concentrations of rutiles from different geological environments. *Mineral. Petrol.*, **45**, 1-9.
- Johnson, O.W., DeFord, J., Shaner, J.W. (1973): Experimental technique for the precise determination of hydrogen and deuterium concentration in rutile. *J. Appl. Phys.*, **44**, 3008-3012.
- Kronenberg, A.K. (1994): Hydrogen speciation and chemical weakening of quartz. in "Silica", P.J. Heaney et al., eds. *Rev. Mineral.*, **29**, 123-176.
- Kronenberg, A.K., Castaing, J., Mitchell, T.E., Kirby, S.H. (2000): Hydrogen defects in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and water weakening of sapphire and alumina ceramics between 600 and 1000°C - I. Infrared characterization of defects. *Acta Mater.*, **48**, 1481-1494.
- Libowitzky, E. & Beran, A. (2004): IR spectroscopic characterization of hydrous species in minerals. in "Spectroscopic methods in mineralogy", A. Beran & E. Libowitzky, eds. *EMU Notes Mineral.*, **6**, 227-279.
- Libowitzky, E. & Rossman, G.R. (1997): An IR absorption calibration for water in minerals. *Am. Mineral.*, **82**, 1111-1115.
- Losos, Z. & Beran, A. (2004): OH defects in cassiterite. *Mineral. Petrol.*, **81**, 219-234.
- Maldener, J., Rauch, F., Gavranic, M., Beran, A. (2001): OH absorption coefficients of rutile and cassiterite deduced from nuclear reaction analysis and FTIR spectroscopy. *Mineral. Petrol.*, **71**, 21-29.
- Moon, A.R. & Phillips, M.R. (1991): Defect clustering in H,Ti:  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. *J. Phys. Chem. Solids.*, **52**, 1087-1099.
- Moon, A.R. & Phillips, M.R. (1994): Defect clustering and color in Fe,Ti:  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. *J. Amer. Ceram. Soc.*, **77**, 356-367.
- Mychaluk, K.A. (1995): The Yogo sapphire deposit. *Gems Gemology*, **31**, 28-41.
- Paterson, M.S. (1982): The determination of hydroxyl by infrared absorption in quartz, silicate glasses and similar materials. *Bull. Minéral.*, **105**, 20-29.
- Peretti, A., Schmetzer, K., Bernhardt, H.-J., Mouawad, F. (1995): Rubies from Mong Hsu. *Gems Gemology*, **31**, 2-26.
- Potter, R.M. & Rossman, G.R. (1979): The tetravalent manganese oxides: identification, hydration, and structural relationships by infrared spectroscopy. *Am. Mineral.*, **64**, 1199-1218.
- Redhammer, G.J., Beran, A., Dachs, E., Amthauer, G. (1993): A Mössbauer and X-ray diffraction study of annites synthesized at different oxygen fugacities and crystal chemical implications. *Phys. Chem. Minerals*, **20**, 382-394.
- Skogby, H. & Rossman, G.R. (1989): OH in pyroxenes: An experimental study of incorporation mechanisms and stability. *Am. Mineral.*, **74**, 1059-1069.
- Smith, C.P. (1995): A contribution to understanding the infrared spectra of rubies from Mong Hsu, Myanmar. *J. Gemology*, **24**, 321-335.
- Smith, C.P., Kammerling, R.C., Keller, A.S., Peretti, A., Scarratt, K.V., Khoa, N.D., Repetto, S. (1995): Sapphires from southern Vietnam. *Gems Gemology*, **31**, 168-186.
- Vlassopoulos, D., Rossman, G.R., Haggerty, S.E. (1993): Coupled substitution of H and minor elements in rutile and the implications of high OH contents in Nb- and Cr-rich rutile from the upper mantle. *Am. Mineral.*, **78**, 1181-1191.
- Volynets, F.K., Sidorova, Y.A., Stsepuro, N.A. (1972): OH-groups in corundum crystals grown by the Verneuil technique (in Russian). *J. Appl. Spectr.*, **17**, 1088-1091.
- Wieczorek, A., Libowitzky, E., Beran, A. (2004): A model for the OH defect incorporation in kyanite based on polarized IR spectroscopic investigations. *Schweiz. Mineral. Petrogr. Mitt.*, **84**, 333-343.

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