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Structure of Si_2N_2O

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The crystal structure of silicon oxynitride has been determined by means of X-ray crystallographic methods. The crystals are orthorhombic and the space group is $Cmc2_1$. The unit cell dimensions are:

$a = 8.843 \pm 0.005$ Å, $b = 5.473 \pm 0.005$ Å, $c = 4.835 \pm 0.005$ Å

and there are four formula units in the cell.

The structure may be described as being built up by distorted SiN_3O tetrahedra, linked together to give an infinite threedimensional network. The silicon and nitrogen atoms are situated in infinite two-dimensional puckered layers which are linked together by oxygen atoms bonded to silicon atoms from two adjacent layers. Silicon – oxygen distances are 1.623 Å and the angle Si–O–Si is 147.7°. Silicon–nitrogen distances have a mean value of about 1.72 Å.

Silicon oxynitride is a refractory material consisting of colorless microcrystals with a hardness above that of quartz. The shape of single crystals is needles or plates. As already mentioned elsewhere [1] single crystals have been synthesised by nitriding silicon-silica powder at 1450°C in an argon-atmosphere with 5 % nitrogen. This gas is purified from oxygen in an absorption tower containing copper(I) oxide. The rate of gas should be about 10 ml/min in a tube with an inner diameter of 30 mm. The weight proportion silicon-silica is 1:1 and a sample of 3–4 g is reacted for 10 h. Many of the crystals are defect but single crystals suitable for X-ray investigations are grown as long needles.

STRUCTURE DETERMINATION

The lattice constants of silicon oxynitride were determined from a powder photograph taken in a Guinier type focusing camera using Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The powder diffraction data are listed in Table 1. The powder pattern could be indexed on the basis of an orthorhombic unit cell, with $a = 8.843 \pm 0.005$ Å, $b = 5.473 \pm 0.005$ Å, and $c = 4.835 \pm 0.005$ Å. The cell dimensions are compared in Table 2 with those obtained by Forgeng and Decker.[2] The composition was established by chemical analysis and the

Table 1. X-Ray powder diffraction data for Si_2N_2O. Guinier camera. Cu$K\alpha'$ radiation.

h	k	l	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	I	d (Å)	h	k	l	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	I	d (Å)
1	1	0	272	274	st	4.68	6	0	0	2739	2737	m	1.473
2	0	0	302	304	v st	4.44	1	3	2	2883	2878	m	1.435
1	1	1	528	528	v st	3.36	0	2	3	3087	3081	st	1.387
0	2	0	792	793	w	2.739	5	1	2	3120	3115	v w	1.380
3	1	0	882	882	m	2.597	3	1	3	3171	3170	st	1.369
0	0	2	1016	1017	st	2.419	0	4	0		3174		
0	2	1	1046	1048	st	2.383	2	2	3	3381	3385	m	1.326
3	1	1	1137	1137	m	2.285	0	4	1	3431	3428	w	1.316
4	0	0	1216	1216	w	2.211	2	4	0	3485	3478	m	1.306
1	1	2	1290	1291	m	2.147	3	3	2		3486		
2	0	2	1321	1321	w	2.121	5	3	0	3682	3685	m	1.270
2	2	1	1357	1352	m	2.093	6	0	2	3755	3753	m	1.258
0	2	2	1812	1810	m	1.811	6	2	1	3786	3784	m	1.253
1	3	0	1861	1861	m	1.787	7	1	0	3927	3923	v w	1.230
3	1	2	1901	1899	m	1.768	0	0	4	4072	4067	w	1.208
5	1	0	2102	2099	m	1.681	7	1	1	4187	4177	w	1.191
2	2	2	2113	2114	m	1.677	0	4	2		4190		
1	3	1		2115			5	1	3	4392	4386	w	1.163
4	0	2	2237	2233	v w	1.630	4	4	0		4390		
4	2	1	2265	2264	w	1.620	2	4	2	4499	4494	m	1.149
5	1	1	2353	2353	m	1.589	6	2	2	4549	4546	w	1.143
3	3	0	2472	2469	m	1.550	5	3	2	4697	4702	m	1.125
1	1	3	2565	2562	w	1.522	3	3	3	4747	4757	w	1.119

Table 2. Lattice constants.

Idrestedt – Brosset		Vorgeng – Decker [2]	
a =	8.843 ± 0.005 Å	a =	5.498 ± 0.005 Å
b =	5.473 ± 0.005 Å	b =	8.877 ± 0.005 Å
c =	4.835 ± 0.005 Å	c =	4.853 ± 0.005 Å
V =	234.0 Å^3	V =	236.9 Å^3
Z =	4		

results were compared with compositions calculated from the formulae Si_2N_2O and Si_2NO (weight percentage):

	Silicon	Nitrogen	Oxygen
Observed	53.5	25.7	—
Si_2N_2O	56.07	27.96	15.97
Si_2NO	65.18	18.56	16.25

The density of both powder and single crystals was determined to be 2.77 g cm^{-3} and 2.87 g cm^{-3}, respectively. This corresponds to four Si_2N_2O per unit cell, the calculated density being 2.84 g cm^{-3}.

With Cu$K\alpha$ radiation the linear absorption coefficient $\mu = 109$ cm^{-1}.

The structure determination was based on single crystal measurements, the crystal used being cylindrical with the dimensions 0.04 × 0.04 × 0.08 mm. X-Ray photographs were taken in an integrating Weissenberg camera, using multiple film technique and Cu$K\alpha$ radiation. The intensities were estimated by visual comparison with a standard intensity scale. The $|F|^2$ values on a relative scale were calculated from the relative intensities using polarisation and Lorentz' factors given by Lu.[3] The crystals were rotated around the a-axis ($h = 0-5$) and the c-axis ($l = 0-3$). The corrections for absorption were applied for intensities obtained around the a-axis by a method due to Albrecht.[4] Intensities obtained from rotating around the c-axis did not need correction as this was below 3 %. The structure factors were placed on an absolute basis by Wilson's method [5] and B for the temperature factor correction, $\exp[-B \sin^2\Theta \cdot \lambda^{-2}]$, was found to be 0.15 from the relevant graph.

The following systematic extinctions were found

$$hkl: \; h + k = 2n$$
$$h0l: \; l = 2n$$

which satisfies three different space groups:

Cmcm (No. 63), *Cmc2* (No. 40) and *Cmc2*$_1$ (No. 36).[6] An intensity distribution curve (according to Howells *et al.*[7]) indicated the lack of a centre of symmetry (Fig. 1) but it was not possible to come to a definite conclusion since the curve differs from both theoretical curves.

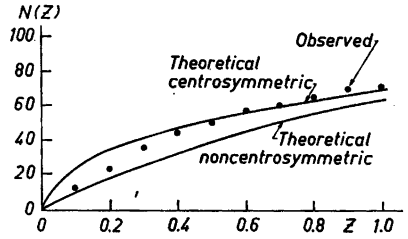

Fig. 1. Test of symmetry.

The two-dimensional Patterson projections on (001) and (100) (Figs. 2 and 3) are consistent with the space group *Cmc2*$_1$ (No. 36)[6] only. It was found that

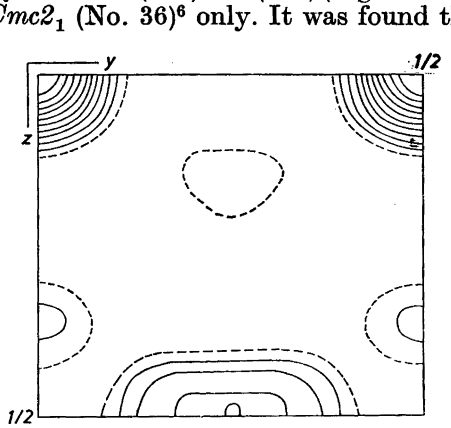

Fig. 2. Patterson projection (100).

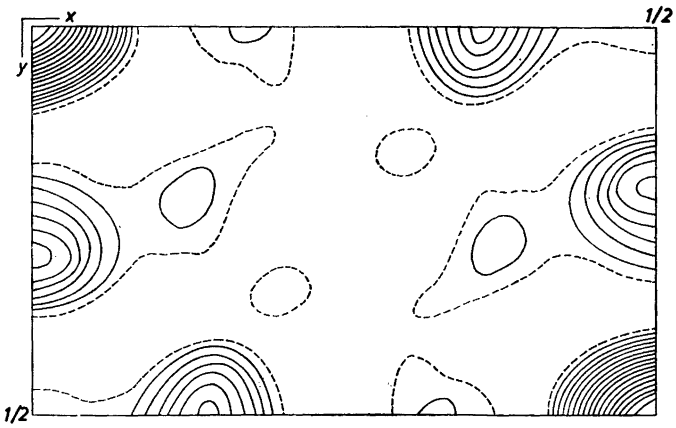

Fig. 3. Patterson projection (001).

the silicon atoms occupy the positions 8*b*, the oxygen atoms 4*a* and the nitrogen atoms 8*b*. From the three-dimensional Patterson synthesis the silicon parameters were determined. The signs of the structure factors were calculated using these silicon parameters, and Fourier syntheses were performed from which the positions of the silicon and the oxygen atoms were derived. The nitrogen positions were found from a difference synthesis $F_{obs}-F_{calc}$. A three-dimensional electron density synthesis then gave fairly accurate parameters for all atoms.

REFINEMENT OF THE STRUCTURE

The structure was refined by means of a structure factor least-squares refinement. After 17 least-squares refinement cycles, the shift in positional parameters was less than one twentieth of the standard deviation and so the refinement was concluded. The final parameters and the isotropic temperature factors are shown in Table 3. There is a large difference between the temperature factors of the nitrogen atoms compared with those of the silicon and oxygen atoms. The calculated structure factors and phase angles, together

Table 3. Final parameters for Si_2N_2O. Space group $Cmc2_1$.

Position [8]	Atom	Parameter			Standard deviation			Temperature factor	
		x	y	z	σ_x	σ_y	σ_z	B (Å^2)	σ_B (Å^2)
8 *b*	Si	0.1763	0.1509	0.2898	0.0007	0.0006	0.0023	0.42	0.06
8 *b*	N	0.218	0.121	0.642	0.003	0.002	0.003	1.54	0.30
4 *a*	O	0	0.214	0.230	0	0.002	0.003	0.35	0.22

Table 4. Structure factors.

h k l	F_{obs}	F_{calc}	α°(*hkl*)	*h k l*	F_{obs}	F_{calc}	α°(*hkl*)
0 0 2	82.1	93.9	179	2 4 4	15.5	12.4	57
0 0 4	42.9	41.4	53	2 4 5	14.0	15.1	272
0 0 6	40.8	37.3	265	2 6 0	21.0	20.2	180
0 2 0	43.4	44.5	180	2 6 1	13.2	15.4	208
0 2 1	61.4	63.8	216	2 6 2	17.8	19.7	28
0 2 2	33.7	34.1	12	2 6 3	22.0	20.7	33
0 2 3	69.0	73.4	44	3 1 0	49.9	53.7	180
0 2 4	21.0	19.0	209	3 1 1	37.4	36.6	43
0 2 5	41.7	39.8	234	3 1 2	33.5	32.5	16
0 4 0	54.5	54.5	180	3 1 3	47.4	48.5	239
0 4 1	39.1	43.8	8	3 1 4	25.6	24.0	249
0 4 2	31.8	33.4	13	3 1 5	34.1	34.7	76
0 4 3	32.4	31.0	211	3 3 0	56.0	55.9	0
0 4 4	26.9	26.0	259	3 3 1	24.5	22.6	21
0 4 5	20.9	20.2	60	3 3 2	46.2	45.0	208
0 6 0	30.1	30.6	0	3 3 3	24.4	23.1	210
0 6 1	17.6	14.1	58	3 3 4	34.4	37.4	68
0 6 2	32.4	30.3	213	3 3 5	11.4	12.2	29
0 6 3	27.2	25.1	242	3 5 0	14.0	11.5	0
1 1 0	37.1	37.0	0	3 5 1	41.3	45.6	196
1 1 1	44.4	51.2	189	3 5 2	11.0	9.4	136
1 1 2	21.9	21.8	190	3 5 3	42.3	41.6	40
1 1 3	32.5	32.8	22	4 0 2	26.7	27.4	96
1 1 4	11.9	11.9	51	4 0 4	23.4	19.9	251
1 1 5	17.5	15.7	218	4 2 0	10.2	8.3	180
1 1 6	9.8	9.1	263	4 2 1	22.9	21.7	348
1 3 0	40.5	41.7	180	4 2 2	10.4	8.3	324
1 3 1	9.2	9.1	321	4 2 4	11.8	8.4	125
1 3 2	32.4	31.5	14	4 2 5	12.8	13.3	111
1 3 3	9.9	9.8	101	4 4 0	8.0	8.4	0
1 3 4	18.3	19.0	223	4 4 2	19.9	17.2	221
1 3 5	7.5	7.7	283	4 4 3	8.3	7.7	92
1 5 0	9.3	7.3	0	4 4 4	12.8	14.9	28
1 5 1	18.6	16.7	23	4 6 0	9.0	10.9	180
1 5 2	9.1	7.5	180	4 6 1	15.8	16.5	170
1 5 3	20.7	17.8	234	4 6 2	7.9	9.2	18
1 5 4	4.8	6.8	343	5 1 0	42.9	44.6	0
1 7 0	9.1	9.0	0	5 1 1	47.3	43.5	200
2 0 2	25.2	23.8	356	5 1 2	28.1	26.5	182
2 0 4	23.1	26.0	279	5 1 3	42.5	42.5	34
2 0 6	27.3	31.8	103	5 1 4	14.0	13.9	64
2 2 0	6.6	6.3	180	5 1 5	23.5	22.9	223
2 2 1	30.6	29.6	72	5 3 0	52.8	53.9	180
2 2 2	9.8	10.6	288	5 3 1	14.3	10.9	296
2 2 3	44.4	44.8	236	5 3 2	34.8	38.8	12
2 2 4	12.8	12.1	99	5 3 3	16.0	15.4	75
2 2 5	24.9	24.4	60	5 3 4	22.3	23.6	233
2 4 0	47.3	48.7	0	5 5 1	28.9	24.5	26
2 4 1	13.0	12.4	205	5 5 2	9.7	7.1	216
2 4 2	32.7	35.2	50	5 5 3	21.7	28.9	231
2 4 3	15.2	14.0	67				

with the observed structure factors are listed in Table 4. Calculated structure factors have been corrected for thermal vibrations. An isotropic temperature factor has been applied, although from the positions of the different atoms, one could assume that the magnitudes of the thermal vibrations were somewhat different in the x- and z-directions.

The standard deviations are 0.007 Å in Si—O and 0.01_4 Å in Si—N distances. Between atoms related by symmetry, the standard deviations are 0.01_5 Å in Si—Si and 0.02_4 Å in O—O distances. The standard deviation for the Si—O—Si angle is 1°. The R-factor, including observed reflections only, was 0.075.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal is based on a three dimensional network of SiN_3O tetrahedra. The structure is shown in three projections. Figs. 4 and 5 show (010) and (001)

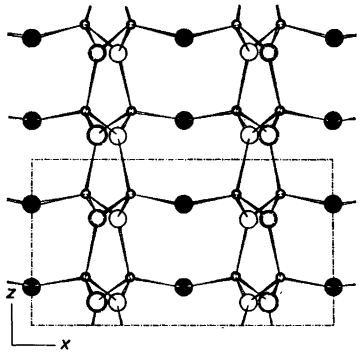

Fig. 4. Projection of the structure along the b-axis.

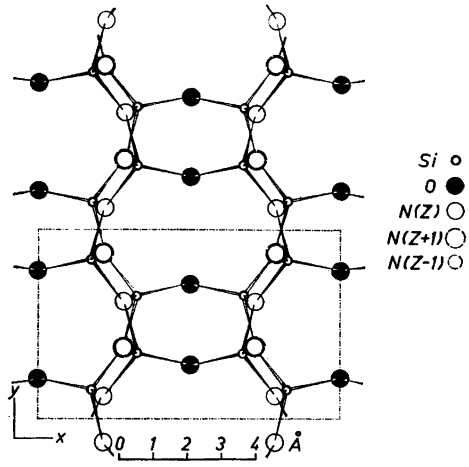

Fig. 5. Projection of the structure along the c-axis.

projections, respectively, the dimensions of one unit cell being denoted by broken lines. There are two special features: The oxygen atoms are arranged in definite layers perpendicular to the (100) direction and the silicon and nitrogen atoms form a parallel layer between two oxygen layers. Thus, successive silicon-nitrogen layers are linked together by oxygen atoms bound to two silicon atoms in adjacent layers. Fig. 6 shows one silicon-nitrogen-oxygen layer viewed from the crystallographic a-direction.

The interatomic distances and interatomic angles are listed in Table 5. In Fig. 7 the distances and angles in one tetrahedron are shown.

Si—O distances in this structure and in silicate structures show good agreement. In framework structures the Si—O distances have a mean value

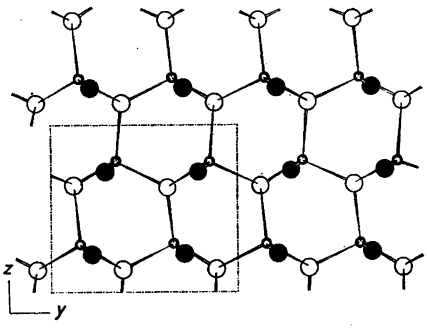

Fig. 6. Projection of a layer of the structure along the *a*-axis.

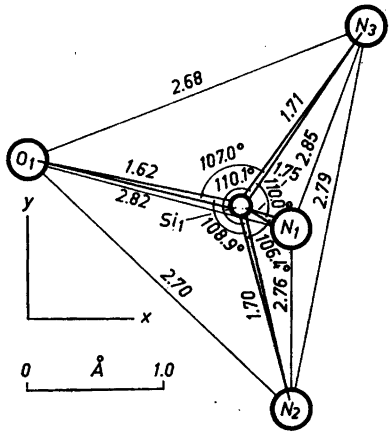

Fig. 7. The tetrahedron formed around a silicon (Si_1) atom.

of 1.61 Å as compared with 1.63 Å in structures with isolated teterahedra. In *α*-quartz Smith and Alexander [8] found the Si—O distances to be 1.617 and 1.597 Å and Si—O—Si angles to be 144.0°, compared with 1.623 Å and 147.7° in Si_2N_2O. The silicon-nitrogen distances are 1.70, 1.71, and 1.75 Å which are very close to the silicon-nitrogen distances, 1.72 and 1.75 Å, found in Si_3N_4 structures by Hardie and Jack.[7]

Table 5. Interatomic distances and angles.

a. Interatomic distances (Å).

Si_1-O_1	1.623	± 0.007
Si_1-N_1	1.75	± 0.02
Si_1-N_2	1.70	± 0.01
Si_1-N_3	1.71	± 0.01
O_1-N_1	2.82	± 0.02
O_1-N_2	2.70	± 0.02
O_1-N_3	2.68	± 0.01
N_1-N_2	2.76	± 0.03
N_1-N_3	2.85	± 0.03
N_2-N_3	2.79	± 0.02
Si_1-Si_3	3.12	± 0.02
Si_1-Si_2	2.93	± 0.02
O_1-O_2	3.37	± 0.03

(shortest Si—Si distance)
(shortest O—O distance)

b. Interatomic angles (°).

$Si_1-O_1-Si_3$	147.7 ± 1.3
$N_1-Si_1-N_2$	106.4
$N_1-Si_1-N_3$	110.0
$N_2-Si_1-N_3$	110.1
$N_1-Si_1-O_1$	113.4
$N_2-Si_1-O_1$	108.9
$N_3-Si_1-O_1$	107.0

c. Atomic positions used in Table 5, a and b

Atom	Parameter		
	x	*y*	*z*
Si_1	0.1763	0.1509	0.2898
Si_2	0.1763	−0.1509	0.2898
Si_3	−0.1763	0.1509	0.2898
N_1	0.218	0.121	0.642
N_2	0.218	−0.121	0.142
N_3	0.282	0.379	0.142
O_1	0	0.214	0.230
O_2	0	−0.214	−0.270

These comparisons show the structural relationship between silicon oxynitride, silica, and silicon nitride. The chemical and physical properties of these compounds are also very similar. Finally may be observed that silicon oxynitride seems to occur in at least two modifications: a normal form (cell dimensions $a \times b \times c$) and a form with a superstructure (cell dimensions $a \times 2b \times 4c$). An investigation of the latter structure is intended.

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