The Occurrence of OH Absorptions in Phenakite—an IR Spectroscopic Study

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With 3 Figures

Summary

IR spectra of phenakite single crystals from different localities show a distinct variability in the region of the OH stretching fundamental. Minute hydrous mineral phases (tourmaline, bertrandite) are included in Piracicaba phenakite. Structural OH, ranging up to 0.005 equivalent wt.% H_2O, is characterized by two extremely pleochroic bands centered at 3380 and 3120 cm^{-1}. On the basis of their pleochroic scheme it is proposed that ($\Box O_2(OH)_2$) and ($\Box O_3(OH)$) tetrahedra occur as structural elements, assuming that the vacancies are on Be sites.

Zusammenfassung

Das Auftreten von OH Absorptionen in Phenakit—eine IR spektroskopische Untersuchung

Die IR Spektren von Phenakit-Einkristallen verschiedener Vorkommen zeigen im Bereich der OH-Streckschwingungen eine deutliche Variabilität. Piracicaba Phenakit enthält feinste Einschlüsse von OH-hältigen Mineralphasen (Turmalin, Bertrandit). Strukturell gebundene OH-Gruppen (bis 0,005 äquivalente Gew.% H_2O) sind durch zwei extrem pleochroitische Banden bei 3380 und 3120 cm^{-1} charakterisiert. Unter der Annahme von Be-Leerstellen werden aufgrund des Pleochroismus dieser Banden ($\Box O_2(OH)_2$) und ($\Box O_3(OH)$) Tetraeder als strukturelle Baueinheiten vorgeschlagen.

Introduction

The system $BeO-Al_2O_3-SiO_2-H_2O$ (BASH) includes several well-formed, stoichiometric and ordered crystal phases in a variety of structures. Over the past several years, minerals in this system, including phenakite, Be_2SiO_4, have been subject of extensive experimental examination as well as of theoretical consideration

(*Hazen* and *Au*, 1986, *Kogure* and *Takéuchi*, 1986, *Hazen* and *Finger*, 1987, *Hazen*, 1988, *Yeganeh-Haeri* and *Weidner*, 1989). One of the principal objectives of these papers is to give a contribution to the understanding of the physical properties at different temperatures and pressures. It is known that the presence of small amounts of water in nominally anhydrous silicate phases has considerable effects on their physical properties (cf. *Griggs*, 1967). The fact that the content of structural OH groups in phenakite is extremely small, coupled with the presence of fluid inclusions and included hydrous minerals, makes the study of the OH incorporation a difficult one.

Sample Description and Experimental

IR spectroscopy provides an extremely sensitive method for detecting trace hydrogen bonded to oxygen in the structure of various anhydrous minerals (cf. *Rossman*,

Table 1. *Data on phenakite*

Sample localities:
    San Miguel di Piracicaba, Minas Gerais, Brazil
    Habach Valley, Pinzgau, Austria
    Takowaja Valley, Urals, USSR
Crystallographic data:
    Unit cell dimensions — $a(\text{Å}) = 12.472(2)$, $c(\text{Å}) = 8.251(1)$
    (Downs and Gibbs, 1987).
    Space group — $R\bar{3}$
Chemical composition:
    Microprobe analyses of the samples revealed no chemical impurities.
    Calculated analytical H_2O^+ content (wt.%) using ε of bertrandite $= 835 \, \text{l.mol}^{-1}.\text{cm}^{-2}$ —
    Piracicaba: 0.003, Habach Valley: 0.005, Takowaja Valley: No OH detectable
Wavenumber positions (cm^{-1}):

phenakite			bertrandite		tourmaline	
Piracicaba	Habach V.	Takowaja V.	Pisek, CSR	powder data (Moenke, 1974)	elbaite (Gonzalez-Carreno et al., 1988)	Fe-elbaite
3650 st, n			3650 sh	3650 w, b	3650 st, n	
3635 st, n						
3625 vst, n			3625 vst, n	3620 w, b		
3595 st, n			3600 st, n			3595 st, n
3580 st, n			3580 st, n	3585 st, b	3585 st, n	
3565 w, n						3560 w, n
			3550 vst, n	3550 st, b		
			3515 vst, n			
3490 w,b						3490 st, n
					3465 st, n	
		3400 vw, vb	3410 w, vb			
3380 st, b	3380 vw, b					
3120 w, b	3120 st, b					

vst-very strong, st-strong, w-weak, vw-very weak, vb-very broad, b-broad, n-narrow, sh-shoulder (wavenumber position is estimated).

1988). *Wilkins* and *Sabine* (1973) first reported "evidence of OH in phenakite from the Pikes Peak region, Colorado". In the present paper a polarized IR study of the OH absorption spectrum in phenakite is reported and a model for the OH positions in the structure is proposed. The natural single crystals used for this work come from three localities: (1) San Miguel di Piracicaba, Brazil, (2) Habach Valley, Austria, (3) Takowaja Valley, USSR (see also Table 1). The crystals are colourless, transparent and visually free of defects. Under the microscope, also the clearest parts of the available Piracicaba crystal show tiny inclusions of solid phases, a few μm in size. Crystals from Habach Valley proved in parts to be absolutely free from impurities, Takowaja Valley phenakite shows irregulary distributed fluid inclusions. Plane-parallel slabs of the crystals were polished parallel to the c-axis. The diameter of the circular measuring area was varied from 2 mm to 0.2 mm. Because of the low OH concentrations encountered in the phenakites, a minimum thicknes of 3.0 mm was required for the samples. Non-polarized and polarized IR spectroscopic measurements were performed with a computer-controlled IR spectrophotometer Perkin-Elmer 580 B, Interdata 6/16 and a wire grid polarizer (Au on AgBr). Spectra were recorded after rotation of the polarizer by steps of 10° with 2 cm^{-1} resolution. Unpolarized spectra of small parts of Piracicaba phenakite were obtained with a Nicolet 60 SX Fourier transform IR spectrophotometer. The crystals were anaylsed by electron microprobe and checked for chemical homogenity; no impurities are detectable by electron microprobe.

A (semi) quantitative OH determination performed with non-polarized IR radiation yielded an analytical H_2O^+-content of 0.003 wt.% for Piracicaba phenakite, and 0.005 wt.% for Habach Valley phenakite. No OH is detectable in the crystal from Takowaja Valley (see Table 1). The equivalent H_2O^+ values were evaluated on the basis of Beer's law using bertrandite, $Be_4Si_2O_7(OH)_2$ as an OH standard. Assuming a stoichiometric composition the integral molar extinction coefficient ε, determined from the non-polarized absorption spectrum of a small colourless crystal fragment from Pisek, CSR, amounts to 835 l.mol^{-1}.cm^{-2} (see Table 1).

Results

Non-polarized IR spectra of phenakite samples polished parallel to the c-axis are summarized in Fig. 1. The Piracicaba phenakite shows a triplet of very sharp absorption bands centered at 3650, 3635, 3625 cm^{-1} and a doublet at 3595, 3580 cm^{-1}. A single band is centered at 3490 cm^{-1} (see also Table 1). Using polarized IR radiation no significant pleochroism of these bands was observed. In contrast, a strong broad band with an absorption maximum at 3380 cm^{-1} and a weak band at 3120 cm^{-1} show a very strong pleochroism. Figure 2 shows that the absorption band at 3380 cm^{-1} has maximum absorption when the electric vector $\bar{E}$ of the polarized radiation vibrates parallel to the c-axis. The band at 3120 cm^{-1} has maximum absorption when $\bar{E}$ vibrates perpendicular to the c-axis. None of the non-pleochroic bands were observed in the spectrum of the Habach Valley phenakite (Fig. 1). The weak band of the Habach Valley sample at 3380 cm^{-1} and the strong band at 3120 cm^{-1} show the same pleochroic behaviour as the equivalent bands of the Piracicaba sample. The spectrum of the Takowaja Valley phenakite is characterized by a very weak and broad absorption with a maximum centered at c. 3400 cm^{-1}; the sample
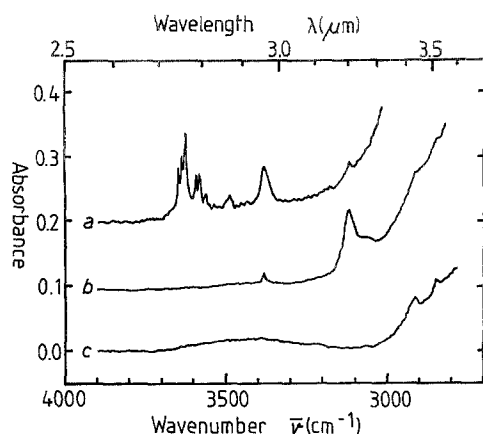
Fig. 1. Non-polarized IR absorption spectra of doubly polished phenakite slabs cut parallel to the c-axis; computer replot from accumulated scans.
(a) Piracicaba, Brazil, t = 4.945 mm,
(b) Habach Valley, Austria, t = 5.710 mm,
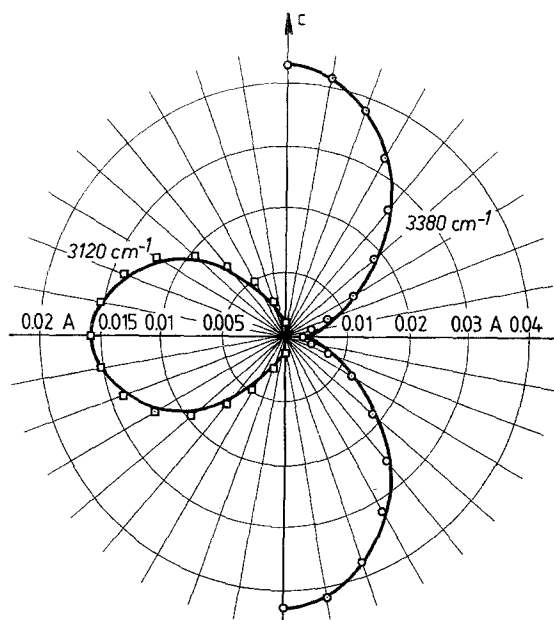(c) Takowaja Valley, USSR, t = 3.265 mm

Fig. 2. Radiants of OH absorbances A (half absorption figures) on a Piracicaba phenakite slab polished parallel to the c-axis, t = 4.945 mm; symbol circle: observed absorption values of the 3380 cm^{-1} band, symbol square: observed absorption values of the 3120 cm^{-1} band, continuous line drawings correspond to calculated absorption values (modified equation of *Strens* et al., 1982, see text)

is also characterized by absorptions in the 2900 cm^{-1} region (again Fig. 1). Probably, these two non-pleochroic absorptions of the Takowaja Valley phenakite are due to the fine-sized fluid inclusions containing water and hydrocarbon. Absorption bands at around 3650, 3625, 3600, 3580, 3560, 3515, 3490, and 3465 are most prominent in the spectra of elbaite—Fe-elbaite (*Gonzalez-Carreno* et al., 1988) and bertrandite (this study, *Moenke*, 1974). Correspondence is found between most of these bands and the Piracicaba phenakite spectrum in the range from 3650 to 3450 cm^{-1} (see Table 1); therefore, tourmaline and bertrandite are likely candidates for included hydrous mineral phases in very small amounts.

Regarding the characteristic pleochroic scheme of the both bands at 3380 and 3120 cm^{-1}, calculations on the basis of the "electric dipole transition model" (*Strens* et al., 1982) reveal an excellent agreement between calculated and observed absorptions. The equation $A = \log(T' \cos^2\theta + T'' \sin^2\theta)^{-1}$ was used in a modified form, where A means absorbance, T' represents I/I_0 parallel to c, T'' represents I/I_0 perpendicular to c, θ measures the angle formed by the c-axis and the electric vector $\bar{E}$ of the polarized radiation (see Fig. 2). The conclusion regarding the origin of these

two bands at 3380 and 3120 cm^{-1} in the Piracicaba and in the Habach Valley phenakite must be that these absorptions are due to structural OH groups.

Discussion

The absorption bands at 3380 and 3120 cm^{-1} are presumed to be an intrinsic feature of phenakite itself. By considering the structure in keeping with the pleochroic scheme of the bands it is relevant to propose a model for the OH positions.

The crystal structure of phenakite was determined by *Bragg* and *Zachariasen* (1930) and first refined by *Zachariasen* (1972). Further refinements were performed under room conditions by *Downs* and *Gibbs* (1987), at high pressures by *Hazen* and *Au* (1986), *Kogure* and *Takéuchi* (1986) and at high temperatures by *Hazen* and *Finger* (1987). (The structural parameters used in this work refer to *Downs* and *Gibbs*). The three symmetrically distinct cations in the phenakite structure, two Be and one Si, are each coordinated by a tetrahedron of oxygens; each of the four crystallographically different oxygens is bonded to two Be and one Si disposed at the corners of a quasi-planar triangle. The coordination triangles about O(1), O(3), and O(4) lie in a plane parallel to the c-axis, whereas the coordination triad about O(2) lies in a plane perpendicular to the c-axis. The O(2) oxygen is located almost exactly on a threefold screw axis and has two neighbours of the same kind of atoms at a distance of 2.750 Å which is the shortest interpolyhedral O–O distance found in a silicate (*Zemann*, 1986). Bond valence calculations (*Brown* and *Altermatt*, 1985) yield valence sums of 1.984 for O(1), 1.980 for O(2), 1.919 for O(3), and 1.952 for O(4), revealing practically no deficient oxygen.

The pleochroic scheme of the two OH absorption bands allows to impose defined constraints on the orientation of the OH dipoles. The extremely high pleochroic ratio (cf. *Rouxhet*, 1970) of the band at 3380 cm^{-1} requires a strong orientation of the OH dipole parallel to the c-axis, the extremely strong pleochroism of the band at 3120 cm^{-1} requires an OH direction strictly perpendicular to the c-axis. As a rule, the donator oxygen of an OH group is the top of a flat distorted trigonal pyramid. Regarding the structure of phenakite, the oxygens lie in the centre of a quasi-planar coordination triangle. Because valences of the silicons are significantly higher than those of the nearly equidistant berylliums, a significant deviation of the OH direction from the normal to the cation planes is to be expected. These facts are neither in coincidence with the observed pleochroism of both absorption bands nor with the usual coordination behaviour of structural OH groups.

On the basis of the relation diagram given by *Novak* (1974) the band at 3380 cm^{-1} requires an O–O distance of c. 2.78 Å and the band at 3120 cm^{-1} requires an O–O distance of c. 2.67 Å. Considering these distances in a geometrically plausible model which is consistent with the pleochroic scheme, it follows that an OH incorporation in the structure of phenakite is easy to provide under the assumption of an incomplete occupancy of the cation positions; no plausible model is derivable, assuming a charge imbalance in cation sites.

To facilitate the discussion, Fig. 3 presents in a schematic diagram the most probable orientation of the OH dipoles. The pleochroism of the band at 3380 cm^{-1} requires a strong orientation of the OH dipole parallel to the c-axis. Under the assumption of vacancies in the Be(1) lattice, the O(4) oxygen can easily act as a
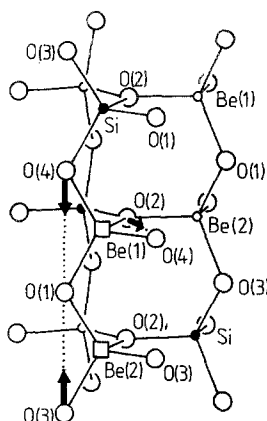
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Fig. 3. Part of the phenakite structure (modified after *Zemann*, 1986) showing possible OH dipole directions (represented as arrows) in $\square O_4$ tetrahedra with Be vacancies. The direction of the dipole along O(4)–O(1), and O(3)–O(1), respectively results from the pleochroism of the band at 3380 cm^{-1}, the direction of the dipole along O(2)–O(4) results from the pleochroism of the band at 3120 cm^{-1}

donator oxygen of an OH group bridging along the practically vertical tetrahedral edge to the O(1) oxygen. The O(4)–O(1) distance of 2.766 Å is in excellent agreement with the expected value of *Novak*'s (1974) diagram. Assuming vavancies in the Be(2) lattice instead of Be(1) vacancies, the position and the pleochroism of the band at 3380 cm^{-1} would also be consistent with an OH dipole direction along the O(3)–O(1) tetrahedral edge (2.762 Å) with O(3) acting as donator oxygen. The pleochroic behaviour of the band at 3120 cm^{-1} which requires a strong orientation of the OH dipole perpendicular to the c-axis indicates that an H atom is located on a horizontal tetrahedral edge. Under the assumption of Be(1) vacancies the O(2) oxygen is an ideal candidate for a partial OH replacement. The distance O(2)–O(4) measures 2.660 Å and is in best coincidence with the band position. It is evident that some close similarities in the geometrical and electrostatic behaviour exist between the three modes of OH replacement. On the basis of the proposed vacancy model the three donator oxygens are coordinated by 1 Be and 1 Si and it is important to note, that in all three cases the OH dipoles show a strong deviation from the normal to the Be-Si line in the direction of the low valent Be. The Be-O-H angles measure 83.7° for O(2), 89.7° for O(3), and 89.5° for O(4), the Si-O-H angles measure 156.0° for O(2), 146.6° for O(3), and 147.0° for O(4).

Probably, there are ($\square O_2(OH)_2$) tetrahedra with a specific combination of H positions as well as simple ($\square O_3(OH)$) tetrahedra as structural elements (cf. *Beran* and *Putnis*, 1983, *Beran* and *Zemann*, 1986). The fact that there are different combinations of such tetrahedra possible in phenakite is clearly demonstrated by the different intensity distribution of the two OH absorption bands in crystals from Piracicaba and Habach Valley.

Acknowledgements

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