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The structure of hemimorphite

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With 1 figure

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Auszug

Die Struktur von Kieselzinkerz, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$, wurde auf Grund von *hk*0- und 0*kl*-Projektionen der Elektronendichte neu bestimmt. Das Si_2O_7-Ion besteht aus zwei SiO_4-Tetraedern mit einem gemeinsamen Sauerstoffatom; der Si—O—Si-Winkel ist 133°, der Si—O-Abstand vom gemeinsamen O-Atom 1,72 Å; die übrigen Si—O-Abstände sind 1,60 und 1,62 Å.

Nach vorläufigen Ergebnissen einer gemeinsam mit H. Lynton angestellten Untersuchung hat der Thortveitit, $Sc_2Si_2O_7$, nicht die Symmetrie $2/m$ und ist der Winkel Si—O—Si entgegen früheren Annahmen kein rechter.

Abstract

The structure of hemimorphite, $Zn_4(OH)_2Si_2O_7 \cdot H_2O$, has been redetermined by means of *hk*0 and 0*kl* electron-density projections. The Si_2O_7 ion consists of two SiO_4 tetrahedra with a shared corner; the Si—O—Si angle is 133° and the Si—O distances are 1.72 Å (central) and 1.60, 1.62 Å (peripheral).

Preliminary results for thortveitite, $Sc_2Si_2O_7$, (with H. Lynton) show that the crystals do not have $2/m$ symmetry and that the Si—O—Si angle is not 180° as formerly supposed.

Introduction

Earlier investigations of hemimorphite, $Zn_4(OH)_2Si_2O_7 \cdot H_2O$ (Ito and West, 1932), and thortveitite, $Sc_2Si_2O_7$ (Zachariasen, 1930), indicated linear Si—O—Si bonds in the pyrosilicate groups. On the other hand in the melilites (Warren, 1930; Warren and Trautz, 1931), lawsonite (Wickman, 1947), tilleyite (Smith, 1953) and epidote (Ito, Morimoto and Sadanaga, 1954) the reported Si—O—Si angles range from 131° to 165°; moreover in X_2O_7 groups of other kinds the X—O—X angle is usually considerably less than 180°. Accordingly, as already reported briefly (Barclay, Cox and Lynton, 1956) we have undertaken a re-examination of hemimorphite and thortveitite.

Experimental

The material used was from the Glencrieff Mine, Wanlockhead. Spectroscopic examination (for which we are indebted to Dr. P. G. HARRIS) showed that the concentrations of impurities (Ge, Fe, Cu and In) in no case exceeded $0.1^0/_0$. X-ray examination of single crystals confirmed the cell dimensions and space group assigned by ITO and WEST, the results being as follows:

$$\text{Orthorhombic, } Imm\ (C_{2v}^{20});\ Z = 2$$

density (calc) 3.48, (obs) 3.45 g/cm^3.

Cell dimensions

	BARCLAY and COX	ITO and WEST
$a =$	8.37 Å	8.38 Å
$b =$	10.67	10.70
$c =$	5.10	5.11

Table 1. *Comparison of observed and calculated structure factors*

(a) 0kl zone

0 k l	F_{obs}	F_{calc}	0 k l	F_{obs}	F_{calc}
0 0 2	223	218	0 1 1	84	89
0 0 4	136	120	0 1 3	65	72
0 0 6	74	86	0 1 5	42	42
0 0 8	44	44			
			0 3 1	123	133
0 2 0	88	105	0 3 3	108	92
0 2 2	51	60	0 3 5	82	72
0 2 4	45	36	0 3 7	33	35
0 2 6	36	37			
			0 5 1	51	48
0 4 0	83	98	0 5 3	67	67
0 4 2	103	94	0 5 5	40	32
0 4 4	95	87			
0 4 6	53	53	0 7 1	87	83
			0 7 3	38	37
0 6 0	191	207	0 7 5	42	40
0 6 2	144	141			
0 6 4	105	96	0 9 1	91	88
0 6 6	71	63	0 9 3	42	51
			0 9 5	55	46
0 10 0	73	69			
0 10 2	79	74	0 11 1	20	17
0 10 4	77	71			
0 10 6	35	42	0 13 1	44	47
0 12 0	67	68	0 15 1	42	44
0 12 2	70	62			
0 12 4	57	52			
0 16 0	25	41			

Note: for the 0kl zone F is complex; phase angles have not been included in the table.

(b) hk0 zone

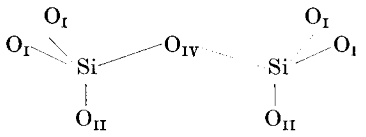
h k 0	F_{obs}	F_{calc}	h k 0	F_{obs}	F_{calc}
0 2 0	82	-106	1 1 0	86	78
0 4 0	91	-100	1 3 0	117	-142
0 6 0	167	207	1 5 0	44	27
0 8 0	-	- 1	1 7 0	48	46
0 10 0	69	- 69	1 9 0	48	- 42
0 12 0	68	68	1 11 0	-	- 15
			1 13 0	25	27
2 0 0	114	-117			
2 2 0	78	73	3 1 0	35	- 31
2 4 0	43	42	3 3 0	116	115
2 6 0	83	- 70	3 5 0	53	- 47
2 8 0	49	35	3 7 0	-	1
2 10 0	26	29	3 9 0	50	46
2 12 0	40	- 39			
			5 1 0	95	84
4 0 0	116	111	5 3 0	169	-177
4 2 0	10	- 5	5 5 0	35	30
4 4 0	67	- 57	5 7 0	73	83
4 6 0	82	83	5 9 0	77	- 90
4 8 0	17	17			
4 10 0	48	- 51	7 1 0	23	- 21
4 12 0	35	37	7 3 0	57	57
			7 5 0	-	- 10
6 0 0	93	96	7 7 0	30	- 33
6 2 0	27	- 20	7 9 0	50	50
6 4 0	19	- 15			
6 6 0	52	51	9 1 0	37	31
			9 3 0	51	- 48
8 0 0	34	- 35	9 5 0	-	2
8 2 0	21	19	9 7 0	48	45
8 4 0	-	14			
8 6 0	31	- 31			
10 0 0	84	81			
10 2 0	19	- 16			
10 4 0	41	- 46			

The hemimorphic nature of the crystals is perhaps too well established to be in need of further proof, but in fact a Wilson plot (WILSON, 1949) of the $0kl$ intensities confirmed the absence of a symmetry centre. The majority of the intensity measurements were made with copper $K\alpha$ radiation, but a few additional measurements in the $0kl$ zone were made with molybdenum $K\alpha$ radiation. 51 intensities were used for the $hk0$ projection and 43 for the $0kl$. All intensities were estimated visually from Weissenberg photographs, but in addition 25 of the $0kl$ intensities were measured on a Geiger-counter diffractometer; the reasonably low value (0.085) of the disagreement index $\Sigma||F|\,(\text{Geiger}) - |F|\,(\text{visual})|/\Sigma|F|\,(\text{Geiger})$ for these 25 reflections showed that the visual estimations were of good accuracy. The structure factors, put on an absolute scale by means of the Wilson plot, are given in Table 1.

The structure analysis

The unit cell contains the following atoms (see formula below):

8 Zn and 8 O_I in general positions;
4 Si, 4 O_{II} and 4 O_{III} (in OH) in mirror planes;
2 O_{IV} and 2 O_V (in H_2O) on two-fold axes.



The $0kl$ projection was studied first and from a Patterson synthesis the fractional coordinates of the Zn atoms were found to be $y = 0.16$ and $z = 0$; by means of Fourier electron-density and difference maps the y and z coordinates of the other atoms were found (Table 2). From this projection alone (Fig. 1) the subscripts of the last three oxygens could not be assigned at this stage, except that it was clear that the

Table 2. *Atomic coordinates (fractional)*

atom	x	y	z
Zn	0.204	0.160	0.000
Si	0.000	0.148	0.503
O_I	0.160	0.205	0.637
O_{II}	0.000	0.155	0.190
O_{III} (OH)	0.308	0.000	0.952
O_{IV}	0.000	0.000	0.637
O_V (H_2O)	0.500	0.000	0.558

one with coordinates (0, 0.952) could not be O_{IV} as it is much too far from the silicon atoms.

Electron-density and difference maps were then made for the *hk*0 projection and these, combined with the previous results, led to the final coordinates of Table 2. The second projection showed clearly that O_{III} does not lie on a symmetry axis and therefore must be OH. The discrimination between O_{IV} and O_V was not immediately obvious since the results of the two projections could equally validly have been combined to give these atoms coordinates (0.500, 0, 0.637) and (0, 0, 0.558) in which case the Si—O_{IV}—Si bonds would have been nearly linear. However calculation showed that these coordinates would lead to the impossibly short H_2O—OH distance of 2.30 Å and they were therefore rejected.

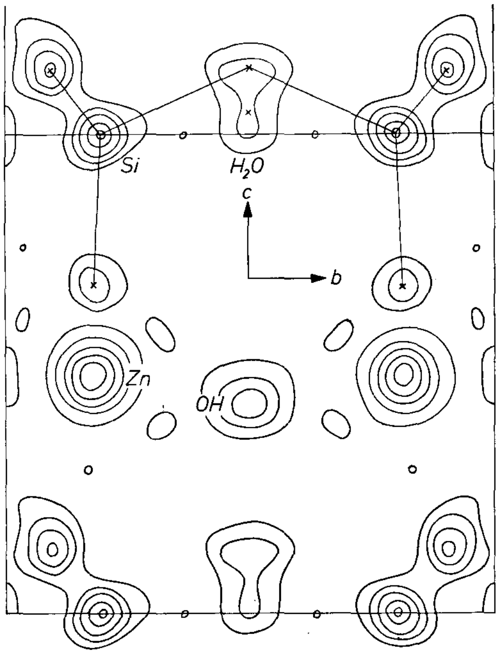


Fig. 1. The electron-density map of hemimorphite projected on (100). The origin of coordinates is at the centre of the half cell (of sides $\frac{1}{2}b$ and c).

The structure factors calculated from the coordinates of Table 2, with a temperature factor $B = 1.2$ Å^2 for all atoms, are shown in Table 1. The disagreement indices are 0.09 and 0.10 for 0*kl* and *hk*0 respectively.

Results of the analysis

The interatomic distances and angles in the pyrosilicate ion are as follows:

$Si—O_{I}$	1.62 Å	$O_{I} \cdots O_{I}$	2.68 Å
$Si—O_{II}$	1.60 Å	$O_{I} \cdots O_{II}$	2.70 Å
$Si—O_{IV}$	1.72 Å	$O_{I} \cdots O_{IV}$	2.56 Å
$Si \cdots Si$	3.16 Å	$O_{II} \cdots O_{IV}$	2.82 Å
$Si—O_{IV}—Si$	133°	$O_{I}—Si—O_{IV}$	100°
$O_{I}—Si—O_{I}$	$111^1/_2$	$O_{II}—Si—O_{IV}$	116
$O_{I}—Si—O_{II}$	$112^1/_2$		

The distortion of the SiO_4 groups from the regular tetrahedral form is thus quite small, but the central Si—O—Si angle is very significantly larger than tetrahedral.

Each zinc atom is surrounded approximately tetrahedrally by four oxygen atoms at the following distances:

$$O_{I}\ 1.95,\ 1.96;\ O_{II}\ 1.96;\ O_{III}\ 1.93\ \text{Å}.$$

The water molecules lie in channels parallel to the *c* axis, where they are held by two bonds to OH ions of length 2.57 Å. The calculated angle between these two bonds is 78°, which seems rather small, and it is possible that the z coordinate of the water molecule (O_V) is somewhat in error.

There are no other O · · · O distances less than 3 Å.

Thortveitite

Thortveitite, $Sc_2Si_2O_7$, is monoclinic, space group *Cm*, *C*2 or *C*2/*m* with two formula-weights in the unit cell. In the absence of evidence to the contrary it has been assumed hitherto that the symmetry is 2/*m* and consequently that the Si—O—Si bonds are collinear. With Dr. H. Lynton we have re-examined this mineral, and although we have not yet completed our analysis, the statistical evidence favours the space group *Cm*, the symmetry of which does not require the Si—O—Si bonds to be collinear.

Wilson plots of the *hk*0 and *h*0*l* intensities indicate that neither of these projections is centrosymmetrical. However the numbers of intensities available in the two zones (35 and 38 respectively) are too small to give entirely satisfactory statistical results and we have therefore embarked on a three-dimensional analysis. A reasonable interpretation of the Patterson synthesis (about 250 terms) with space-group *Cm* has been made, but detailed analysis is difficult because the symmetry of the structure is nearly $C2/m$. The silicon atoms and the central oxygen atom lie in the mirror plane but it is not yet possible to assign reliable values to the Si—O—Si angle and the bond distances.

Discussion

The bond lengths and angles obtained from the more recent structure analyses of substances containing Si_2O_7 groups are summarised below.

	Si—O (central)	Si—O (peripheral)	Si—O—Si
Lawsonite (Wickman, 1947)	1.59 Å	1.65 Å	150°
Tilleyite (Smith, 1953)	1.65 Å	1.58—1.62 mean 1.60	167
Epidote (Ito *et al.*, 1954)	1.60, 1.70 mean 1.65	1.59—1.66 mean 1.63	155
Zoisite (Fesenko *et al.*, 1956)	1.63, 1.67 mean 1.65	1.53—1.68 mean 1.62	161
Hemimorphite (Barclay and Cox, 1959),	1.72	1.60, 1.62 mean 1.61	133

Although the environments of the pyrosilicate ions in the various structures are different and the accuracy of the analyses varies, it is clear from these figures that the configuration and dimensions of the ion are much the same in all structures, the Si—O—Si angle being, as would be expected, more sensitive than the bond lengths to environmental effects. The figures suggest that the results for lawsonite may be in error, since it is very unlikely that the central Si—O bonds are shorter than the peripheral ones.

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