The Crystal Structure of $\beta$-Si$_3$N$_4$

O. Borgen and H. M. Seip

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

The crystal structure of $\beta$-Si$_3$N$_4$ 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 $\beta$-Si$_3$N$_4$ have been grown$^3$ 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 $\alpha$- and $\beta$-Si$_3$N$_4$.

The crystal structure of $\beta$-Si$_3$N$_4$ 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 $\mu$ 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$^1$.

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,

$\text{N in (c)} \quad x = 1/2 \quad y = 2/3 \quad z = 1/4$

$\text{N in (h)} \quad x = 0.321 \quad y = 0.025 \quad z = 1/4$

$\text{Si in (h)} \quad x = 0.174 \quad y = -0.234 \quad z = 1/4$

The coordinates of $\text{N in (h)}$ are somewhat different from those of Hardie and Jack$^4$.

$\text{N in (h)} \quad x = 0.333 \quad y = 0.033 \quad z = 1/4$

$\text{Si in (h)} \quad x = 0.172 \quad y = -0.231 \quad z = 1/4$

The final reliability factor was $R = \Sigma |\Delta F| / \Sigma |F_o| = 0.109$.

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

The interatomic distances within the distorted Si$_3$N$_4$ tetrahedron (see Fig. 1) are given below.

\begin{align*}
\text{Si} - \text{N(1)} & = 1.72_{o} \text{ Å} \\
\text{Si} - \text{N(2A)} = \text{Si} - \text{N(2B)} & = 1.75_{o} \text{ Å} \\
\text{Si} - \text{N(2C)} & = 1.71_{o} \text{ Å} \\
\text{N(1)} - \text{N(2A)} = \text{N(1)} - \text{N(2B)} & = 2.89_{o} \text{ Å} \\
\text{N(1)} - \text{N(2C)} & = 2.77_{o} \text{ Å} \\
\text{N(2A)} - \text{N(2B)} & = 2.91_{o} \text{ Å} \\
\text{N(2C)} - \text{N(2A)} = \text{N(2C)} - \text{N(2B)} & = 2.76_{o} \text{ Å}
\end{align*}

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


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