Crystal structure of wiserite

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Abstract

The discovery of excellent crystals at the Kombat mine, Namibia, permitted the crystal structure of wiserite, a rare manganese borate, to be solved. The cell parameters of wiserite are $a = 20.192(6)$, $c = 3.281(2)$ Å; space group $P4/n$ (C_{4h}^3); $Z = 2$. The crystal structure was solved by direct methods and was refined to $R = 0.058$ for 2931 reflections. The general formula of this mineral is

$$\{(Mn,Mg)_{14}(B_2O_5)_4(OH)_8\}\{[Si_{1-x}Mg_x][O_{1-x}(OH)_x]_4Cl_{2x}\}$$

with $x \simeq 0.5$.

The wiserite structure consists of an ordered three-dimensional network with formula $[Mn_{14}(B_2O_5)_4(OH)_8]^{4+}$. With minor restrictions, wiserite is another member of the mineral group with the 3-Å wallpaper structure. Three-fourths of the Mn atoms are octahedrally coordinated by O and OH; and a quarter of the Mn atoms are five-coordinated. Mn-O distances range from 2.09 to 2.30 Å. The two BO_3 groups are linked to form B_2O_5 dimers with $(B-O)_{nonbridging}$ ranging from 1.35 to 1.38 Å and $(B-O)_{bridging}$ ranging from 1.40 to 1.41 Å. Channels parallel to [001] contain (SiO_4) and $Mg(OH)_4$ groups as well as Cl atoms.

Introduction

Wiserite is a very rare hydrated borate of manganese containing minor amounts of Mg, Si, Ca, Fe, and Cl. Data compiled from the literature as well as new mineralogical, chemical, and physical data have been reported by Dunn et al. (1989). Superior crystals recently discovered at the Kombat mine in Namibia made determination of the crystal structure possible. The structure was solved to resolve ambiguities about the average chemical formula of wiserite.

Experimental details

Preliminary X-ray investigations of approximately a dozen wiserite crystals from the Kombat mine were carried out by oscillation and Weissenberg film methods. These investigations confirmed the lattice parameters, Laue symmetry, and extinction rules reported by Dunn et al. (1989). However, rotation photographs of three crystals with the fourfold axis as rotation axis, exposed for ~200 h, show very faint streaks, not resolved into single spots, indicating that the lattice constant c of these crystals is a quadruple of 3.281(2) Å.

A cut crystal chip with the approximate dimensions 0.1 × 0.1 × 0.3 mm, showing no multiplicity of c, was used for the structure determination. The X-ray intensity data (Mo$K\alpha$ radiation, graphite monochromator) were collected with a Stoe four-circle diffractometer. Conditions

for intensity measurements include scan-speed ratio $2\theta{:}\omega = 1{:}1$, 50 steps for each reflection (increased for $\alpha_1 - \alpha_2$ splitting), step width = 0.035°, step time = 0.5 to 1.5 s, eight steps at each side for background correction. Three standard reflections were measured in intervals of 120 min and showed no significant intensity variation. A total of 5489 reflections ($h, k, \pm l$) up to $2\theta = 75°$ were collected. Corrections were applied for Lorentz and polarization effects and for absorption (Gaussian integration, minimum and maximum transmission factors 0.24 and 0.41, respectively; $\mu(MoK\alpha) \simeq 63.5$ cm⁻¹). Symmetry-related reflections were averaged, yielding a unique data set of 3541 reflections ($R_{int} = 0.047$) of which 2931 had $F_o > 3\sigma(F_o)$ and were treated as observed reflections in all calculations (program strucsy, Stoe and Cie, 1984). Complex scattering functions for neutral atoms were obtained from the *International Tables for X-ray Crystallography* (1974).

The positions of the Mn atoms were found by direct methods; those of all the other atoms by subsequent Fourier and difference-Fourier summations. The structure parameters for all atoms were fit by least-squares techniques; the ratio of maximum least-squares shift to error in the last cycle of refinement (Δ/σ) was $<10^{-3}$. The isotropic secondary extinction factor was refined to a value of $3.2(9) \times 10^{-6}$ (Zachariasen, 1967). The reliability indices were $R = 0.059$ and $wR = 0.058$, $w = [\sigma(F_o)]^{-2}$ for 140 variables. A final difference-Fourier summation showed minimum and maximum heights of 3.0 and -4.4

TABLE 1. Fractional atomic coordinates and anisotropic temperature factors of wiserite

Atom	Position	x	y	z	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	4d	0.0	0.0	0.0	0.0177(4)	0.0188(4)	0.0255(6)	−0.0004(3)	−0.0002(4)	−0.0012(4)
Mn(2)	8g	0.26828(3)	0.03228(3)	0.95605(22)	0.0098(2)	0.0109(2)	0.0125(3)	−0.0005(2)	−0.0001(2)	−0.0003(2)
Mn(3)	8g	0.11177(3)	0.08627(3)	0.46820(21)	0.0097(2)	0.0117(2)	0.0124(3)	0.0001(2)	−0.0002(2)	−0.0004(2)
Mn(4)	8g	0.24572(3)	0.88625(3)	0.43468(24)	0.0187(3)	0.0137(3)	0.0170(3)	−0.0001(2)	−0.0045(3)	0.0020(3)
B(1)	8g	0.9589(2)	0.1203(2)	0.4130(15)	0.0106(16)	0.0091(15)	0.0087(18)	0.0011(12)	−0.0020(14)	0.0001(14)
B(2)	8g	0.8637(2)	0.0487(2)	0.1100(15)	0.0063(15)	0.0111(16)	0.0105(19)	0.0009(12)	−0.0009(13)	−0.0016(15)
OH(1)	8g	0.1085(1)	0.1555(1)	0.9665(11)	0.0129(12)	0.0092(11)	0.0169(16)	0.0021(9)	0.0005(11)	−0.0012(11)
OH(2)	8g	0.2174(1)	0.0811(1)	0.4596(11)	0.0099(11)	0.0123(12)	0.0143(15)	0.0006(9)	−0.0008(11)	−0.0010(11)
O(1)	8g	0.8952(1)	0.1051(1)	0.2650(12)	0.0104(12)	0.0086(12)	0.0258(19)	0.0013(10)	−0.0041(12)	−0.0063(12)
O(2)	8g	0.3146(1)	0.9717(1)	0.4601(10)	0.0074(10)	0.0134(11)	0.0142(16)	0.0016(9)	0.0015(10)	−0.0020(11)
O(3)	8g	0.0032(1)	0.0707(1)	0.4817(10)	0.0076(10)	0.0089(11)	0.0150(15)	0.0007(8)	−0.0018(10)	0.0000(10)
O(4)	8g	0.2038(1)	0.9437(1)	0.9416(11)	0.0073(10)	0.0138(12)	0.0157(15)	0.0002(9)	0.0003(10)	0.0004(11)
O(5)	8g	0.1034(1)	0.0078(1)	0.9724(11)	0.0092(11)	0.0098(11)	0.0161(15)	0.0010(9)	−0.0013(11)	−0.0010(11)
O(6)	8g	0.2980(3)	0.8168(3)	0.7822(18)	0.0335(26)	0.1147(53)	0.0604(41)	0.0417(30)	0.0248(27)	0.0640(40)
Me	2a	0.75	0.25	0.0	0.0086(6)	0.0086(6)	0.0331(17)	0.0	0.0	0.0
Cl(1)	2c	0.75	0.75	0.7714(89)	0.0423(67)					
Cl(2)	2c	0.75	0.75	0.2709(106)	0.0463(80)					
Cl(3)	2c	0.75	0.75	0.5230(96)	0.0367(71)					
Cl(4)	2c	0.75	0.75	0.0206(113)	0.0592(81)					

Note: Occupation of Me = 0.5(1)Mg + 0.5(1)Si. The occupation factors for Cl(1) to Cl(4) are 0.20(3); for all other atoms, 1.0. The temperature factors are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$. Numbers in parentheses are esd's.

$e/\text{Å}^3$. The final atomic parameters are listed in Table 1, selected interatomic distances and angles in Table 2, and the structure factors in Table 3.[1]

DESCRIPTION AND DISCUSSION

Figure 1 shows the structure of wiserite. The Mn(1) to Mn(4) polyhedra share edges to form a framework with large channels. This framework is another example of the 3-Å wallpaper structure (Moore and Araki, 1974). The B_2O_5 groups and the Me and Cl atoms are located at distinct positions within the channels.

The Mn atoms in wiserite are six- and five-coordinated by O atoms. The mean Mn-O distances in the $Mn(2)O_6$ and $Mn(3)O_6$ octahedra are 2.206 Å and agree with the expected value of 2.21 Å (Peacor, 1972). The mean Mn-O distance in the $Mn(1)O_6$ octahedra (2.149 Å), however, is short. Mn(1) is bonded to six oxygen atoms, whereas Mn(2) and Mn(3) are each bonded to three oxygen atoms and three hydroxyls. Differences in anion coordination as well as minor substitution in the Mn(1) site by Mg are assumed to be responsible for the differences in the mean Mn-O distances. Partial substitution of Mg in Mn(1), suggested by the chemical analyses, would diminish the mean distance to the coordinating oxygen atoms for the average structure model. Accordingly, a greater vibration of the oxygen atoms parallel to the metal-oxygen bond should be observed to compensate for the local distortions.

Mn(4) is coordinated to five oxygen atoms, forming a tetragonal pyramid. Three of these oxygen atoms, O(2) and O(4) are also bonded to two Mn atoms, and one B atom. Two of the oxygen atoms, O(6), are also shared with the Me site (Mg,Si). A sixth oxygen atom, Mn(4)-

O(6), is at a distance of 2.77 Å. Two examples of five-fold coordination of Mn^{2+} by oxygen are given by Peacor (1972): $Bi_2Mn_4O_{10}$ (Niizeki and Wachi, 1968) and $HoMn_2O_5$ (Quezel-Ambrunaz et al., 1964). Although these two compounds are quoted by Peacor (1972) as examples of Mn^{2+} compounds, the possibility of the presence of

TABLE 2. Selected interatomic distances (Å) and angles (°) in wiserite

Mn(O,OH)$_x$ polyhedra					
Mn(1)-O(3)	2.131(3) 2×		Mn(3)-OH(1)	2.152(3)	
-O(3')	2.221(3) 2×		-OH(1')	2.160(3)	
-O(5)	2.095(3) 2×		-OH(2)	2.135(3)	
			-O(3)	2.215(3)	
Mn(2)-OH(1)	2.178(2)		-O(5)	2.278(3)	
-OH(2)	2.164(6)		-O(5')	2.297(3)	
-OH(2')	2.181(3)				
-O(2)	2.241(3)		Mn(4)-O(2)	2.218(3)	
-O(2')	2.260(3)		-O(4)	2.163(3)	
-O(4)	2.214(2)		-O(4')	2.197(3)	
			-O(6)	2.094(6)	
			-O(6')	2.296(5)	
Borate group					
B(1)-O(1)	1.408(5)		O(1)-B(1)-O(2)	115.2(3)	
-O(2)	1.348(5)		-O(3)	120.0(3)	
-O(3)	1.362(5)		O(2)-B(1)-O(3)	125.0(4)	
B(2)-O(1)	1.401(5)		O(1)-B(2)-O(4)	113.7(3)	
-O(4)	1.381(5)		-O(5)	122.5(4)	
-O(5)	1.347(5)		O(4)-B(2)-O(5)	123.8(4)	
			B(1)-O(1)-B(2)	135.7(7)	
Me (= Mg,Si) tetrahedron					
Me-O(6)	1.808(5) 4×		O(6)-Me-O(6)	99.0(5) 4×	
			-O(6')	133.5(5) 2×	
Cl(OH)$_x$ polyhedra					
Cl(1)-OH(1)	3.541(7) 4×		Cl(2)-OH(1)	3.522(7) 4×	
-OH(2)	3.555(6) 4×		-OH(2)	3.584(8) 4×	
Cl(3)-OH(1)	3.792(13) 4×		Cl(4)-OH(1)	3.435(2) 4×	
-OH(1')	3.822(13) 4×		-OH(2)	3.870(15) 4×	
-OH(2)	3.474(2) 4×		-OH(2')	3.814(13) 4×	

Note: Numbers in parentheses are esd's.

[1] A copy of Table 3 may be ordered as Document AM-89-424 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.
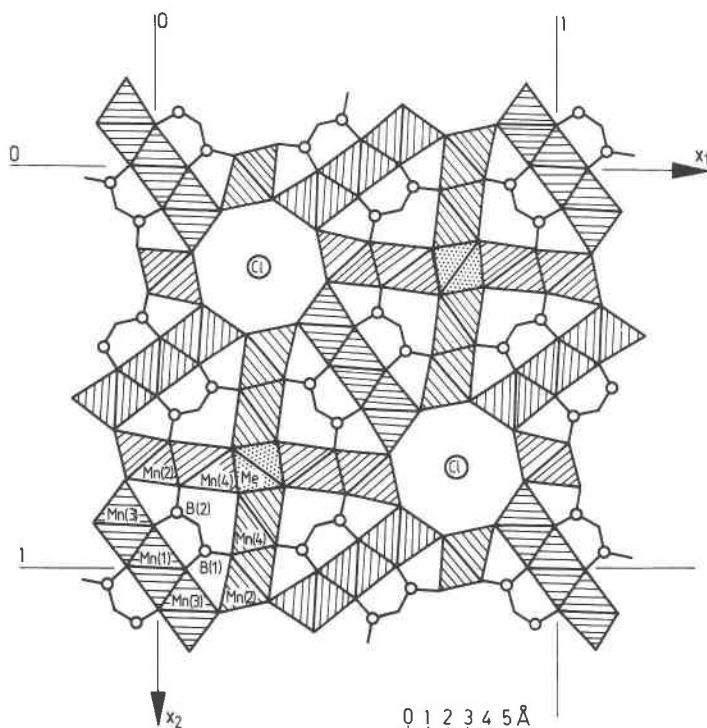
Fig. 1. The crystal structure of wiserite projected parallel to [001].

some Mn^{3+} in both of these ceramic phases must be considered, thereby casting doubt on the meaningfulness of the comparison.

Approximately a dozen borate minerals with distinct B_2O_5 groups have been described; the crystal structures of only two have been determined accurately, suanite (Takéuchi, 1952) and szaibelyite = ascharite (Takéuchi, 1957; Peng et al., 1963; Kudoh and Takéuchi, 1973; Takéuchi and Kudoh, 1975). A feature, common to these two structures as well as to that of wiserite is that the angles between the direction normals to the planar BO_3 groups range from 20° to 50°. This orientation of the two BO_3 triangles may be due to the resonance of the electron orbitals of these two groups. The variability of the B-O-B angles is small: 130(10)°. The deviation of the B-O-B angle from 180° is caused by the unbonded lone-pair electrons at the oxygen atom and their space requirements. Taking into account the lone-pair electrons, these oxygen atoms have a slightly distorted triangular planar environment.

The Me position has the point symmetry $\bar{4}$ with four Me-O(6) distances of 1.81 Å; the coordination polyhedron is a strongly flattened MeO_4 tetrahedron. The mean [4]Si-O bond length, given in the literature, is 1.63(3) Å (Correns, 1968), the mean [4]Mg-O bond length is 1.94(5) Å. This latter value was calculated from "normal" spinel $MgAl_2O_4$, with Mg-O = 1.93 Å (Fischer, 1967) and Mg-O = 1.95 Å (Zorina and Kvitka, 1969); from MgV_2O_4 with Mg-O = 1.96 Å (Plumier and Tardieu, 1963); from åk-

ermanite, $Ca_2Mg(Si_2O_7)$, with Mg-O = 1.88 Å (Smith, 1953); and from magnesian merrihueite $K_2^{[6]}Mg_2$ ([4]Mg_3 $Si_{12}O_{30}$), with [4]Mg-O = 1.96 Å (Khan et al., 1972).

There are two reasons for the assumption that the position Me is occupied by Mg and Si atoms in a 1:1 ratio: (1) The site occupancy for Mg and Si at the Me position, determined by least-squares refinement is 0.5 for both elements. (2) The Si occupancy of the Me site approximately agrees with the chemical analyses.

The mean Me-O distance, 1.81 Å, in the distorted MeO_4 tetrahedron is short if compared to the mean [4]Mg-O distance and long if compared to the [4]Si-O distance. The O(6) atom has a large thermal-vibration amplitude, 0.40 Å, parallel to the Me-O bond, whereas the amplitude normal to this direction is only 0.12 Å. This suggests that O(6) may be positionally disordered with two Me-O distances. At least partial order in the arrangement of the Me position might be one reason for the weak interlayer reflections observed for long-time X-ray exposures.

The channels parallel to the fourfold axes at (¼, ¼, z) and (¾, ¾, z) have diameters of approximately 6 Å. Four positions within these channels with point symmetry 4 are partially occupied by Cl atoms. These Cl atoms are bonded to the framework by eight to twelve Cl···H-O bonds. Comparable situations in the coordination chemistry of Cl atoms were observed in the following ordered structures: $MgCl_2\cdot12H_2O$ (Sasvari and Jeffrey, 1966), $AlCl_3\cdot6H_2O$ (Andress and Carpenter, 1934; Buchanan and Harris, 1968), $HCl\cdot6H_2O$ (Taesler and Lundgren, 1978),

hydrochlorborite, $Ca_2[B_3O_3(OH)_4 \cdot OB(OH)_3]Cl \cdot 7H_2O$ (Brown and Clark, 1978), $MgCl_2 \cdot 6H_2O$ (Andress and Gundemann, 1934; Agron and Busing, 1985), and $CaCl_2 \cdot 6H_2O$ and $SrCl_2 \cdot 6H_2O$ (Agron and Busing, 1986). In all these compounds the distance from the acceptor Cl atoms to the donor O atoms of the hydrogen bonds are within the range 2.9 Å to 3.2 Å, irrespective of the coordination polyhedron and the coordination number. In wiserite, however, the $Cl \cdots H-O$ distances are within the range 3.4 Å to 3.9 Å, and all the Cl atoms have large thermal-vibrational amplitudes. It is assumed that the positional coordinates of the Cl atoms are for an average position and that in reality, these atoms are drawn toward a distinct number of oxygen atoms, so that the distances $Cl \cdots H-O$ are shortened to a length comparable to those observed in the above-cited crystal structures. An attempt to refine anisotropic displacement factors for the Cl atoms failed, with some factors having negative signs.

As mentioned above, single-crystal rotation photographs, made with $CuK\alpha$ radiation and rotation axis [001], showed a quadrupling of the c axis as indicated by very faint streaks. The quadrupling may be due to the ordering of the Mg and Si atoms at the Me position as well as an ordering of the Cl atoms.
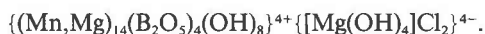
The Kombat wiserite has the complex formula

$$\{(Mn,Mg)_{14}(B_2O_5)_4(OH)_8\}\{[Si_{1-x}Mg_x][O_{1-x}(OH)_x]_4Cl_{2x}\}$$

with $x \simeq 0.5$, which is in agreement with the formulas of hypothetical end-members:
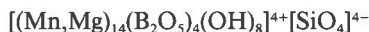
$$[(Mn,Mg)_{14}(B_2O_5)_4(OH)_8]^{4+}[SiO_4]^{4-}$$

and

$$\{(Mn,Mg)_{14}(B_2O_5)_4(OH)_8\}^{4+}\{[Mg(OH)_4]Cl_2\}^{4-}.$$

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