

Guildite, a layer structure with a ferric hydroxy-sulphate chain and its optical absorption spectra¹

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Abstract

Guildite, $\text{Cu}^{2+}\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})\cdot 4\text{H}_2\text{O}$, from the United Verde Mine, Jerome, Arizona, is monoclinic, space group $P2_1/m$, with cell dimensions $a = 9.786(2)$, $b = 7.134(1)$, $c = 7.263(1)\text{Å}$, $\beta = 105.28(1)^\circ$, $Z = 2$. The crystal structure has been determined by Patterson and Fourier syntheses and refined by the method of least squares to an R factor of 0.056 for 942 reflections, measured on an automatic single-crystal diffractometer. The crystal structure contains an octahedral-tetrahedral chain, which consists of zig-zag chains of $[\text{FeO}_5(\text{OH})]$ octahedra sharing the (OH) corner; two pairs of octahedral corners on either side of this chain are shared by $\text{S}(1)\text{O}_4$ and $\text{S}(2)\text{O}_4$ tetrahedra. These chains are crosslinked through corner-sharing *trans*- $[\text{CuO}_2(\text{H}_2\text{O})_4]$ octahedra into corrugated sheets parallel to the (001) plane. Adjacent sheets are hydrogen-bonded through water molecules. The average $\text{Fe}^{3+}-\text{O}$ and $\text{S}-\text{O}$ bond lengths are 2.005 and 1.472Å respectively. Cu^{2+} shows the usual Jahn-Teller distortion with four short $\text{Cu}-\text{O}(W)$ bonds (av. 1.985Å) and two long $\text{Cu}-\text{O}$ bonds (av. 2.264Å).

The pleochroism in guildite is similar to that of other materials containing hydroxobridged Fe^{3+} chains. Intense color and the highest refractive index occur when the vibration direction of the incident light is along the chain direction. An intense absorption band at 430 nm and a band at 874 nm are due to Fe^{3+} , whereas broad absorption bands at 1285 nm and 780 nm have been assigned to Cu^{2+} . Additional bands, including a sharp band at 1953 nm, are due to (OH) ions and water molecules.

Introduction

Guildite is a secondary hydrated basic copper ferric sulphate mineral, formed as a result of a mine fire at the United Verde Mine, Jerome, Arizona, in association with coquimbite, $\text{Fe}_{2-x}\text{Al}_x(\text{SO}_4)_3\cdot 9\text{H}_2\text{O}$, and ransomite, $\text{CuFe}_2(\text{SO}_4)_4\cdot 6\text{H}_2\text{O}$ (Lausen, 1928). Lausen (1928) originally proposed a complex chemical formula for guildite, $(\text{Cu},\text{Fe})_8(\text{Fe},\text{Al})_4(\text{SO}_4)_7\text{O}_2\cdot 17\text{H}_2\text{O}$. The unit-cell dimensions and space group were determined by Laughon (1970), who proposed a simplified chemical formula, $\text{CuFe}(\text{SO}_4)_2(\text{OH})\cdot 4\text{H}_2\text{O}$, which is consistent with the density, the measured cell volume, and symmetry requirements of the

space group. Our structure determination has confirmed the formula proposed by Laughon (1970). We have also interpreted the optical absorption spectra of guildite in view of its crystal structure.

Experimental

A single-crystal fragment of type guildite (NMNH #95950) from the United Verde Mine measuring $0.20 \times 0.20 \times 0.25$ mm was mounted on the Syntex PI automatic single-crystal diffractometer, with the long axis parallel to the phi-axis of the diffractometer. The unit-cell dimensions were determined by the least-squares refinement of 15 reflections with 2θ values between 25 and 35° measured on the diffractometer, using $\text{MoK}\alpha$ radiation. Our cell dimensions [$a =$

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9.782(7), $b = 7.145(5)$, $c = 7.264(4)$ Å, $\beta = 105.36(5)^\circ$] are in agreement with those determined by Laughon (1970); however, since his cell dimensions are more precise than ours, we have used them (Table 1) for the following structure determination. The intensities of all reflections within $2\theta \leq 50^\circ$ were measured on the diffractometer by the 2θ - θ method, using MoK α radiation (50 kV, 12.5 mA), monochromatized by reflection from a graphite "single" crystal and a scintillation counter. A variable scan rate was used, the minimum rate being $2^\circ/\text{min}$. A total of 942 reflections were measured, out of which 120 were below $3\sigma(I)$, where $\sigma(I)$ is the standard deviation of the intensity, I , as measured by the counting statistics. All reflections were corrected for Lorentz and polarization factors. An approximate absorption correction was made, assuming the crystal to be a sphere with an average diameter of 0.216 mm.

The optical absorption spectra of guildite were recorded at room temperature. Experimental details have been previously described (Rossman, 1975).

Determination and refinement of the crystal structure

The position of one iron, one copper, and two independent sulphur atoms were determined from a three-dimensional Patterson map. A difference Fourier synthesis yielded the positions of all the oxygen atoms. The positional and thermal parameters of all non-hydrogen atoms were refined by the method of least squares, using the program RFINE (Finger, 1968), to an R factor of 0.084. A difference Fourier synthesis calculated at this stage showed the locations of three out of seven hydrogen atoms, which were stereochemically acceptable. However, an attempt to refine the hydrogen positions did not succeed. Hence, all the hydrogen positions were held constant with an isotropic temperature factor, $B = 3.5 \text{ \AA}^2$, while the non-hydrogen positions were refined with anisotropic temperature factors. However, some of the aniso-

Table 2. Guildite: atomic positional and thermal parameters (standard deviations in parentheses)

Atom	x	y	z	B eq.*
Fe	0	0	0	0.78(2)
Cu	0.3497(1)	0.25	0.6224(1)	1.25(2)
S(1)	0.0180(2)	0.25	0.6362(3)	0.71(3)
S(2)	0.7056(2)	0.25	0.8828(3)	0.74(3)
O(1)	0.1172(6)	0.25	0.5163(8)	1.15(10)
O(2)	0.0489(4)	0.0812(5)	0.7612(5)	1.27(7)
O(3)	0.8727(6)	0.25	0.5223(8)	1.33(10)
O(4)	0.7944(4)	0.0798(5)	0.8903(5)	1.28(7)
O(5)	0.5967(6)	0.25	0.7028(8)	1.21(10)
O(6)	0.6436(6)	0.25	0.433(8)	1.82(11)
(OH)	0.0487(5)	0.25	0.1148(7)	0.77(9)
O(W1)	0.3731(7)	0.25	0.3548(9)	5.12(24)
O(W2)	0.6498(5)	0.234(7)	0.3773(9)	4.10(13)
O(W3)	0.3549(6)	0.25	0.9039(9)	3.40(17)
H(1)	0.035	0.25	0.229	5.12(24)
H(2)	0.738	0.061	0.443	3.5
H(3)	0.445	0.25	0.902	3.5

*Equivalent isotropic temperature factor, calculated from anisotropic temperature factors.

tropic thermal parameters turned out to be negative, probably caused by the inadequate absorption correction.

The refinement converged to an R factor of 0.056 for 942 reflections. Thirtyseven reflections with $\Delta F > 10.0$ were removed from the final refinement. The atomic scattering factors for Cu, Fe, S and O were taken from Cromer and Mann (1968). Anomalous dispersion corrections were made according to Cromer and Liberman (1970). All observed structure factors, (F_o 's) were weighted by $1/\sigma^2(F_o)$, where $\sigma(F_o)$ is the measured standard deviation of F_o . The final atomic parameters are listed in Table 2. Since all the anisotropic thermal parameters are not physically meaningful, an equivalent isotropic temperature factor, calculated from the anisotropic temperature factors (Hamilton, 1959), is listed. The observed and calculated structure factors are listed in Table 3², and the bond lengths and angles with their estimated standard deviations in Table 4. The average error in Cu-O, Fe-O and S-O bond lengths are 0.004, 0.006, and 0.005 Å and in O-Fe-O, O-Cu-O and O-S-O angles 0.2, 0.2, and 0.3° respectively.

Description of the crystal structure

The crystal structure of guildite consists of an octahedral-tetrahedral chain, consisting of $[\text{Fe}^{3+}\text{O}_6$

² To obtain a copy of this table, order Document AM-78-069 from the Business Office, Mineralogical Society of America, 1909 K Street NW, Washington, DC 20006. Please remit \$1.00 in advance for the microfiche.

Table 1. Guildite: crystal data

Guildite, $\text{CuFe}(\text{SO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$: United Verde Mine, Jerome, Arizona,	
NMNH #95950 Honey yellow platy prisms	
Monoclinic, $2/m$	Cell volume: 489.08 \AA^3
a : 9.786(2) Å	Cell content: $2[\text{CuFe}(\text{SO}_4)_2(\text{OH}) \cdot 4\text{H}_2\text{O}]$
b : 7.134(1)	D_m : $2.695(10) \text{ g cm}^{-3}$
c : 7.263(1)	D_x : 2.717 g cm^{-3}
β : $105.38(1)^\circ$	μ (MoK α): 44.06 cm^{-1}
Space group: $P2_1/m$	
(Laughon, 1970).	

Table 4. Guildite: interatomic distances (Å) and angles (°) (standard deviations in parentheses)

The Fe Octahedron			
Fe-(OH)	1.976(2) (x2)	(OH)-Fe-0(2)	91.5(2) (x2)
Fe-0(2)	2.002(4) (x2)	(OH)-Fe-0(2')	88.5(2) (x2)
Fe-0(4)	2.038(4) (x2)	(OH)-Fe-0(4)	89.1(2) (x2)
Mean	2.005	(OH)-Fe-0(4')	90.9(2) (x2)
		0(2)-Fe-0(4)	89.1(2) (x2)
		0(2)-Fe-0(4')	90.9(2) (x2)
(OH)-0(2)	2.849(7) (x2)	Mean	90.0
(OH)-0(2')	2.776(6) (x2)		
(OH)-0(4)	2.816(5) (x2)		
(OH)-0(4')	2.862(6) (x2)		
0(2)-0(4)	2.834(5) (x2)		
0(2)-0(4')	2.879(6) (x2)		
Mean	2.836		
The Cu Octahedron			
Cu-0(1)	2.200(6)	0(1)-Cu-0(W1)	92.1(3)
Cu-0(5)	2.328(6)	0(1)-Cu-0(W2)	89.8(1) (x2)
Cu-0(W1)	2.016(8)	0(1)-Cu-0(W3)	96.0(3)
Cu-0(W2)	1.951(5) (x2)	0(5)-Cu-0(W1)	82.3(3)
Cu-0(W3)	2.021(8)	0(5)-Cu-0(W2)	90.2(1) (x2)
Mean	2.078	0(5)-Cu-0(W3)	89.6(2)
		0(W1)-Cu-0(W2)	89.8(2)
		0(W2)-Cu-0(W3)	90.2(2)
0(1)-0(W1)	3.037(11)	Mean	90.0
0(1)-0(W2)	2.935(6) (x2)		
0(1)-0(W3)	3.139(8)		
0(5)-0(W1)	2.868(8)		
0(5)-0(W2)	3.014(9) (x2)		
0(5)-0(W3)	3.073(10)		
0(W1)-0(W2)	3.125(9)		
0(W2)-0(W3)	2.818(8) (x2)		
Mean	2.992		
The S(1) Tetrahedron			
S(1)-0(1)	1.463(7)	0(1)-S(1)-0(2)	107.5(2) (x2)
S(1)-0(2)	1.493(4) (x2)	0(1)-S(1)-0(3)	111.7(4)
S(1)-0(3)	1.440(6)	0(2)-S(1)-0(3)	110.9(2) (x2)
Mean	1.472	0(2)-S(1)-0(2')	108.3(3)
		Mean	109.5
0(1)-0(2)	2.384(7) (x2)		
0(1)-0(3)	2.402(9)		
0(2)-0(2')	2.420(6)		
0(2)-0(3)	2.416(6) (x2)		
Mean	2.404		
The S(2) Tetrahedron			
S(2)-0(4)	1.488(4) (x2)	0(4)-S(2)-0(5)	108.4(2) (x2)
S(2)-0(5)	1.457(5)	0(4)-S(2)-0(6)	109.6(2) (x2)
S(2)-0(6)	1.454(8)	0(4)-S(2)-0(4')	109.5(2)
Mean	1.472	0(5)-S(2)-0(6)	111.2(4)
		Mean	109.5
0(4)-0(5)	2.389(6) (x2)		
0(4)-0(6)	2.405(8) (x2)		
0(4)-0(4')	2.431(5)		
0(5)-0(6)	2.402(9)		
Mean	2.404		

(OH)] octahedra and two different types of [SO₄] tetrahedra sharing corners; these chains are cross-linked by [CuO₂(H₂O)₄] octahedra into sheets parallel to the (001) plane.

The octahedral-tetrahedral chains

The octahedral-tetrahedral chains running parallel to the *b* axis (7.134 Å) (Fig. 1), are similar to those found in a large number of ferric hydroxy-sulphate phases (Süsse, 1971), as well as transition metal phosphates (Moore, 1970). In guildite, these chains consist of zig-zag chains of [FeO₆(OH)] octahedra shar-

ing the (OH) corner; two pairs of octahedral corners on either side of this chain are shared by [S(1)O₄] and [S(2)O₄] tetrahedra. In this respect, the chain is different from the octahedral-tetrahedral chain found in Fe(OH)SO₄ (Johansson, 1962) in having additional sulphate groups as chain components. Topologically, the chain is identical to the one found in jahnsite, [Mg(H₂O)₄]₂[CaMnFe³⁺(OH)₂(PO₄)₄], and overite, [Mg(H₂O)₄]₂[Ca₂Al₂(OH)₂(PO₄)₄], (Moore and Araki, 1974, 1977). These chains, 9.786 Å apart in the structure, are cross-linked through isolated [CuO₂(H₂O)₄] octahedra, sharing the oxygen atom corners with S(1)O₄ and S(2)O₄ tetrahedra (Figs. 2 and 3). Three different types of water molecules [W(1), W(2) and W(3)] are coordinated to the copper atom only.

The layer structure

The dominant feature of the structure is the corrugated octahedral-tetrahedral layers (shown projected end-on in Fig. 2). These layers consist of eight-membered rings, consisting of two Fe and two Cu octahedra and four sulphate tetrahedra, with the sequence-Fe-S-Cu-S-Fe-S-Cu-S-. The layers are parallel to (001) and are cross-linked to adjacent layers through hydrogen bonds, accounting for the perfect (001) cleavage. A similar layer structure con-

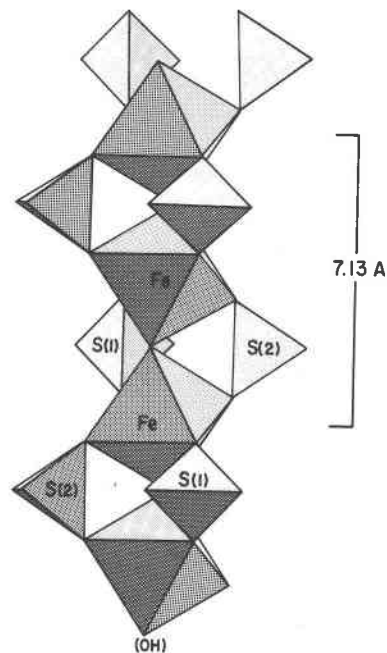


Fig. 1. The ferric hydroxy-sulphate chain parallel to the *b* axis in guildite.

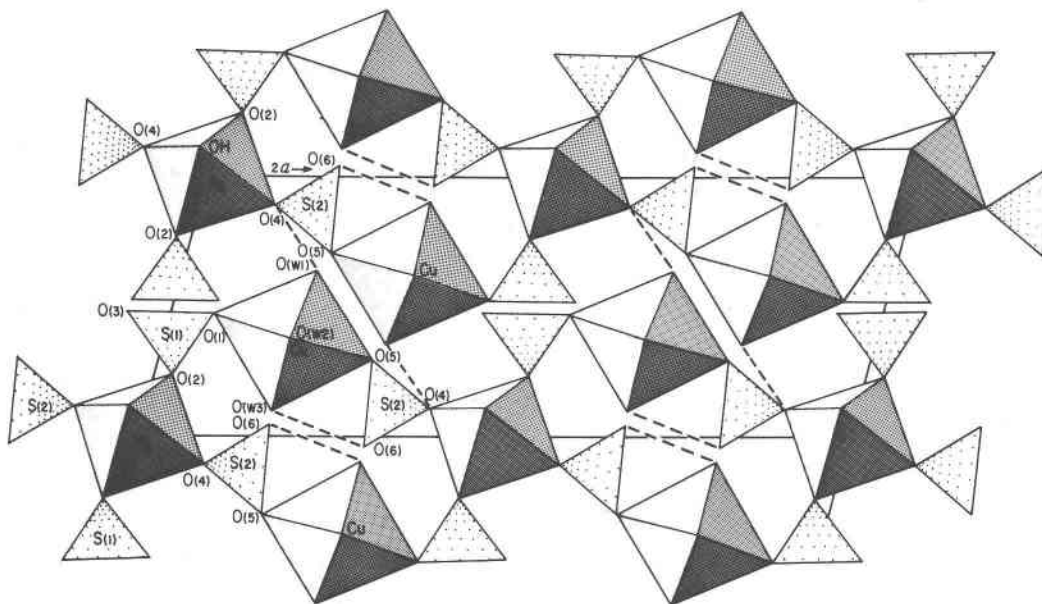


Fig. 2. A view of the layer structure of guildite, composed of ferric hydroxy-sulphate chains (projected end-on) linked by Cu octahedron. Note the eight-membered octahedral-tetrahedral rings and the inter-layer hydrogen bonds.

taining a twelve-membered octahedral-tetrahedral ring has been found in kornelite, $[\text{Fe}_2^{3+}(\text{H}_2\text{O})_6(\text{SO}_4)_3] \cdot 1.25 \text{H}_2\text{O}$ (Robinson and Fang, 1973).

Dimensions and distortions of the $[\text{FeO}_5(\text{OH})]$ and $[\text{CuO}_2(\text{H}_2\text{O})_4]$ octahedra and the $[\text{SO}_4]$ tetrahedra

The $[\text{FeO}_5(\text{OH})]$ octahedron with the point symmetry $\bar{1}$ is nearly regular, with an average Fe–O distance of 2.005Å. The Fe–(OH) distance (1.976Å) is significantly shorter than the Fe–O distances (2.002 and 2.038Å). The O–Fe–O angles vary from 88.5 to 91.5°.

The $[\text{CuO}_2(\text{H}_2\text{O})_4]$ octahedron with point symmetry m is in fact a tetragonal bipyramid; four water molecules surround the copper atom in a nearly regular square plane [av. Cu–O(H_2O) distance 1.985Å]; two oxygen atoms at distances of 2.200 and 2.328Å complete the octahedron. The Jahn-Teller distortion of the Cu^{2+} ion is indicated by these two long Cu–O bonds. The O–Cu–O angles vary from 82.3 to 96.0°.

The two crystallographically-different sulphate groups have the point symmetry m and average S–O distance of 1.472Å. Within each sulphate tetrahedron three oxygen corners are shared with Fe^{3+} or Cu^{2+} octahedron, the fourth oxygen corner being free; the free oxygen corner is the recipient of hydrogen bonds. The non-bridging S–O bond within each tetrahedron is shorter than the bridging S–O bonds.

The stereochemical features of the $[\text{CuO}_2(\text{H}_2\text{O})_4]$ octahedron and the two sulphate tetrahedra in guildite are very similar to those found in ransomite, $\text{CuFe}_2(\text{SO}_4)_4 \cdot 6\text{H}_2\text{O}$ (Wood, 1970). Ransomite possesses a different type of sheet structure, consisting of iron octahedral bands, one octahedron wide and two deep, connected by two types of corner-sharing sulphate tetrahedra; these bands are connected into a sheet through corner-sharing Cu-octahedra.

Hydrogen bonding

Out of the seven hydrogen atoms, three involved in relatively short hydrogen bonds have been located with some certainty. A hydrogen bond within the ferric hydroxy-sulphate chain involves the (OH) ion donating a hydrogen to a corner of the $[\text{S}(1)\text{O}_4]$ tetrahedron [(OH)–O(1) = 2.812Å].

Within the layer structure, the water molecule $W(2)$ donates a hydrogen to the non-bridging corner of the $[\text{S}(1)\text{O}_4]$ tetrahedron [$W(2)$ –O(3) = 2.690Å] and another hydrogen to $W(1)$ [$W(2)$ – $W(1)$ = 3.125Å]. The water molecule $W(3)$ donates one hydrogen to the non-bridging corner of $[\text{S}(2)\text{O}_4]$ tetrahedron [$W(3)$ –O(6) = 2.730Å] and the other hydrogen atom to a corner of the $[\text{S}(1)\text{O}_4]$ tetrahedron [$W(3)$ –O(2) = 3.154Å].

The hydrogen bonds holding the layers together involve two hydrogen atoms belonging to the water

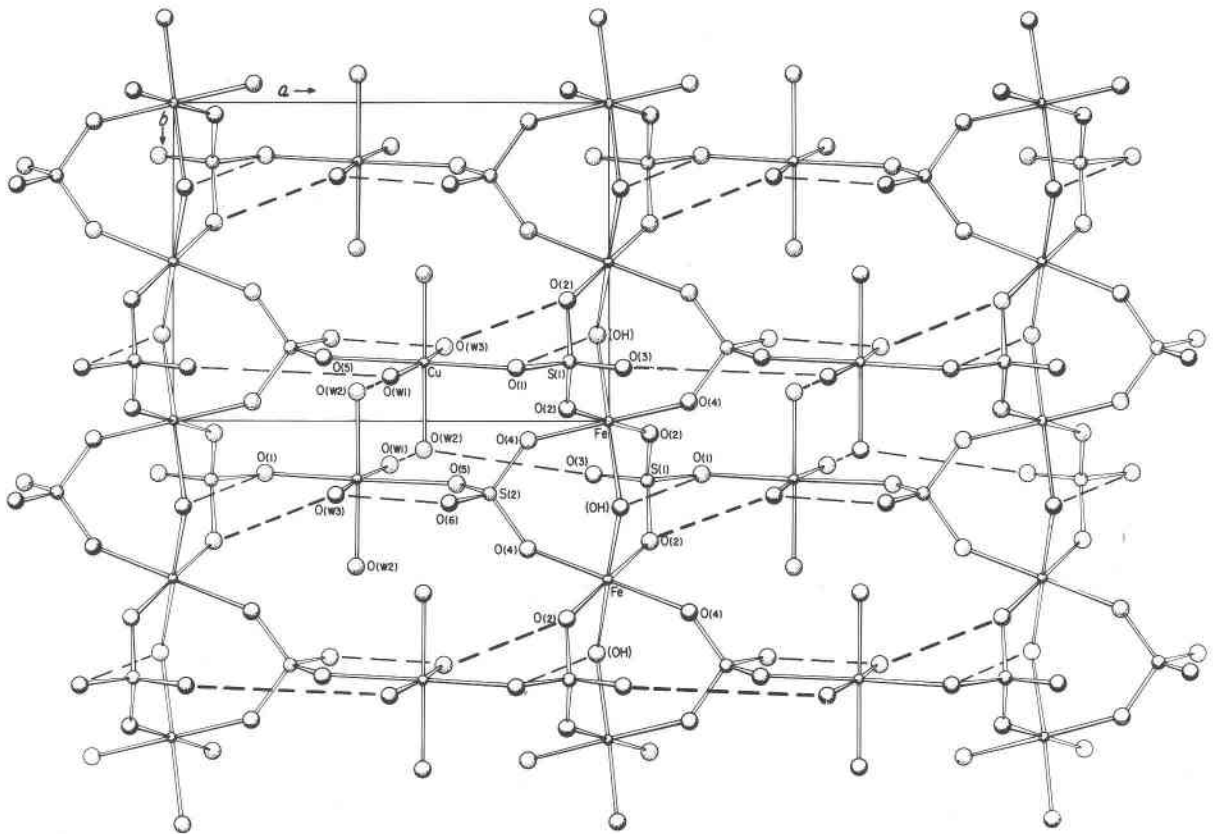


Fig. 3. A view of the guildite structure approximately down the c axis, showing the linking of the ferric hydroxy-sulphate chains through $[\text{CuO}_2(\text{H}_2\text{O})_4]$ octahedra and intra-layer hydrogen bonds.

molecule $W(1)$, which are donated to the mirror-related corners of the $S(2)$ tetrahedra belonging to the adjacent Cu,Fe hydroxy-sulphate layer [$W(1)$ -O(4) = 3.140Å].

Optical absorption spectra

The pleochroism of guildite is similar to that of other materials containing hydroxobridged Fe^{3+} chains. Intense color occurs only when the vibration

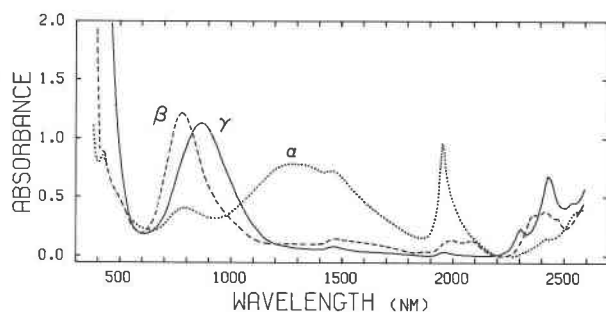


Fig. 4. Optical absorption spectrum of guildite; crystal thickness 150 μm .

direction of the incident light is along the chain direction ($E \parallel b$). The absorption spectrum (Fig. 4) contains contributions from Fe^{3+} , Cu^{2+} , H_2O , and OH^- . An analysis of the general features of the spectra of hydroxobridged chains of Fe^{3+} has been presented (Rossman, 1975, 1976), which can be used to identify the Fe^{3+} contributions to the guildite spectrum.

A salient feature of the hydroxobridged Fe^{3+} chain spectra is a strong relatively narrow absorption band at ~ 430 nm assigned to the ${}^6A_{1g} \rightarrow ({}^4A_{1g}, {}^4E_g)$ transition of Fe^{3+} , polarized along the chain direction. It occurs at 430 nm in the guildite spectrum polarized $E \parallel b$. The peak of the band is off scale in Figure 4, but weak components of the transition are found at 430 nm in the α and β spectra. The ϵ value, approximately 33 in γ , is similar to that found for other hydroxobridged Fe^{3+} chains such as in butlerite and parabutlerite, and for the two-dimensional sheet of hydroxobridged Fe^{3+} in jarosite (Rossman, 1976, 1977).

By analogy to the spectra of butlerite, parabutlerite, and stewartite, the lowest-energy Fe^{3+} absorption band is predicted to occur in the range 880–

920 nm, and is expected to be polarized in the direction of the chain. The band at 874 nm ($E \parallel b$) best satisfies this prediction and is accordingly assigned to Fe^{3+} . The ϵ value is approximately 9.4, which is somewhat higher than the value of 2.4 found in butlerite and parabutlerite, although absorption from Cu^{2+} may in part contribute to the absorption in this region.

The Cu^{2+} absorption features must then be the remaining broad absorption bands at 1285 nm, most intense in α , and at 780 nm in β . The ϵ values for these bands are 7.1 and 10.3 respectively, in the most intense direction. The polarization of the higher-energy 780 nm band corresponds to the direction of intermediate compression of the CuO_6 polyhedron, whereas the 1285 nm band is polarized in the direction of maximum extension.

Overtones and combinations of infrared absorptions contribute the remaining spectroscopic features in the 1000 to 2600 nm range. The combination mode involving stretching and bending of H_2O at 1953 nm in α is the most prominent.

Optical orientation

The direction of the most intense color, b , corresponds to the greatest index of refraction, γ . Because the (100) cleavage slab provides an almost exactly centered Bxo orientation ($\beta\gamma$), β must be oriented almost exactly along c .

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