CRYSTAL STRUCTURES OF WILLEMITE $Zn_2[SiO_4]$ AND ITS GERMANIUM ANALOG $Zn_2[GeO_4]$

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The lattice constants are as follows: Si willemite, a_{hex} = 13.93, c_{hex} = 9.31 Å, a_{rh} = 8.63 Å, α = 107°52';Ge willemite, a_{hex} = 14.27, c_{hex} = 9.56 Å, a_{rh} = 8.84 Å, α = 107°42'. Space group $R\bar{3}$. The structures were solved by the "heavy atom" method with subsequent refinement of the atomic coordinates with three-dimensional sets of reflections by the method of least squares to R_{hkl} = 14.3% with 250 independent hk0–hk6 independent reflections for willemite and R_{hkl} = 13.3% with 226 hk0, hk3, hk6 and hk9 reflections for its germanium analog. The $[Zn_4O_{12}]$ metachains are entwined around the $3_1(3_2)$ axes and are encrusted with Si(Ge) orthotetrahedra. Each oxygen atom is at the center of an almost equilateral Zn – Zn – Si(Ge) triangle, and each cation is in a tetrahedral environment of oxygen atoms. The interatomic separations, calculated from the final coordinates, are as follows: Si – O = 1.58–1.68 Å; Ge – O = 1.74–1.78 Å; Zn – O = 1.89–2.02 Å; these values are consistent with those normally encountered.

Willemite (zinc silicate $Zn_2[SiO_4]$) is a fairly rare mineral,[1] which only sometimes forms substantial accumulations in oxidation zones of lead-zinc deposits. The structure of willemite was proposed in 1926 by Bragg and Zachariasen [1] by analogy with the structure of phenakite $Be_2[SiO_4]$ and has not been verified or refined. We had at our disposal crystals of synthetic willemite and its germanium analog $Zn_2[GeO_4]$ from the hydrothermal synthesis laboratory at the Institute of Crystallography, Academy of Sciences of the USSR.

Transparent single crystals of both willemites with dimensions of 0.1 × 0.1 × 0.15 mm were selected for x-ray investigation. The parameters of the double-centered hexagonal and primitive rhombohedral cells of the crystals (rotational x-ray diagrams) are shown in Table 1.

The experimental material comprised the reflections from eight Weissenberg scans (molybdenum radiation) of the hk0–hk6 layers [max $(\sin\theta)/\lambda$ = 0.97], and 0kl [max $(\sin\theta)/\lambda$ = 1.03] for its germanium analogy. With the latter the hk$l$ reflections with $L \neq 3n$ are extinguished, in contrast to the silicon willemite, where these reflections are only considerably weakened, i.e., have a clearly defined pseudoparameter of $c' = c/3$. The reflection intensities were assessed against a standard $\sqrt{2}$ blackness scale. The Laue class and the integral extinctions $-h + k + l \neq 3n$ established the x-ray group $R\bar{3}$, comprising two Fedorov groups $C_{3i}^2 = R\bar{3}$ and $C_3^4 = R3$. The choice in favor of the centrosymmetrical group was made on the basis of curves for the statistical distribution of the hkL intensities (L = 3n).

The structures were interpreted by means of the "heavy atom" method in accordance with the previously calculated [2] "weight criterion" $r = (\Sigma f m^2/\Sigma f_l^2)^{1/2}$ (for willemite, $r \approx 4$), i.e., after the heavy atoms had been localized by Patterson projections the positions of the remaining basis atoms were determined by the method of successive approximations.

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[1] The crystals of willemite are colorless or yellow-brown, sometimes with a greenish or reddish hue (MnO impurity). N_g = 1.719-1.723 and N_p = 1.691-1.694. Specific gravity 3.89-4.18, hardness 5-6, brittle, clear cleavage along (0001).

TABLE 1. Unit Cell Parameters

Phases	Hexagonal cell	Rhombohedral cell
Si willemite, $Zn_2[SiO_4]$	$a = 13.931 \pm 0.001$ Å*, $c = 9.307 \pm 0.003$	$a = 8.628$ Å, $\alpha = 107°52'$
Ge willemite, $Zn_2[GeO_4]$	$a = 14.269 \pm 0.001$ Å, $c = 9.559 \pm 0.003$	$a = 8.836$ Å, $\alpha = 107°42'$
	$Z = 18$	$Z = 6$

*The hexagonal cell parameters were refined on a DRON-1 diffractometer with CuKα radiation.

TABLE 2. Coordinates of Basis Atoms in Si Willemite ($Zn_2[SiO_4]$) and Ge Willemite ($Zn_2[GeO_4]$) Structures

Atoms	$Zn_2[SiO_4]$			Atoms	$Zn_2[GeO_4]$		
	x/a	y/a	z/c		x/a	y/a	z/c
Si	0.459	0.225	0.051	Ge	0.465	0.229	0.056
Zn_1	0.793	0.562	0.385	Zn_1	0.798	0.562	0.389
Zn_2	0.128	0.897	0.720	Zn_2	0.132	0.896	0.723
O_1	0.329	0.019	−0.027	O_1	0.317	0.005	−0.034
O_2	0.614	0.307	0.258	O_2	0.625	0.312	0.272
O_3	0.971	0.639	0.640	O_3	0.973	0.641	0.636
O_4	0.553	0.229	−0.092	O_4	0.579	0.249	−0.078

TABLE 3. Interatomic Separations (Å) in Structure of Willemite $Zn_2[SiO_4]$

Si-tetrahedron		Zn_1-tetrahedron		Zn_2-tetrahedron	
$Si-O_1$	1.58	Zn_1-O_2	1.98	Zn_2-O_3	1.97
$Si-O_2$	1.66	Zn_1-O_3	2.02	Zn_2-O_1	2.02
$Si-O_3'$	1.66	Zn_1-O_2'	2.00	Zn_2-O_1'	1.98
$Si-O_4'$	1.68	Zn_1-O_4'	1.90	Zn_2-O_4''	1.93
O_1-O_2	2.70	O_2-O_3	3.38	O_3-O_1	3.37
O_1-O_3'	2.76	O_2-O_2'	3.36	O_3-O_1'	3.26
O_1-O_4	2.57	O_2-O_4'	2.92	O_3-O_4''	3.13
O_2-O_3'	2.74	O_3-O_2'	3.27	O_1-O_1'	3.37
O_2-O_4	2.73	O_3-O_4'	3.22	O_1-O_4''	3.21
$O_3'-O_4$	2.59	$O_2'-O_4'$	3.15	$O_1'-O_4''$	2.96
Mean separations					
$Si-O$	1.65	Zn_1-O	1.97	Zn_2-O	1.97
$O-O$	2.68	$O-O$	3.22	$O-O$	3.22

The mean Si–O, Ge–O, and Zn–O separations given in Tables 3 and 4 agree closely with the cation radii according to Arens: Si, 0.42 Å; Ge, 0.53 Å; Zn, 0.74 Å.

The models obtained from an analysis of the projections were refined (in the hexagonal arrangement of the $R\bar{3}$ group) by the method of least squares using three-dimensional sets of intensities. The final divergence factors R_{hkl}, calculated from the refined coordinates (Table 2), were as follows: 14.3% for silicon willemite (250 independent nonzero reflections); 13.3% for its germanium analog (226 reflections). All the computations were performed at the Moscow State University Computer Center on M-20 and BÉSM-4 electronic computers using programs compiled by Tarnopol'skii and Andrianov [3], and Tovbis and Shchedrin [4]. The interatomic separations, calculated from the final coordinates, are given in Tables 3 and 4.

In the willemite structure the atoms are arranged in layers at six equally separated levels along the c axis, and this determines the cleavage of the crystals along (0001). At each level the oxygen atom forms the center of a horizontal almost equilateral Zn – Zn – Si(Ge) triangle, and each cation is in a tetrahedral environment of $O_{1,2,3,4}$ atoms. The horizontal triangles are superimposed on each other, and 1Si + 2Zn alternate in the trigonal prism formed and along any of its vertical edges, i.e., the 3_1 screw axis (3_2 in the central prism) coincides with the O – O – O axis of the prism (Fig. 1). The cation tetrahedra are arranged in columns along each edge of the prism, and the vertical edges continue in straight lines parallel to the $3_1(3_2)$ axis (Fig. 2). Both in hodgkinsonite [5] and clinohedrite [6] and in willemite extending along the $3_1(3_2)$ axis there is a metachain with units of two Zn tetrahedra, which are entwined about the $3_{1,2}$ axes within the trigonal prisms and are encrusted with 3Si(Ge) orthotetrahedra. The identity parameter c = 9.31 Å (c = 9.56 Å in the germanium willemite) requires an increment of the $[Zn_2O_6]$ metachain which encrusts the Si(Ge) tetrahedron. Three 1Si + 2Zn tetrahedra (valence balance 2 = 4/4 + 2 · 2/4) converge on each of the four kinds of oxygen atoms.

In the willemite lattice six 3_1 and 3_2 screw axes surround the central $\bar{3}$ axes (the special point of

TABLE 4. Interatomic Separations (Å) in Structure of Germanium Willemite $Zn[GeO_4]$

Ge-tetrahedron		Zn_1-tetrahedron		Zn_2-tetrahedron	
$Ge—O_1$	1.76	$Zn_1—O_2$	1.94	$Zn_2—O_3$	2.02
$Ge—O_2$	1.74	$Zn_1—O_3$	2.00	$Zn_2—O_1$	1.98
$Ge—O_3'$	1.76	$Zn_1—O_2'$	2.01	$Zn_2—O_1'$	1.91
$Ge—O_4$	1.78	$Zn_1—O_4'$	1 89	$Zn_2—O_4''$	1.96
$O_1—O_2$	2.72	$O_2—O_3$	3.32	$O_3—O_1$	3.30
$O_1—O_3'$	2.73	$O_2—O_2'$	3.36	$O_3—O_1'$	3.10
$O_1—O_4$	2.86	$O_2—O_4'$	3.08	$O_3—O_4''$	3.02
$O_2—O_3'$	2.93	$O_3—O_2'$	3.32	$O_1—O_1'$	3.36
$O_2—O_4$	2.85	$O_3—O_4'$	3.18	$O_1—O_4''$	3.07
$O_3'—O_4$	2.70	$O_2'—O_4'$	3.08	$O_1'—O_4''$	2.98
Mean separations					
Ge—O	1.76	$Zn_1—O$	1.96	$Zn_2—O$	1.97
O—O	2.80	O—O	3.32	O—O	3.14

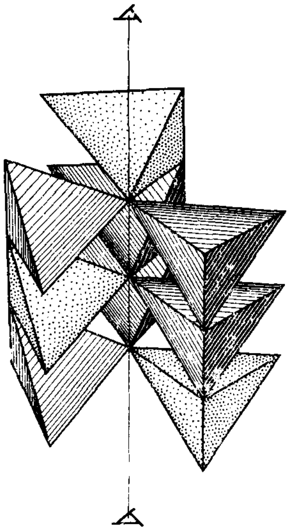

Fig. 2. Columns of cation tetrahedra around 3_1 axis.

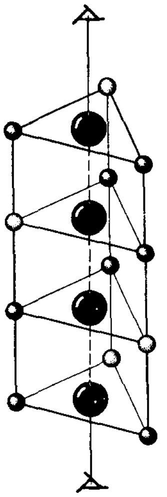

Fig. 1. Trigonal prism, formed by superimposition of Zn — Zn — Si(Ge) triangles.

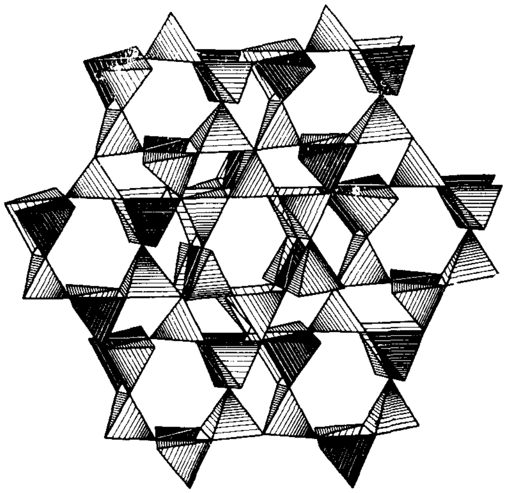

Fig. 3. Rhombohedral structure of willemite with broad channels of six-cornered cross section around the $\bar{3}$ axes, between which the columns of cation tetrahedra are entwined about the three screw axes (3_1 on the right and 3_2 on the left).

which is taken as the origin of the coordinates), and wide channels with diameter up to 5.5 Å and open walls constructed from six columns of cation tetrahedra (Fig. 3) pass along these $\bar{3}$ axes. If the main characteristic in willemite is considered to be these columns with the 2Zn + 1Si unit and these tetrahedra are further identified (which is particularly easy for zinc and germanium willemites by x-ray analysis), then simultaneously with the reduction of the c parameter by a factor of three the rhombohedral character is lost and the cell becomes a primitive hexagonal $P\bar{3}$ cell.

The structural analogy between willemite and phenakite Be_2SiO_4 is yet another example of the formal similarity in the crystal chemistry of beryllium and zinc silicates as illustrated by the following pairs: bromellite BeO — zincite ZnO; euclase $AlBeSiO_4(OH)$ — clinohedrite $CaZnSiO_4(OH)$ and to a lesser degree bertrandite $Be_4Si_2O_7(OH)_2$ — calamine $Zn_4Si_2O_7(OH)_2H_2O$.

Willemite and its germanium analog complete the isostructural series: $Li_2[BeF_4]$ — $Li_2[WO_4]$ — $Li_2[MoO_4]$ — $Be_2[SiO_4]$ — $Zn_2[SiO_4]$ $(Zn, Mn)_2[SiO_4]$ — $Zn_2[GeO_4]$.

If the crystallochemical roles of silicon and zinc are equated, the structure can be assigned to a framework structure of tetrahedra with the $(Zn, Si)_3O_4$ formula. If it is classified as a silicon — oxygen radical, the $Zn_2[SiO_4]$ together with phenakite

$Be_2[SiO_4]$ form an isolated group of hexagonal orthosilicates, which differ greatly from the rhombic orthosilicates of the olivine group.

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LITERATURE CITED

1. W. L. Bragg and W. H. Zachariasen, Proc. Roy. Soc., A113 (1926).
2. M. A. Simonov, Thesis, Institute of Crystallography, Academy of Sciences of the USSR, Moscow (1969).
3. B. L. Tarnopol'skii and V. I. Andrianov, Zh. Strukt. Khim., 4, No. 3, 434 (1963).
4. A. B. Tovbis and B. M. Shchedrin, Complex of Programs for Solution of Problems in Structural Analysis of Crystals [in Russian], VTs MGU, Moscow (1968).
5. L. P. Solov'eva and N. V. Belov, Dokl. Akad. Nauk SSSR, 152, No. 2, 327 (1963) [Sov. Phys.–Dokl., 8, 867 (1964)].
6. A. V. Nikitin and N. V. Belov, Dokl. Akad. Nauk SSSR, 148, No. 6, 1386 (1963).