The Space Group of β-Si$_3$N$_4$

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Abstract

A new preparation of pure β-Si$_3$N$_4$ powder has permitted a study of the material by convergent-beam electron diffraction. This study has confirmed its classification in the space group $P6_3/m$.

Introduction

Silicon nitride is rapidly becoming one of the more important engineering ceramics. Two polymorphs, α- and β-Si$_3$N$_4$, are known (Ruddlesden & Popper, 1958) and the conditions for their preparation and stability are currently the subject of intensive research. The crystal structure of α-Si$_3$N$_4$ is now well known (Kato, Inoue, Kijima, Kawada & Tanaka, 1975); however, the difficulty of preparing good single crystals of β-Si$_3$N$_4$ has hindered an accurate structure determination. On the basis of a study of an impure powder, Hardie &

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Jack (1957) reported an approximate structure with symmetry $P6_3/m$. Subsequently Borgen & Seip (1961) redetermined the structure using diffraction data from a small single crystal. They used only $hk0$ reflections, as the mirror plane (in space group $P6_3/m$) fixes the z coordinates of all the atoms. Wild, Grieveson & Jack (1972) subsequently published a more precise structure, still with the same space group, that differed significantly from that of Borgen & Seip. Recently Grun (1977) proposed a slightly different structure, based on refinement of single-crystal X-ray data, with space group $P6_3$. This structure differed from that of Wild *et al.* (1972) mainly in displacements of three quarters of the N atoms by approximately 0·05 Å along the c axis. These displacements in turn result in changes in Si–N bond lengths by about the same amount. Thus two Si–N bond lengths of 1·730 Å in the Wild *et al.* (1972) structure become 1·689 and 1·763 Å in the Grun (1977) structure. As a knowledge of accurate bond lengths and bond angles plays a central role in discussions of bonding in crystals we have examined this structure using convergent-beam electron diffraction (CBED).
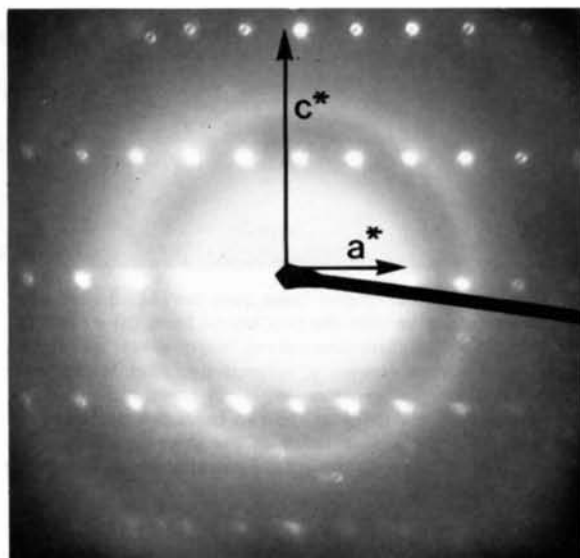

Fig. 1. The 'selected-area' pattern from the [11$\bar{2}$0] zone setting of Si$_3$N$_4$, used for the convergent-beam studies. The rectangular cell shown ($a^* \times c^*$) corresponds to the real-space cell of $a = 6\cdot6$, $c = 2\cdot9$ Å.
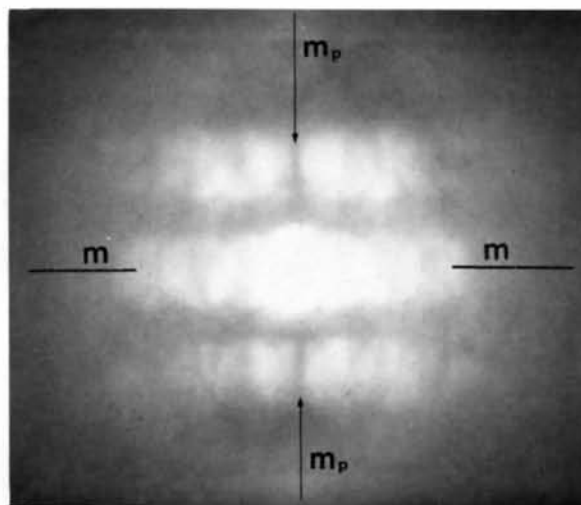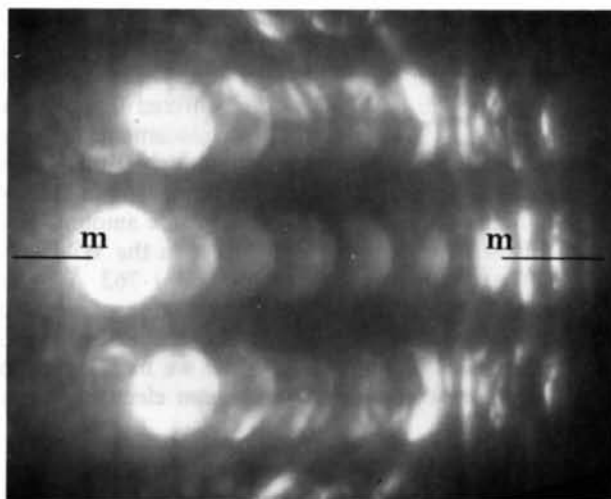

Fig. 2. The zone-axis convergent-beam pattern for [11$\bar{2}$0]. The lines m and m_p show the mirror lines which are only crudely visible in the pattern; the mirror line across m–m is partly obscured by the slight mis-setting of the illumination aperture relative to the zone axis. The extinction of intensity in the 0001/000$\bar{1}$ reflexions is clearly seen at the ends of the arrows m_p.

In the technique of CBED, unlike X-ray diffraction, the symmetry elements of a structure are examined directly and, in the case of a material such as Si$_3$N$_4$ where there is no great range over atomic number ($Z = 14$, 7 and for Si and N), mirror symmetries may be determined to a high accuracy.

Experiments and results

Si$_3$N$_4$ (from the Ventron Corporation) consisting of approximately equal amounts of α- and β-Si$_3$N$_4$ was converted to β-Si$_3$N$_4$ (as revealed by X-ray powder diffraction) after heating at 1973 K for 10 h in a 90% N$_2$ + 10% H$_2$ mixture. The resulting powder was found by electron microscopy to consist of platelets with faces parallel to the c axis. This morphology gave convenient access to the reflexions of the [11$\bar{2}$0] zone.

(a)
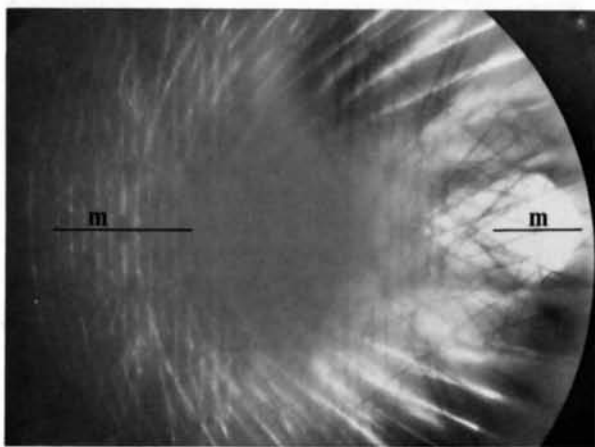
(b)

Fig. 3. The horizontal mirror line, scarcely discernible from Fig. 2, is made obvious in (a) and (b); these are convergent-beam patterns taken with the incident beam tilted to the zone axis, but symmetrically disposed across the mirror line, a^* (see text).
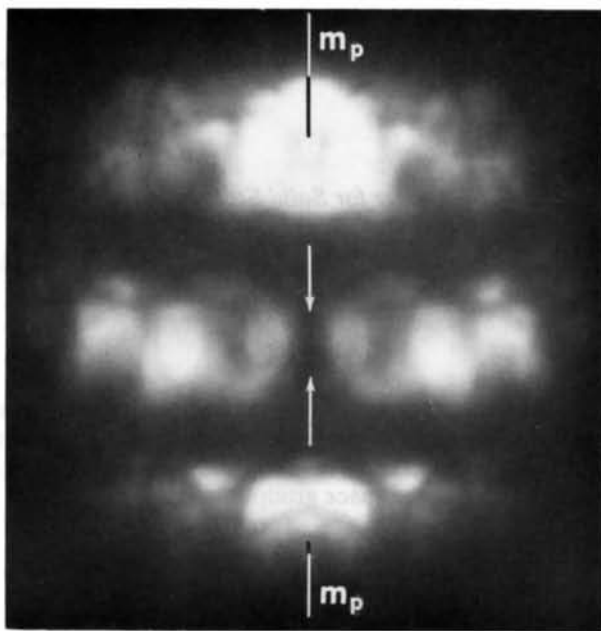

Fig. 4. The convergent-beam pattern taken with the incident cone of electrons tilted from the zone axis in the perpendicular direction from Fig. 3, *i.e.* symmetrically disposed about the c^* axis. Note the extinction at the 0001 position (indicated by arrows).
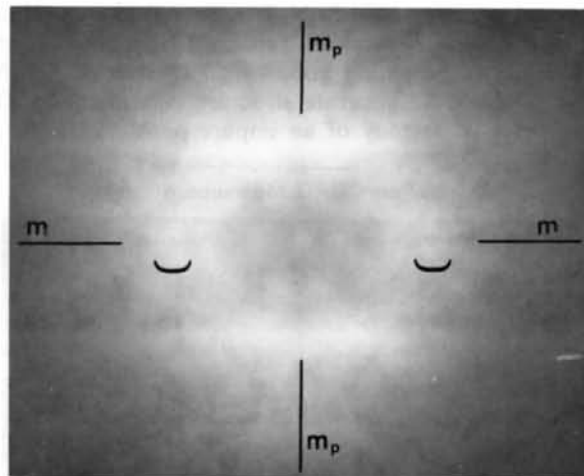

Fig. 5. Wide-angle convergent beam from the [11$\bar{2}$0] zone axis. In this pattern can be seen the two mirror lines, (a) m–m and (b) m_p–m_p, from the three-dimensional mirror plane, and from the *projective* mirror symmetry, respectively. Also, it can be seen that the symmetry across m_p–m_p is not exact, but is broken by the differences occurring at the two bracketed positions in the picture. This break is a result of the three-dimensional interaction of electrons with the crystal potential within the dynamic scattering process.

The preparation was examined in a JEOL 100B electron microscope, set up for convergent-beam diffraction (Goodman, 1980). Results are shown in Figs. 1–5.

Fig. 1 shows the 'selected-area' point pattern from the [11$\bar{2}$0] zone axis. This serves to show the rectangular cell dimensions 6·6 × 2·9 Å (*i.e.* $\sqrt{3}a/2$ × *c*). The scale of the diffraction pattern is given by the carbon halo shown which corresponds to the *c*–*c* spacing of 2 Å. In the remaining figures the CBED–Kossel pattern (wide-angle convergent beam) and apertured convergent-beam patterns display the relevant symmetry elements, as follows:

1. The [11$\bar{2}$0] zone-axis pattern of Fig. 2 shows the 2*m* symmetry of the projection. Note the 000*l*, *l* = 2*n* absences indicated by the dark band through the 0001 position.

2. Fig. 3(*a*) and (*b*) shows the patterns obtained from thin and thick crystals when the incident cone of electrons is parallel to the {000*l*} planes but tilted several degrees to the [11$\bar{2}$0] zone axis. This tilting increases the sensitivity of the pattern to any deviation from an [0001] mirror symmetry, by greatly increasing the zone of visible reflexions. In particular, the large tilt and large incident-cone semi-angle used for Fig. 3(*b*) bring up very many sharp defect lines within and around the direct (0000) beam. With these data we can verify the mirror plane in question (*i.e.* the mirror plane specific to *P*6$_3$/*m* and absent from *P*6$_3$) to a high accuracy; certainly deviations of the order reported by Grun (1977) can be ruled out by this direct observation.

3. Fig. 4, taken with a tilt along the second axis, *i.e.* with the incident cone parallel to the {*hh*00} planes, shows the projective symmetry of the twofold screw axis. The absence of intensity at the 0001 position is in agreement with the twofold screw operator.

4. The wide-angle convergent-beam pattern of Fig. 5 which was taken at the [11$\bar{2}$0] zone-axis setting has low contrast but an approximate 2*m* symmetry (the symmetry of the projection) can be seen. However, upon closer examination only the symmetry across the [0001]* line is exact.

Across the [1$\bar{1}$00]* axis a break in the symmetry (indicated on the figure) is in agreement with the well-known three-dimensional character of fast-electron-interaction crystal potential, and with the fact that its origin is not a mirror plane but the *projective* symmetry of a diad axis.

Conclusion

The above examination of β-Si$_3$N$_4$ shows accurate agreement with the *P*6$_3$/*m* space group.

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The Structure of Cs₃CoCl₅ at 295 K: A Neutron Diffraction Study

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Abstract

The crystal structure of Cs₃CoCl₅ [tetragonal, *I*4/*mcm*, $a = 9\cdot2315$ (15), $c = 14\cdot5535$ (24) Å, $U = 1240\cdot3$ Å³, $Z = 4$] has been determined at 295 K by the use of high-accuracy single-crystal neutron diffraction data. Automatic diffractometry has provided Bragg intensities for 490 independent reflections with $0 < \sin\theta/\lambda \le 0\cdot690$ Å⁻¹, after equivalent reflections had been averaged. The structure was refined by full-matrix least-squares methods to *R* 0·023 and χ 1·454. Thermal-vibration parameters have been accurately

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