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Trace hydrogen in the olivine-type minerals chrysoberyl, Al_2BeO_4 and sinhalite, MgAlBO_4 – a polarized FTIR spectroscopic study

by Peter Bauerhansl¹ and Anton Beran¹

Abstract

Polarized FTIR spectra of the olivine-type minerals chrysoberyl, Al_2BeO_4 and sinhalite, MgAlBO_4 show the existence of absorption bands in the region of the OH stretching fundamental. Strongly pleochroic bands centered at 3234/3219 and 3135 cm^{-1} in chrysoberyl from Ouro Preto, Brazil and at 3509 and 3474 cm^{-1} in sinhalite from Sri Lanka are attributed to OH dipoles oriented parallel to [100]. Under the assumption of vacancies on the X-sites ($X = \text{Be}$ and B , respectively), it is proposed that O1 is partially replaced by OH groups pointing to the X-vacancy. Probably this model, which is also in agreement with results obtained for forsterite, represents a predominating incorporation mode for trace hydrogen in olivine-type structures.

Keywords: chrysoberyl, sinhalite, olivine-type structure, trace hydrogen, FTIR spectroscopy.

Introduction

In view of the elucidation of the role of "water" in the Earth's mantle a great deal of attention has been devoted to crystal chemical aspects of the specific hydrogen incorporation modes in olivine. The interpretation and understanding of deformation processes, rheological laws and solid state conductivity of the upper mantle hinges upon trace amounts of hydrogen to an extent far out of proportion to its low concentration. Olivine may indeed be an essential storage site for trace hydrogen in the upper mantle (BELL and ROSSMAN, 1992; BAI and KOHLSTEDT, 1993; LIBOWITZKY and BERAN, 1995; KOHLSTEDT et al., 1996).

The recognition of trace hydrogen in olivine was based on the observation of a series of OH absorption bands in the 3670–3220 cm^{-1} wavenumber range (BERAN and PUTNIS, 1983; MILLER et al., 1987; BAI and KOHLSTEDT, 1993; LIBOWITZKY and BERAN, 1995). On the basis of polarized IR measurements and under the assumption of Si- and M-site vacancies, BERAN and PUTNIS (1983) derived a model for the OH incorporation in olivine.

They proposed that $[\text{O}(\text{OH})_3]$ - and $[\text{O}_2(\text{OH})_2]$ -tetrahedra with a specific combination of hydrogen positions occur as structural elements, assuming that vacancies are on Si-sites. According to this model, O1 and O2 oxygens are partially replaced by OH dipoles pointing to a vacant Si-site. Hydrogen is also located on the "vertical" tetrahedral O3–O3' edge and on the "horizontal" O1–O2 edge, where O3 as well as O3' and O1 as well as O2, respectively behave as probable donor-acceptor oxygens. If M2-site vacancies were assumed $[\text{SiO}_3(\text{OH})]$ - and $[\text{SiO}_2(\text{OH})_2]$ -tetrahedra occur as structural elements. MILLER et al. (1987) noted that in polarized IR spectra the majority of OH absorption bands of olivines from different geologic occurrences are inclined toward [100]. SYKES et al. (1994) published IR spectroscopic data of a B-containing olivine with unusually high contents of H and F. The polarized IR spectrum corresponding to [100] shows the most intense and significant OH absorption maxima. The majority of pleochroic OH absorption bands in near end-member forsterite as reported by LIBOWITZKY and BERAN (1995) are attributed to OH dipoles

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oriented parallel to [100]. Under the assumption of vacancies on Si- and M-sites it was deduced that mainly O1 oxygens are partially replaced by OH defects pointing to the vacant Si-site. Explaining the pleochroic behaviour of bands with a significant component also parallel to [001], it was further proposed that O3 acts as donor oxygen of OH dipoles lying near the O3–O1 tetrahedral edge or pointing to a vacant M2-site. Also O2 can act as donor oxygen of an OH group oriented along the O2–O3 edge of a vacant M1 octahedron.

Mineral phases with close-packed crystal structures in the system $\text{BeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$, including chrysoberyl, have been subject of extensive experimental examination with a definite interest in their physical properties at different temperature and pressure conditions (AU and HAZEN, 1985; HAZEN and FINGER, 1987). As reported by STOCKTON and KANE (1988) absorption features of chrysoberyls in the 3300–2800 cm^{-1} region, attributed to the presence of "water", also provide a gemological means to distinguish natural from synthetic alexandrites.

The aim of this paper is to present a polarized IR spectroscopic study of the olivine-type minerals chrysoberyl, Al_2BeO_4 and sinhalite, MgAlBO_4 , both mineral phases containing trace amounts of hydrogen, and to compare the incorporation mode of trace hydrogen in these minerals with respect to olivine.

Sample description and experimental

The chrysoberyl single crystals used for the polarized measurements come from a locality near Ouro Preto, Brazil. A suite of ten additional gem quality crystals, cut chrysoberyls and alexandrites from Brazil, the Ural mountains, and from Sri Lanka were also studied for comparison. A single crystal piece of sinhalite from Sri Lanka with an approximate size of about 1 · 1 · 0.5 cm with oriented cut faces was provided by *G.R. Rossman* (Pasadena) for the polarized measurements. Five additional cut stones from Sri Lanka were available for comparative measurements. Under the binocular microscope the yellowish-green chrysoberyl and the brown sinhalite material used for the polarized measurements proved in large parts to be free from impurities and inclusions. The crystals were analysed by a Jeol JSM-6400 scanning electron microscope equipped with a Link energy-dispersive system. Using a natural garnet standard, 1.0 wt% Fe_2O_3 , 0.2 wt% TiO_2 and traces of Cr were determined for the Brazilian chrysoberyl. No other elements except for Fe (2.0

wt% Fe_2O_3) were detected in the Sri Lanka sinhalite crystal piece. The chrysoberyl crystals used for the polarized FTIR measurements were oriented by the X-ray precession and Weissenberg method. Subsequently, two slabs, parallel (010) and (001) were cut with a low-speed diamond saw and polished to a thickness of 0.118 cm each. In two sequences of preparation, the sinhalite piece was attached with the existing (010) and (001) face on a sample grinder and cut and polished on the both opposite sides to a final thickness of 0.987 and 1.198 cm, respectively. The orientation of the faces was proved with a small separated crystal fragment by the X-ray precession method. The indices refer to the lattice constants $a_0 = 4.424(1)$, $b_0 = 9.396(1)$, $c_0 = 5.471(2)$ Å, space group *Pbnm* for chrysoberyl (HAZEN and FINGER, 1987) and $a_0 = 4.3320(4)$, $b_0 = 9.8819(5)$, $c_0 = 5.6813(4)$ Å for sinhalite (HAYWARD et al., 1994).

Single crystal FTIR spectra were recorded by means of the Perkin-Elmer FTIR-spectrometer 1760 X equipped with a gold wire grid polarizer.

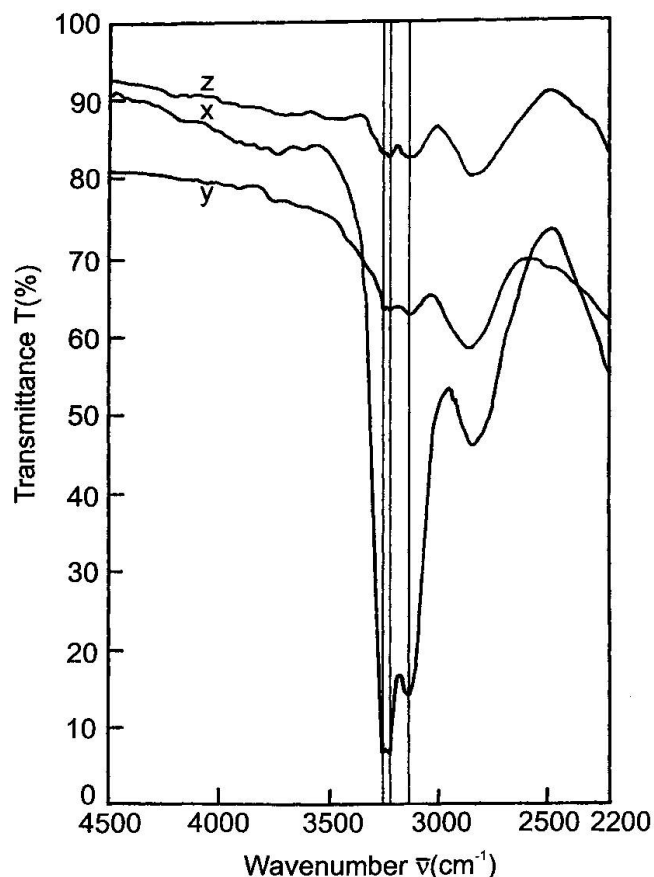


Fig. 1 Polarized FTIR spectra of oriented chrysoberyl single crystal sections (thickness 0.118 cm). The x-spectrum (*E* vibrates parallel to [100]) was measured on (010) and (001), the y-spectrum (*E* parallel [010]) on (001) and the z-spectrum (*E* parallel [001]) on (010). The vertical thin lines indicate maximum band positions at 3234, 3219 and 3135 cm^{-1} .

Background and sample spectra were obtained from 64 scans each with 4 cm^{-1} resolution. Polarized spectra were recorded for the x- and z-direction in (010) and for the x- and y-direction in (001). The x-, y- and z-spectra for chrysoberyl are given in figure 1 and for sinhalite in figure 2. For the determination of the absorbance values the baseline method was used, drawing a straight line through two reproducible points of the spectrum; this was provided in the $3500\text{--}3000\text{ cm}^{-1}$ range for chrysoberyl and in the $3600\text{--}3400\text{ cm}^{-1}$ range for sinhalite, following also the strongly decreasing transmittance in the x-spectrum of sinhalite. Data handling and calculations were managed by the program IRDM (Perkin-Elmer). Deuteration experiments on chrysoberyl crystals were carried out in a quartz glass tube at $T = 1000\text{ }^{\circ}\text{C}$ and $P_{\text{tot}} = P_{\text{D}_2\text{O}} = 1\text{ bar}$ for six days.

Results

CHRYSOBERYL

The FTIR spectrum of the Ouro Preto chrysoberyl in the region of the OH stretching fundamental consists of two strong absorption bands (Fig. 1). The high-energy band is in fact a doublet with maxima at 3234 and 3219 cm^{-1} , the

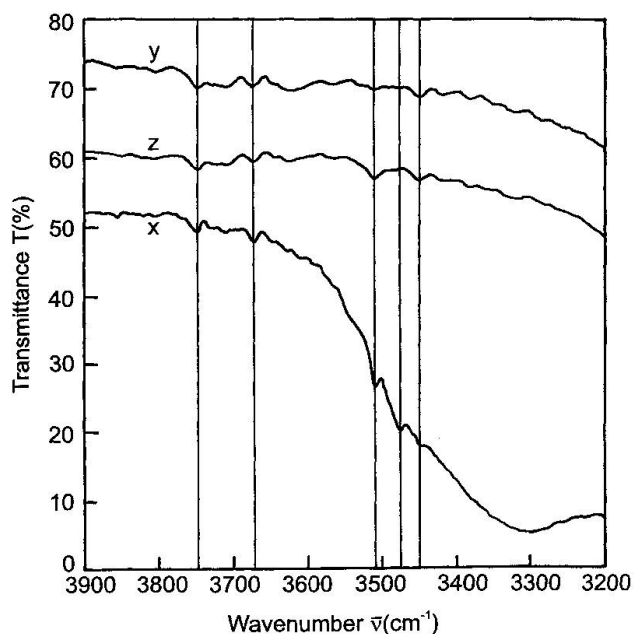


Fig. 2 Polarized FTIR spectra of oriented sinhalite single crystal sections (normalized thickness 1.0 cm). The x-spectrum (\mathbf{E} vibrates parallel to $[100]$) was measured on (010) and (001), the y-spectrum (\mathbf{E} parallel $[010]$) on (001) and the z-spectrum (\mathbf{E} parallel $[001]$) on (010). The vertical thin lines indicate maximum band positions at 3740 , 3670 , 3509 , 3474 and 3445 cm^{-1} .

low-energy band is centered at 3135 cm^{-1} . There is also a band at 2840 cm^{-1} . Comparing the non-polarized spectrum of the Ouro Preto crystal with spectra of samples from other localities, it appeared that an absorption band around 3230 cm^{-1} is a characteristic feature present in all natural chrysoberyl crystals. Crystal fragments from the Ouro Preto material were checked for dehydration performed after a series of 8 hours heating steps with temperature intervals of $100\text{ }^{\circ}\text{C}$. After the heat treatment at $700\text{ }^{\circ}\text{C}$ the split high-energy band merges to one maximum at 3228 cm^{-1} . The low-energy band slightly increases in intensity and shows a significant shift to lower wavenumbers; after the $1100\text{ }^{\circ}\text{C}$ heating step this band is situated at 3083 cm^{-1} . Further heating reduces the intensities of both bands and heating temperatures of $1200\text{ }^{\circ}\text{C}$ for 36 hours causes the two absorption bands to disappear. Deuteration experiments were performed on one crystal fragment. The resulting spectrum shows additional bands at 2410 and 2318 cm^{-1} which directly proves by the appropriate OH/OD factor that hydrogen has partially exchanged with deuterium.

As evident from the x-spectrum in figure 1 the bands at $3234/3219$ and 3135 cm^{-1} show maximum absorption when the vector \mathbf{E} of the polarized radiation vibrates parallel to $[100]$ (BAUERHANSL and BERAN, 1993). The band at around 2840 cm^{-1} does not respond to deuteration experiments and shows no orientation dependent changes of its intensity. For these reasons, this band is assigned to combination modes of lattice vibrations (probably third overtone of the ν_3 stretching vibration of the BeO_4 unit) and is not further discussed.

SINHALITE

The sinhalite spectrum shows extremely weak but distinct absorption bands at 3509 , 3474 and 3445 cm^{-1} (Fig. 2). Because of the low hydrogen concentration encountered in the Sri Lanka material, a sample thickness of approximately 1 cm is required for the polarized measurements. Significant bands at 3509 cm^{-1} are observable in the x- and, more weakly, in the z-spectrum. The band at 3474 cm^{-1} shows maximum absorption when the vector \mathbf{E} of the polarized radiation vibrates parallel to $[100]$ (x-spectrum), no absorptions exist in the y- and z-spectrum. The band at 3445 cm^{-1} shows a practically isotropic absorption behaviour. This absorption band is consistent with the presence of "non-structural" OH defects associated with dislocations on subgrain boundaries, also described in olivine by BERAN and PUTNIS (1983). Our conclusion regarding the origin of the

strongly pleochroic absorption bands at 3509 and 3474 cm^{-1} in crystal parts free from impurities, is that these bands are caused by stretching vibrations of structural OH groups. A strong increase of the background absorption below 3650 cm^{-1} is observed in the x-spectrum, revealing an additional broad band centered around 3300 cm^{-1} . An assignment of this broad band absorption to hydrogen bonded structural OH groups is of speculative character and is not discussed in detail.

Non-pleochroic bands at around 3740 and 3670 cm^{-1} are significantly present in turbid crystal parts and are apparently due to contaminating OH bearing phases (probably clay minerals). No correlation does exist between these two bands and the absorption features at 3509, 3474 and 3445 cm^{-1} .

Discussion

The structures of chrysoberyl, Al_2BeO_4 and sinhalite, MgAlBO_4 have the olivine topology (HAZEN and FINGER, 1987; HAYWARD et al., 1994). One formula unit M_2XO_4 contains two crystallographically different M-sites; M1 on a centre of symmetry (Al in chrysoberyl and sinhalite), M2 in a mirror plane (Al in chrysoberyl and Mg in sinhalite). X (Be and B, respectively) is also placed in the mirror plane. Two of the three oxygen positions, O1 and O2, are localized in a mirror plane, while the third, O3, occupies a general position. All of the oxygens are coordinated by three M and one X in a distorted tetrahedron. A crystal chemically plausible model for the incorporation mode of OH defects in chrysoberyl and sinhalite, based on the FTIR spectroscopic measurements, is derivable in association with the presence of vacancies in the cation lattice. No plausible model is derivable under the assumption of a complete occupancy of all cation positions. It is further assumed that the OH incorporation is critically influenced by the presence of minor elements on the M-sites, notably by the oxidation state of Fe.

The relation proposed by PATERSON (1982) was used for the determination of the integral molar absorptivity ϵ_i and the trace hydrogen content (as H_2O) was estimated on the basis of the Lambert-Beer law. For chrysoberyl the bands centered at 3234 and 3135 cm^{-1} were assumed and for sinhalite the two pleochroic bands at 3509 and 3474 cm^{-1} . The integral absorbance was measured with polarized radiation. The $\epsilon_i(\text{H}_2\text{O})$ value for chrysoberyl results to 163'800 and 193'500 $\text{l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-2}$, respectively and for sinhalite to 81 300 and 91 800 $\text{l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-2}$, respectively. The corresponding H_2O content is calculated to values

at around 50 ppm for chrysoberyl, and to 0.5 ppm for sinhalite.

The pleochroic scheme of the OH absorption bands allows certain constraints to be imposed on the orientation of the OH defects. A common feature for both mineral phases is the extremely strong pleochroism of the two bands with maxima at 3234/3219 and 3135 cm^{-1} in chrysoberyl, and the bands at 3509 and 3474 cm^{-1} in sinhalite, indicating for both minerals a strongly preferred orientation of the OH dipole direction parallel to [100]. If we assume vacancies in the X-position (V_X), an OH direction along the line O1- V_X with O1 acting as donor oxygen would be a plausible model to explain the observed pleochroism. If we assume vacancies in the M-site positions instead of X-vacancies, no plausible model would be consistent with the observed OH dipole direction.

The O1- V_X line is practically parallel to [100] and O1 is coordinated by three M-atoms, two M1 and one M2, forming the top of a (slightly distorted) trigonal pyramid, thus being an "ideal" candidate for a partial OH replacement with "Mg(OH)₂-type" coordination (Fig. 3). Distinct from O1, the lines connecting O2 with V_X and O3 with V_X are strongly deviating from the lines normal to the plane of their coordinating M-sites, which do not point to the center of the [$\text{V}_\text{X}\text{O}_4$]-tetrahedra. In the definite case, represented by the two bands in chrysoberyl and by the 3474 cm^{-1} band in sinhalite, the OH dipole direction is practically perpendicular to the plane of the three surrounding M-sites. A very similar situation holds for the 3509 cm^{-1} band in sinhalite, but with a significant deviation of the OH dipole direction from

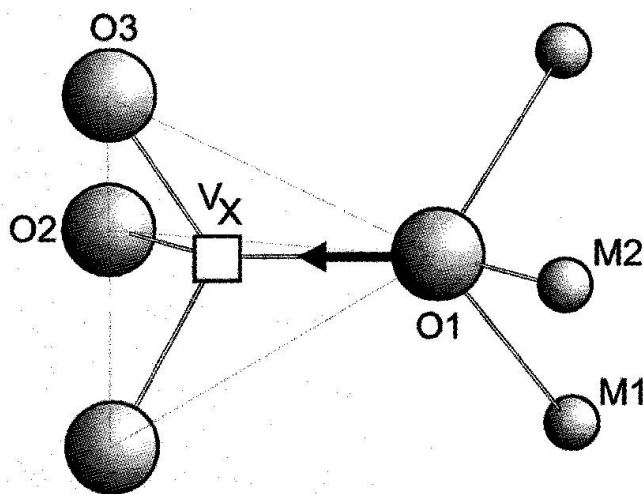


Fig. 3 Schematic diagram of a part of the olivine-type structure of chrysoberyl and sinhalite (view approximately along [010]) with an X-vacancy (V_X , X = Be and B, respectively) showing the proposed OH dipole direction along O1- V_X (practically parallel [100]).

the O1- V_x line, clearly required by the absorption component in the z-spectrum.

In both minerals, the presence of OH absorption bands at different wavenumbers may be explained by deviations of the OH positions from the ideal O1 coordinate, due to local distortions of the tetrahedral oxygens coordinating the vacant X-site. In chrysoberyl the OH groups apparently point to three oxygens in equal distances, which strongly reduces the energy of the OH stretching vibration (NAKAMOTO et al., 1955). Local charge balances along with varying M-O distances may also influence the energy of the OH stretching vibration. Probably the higher wavenumber position of the OH bands in sinhalite is caused by both, the presence of weak hydrogen bonds in strongly distorted oxygen tetrahedra and the lower valence sum on O1. However, despite the greater valence deficiency of O3 (coordinated by two Mg and one Al in the ideal structure of sinhalite) compared to that of O1 and O2 (coordinated by one Mg and two Al), no model consistent with the obtained results is derivable with O3 acting as donor oxygen. This indicates that bond valence calculations are not the method to be definitely applied for the prediction of OH defect positions. Considering the extremely small OH concentration observed in sinhalite, in accordance with the results of HAYWARD et al. (1994) it is highly probable that the M2-site in sinhalite can also accept small amounts of Al^{3+} , Fe^{2+} , Fe^{3+} and Cr^{3+} , thus creating a "chrysoberyl environment".

The band at 3083 cm^{-1} observed in chrysoberyl after the heat treatment at $1100\text{ }^\circ\text{C}$ is explained by conversion of hydrogen to a "deviating" O1 oxygen position. This band follows the general rule of a shift to lower wavenumbers with increasing temperature (AINES and ROSSMAN, 1985). The splitting of the high-energy OH band in Ouro Preto chrysoberyl, with maxima separated by 15 cm^{-1} , is not generally observed and is probably caused by the presence of Fe in one of the M-positions coordinating the donor oxygen. The observation of a splitted band suggests an affinity of substituting Fe to the OH defects, though present in minor amounts (HAMMER et al., 1996).

As a characteristic feature, the OH absorption spectra of chrysoberyl and of sinhalite show maximum absorption when **E** vibrates parallel to [100] and practically no or very weak absorptions when **E** vibrates parallel to [010] and [001]. These observations clearly demonstrate that in these minerals the O1 oxygens are partially replaced by OH groups directly pointing to vacant X-sites. O1 is proposed to be the dominating donor oxygen of OH groups in chrysoberyl and sinhalite. In olivine also other replacement modes occur. However,

this mode of O1 replacement by OH, which has also been observed in Pamir forsterite (LIBOWITZKY and BERAN, 1995) and in Zabargad olivine (BERAN and PUTNIS, 1983), is a predominating incorporation mode for trace hydrogen in olivine-type structures.

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