

shorter (1.80 and 1.83 Å) bond length. In both cases, this displacement is in the direction of the center of the channel. The sites *M1* and *M2*, if idealized, would be situated ~1.90 Å from the O atoms, a distance ~0.11 Å shorter than the average Li–O bond distance found in this structure. This would then be a more unfavorable location for the Li⁺ ion.

Single-crystal d.c. conductivity (Boyce, 1978) and microwave dielectric-constant measurements (Richards, 1978) show no strong anisotropy in this material, suggesting Li⁺ ion paths perpendicular to the channel directions. The Ti site accommodates an ion of radius ~0.69 Å and is sufficiently large for the Li⁺ ion.

Table 2. Bond lengths (Å) and angles (°) in Li₂Ti₃O₇

Ti–O(1)	1.956 (1)	O(1)–Ti–O(1')	96.90 (5)
Ti–O(1')	1.980 (1) × 2	O(1)–Ti–O(2)	90.70 (5)
Ti–O(2)	1.982 (1) × 2	O(1)–Ti–O(2')	80.56 (4)
Ti–O(2')	2.026 (1)	O(1')–Ti–O(1')	96.10 (4)
		O(1')–Ti–O(2)	91.87 (5)
		O(2)–Ti–O(2')	80.56 (4)
		O(2')–Ti–O(2')	95.95 (4)
Li(1)–O(2)	1.80 (2)	O(2)–Li(1)–O(2')	123 (1)
Li(1)–O(2')	2.05 (2) × 2	O(2')–Li(1)–O(2')	92 (1)
Li(1)–O(1)	2.15 (2)	O(2)–Li(1)–O(1)	133 (1)
		O(2')–Li(1)–O(1)	87 (1)
Li(2)–O(2)	1.83 (3)	O(2)–Li(2)–O(2')	125 (1)
Li(2)–O(2')	1.99 (2) × 2	O(2')–Li(2)–O(2')	95 (1)
Li(2)–O(1)	2.26 (4)	O(2)–Li(2)–O(1)	134 (2)
		O(2')–Li(2)–O(1)	82 (1)

In fact, the present structure study obtained the best fit to the experimental data with the model in which Li⁺ ions fill the vacant Ti sites. For Li⁺ ion diffusion perpendicular to the channel directions, the Li⁺ ion would need to hop through the octahedral face shared with the tetrahedron containing the empty *M1* or *M2* sites and then on to the center of the channel to the Li(1) and Li(2) sites. The time spent on *M1* and *M2* is very small as indicated by the very low value of electron density at these sites. Hops from the octahedral site to *M1* are along the *b* direction while those to *M2* are along the *a* direction. Thus, the Li⁺ ion disorder in the channels, the small positive value for the electron density at the *M1* and *M2* sites and the structural arrangement of shared faces between the octahedra and *M1* or *M2* tetrahedra are consistent with the lack of anisotropy in the ionic conductivity of this material.

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The Crystal Structure of β-Si₃N₄; Structural and Stability Considerations Between α- and β-Si₃N₄

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Abstract

β-Si₃N₄, grown from a silicon melt, has space group *P6₃* with *a* = 7.595 (1), *c* = 2.9023 (6) Å, *Z* = 2. *R* = 0.037 for 345 independent reflections. The close relation to the α-Si₃N₄ structure is shown. Madelung energy calculations suggest that β-Si₃N₄ is the more stable form at about 293 K.

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Introduction

The high-temperature ceramic Si₃N₄ is of technological interest because of its good refractory properties. However, the relationship between the two forms α and β is not completely understood. It was supposed that α- and β-Si₃N₄ are low- and high-temperature forms, respectively, but only a transformation from α to β has been observed, never the reverse.

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The synthesis of Si_3N_4 by nitriding pure Si at <1773 K always leads to the α - and β -phases in varying proportions.

Wild, Grieveson & Jack (1972) assumed that α - Si_3N_4 is an oxonitride, but this has been disproved by Blegen (1975) and also by structural results (Kohatsu & McCauley, 1974; Kato, Inoue, Kijima, Yamane & Kawada, 1975). Therefore it is concluded that β - Si_3N_4 is the stable and α - Si_3N_4 a metastable phase of pure Si_3N_4 .

The crystal structure of β - Si_3N_4 has been described by Hardie & Jack (1957), Thompson & Pratt (1967) and Wild *et al.* (1972). All these determinations were based on powder photographs. A structure investigation from single-crystal data (Borgen & Seip, 1961) used only the $hk0$ reflections, because the centrosymmetric space group $P6_3/m$ was assumed.

This paper describes an attempt to clarify the stability relations between α - and β - Si_3N_4 by Madelung energy computations. For this it was necessary to have a structure determination for both phases. A single-crystal structure determination for α - Si_3N_4 has been published by Kato *et al.* (1975); a comparable structure refinement of β - Si_3N_4 is described in the first part of this paper.

Structure refinement of β - Si_3N_4 : experimental

Single crystals of β - Si_3N_4 were obtained by a method similar to that described by Inomata & Yamane (1974). A silicon nitride crucible containing pure Si was heated in an electric resistance furnace at about 1823 K for 6–10 h in a nitrogen atmosphere (10^5 Pa) (Grün, 1979).

A Si_3N_4 film forms at the surface of the Si melt, so that further nitrogen diffusion into the melt is restricted. Single crystals of β - Si_3N_4 then grow into the Si melt. After cooling, the rest of the Si melt is removed by a mixture of HF and HNO_3 to yield colourless, transparent crystals several mm long, with a diameter up to 0.5 mm.

Preliminary information about the cell dimensions and symmetry were taken from precession photographs of about 25 crystals. The Laue group is $6/m$. From the intensity distribution and the systematic extinctions ($00l$ with $l = 2n - 1$), the space groups $P6_3$ and $P6_3/m$ were possible. The crystal chosen for the subsequent structural work was cylindrical, 370 μm long with a diameter of 160 μm .

Intensities were collected on a four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å, graphite

monochromator), θ - 2θ step-scan mode ($\theta = 40^\circ$) with 60 steps of 0.01° and 1 s counting time per step. The background was measured for 6 s at each end of the scanning interval.

The cell dimensions in Table 1 were obtained by a least-squares procedure from 12 reflections. Lorentz-polarization and absorption corrections for the 2853 measured intensities were made. The individual values of the squared structure amplitudes and their e.s.d.'s were averaged for symmetrically equivalent reflections. This reduction gave 345 structure amplitudes of which 19 with $F_o^2 < 1.5\sigma(F_o^2)$ were classified as unobserved.

The following computer programs were used: *DATAPH* (Coppens, Leiserowitz & Rabinovich, 1965) for Lorentz-polarization, absorption and extinction corrections; *ORFLS* (Busing, Martin & Levy, 1962; modified by W. C. Hamilton and J. A. Ibers) for least-squares refinement; *SFS* (Neukäter & Biedl, unpublished) for the Fourier synthesis; *SADIAN* (Baur & Wenninger, unpublished) for calculation of the interatomic distances and bond angles.

Scattering factors, from *International Tables for X-ray Crystallography* (1962), were interpolated for $\text{Si}^{4/3+}$ and N^- ions. This follows from the assumption of an ionic bonding character of 30% according to the difference in the Pauling electronegativity between Si and N.

In the refinement, $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$ (for $F_o = 0$, $w = 0$) was minimized. Full-matrix least-squares refinement with anisotropic temperature factors gave a final $R = 0.037$ and $R_w = 0.062$.

An extinction correction was made (Zachariasen, 1963). With $E = (18 \pm 2) \times 10^{-8}$, the maximum change of F_o was about 40% for the 002 reflection.

The positional parameters of Wild *et al.* (1972) were taken as a starting model. Atom parameters, interatomic distances and bond angles are listed in Tables 2 and 3.* The maxima of the electron density in the final Fourier synthesis were $<0.4 \text{ e } \text{Å}^{-3}$.

Description of the β - Si_3N_4 structure and discussion

The structure is similar to phenacite. It consists of SiN_4 tetrahedra and the sharing coefficient (Zoltai, 1960) is 3. The Si_3N groups are nearly planar and the slightly distorted tetrahedra are oriented with one edge parallel to c .

The atomic arrangement of one unit cell is shown in Fig. 1 which includes some N positions from neigh-

Table 1. *Crystal data of β - Si_3N_4*

$a = 7.595$ (1) Å	$V = 144.98$ (5) Å ³
$c = 2.9023$ (6)	$Z = 2$
$c/a = 0.3821$ (1)	Space group: $P6_3$

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34142 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic parameters and anisotropic temperature factors of β -Si₃N₄ (all values $\times 10^4$)

	x/a	y/a	z/c	Anisotropic temperature factors of β -Si ₃ N ₄ in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.					
				β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si	7686 (1)	1744 (1)	2500	23 (1)	23 (1)	88 (8)	12 (1)	-6 (9)	-12 (9)
N(1)	298 (3)	3294 (3)	2628 (20)	27 (3)	26 (3)	102 (20)	11 (2)	-36 (24)	-37 (21)
N(2)	6667	3333	2392 (55)	29 (3)	29 (3)	126 (40)	15 (2)	0	0

bouring cells. In this ORTEP plot (Johnson, 1965) the atoms are represented by thermal ellipsoids at the 99.9% probability level.

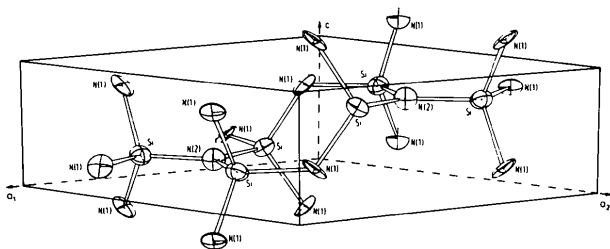
Fig. 2 shows a projection down c of a unit-cell layer, where spheres indicate the Si and N atoms with radii of about 0.80 and 1.00 Å respectively. These radii have been interpolated from the atomic and ionic radii (Si⁴⁺, N³⁻) by supposing an ionic character of 30%. Fig. 2 shows that there are two straight channels through the structure, one located around the origin with a radius of 1.50 Å, the other with dimensions 1.00 \times 2.40 Å in the middle of the unit cell.

Table 3. Interatomic distances (Å) and bond angles (°) of β -Si₃N₄

Si-N(1) ⁱ	1.728 (2)	Si-N(1) ⁱⁱⁱ	1.767 (5)
Si-N(1) ⁱⁱ	1.704 (5)	Si-N(2)	1.730 (1)
	Angle	N-N distance	
N(1) ⁱⁱⁱ -Si-N(1) ⁱ	109.4 (2)	2.801 (5)	
N(1) ⁱⁱ -Si-N(2)	109.7 (5)	2.808 (9)	
N(1) ⁱ -Si-N(1) ⁱⁱ	113.5 (2)	2.902 (8)	
N(1) ⁱ -Si-N(2)	106.7 (1)	2.774 (1)	
N(1) ⁱ -Si-N(1) ⁱⁱ	106.6 (2)	2.801 (5)	
N(2)-Si-N(1) ⁱⁱ	110.8 (5)	2.878 (9)	
	Angle	Si-Si distance	
Si ^{iv} -N(1)-Si ^{vi}	125.1 (3)	3.046 (1)	
Si ^{iv} -N(1)-Si ^v	113.5 (1)	2.902 (0)	
Si ^{vi} -N(1)-Si ^v	121.3 (3)	3.046 (1)	
Si-N(2)-Si ^{vii}	119.97 (4)	2.996 (1)	

Equivalent positions

- (i) $x + 1, y, z$ (ii) $x - y, -y, z + 0.5$
 (iii) $x - y, -y, z - 0.5$ (iv) $-x, y - x, z + 0.5$
 (v) $-x, y - x, z - 0.5$ (vi) $x - 1, y, z$
 (vii) $-y, y - x, z$

Fig. 1. Atomic arrangement of the unit cell of β -Si₃N₄ including some N atoms from neighbouring cells.

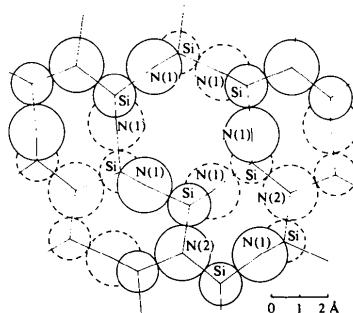
In previous structure determinations of β -Si₃N₄, the centrosymmetric space group $P6_3/m$ was chosen. But the deviations of the z parameters from the special position $z/c = 0.25$ in $P6_3/m$ are significant (6.6 and 2.0 σ), so that $P6_3$ should be the correct choice.

The Hamilton (1965) significance test also confirmed that the improvement in changing from $P6_3/m$ to $P6_3$ is more than 99.5% significant.

An $N(z)$ test failed to distinguish between a centrosymmetric or non-centrosymmetric space group. If the centrosymmetric structure is assumed, all atoms are located in a mirror plane, so that the Si₃-N(2) groups have to be planar. This, however, is implausible because the similar Si-N(1) groups are not planar. The deviations of N(1) and N(2) from the corresponding Si₃ plane are 0.048 and 0.040 Å respectively. α -Si₃N₄ has a very similar structure to β -Si₃N₄, although the former contains two rather than only one distinct set of Si₃-N groups (Kato *et al.*, 1975). The corresponding values are 0.035 and 0.17 Å for N(1) and N(2) and 0.003 and 0.35 Å for N(3) and N(4).

Structural relations between α - and β -Si₃N₄

α -Si₃N₄ also consists of SiN₄ tetrahedra, which are arranged in a similar manner as in β -Si₃N₄. Thompson & Pratt (1967) mentioned that α -Si₃N₄ consists essentially of alternate basal layers of β (here called A) and a mirror image of β (called B), so that the c spacing of α -Si₃N₄ is nearly twice that of β -Si₃N₄.

Fig. 2. Projection down c of a unit-cell slice from β -Si₃N₄.

The relationship between the layers *A* and *B* is given by the following transformation of one atom position X_A from *A* to an atom position X_B in *B*:

$$X_B = \begin{pmatrix} -1 & 0 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} X_A + \frac{1}{3} \begin{pmatrix} -1 \\ 1 \\ 3 \end{pmatrix}$$

with

$$X_{A,B} = \begin{pmatrix} x/a \\ y/a \\ z/c \end{pmatrix} \quad (1)$$

Such an *ABA* sequence (a_3 projection) is shown in Fig. 3(a). There the unit cell of the α - Si_3N_4 structure is indicated by dotted lines, and is thus very similar to the equivalent projection of the real α - Si_3N_4 structure (Fig. 3b). The projection down *c* of the two layers *A* and *B* is shown in Fig. 4(a). The unit cell of the α -structure is also indicated by dotted lines to allow comparison with the projection of the real α - Si_3N_4 structure in Fig. 4(b).

In β - Si_3N_4 the tetrahedra are oriented such that the edges are in a straight line parallel to *c*. In the α -structure, on the other hand, there are two sequences of non-equivalent tetrahedra which are distorted with respect to one another by about 60 – 70° around *c*. The edges in the *c* direction are not in a straight line, so that $c(\alpha)$ is almost twice the tetrahedron edge (Fig. 5).

Physicochemical relations of α - and β - Si_3N_4

From the assumption that α is a metastable and β the stable form of Si_3N_4 , it is to be expected that the

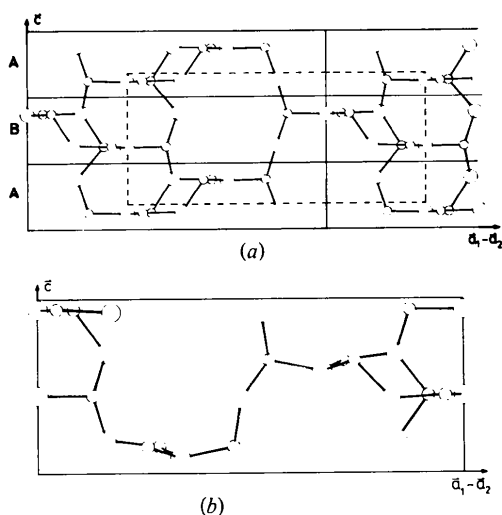


Fig. 3. Projection down a_3 of the *ABA* sequence (a) produced by transformation 1 (see text). The region indicated with dotted lines is equivalent to (b) the projection of the real α - Si_3N_4 unit cell. (Large circles: N, small circles: Si.)

difference of the free energy $\Delta G(\beta - \alpha) = G(\beta) - G(\alpha)$ of the two phases is negative. Its magnitude must be small compared with the enthalpy barrier which results from the reconstructive phase transformation from α to β . For the difference ΔG :

$$\Delta G(\beta - \alpha) = \Delta U_c + \Delta U_e + p\Delta V - T\Delta S, \quad (2)$$

where ΔU_c = covalent part of the lattice energy: negligible, because it is expected that both phases have the same bonding character; this is understandable, because the covalent forces are short range, and in both cases there are nearly equivalent SiN_4 tetrahedra; ΔU_e = electrostatic part of the lattice energy: not negligible, because the range of the electrostatic forces is much greater than to the nearest neighbours, so that it depends on the different crystal structure; ΔV = molar or unit-cell volume: not negligible; ΔS = entropy: can be expected to be small compared to the other effects, because both phases are ordered states and have very similar crystal structures. Therefore:

$$\Delta G(\beta - \alpha) \approx \Delta H = \Delta U_e + p\Delta V. \quad (3)$$

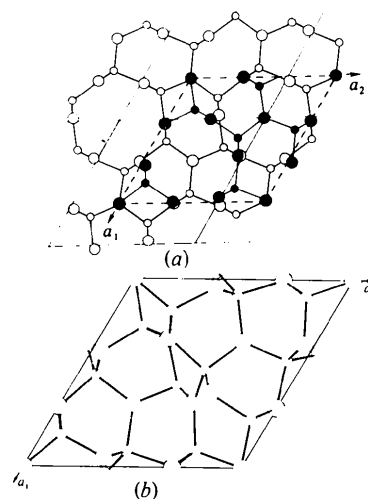


Fig. 4. (a) Projection down *c* of layer *A* (open circles) and layer *B* (full circles) produced by transformation 1 (see text). The region enclosed by dotted lines is equivalent to (b) the projection of the real α - Si_3N_4 unit cell. (Large circles: N, small circles: Si.)

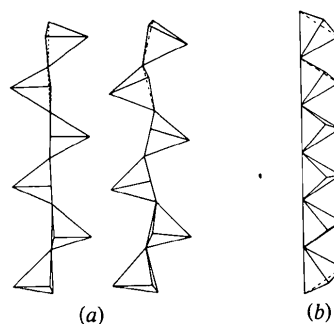


Fig. 5. (a) The two tetrahedra sequences of α - Si_3N_4 along *c* and (b) the one tetrahedron sequence of β - Si_3N_4 along *c*.

To calculate the Madelung energy, including the Born repulsive forces, it is considered that (Pauling, 1968; Cotton & Wilkinson, 1970):

$$U_e = -\frac{MF}{r_o} Z^2 \frac{e^2}{4\pi\epsilon_0} \left(1 - \frac{1}{n}\right). \quad (4)$$

If there are s slightly different bond distances r_i then:

$$U_e = -\frac{MF}{r_m} Z^2 \frac{e^2}{4\pi\epsilon_0} \left(1 - \frac{1}{n}\right) \quad (5)$$

with

$$\frac{1}{r_m} = \frac{1}{s} \sum_{i=1}^s \frac{1}{r_i}.$$

The Madelung factor MF is a function of the distance r_j from one ion to another in the crystal and was calculated with the program *MADKUG* (Neukäter & Roch, unpublished).

The results for one formula unit Si₃N₄ are listed in Table 4. The values for β_c -Si₃N₄ refer to the space group $P6_3/m$. With these values for α - and β -Si₃N₄ both parts in (3) become negative. Therefore β -Si₃N₄ must be the more stable form at about 293 K. The magnitude of this difference is only about 1.3% of the absolute value, so that coexistence of both phases can be presumed. But it is to be expected that the transformation from α - to β -Si₃N₄ is possible and not the reverse, in agreement with the experimental results.

The difference of the lattice energy between the centrosymmetric and the non-centrosymmetric structures of β -Si₃N₄ is very small, so that from the electrostatic point of view a non-centrosymmetric structure would be slightly more favoured.

To calculate the enthalpy difference ΔH from (3) it can be supposed that: (1) The Si-N bonding character is 30% ionic, so that $Z = 0.3$. This follows from the

difference in the Pauling electronegativity. (2) The Born exponent $n = 7$ is nearly the same for both phases (neon configuration of Si and N; Cotton & Wilkinson, 1970). (3) $p = 10^5$ Pa; $T = 298$ K.

Substituting these values in (3) and (5) we obtain: $\Delta H = -(30 \times 10^3 + 0.09)$ J mol⁻¹ ≈ -30 kJ mol⁻¹. The magnitude of this calculated enthalpy difference is of the same order as the accuracy of the measured enthalpy change for the reaction $3\text{Si} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4$, $\Delta H_{298} = -(737 \pm 25)$ kJ mol⁻¹ (Pehlke & Elliott, 1959). In this reaction the α - β difference has not been taken into consideration.

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Table 4. Madelung factors (MF) of α -, β - and β_c -Si₃N₄ (β_c assumes the centrosymmetric space group $P6_3/m$ for β -Si₃N₄), volumes (V_f) of one formula unit of Si₃N₄ and r_m values: see (5)

	MF	r_m (Å)	MF/ r_m (Å ⁻¹)	V_f (Å ³)
α -Si ₃ N ₄	66.4505	1.7430	38.124	73.99
β -Si ₃ N ₄	66.5369	1.7319	38.418	72.49
β_c -Si ₃ N ₄	66.5156	1.7319	38.404	72.49