The Crystal Structure of β-Si_3N_4

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The crystal structure of β-Si_3N_4 is known from studies by Hardie and Jack [1], and Popper and Ruddlesden [2] with X-ray data obtained from powder photographs.

Although crystals of β-Si_3N_4 have been grown[2] by heating silicon in an ammonia atmosphere at 1500°C for three days, no single crystal structure investigation has been published.

A sample of crystals formed spontaneously on a ferrosilicon alloy in air at room temperature [3] has been given us by Prof. K. Grjotheim. The sample contains both α- and β-Si_3N_4.

The crystal structure of β-Si_3N_4 has been reinvestigated by us, using X-ray intensities measured photometrically from integrated Weissenberg films and corrected in the usual way. Needle-formed crystals of diameter about 30 μ were used for this investigation.

We have reaffirmed the space group $P6_3/m$ and unit cell parameters, $a = 7.607$ Å, $c = 2.911$ Å, found by the earlier investigators [1,2].

As the z-coordinates of all atoms are determined by the space group, only the $hk0$-reflections have been utilized in this investigation.

Three cycles of least-squares refinement of the atomic coordinates were made, giving the final values for atoms in different special positions,

N in (c) $x = 1/2$ $y = 2/3$ $z = 1/4$
N in (h) $x = 0.321$ $y = 0.025$ $z = 1/4$
Si in (h) $x = 0.174$ $y = -0.234$ $z = 1/4$

The coordinates of N in (h) are somewhat different from those of Hardie and Jack [1].

N in (h) $x = 0.333$ $y = 0.033$ $z = 1/4$
Si in (h) $x = 0.172$ $y = -0.231$ $z = 1/4$

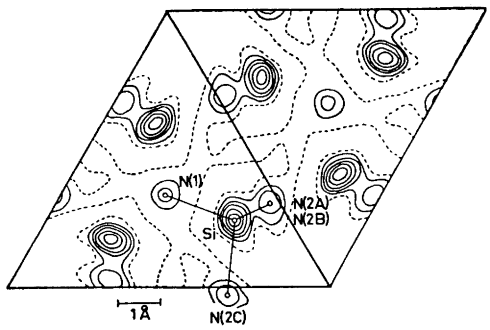

Fig. 1. Electron density projection of β-Si_3N_4 on (001).

The final reliability factor was $R = \Sigma \mid \Delta F \mid / \Sigma \mid F_0 \mid = 0.109$.

An electron density projection on (001), calculated before the least-squares refinement, is shown in Fig. 1.

The interatomic distances within the distorted SiN_4 tetrahedron (see Fig. 1) are given below.

Si – N(1)	1.72_0 Å
Si – N(2A) = Si – N(2B)	1.75_8 Å
Si – N(2C)	1.71_1 Å
N(1) – N(2A) = N(1) – N(2B)	2.89_3 Å
N(1) – N(2C)	2.77_4 Å
N(2A) – N(2B)	2.91_1 Å
N(2C) – N(2A) = N(2C) – N(2B)	2.76_7 Å

The standard deviations of the above distances are estimated to be less than 0.015 Å.

1. Hardie, D. and Jack, K. H. *Nature* **180** (1957) 332.
2. Ruddlesden, S. N. and Popper, P. *Acta Cryst.* **11** (1958) 465.
3. Grjotheim, K., Johnson, E. and Krohn, C. *Nature* **190** (1961) 23.

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