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The Crystal Structure of Zn_2SiO_4-II, a High-Pressure Phase of Willemite

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The crystal structure of Zn_2SiO_4-II, a high-pressure form of willemite, has been determined with three-dimensional X-ray diffraction data. The crystal is tetragonal with $a=7{\cdot}0069$, $c=6{\cdot}4637$ Å at 20°C and space group $I\bar{4}2d$. The structure was refined by the least-squares method down to an R value of 0·081 for the 90 reflexions collected photographically. Oxygen atoms are approximately in a body-centred cubic arrangement. Both Zn and Si atoms have tetrahedral surroundings of oxygen. All Zn–O distances are normal for the tetrahedrally coordinated Zn atom, having a mean value of 1·98 Å. The Si–O distance, 1·62 Å, is also in good agreement with the expected value.

Introduction

A comprehensive study of the high-pressure phase transformation in the zinc-silicate system was carried out by Syono, Akimoto & Matsui (1970). They described five polymorphs of Zn_2SiO_4 designated as I to V in the order of increasing pressure. Phase I is identical with the mineral willemite, and transforms to phase II at about 30 kbar. Zn_2SiO_4-II becomes unstable above about 80 kbar and is considered to decompose into phase III and a small amount of ZnO, resulting in nonstoichiometric composition of phase III. Phase IV is also considered to be non-stoichiometric. Phase V was obtained above about 130 kbar at 900°C, and has the stoichiometric composition Zn_2SiO_4.

Among these five phases, the structures of I and V are known. Willemite is isomorphous with phenakite Be_2SiO_4 (Bragg & Zachariasen, 1930); accurate atomic parameters were determined recently by Hang, Simonov & Belov (1970). The structure has fairly large open spaces around the threefold axes of rotation. Phase V has the modified spinel structure (Syono *et al.*, 1970), which is based on the closest packing of oxygen atoms (Morimoto, Akimoto, Koto & Tokonami, 1969). The Zn atoms are surrounded tetrahedrally in I and octahedrally in V. It is of interest to know the coordinations for the Zn atoms and the packing mode of oxygen atoms in the intermediate phases. Consequently, the structure Zn_2SiO_4-II was determined as a part of a systematic study of various phases in Zn_2SiO_4.

Experimental

The specimens investigated were quenched crystals of Zn_2SiO_4-II, which were prepared from artificial willemite at 1400°C and 70 kbar by Syono *et al.* (1970) with the tetrahedral anvil-type high-pressure apparatus. Crystals are colourless and granular in shape. Cell dimensions were determined from Weissenberg photographs and were refined with powder-diffraction data. The number of chemical formulae in a unit cell was determined as uniquely four by assuming the density of Zn_2SiO_4-II to be the same as that of willemite. Systematic absences were observed for hkl with $h+k+l=2n+1$ and for hhl with $2h+l\neq4n$. There are two possible space groups, $I4_1md$ and $I\bar{4}2d$, for these systematic absences and the observed Laue symmetry $4/m$. The true space group was proved to be $I\bar{4}2d$ in the course of structure determination. Crystal data are summarized in Table 1.

Table 1. *Crystal data of* Zn_2SiO_4-II

Crystal system: tetragonal
Space group: $I\bar{4}2d$
Cell dimension at 20°C: $a=7{\cdot}0069\pm0{\cdot}0003$ Å
$c=6{\cdot}4637\pm0{\cdot}0004$
$U=317{\cdot}4$ Å^3
$Z=4$
X-ray density = 4·66 g.cm^{-3}
μ(Cu $K\alpha$) = 216 cm^{-1}

A crystal of dimensions about 0·1 × 0·1 × 0·1 mm was used for intensity measurements. Equi-inclination Weissenberg photographs were taken with Cu $K\alpha$ radiation up to the 4th layer around [001] and up to the 2nd layer around [011], employing the multiple-film technique. Intensities were estimated visually by comparing them with a standard intensity scale, and they were corrected for Lorentz–polarization and spot-shape factors. No corrections were made for absorption factors in view of the small size of the crystal. Observed structure amplitudes were put on the same relative scale by the ordinary layer-scaling procedure. Thus, 90 independent reflexions were obtained.

Structure determination

The three-dimensional Patterson function was synthesized. General positions are 16-fold in both space group $I4_1md$ and $I\bar{4}2d$. Since only eight Zn atoms exist in a unit cell, they should be at special positions. The Patterson function can be explained only by allocating Zn atoms to the 8-fold positions (d) in the space group

$I\bar{4}2d$. Positions of Si and O atoms were also determined unequivocally from the Patterson maps by seeking Zn–Si and Zn–O peaks. Structure factors were calculated with these positional parameters and with the overall temperature factor determined by the statistical method. The *R* value was 0·33.

The structure was refined by the Fourier method and the difference Fourier method, assuming individual isotropic temperature factors, until the *R* value was reduced to 0·17. Five cycles of further refinements were performed with a version (Sakurai, Nakatsu & Iwasaki, 1967) of full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962), using anisotropic temperature factors. The final *R* value was 0·081 for all 90 reflexions. Final positional and thermal parameters with their standard deviations are given in Table 2. Observed and calculated structure factors are listed in Table 3 for comparison.

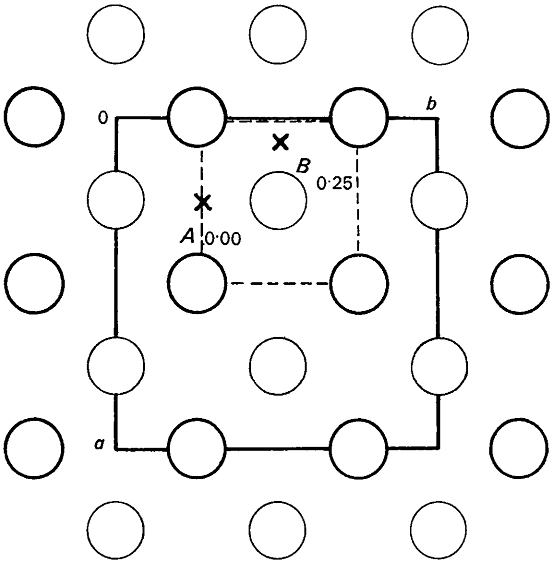

Fig. 1. Relation of the Zn_2SiO_4-II structure to the body-centred cubic packing. Unit cell of Zn_2SiO_4-II is in thick lines and the body-centred cubic cell is in broken lines. *A* and *B* are two types of tetrahedrally-surrounded positions. Heights are indicated in fractions of the body-centre cubic cell edge.

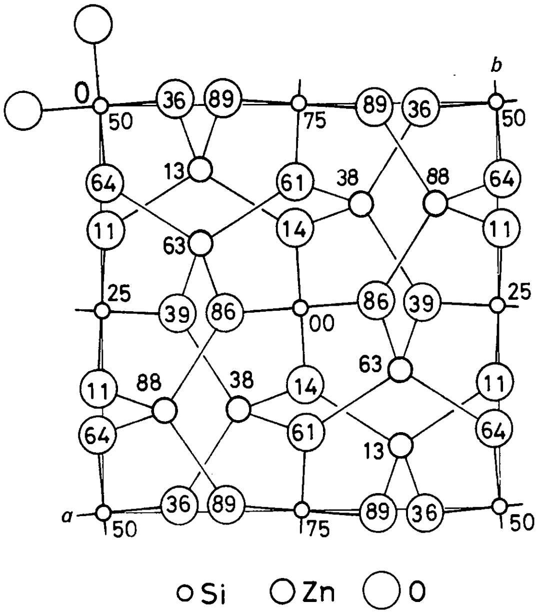

Fig. 2. Projection of the structure along the *c* axis. Numbers are the fractional heights multiplied by 100.

Table 2. *Final atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^4$) *with their e.s.d.'s in parentheses*

Thermal parameters are in the form:

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)\right].$$

	Zn	Si	O
x	1570 (6)	0	3079 (23)
y	2500	0	4890 (31)
z	1250	5000	1376 (45)
B_{11}	3 (8)	8 (13)	34 (27)
B_{22}	8 (7)	8 (13)	49 (28)
B_{33}	18 (15)	18 (39)	68 (68)
B_{12}	0	0	−1 (22)
B_{13}	0	0	−1 (42)
B_{23}	2 (8)	0	−4 (50)

Table 3. *Observed and calculated structure factors*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
2	0	0	74	81	6			43	48	3	2	3	128	133
4			101	93	8			61	59	5			43	47
6			58	52	5	4	1	38	40	7			42	43
8			56	59	7			46	43	4	3	3	50	50
3	1	0	80	78	6	5	1	47	39	6			64	71
5			125	129	2	0	2	24	24	5	4	3	32	33
7			70	64	4			138	145	7			59	60
2	2	0	43	37	6			98	101	6	5	3	21	18
4			44	37	8			63	62	2	0	4	137	121
6			0	5	1	1	2	174	161	4			13	8
8			17	12	3			61	59	6			4	7
5	3	0	58	49	5			25	25	3	1	4	54	60
7			11	13	7			26	24	5			100	98
4	4	0	54	51	4	2	2	91	93	7			58	53
6			135	112	6			41	50	2	2	4	15	11
8			17	16	8			11	12	4			25	19
7	5	0	9	10	3	3	2	59	49	6			47	47
6	6	0	49	42	5			67	67	5	3	4	40	39
1	0	1	7	8	7			46	41	7			8	11
3			68	69	6	4	2	21	17	4	4	4	92	88
5			35	28	5	5	2	108	95	6			55	50
7			35	32	7			56	63	5	0	5	20	19
2	1	1	119	128	1	0	3	51	48	4	1	5	51	55
4			54	53	3			27	29	6			20	19
6			53	59	5			6	10	5	2	5	40	38
8			36	42	7			62	57	4	3	5	34	40
3	2	1	106	114	2	1	3	80	75	6			58	62
5			76	77	4			62	65	5	4	5	33	28
7			73	67	6			20	23	5	1	6	25	26
4	3	1	76	85	8			53	52	5	3	6	38	45

Discussion

The structure is of a new type for silicates. Oxygen atoms are approximately in a body-centred cubic arrangement, with Si and Zn atoms in tetrahedral interstices. Two kinds of tetrahedrally surrounded positions exist in the body-centred cubic packing as indicated by *A* and *B* in Fig. 1. The Si atoms are at the tetrahedral positions of type *A* and the Zn atoms are at the positions of type *B*. Though the tetrahedra around positions *A* and *B* are largely distorted in an ideal body-centred cubic packing, both metal atoms have nearly regular tetrahedral surroundings in the Zn_2SiO_4-II structure due to the shifts of oxygen atoms from the ideal packing. Each oxygen atom is shared by

Table 4. *Interatomic distances and bond angles with their e.s.d.'s in parentheses*

Symmetry code:

i = x, y, z
ii = $-0·5+y, x, -0·25+z$
iii = $0·5-x, 0·5-y, 0·5+z$
iv = $1-y, x, -z$
v = $1-x, 1-y, z$
vi = $1-y, 0·5-x, 0·25+z$
vii = $0·5-x, y, 0·75-z$
viii = $x, 0·5-y, 0·25-z$
ix = $-0·5+y, 0·5-x, 0·5-z$
x = $-0·5+x, -0·5+y, 0·5+z$

$\mathrm{Zn^{i}}$–$\mathrm{O^{i}}$	1·98 (2) Å
–$\mathrm{O^{ii}}$	1·98 (2)
$\mathrm{Si^{i}}$—$\mathrm{O^{iii}}$	1·62 (2)
$\mathrm{O^{i}}$—$\mathrm{O^{iv}}$	2·61 (5)
—$\mathrm{O^{v}}$	2·70 (3)
—$\mathrm{O^{vi}}$	2·99 (5)
—$\mathrm{O^{ii}}$	3·04 (5)
—$\mathrm{O^{vii}}$	3·17 (6)
—$\mathrm{O^{viii}}$	3·35 (4)
—$\mathrm{O^{ix}}$	3·38 (4)

$\mathrm{O^{iii}}$—$\mathrm{Si^{i}}$—$\mathrm{O^{x}}$	113 (1)°
$\mathrm{O^{iii}}$—$\mathrm{Si^{i}}$—$\mathrm{O^{ix}}$	108 (1)
$\mathrm{O^{i}}$—$\mathrm{Zn^{i}}$–$\mathrm{O^{ii}}$	100 (1)
$\mathrm{O^{i}}$—$\mathrm{Zn^{i}}$–$\mathrm{O^{viii}}$	116 (1)
$\mathrm{O^{i}}$—$\mathrm{Zn^{i}}$–$\mathrm{O^{ix}}$	117 (1)
$\mathrm{O^{ii}}$—$\mathrm{Zn^{i}}$–$\mathrm{O^{ix}}$	107 (1)
$\mathrm{Zn^{iii}}$–$\mathrm{O^{vi}}$–$\mathrm{Si^{vii}}$	125 (1)
$\mathrm{Zn^{vi}}$–$\mathrm{O^{vi}}$–$\mathrm{Si^{vii}}$	118 (1)
$\mathrm{Zn^{iii}}$–$\mathrm{O^{vi}}$–$\mathrm{Zn^{vi}}$	115 (1)

one Si atom and two Zn atoms. The projection of the structure along the *c* axis is illustrated in Fig. 2.

Interatomic distances and bond angles are given in Table 4 and illustrated in Fig. 3. The interatomic distances of Zn_2SiO_4-II are quite similar to those of willemite (Hang *et al.*, 1970). The Si–O distance is in good agreement with the value 1·624 Å predicted for the case C.N. = 3 by the formula of Brown & Gibbs (1969). Here, C.N. stands for the mean coordination number of the oxygen ion bonded to Si atoms. The Zn–O distances are also normal for a tetrahedrally coordinated Zn atom. The tetrahedron around the Si atom is a little compressed along the *c* axis. The ZnO_4 tetrahedron is more distorted than that around Si (Table 4).

Note that the tetrahedral coordinations for all metallic atoms, which are observed in the atmospheric-pressure form of Zn_2SiO_4 willemite, are preserved even at 70 kbar. However, a considerable volume change occurs in the phase transformation of Zn_2SiO_4I–II, although there is no change in coordination numbers of both metal ions and the oxygen ion. Volumes for each formula unit are 86·92 Å^3 in willemite and 79·34 Å^3 in phase II. The decrement of volume amounts to 8·8%. This large decrease in volume suggests that the crystal structure of Zn_2SiO_4-II is rather densely packed for the four-coordination structure. Subsequent high-pressure phases of Zn_2SiO_4-III and -IV are supposed to be nonstoichiometric and their densities do not increase much above that of Zn_2SiO_4-II. This implies that Zn^{2+} ions are in the tetrahedrally coordinated sites even above 100 kbar. Since the olivine structure is definitely unstable in Zn_2SiO_4, more than 130 kbar are necessary to bring the Zn atoms into the six coordinations in the modified spinel structure, with a density increase of about 14% (Syono *et al.*, 1970).

Most compounds with the phenakite structure are known to transform directly to the cubic spinel structure at high pressure. (*e.g.*, Li_2MoO_4, Zn_2GeO_4, $LiAlGeO_4$, $LiGaGeO_4$ and $LiZnVO_4$; Rooymans, 1967). Therefore, the mode of high-pressure transformation found in Zn_2SiO_4 is an exceptional case. This exception stems from the fact that the former phenakites consist of cations whose ionic radii do not differ much from each other, whereas the ionic radius ratio of Zn^{2+} to Si^{4+} is too large to be stabilized in the cubic spinel structure.

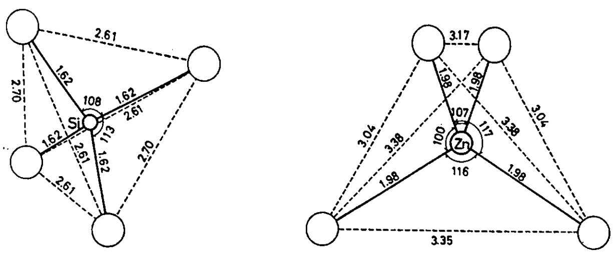

Fig. 3. Bond distances (Å) and angles (°) in (*a*) SiO_4 and (*b*) ZnO_4 tetrahedra.

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