

New Investigation of Willemite

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Abstract. Zn_2SiO_4 , trigonal, $R\bar{3}$, hexagonal axes: $a = 13.948$ (2), $c = 9.315$ (2) Å, $Z = 18$, $D_x = 4.224$ g cm $^{-3}$, $\mu(\text{Cu } K\alpha) = 197.3$ cm $^{-1}$. The structure of willemite has been refined by a full-matrix least-squares method to an R value of 0.032 for 669 structure amplitudes measured with Cu $K\alpha$ radiation (counter techniques). The Si–O bond lengths are 1.628 (3), 1.629 (3), 1.638 (3) and 1.643 (3) Å.

Introduction. The structure of willemite was proposed by Bragg & Zachariasen (1930) and refined by Chin'Hang, Simonov & Belov (1970), using intensities from Weissenberg scans (Mo radiation) assessed against a standard $\sqrt{2}$ blackness scale. Chin'Hang, Simonov & Belov (1970) obtained an R value of 0.143 for 250 reflections by refining the atomic coordinates. Upon examination the Si tetrahedron showed marked irregularity and a rather unusual Si–O bond length of 1.68 Å. Moreover, we could not evaluate the optical properties of willemite from the structural data by means of the point-dipole theory, as is possible for the other orthosilicates (Pohl, Eck & Klaska, 1978). A more accurate structure refinement of willemite therefore seemed necessary.

Crystals of willemite were prepared hydrothermally at 693 K and 500 bar. Typical shapes are prisms elongated along c . The color is yellow-brown. A transparent crystal of approximate dimensions $0.076 \times 0.092 \times 0.126$ mm was selected for single-crystal investigation (mounted on the c axis). The cell parameters (294 K) were derived by the least-squares method from high-angle data for 30 Cu $K\alpha$ reflections in the 2θ range 82 to 136°. The room-temperature intensity data were measured according to the five-point procedure described by Hoppe (1969), on a Siemens off-line three-circle diffractometer, with Cu $K\alpha$ radiation and a graphite monochromator. 692 independent reflections were measured for $l \geq 0$ and $2\theta < 143^\circ$, of which 669 with $I \geq 3\sigma(I)$ were accepted as observed. Lp corrections were applied. The data were corrected for absorption by Burnham's (1961) method. To describe the shape of the crystal, account was taken of 14 plane faces. The structure was refined by full-

Table 1. *Final fractional positional coordinates ($\times 10^4$) for willemite*

Numbers in parentheses represent the standard deviations right-adjusted to the least significant digit of the preceding quantity.

	x	y	z
Si	9839.3 (8)	1955.7 (8)	7494 (1)
Zn(1)	9825.7 (4)	1916.7 (4)	4153.5 (5)
Zn(2)	9769.4 (4)	1919.7 (4)	814.0 (5)
O(1)	1104 (2)	2164 (2)	7505 (3)
O(2)	−42 (2)	3178 (2)	7490 (3)
O(3)	9164 (2)	1256 (2)	8926 (3)
O(4)	9227 (2)	1283 (2)	6036 (3)

matrix least-squares calculations (Busing, Martin & Levy, 1962), initially using the atomic positional parameters of phenacite as given by Zachariasen (1971), transformed to a right-handed set of axes by interchanging the x and y coordinates. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where weights $w = 1/\sigma^2$ were from counting statistics. Scattering factors for Zn, Si and O, and anomalous dispersion terms for Zn and Si, were taken from *International Tables for X-ray Crystallography* (1974).

In the final cycle all atoms were refined with anisotropic temperature factors and a secondary extinction parameter was included. Corrections for extinction were necessary, since otherwise the temperature factors for all atoms would be negative. The final residual for the observed reflections, $R = \sum |F_o| - |F_c| / \sum |F_o|$, was 0.032, the weighted residual, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, was 0.058. Atomic coordinates are given in Table 1.* The principal bond lengths and angles are listed in Table 2.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33740 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances (Å) and bond angles (°)*

Symmetry code

(i)	$1 + x,$	$y,$	z	(iv)	$1 + y,$	$1 - x + y,$	$1 - z$
(ii)	$1 + x - y,$	$x,$	$1 - z$	(v)	$\frac{2}{3} - x + y,$	$\frac{1}{3} - x,$	$z - \frac{2}{3}$
(iii)	$\frac{4}{3} - y,$	$\frac{2}{3} + x - y,$	$z - \frac{1}{3}$	(vi)	$x,$	$y,$	$z - 1$

Si tetrahedron

Si—O(1 ⁱ)	1.638 (3)	O(2 ⁱ)—Si—O(4)	110.5 (2)
Si—O(2 ⁱ)	1.628 (3)	O(2 ⁱ)—Si—O(1 ⁱ)	106.1 (2)
Si—O(3 ⁱ)	1.643 (3)	O(2 ⁱ)—Si—O(3 ⁱ)	110.6 (2)
Si—O(4 ⁱ)	1.629 (3)	O(4 ⁱ)—Si—O(1 ⁱ)	108.4 (2)
		O(4 ⁱ)—Si—O(3 ⁱ)	110.8 (2)
O(1 ⁱ)—O(2 ⁱ)	2.609 (4)	O(1 ⁱ)—Si—O(3 ⁱ)	110.3 (2)
O(1 ⁱ)—O(3 ⁱ)	2.693 (4)		
O(1 ⁱ)—O(4 ⁱ)	2.650 (4)		
O(2 ⁱ)—O(3 ⁱ)	2.689 (4)		
O(2 ⁱ)—O(4 ⁱ)	2.676 (4)		
O(3 ⁱ)—O(4 ⁱ)	2.693 (4)		

Zn(1) tetrahedron

Zn(1)—O(1 ⁱⁱ)	1.949 (3)	O(2 ⁱⁱⁱ)—Zn(1)—O(1 ⁱⁱ)	111.9 (1)
Zn(1)—O(2 ⁱⁱⁱ)	1.946 (3)	O(2 ⁱⁱⁱ)—Zn(1)—O(4 ^{iv})	103.2 (1)
Zn(1)—O(4 ^{iv})	1.953 (3)	O(2 ⁱⁱⁱ)—Zn(1)—O(4 ^{iv})	108.0 (1)
Zn(1)—O(4 ^{iv})	1.950 (3)	O(1 ⁱⁱ)—Zn(1)—O(4 ^{iv})	108.2 (1)
		O(1 ⁱⁱ)—Zn(1)—O(4 ^{iv})	116.4 (1)
O(1 ⁱⁱ)—O(2 ⁱⁱⁱ)	3.227 (4)	O(4 ^{iv})—Zn(1)—O(4 ^{iv})	108.4 (1)
O(1 ⁱⁱ)—O(4 ^{iv})	3.317 (4)		
O(1 ⁱⁱ)—O(4 ^{iv})	3.159 (4)		
O(2 ⁱⁱⁱ)—O(4 ^{iv})	3.154 (4)		
O(2 ⁱⁱⁱ)—O(4 ^{iv})	3.053 (4)		
O(4 ^{iv})—O(4 ^{iv})	3.166 (4)		

Zn(2) tetrahedron

Zn(2)—O(1 ⁱⁱ)	1.941 (3)	O(1 ⁱⁱ)—Zn(2)—O(2 ^v)	108.7 (1)
Zn(2)—O(2 ^v)	1.954 (3)	O(1 ⁱⁱ)—Zn(2)—O(3 ^{vi})	117.0 (1)
Zn(2)—O(3 ^{vi})	1.971 (3)	O(1 ⁱⁱ)—Zn(2)—O(3 ^{vi})	104.7 (1)
Zn(2)—O(3 ^{vi})	1.979 (3)	O(2 ^v)—Zn(2)—O(3 ^{vi})	106.6 (1)
		O(2 ^v)—Zn(2)—O(3 ^{vi})	109.6 (1)
O(1 ⁱⁱ)—O(2 ^v)	3.165 (4)	O(3 ^{vi})—Zn(2)—O(3 ^{vi})	110.1 (1)
O(1 ⁱⁱ)—O(3 ^{vi})	3.336 (4)		
O(1 ⁱⁱ)—O(3 ^{vi})	3.104 (4)		
O(2 ^v)—O(3 ^{vi})	3.146 (4)		
O(2 ^v)—O(3 ^{vi})	3.214 (4)		
O(3 ^{vi})—O(3 ^{vi})	3.237 (4)		

Metal—metal distances along the *c* axis

Si—Zn(1)	3.112 (1)
Si—Zn(2)	3.094 (1)
Zn(1)—Zn(2)	3.112 (1)

Discussion. This investigation was undertaken to obtain accurate atomic parameters in order to provide a structural basis for the evaluation of the optical properties of willemite. By applying the point-dipole theory to orthosilicates (Pohl, Eck & Klaska, 1978), a connection between structural and optical properties can be derived.

The interatomic distances in the Si tetrahedron differ little from those in phenacite as given by Zachariassen (1971): Si—O(1) 1.630, Si—O(2) 1.628, Si—O(3) 1.634, Si—O(4) 1.631 Å. The Zn tetrahedra show only slight deviations from regularity. Differences between the structures of willemite and phenacite may be attributed to the enlarged Zn tetrahedra as compared with the Be tetrahedra.

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References

- BRAGG, W. L. & ZACHARIASEN, W. H. (1930). *Z. Kristallogr.* **72**, 518–528.
- BURNHAM, C. W. (1961). PhD dissertation. Massachusetts Institute of Technology.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- CHIN'HANG, SIMONOV, M. A. & BELOV, N. V. (1970). *Sov. Phys. Crystallogr.* **15**, 387–390.
- HOPPE, W. (1969). *Acta Cryst.* **A25**, 67–76.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- POHL, D., ECK, J. C. & KLASKA, K.-H. (1978). *Acta Cryst.* **A34**, 1027–1028.
- ZACHARIASEN, W. H. (1971). *Sov. Phys. Crystallogr.* **16**, 1021–1025.