becoming about onefold positively charged due to the charge transfer. O(2), being also bonded to B, is then in a favourable electron-state condition. B also binds O(1); however, there is an unpaired electron left on O(1) which can then interact with another free electron of the B atom of the next unit, as discussed above. This interaction leads to the polymerization into chains, and the chains are then held together by the electrostatic forces between Li$^+$ cations and negatively charged O atoms. The model can also be expressed in terms of the bond-strength–bond-valence balance. The sum of the bond strengths of bonds involving B is 2·965, close enough to the valence number 3. For O(1) the sum is 1·845 and for O(2) only 1·12. Assuming that the differences from valence number 2 express the bond strengths of the Li–O(1) (0·155) and Li–O(2^i) (0·88) bonds, the bond-strength sum for Li is 1·035 – matching its valence number of 1 and supporting the importance of the Li–O(2^i) bond.

It must be emphasized here that this attempt to rationalize the chemical bonding in LiBO$_2$ was developed in a straightforward manner just by interpreting the information in the deformation density maps. Clearly, the situation is much more complicated and cannot be easily unravelled in terms of single bonds; but we consider this study to be an example of how knowledge about chemical bonding derived from calculations on diatomic systems can be used beneficially in interpretations of observations in more complex compounds.

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Weak Asymmetry in β-Si₃N₄ as Revealed by Convergent-Beam Electron Diffraction

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Abstract

The thickness dependence of the apparent crystal symmetry in a pure β-Si₃N₄ crystal has been studied by the convergent-beam electron diffraction (CBED) technique. The [11$\bar{2}$0] zone-axis CBED pattern for a thin crystal is compatible with the centrosymmetric space group $P6_3/m$, while that for a thick crystal would require the non-centrosymmetric space group $P6_3$. The thickness dependence of this result is discussed on the basis of the crystal structure of β-Si₃N₄ with space

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group $P6_3$, in which the structure contains a small antisymmetric group of nitrogen atoms.

Introduction

Convergent-beam electron diffraction (CBED) provides a very powerful technique for determining crystal symmetry (Goodman, 1975; Buxton, Eades, Steeds & Rackham, 1976). The crystal point group and the space group can be obtained from the symmetry appearing in the CBED pattern (Tanaka, Saito & Watanabe, 1980; Johnson & Gatehouse, 1980; Bando, Sekikawa, Yamamura & Matsui, 1981).

When carrying out a symmetry determination, the question has been raised as to whether CBED patterns reveal the true crystal symmetry and to what accuracy. If the crystal structure contains a small antisymmetric part due mainly to a small displacement of light atoms in the presence of heavy atoms, the crystal symmetry derived from CBED patterns can plausibly be too high, because it is generally difficult to detect weak pattern asymmetries. It is therefore worthwhile investigating whether the CBED technique is capable of detecting presence or absence of this type of asymmetry. Buxton et al. (1976) examined this for GaAs, where the crystal has a known antisymmetric component, and observed a weak asymmetry over a wide range of specimen thicknesses. Si_3N_4, on the other hand, provides a more complicated structure, for which a small structure asymmetry is in question, and therefore presents a good case for CBED study.

Silicon nitride is of interest for gas turbine and other high-temperature applications. Two polymorphs, α- and β-Si_3N_4, are known. The crystal structure of α-Si_3N_4 was refined by Kato, Inoue, Kijima, Kawada & Tanaka (1975) from single-crystal X-ray diffraction. The crystal is trigonal with space group $P31c$. Wild, Grieveson & Jack (1972) studied the picture of β-Si_3N_4 by X-ray powder diffraction and suggested that the space group was the centrosymmetric one, $P6_3/m$. On the other hand, Grün (1979) determined the structure from single-crystal X-ray diffraction and concluded that the space group was the non-centrosymmetric $P6_3$. Recently, Goodman & O'Keeffe (1980) studied the space group of β-Si_3N_4 by the CBED technique. Their result was consistent with that of Wild et al. (1972). Thus the space group of β-Si_3N_4 still seems controversial.

In the present paper, the space group of β-Si_3N_4 has been redetermined, and special attention has been payed to the thickness dependence of the 'apparent' CBED symmetry. It is shown that for a thin crystal the space group would be allocated to $P6_3/m$, while for a thick one the lower symmetry of $P6_3$ is revealed. The thickness dependence is discussed qualitatively on the basis of the crystal structure determined by Grün

(1979), in which the structure contains a small antisymmetric part due to small displacements of nitrogen atoms from mirror planes.

Experimental

The specimen-preparation method for the β-Si_3N_4 crystal was the same as that reported by Goodman & O'Keeffe (1980); the Si_3N_4 (Venton Corporation) consisting of approximately equal amounts of α- and β-Si_3N_4 was converted to β-Si_3N_4 after heating at 1973 K for 10 h in a 90% N_2 + 10% H_2 mixture. The crystals obtained were as small as a few tens of micrometers in size.

The specimen thus prepared was placed on a holey carbon supporting grid and observed in a Philips EM-400 electron microscope, equipped with both an energy-dispersive X-ray spectrometer and an electron-energy analyzer. The accelerating voltage was 120 kV. The CBED patterns were taken from the specimen fragment oriented along the [0001] and the [11$\bar{2}$0] zone axes. The incident electron-beam diameter was approximately 200 Å at the specimen position. The characteristic X-ray spectrum and the electron energy-loss spectrum were taken from the same specimen used for the CBED observation. No impurities were observed within the detection limit of the present microanalysis.

Results and discussion

Conventional selected-area electron diffraction patterns taken from β-Si_3N_4 crystal fragments indicated that the crystal is hexagonal with lattice parameters $a = 7\cdot60$ and $c = 2\cdot90$ Å. Systematically absent reflections were $l = 2n + 1$ for $00l$. Since the Laue group is $6/m$, the possible space groups are either non-centrosymmetric $P6_3$ or centrosymmetric $P6_3/m$.

In the following interpretation of zone-axis CBED patterns, it is helpful to refer to the relation between crystal point groups and the diffraction groups which have been derived by Buxton et al. (1976). Table 1 shows the relevant data for the present case of space groups $P6_3$ and $P6_3/m$: the diffraction groups, whole pattern symmetries, projection diffraction groups, and projection symmetries, for two zone-axis settings are given. From Table 1, it is clear that if we could examine the presence or absence of a mirror line appearing in the whole pattern symmetry for the [11$\bar{2}$0] zone-axis CBED pattern, we could determine the point group and the corresponding space group directly.

Fig. 1 shows a [0001] zone-axis CBED pattern. The pattern symmetry indicates the presence of a sixfold axis along the incident-beam direction. This confirms that the crystal is not α-Si_3N_4 with trigonal symmetry but is β-Si_3N_4 with hexagonal symmetry.

Table 1. *Symmetries of CBED patterns for two space groups $P6_3/m$ and $P6_3$*

Space group	Point group	Zone axis	Diffraction group	Whole pattern	Projection diffraction group	Projection symmetry
$P6_3/m$	$6/m$	[0001]	61_R	6	61_R	6
		[11$\bar{2}$0]	$2_R mm_R$	m	$2mm1_R$	$2mm$
$P6_3$	6	[0001]	6	6	61_R	6
		[11$\bar{2}$0]	m_R	1	$m1_R$	m

The [11$\bar{2}$0] zone-axis CBED pattern taken from a relatively thin part of the crystal region is shown in Fig. 2, where (*a*) shows a CBED pattern as a whole including zero-layer reflections as well as upper-layer reflections [high-order Laue zone (HOLZ) lines] and (*b*) is a CBED pattern enlarged so as to inspect the fine structure within the zero-layer reflection disks. The intensity distribution in the first HOLZ line indicates the presence of one mirror line perpendicular to the c^* axis as shown in m–m in Fig. 2(*a*). On the other hand, the whole pattern symmetry observed from the zero-layer reflections only is higher, and has two mutually perpendicular mirror lines labelled as m–m and m_p–m_p in Fig. 2(*b*). The additional mirror line m_p suggests that the projection diffraction group is valid for the zero-layer reflections, due to the relatively weak interactions between zero-layer and HOLZ-line reflections. Then the projection symmetry should be $2mm$, and the three-dimensional, or whole, pattern symmetry m, in accord with the observations in Table 1. The result implies that the crystal point group obtained from a thin crystal would be $6/m$ and that the corresponding space group is $P6_3/m$.

The dark bands appearing in the odd-order reflections 00l, such as 001 and 00$\bar{1}$, correspond to dynamic absences as pointed out by Gjønnes & Moodie (1965). The dynamic ab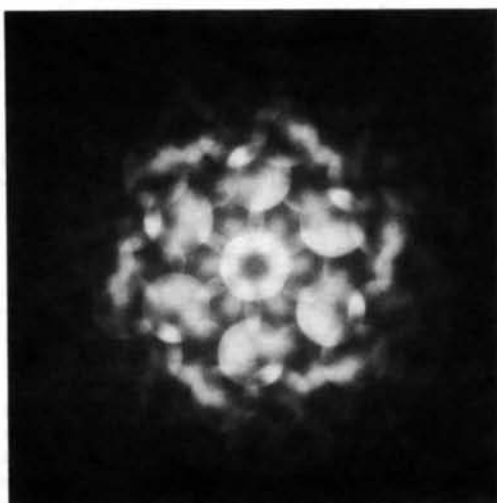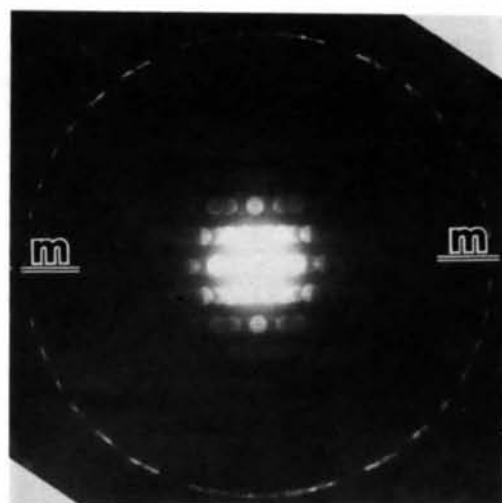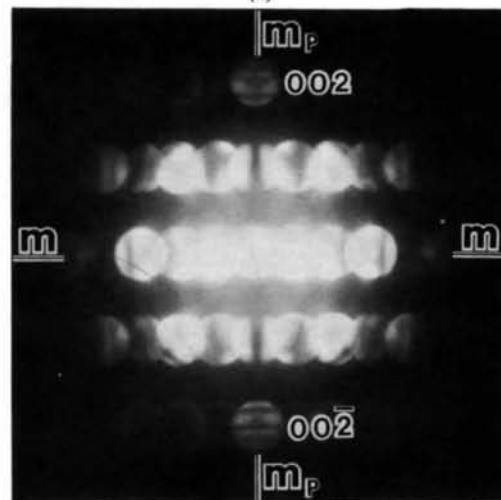sence in the present case is related to kinematically forbidden reflections due to the presence of a 6_3 screw axis parallel to the c axis.

The [11$\bar{2}$0] zone-axis CBED pattern taken from a thick crystal region of the same specimen fragment as

(*a*)

(*b*)

Fig. 2. The [11$\bar{2}$0] zone-axis CBED pattern, taken from a thin crystal region. (*a*) The CBED pattern as a whole including zero-layer reflections as well as a HOLZ line. (*b*) An enlarged CBED pattern showing the fine structure of zero-layer reflection disks. Two mirror lines are indicated as m–m and m_p–m_p, from the three-dimensional mirror symmetry and from the projection mirror symmetry, respectively. The space group is apparently $P6_3/m$ for the thin crystal.

Fig. 1. The [0001] zone-axis CBED pattern of a β-Si_3N_4 crystal. A sixfold axis along the incident-beam direction is present in the pattern.

observed in Fig. 2 is shown in Fig. 3. The intensity distribution appearing in the first HOLZ line in Fig. 3(a) indicates the absence of the mirror line, but the absence is obscure, since the asymmetry between $h1l$ and $h1\bar{l}$ reflections is very weak. The asymmetry is, however, clearly visible in an enlarged zero-layer CBED pattern as shown in Fig. 3(b). The fine structure appearing in the 002 disk differs from that of the $00\bar{2}$ disk, suggesting the lack of the mirror line perpendicular to the c^* axis. Then, the crystal point group obtained from the thick crystal is 6 and the space group is $P6_3$.
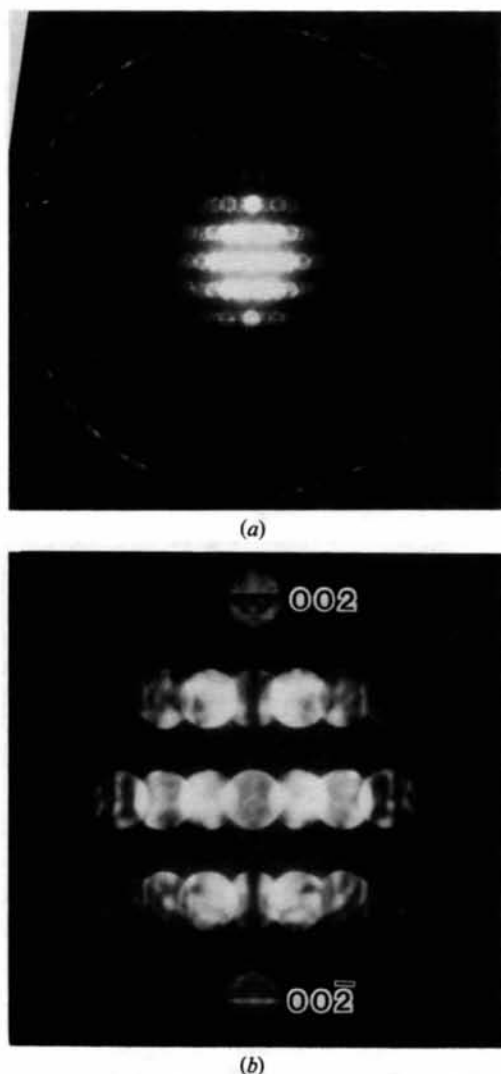

(a)

(b)

Fig. 3. The [11$\bar{2}$0] zone-axis CBED pattern, taken from a thick crystal region. (a) The CBED pattern showing the HOLZ line as well as zero-layer reflections. (b) A CBED pattern enlarged so as to show the fine structure within the zero-layer reflection disks. Note that the asymmetry appearing in the pattern between the 002 and $00\bar{2}$ disks is clearly visible in (b). The lack of mirror line suggests that the space group is $P6_3$.

As shown in Figs. 2 and 3, the space group of β-Si$_3$N$_4$ obtained from thin-crystal data differs from that obtained from thick-crystal data. The thickness dependence of the observable symmetry can be interpreted qualitatively on the basis of the structure of β-Si$_3$N$_4$. The crystal structure of β-Si$_3$N$_4$ consists of corner-sharing SiN$_4$ tetrahedra. The tetrahedra are orientated with one edge parallel to the c axis so that joining of neighboring tetrahedra makes chains parallel to the c axis. Figs. 4(a) and (b) show one of the tetrahedral chains for the structure with space group $P6_3/m$ (Wild et $al.$, 1972) and $P6_3$ (Grün, 1979), respectively. In Fig. 4(a), both silicon and nitrogen atoms are located on mirror planes ($z = \frac{1}{4}$ and $\frac{3}{4}$) normal to the c axis, while in (b), nitrogen atoms are slightly displaced from the mirror planes. The amount of the displacement is approximately 0·05 Å.

Thus, according to the model with the non-centrosymmetric space group, the crystal structure of β-Si$_3$N$_4$ contains a small antisymmetric part. The diffraction asymmetry is small and hard to detect in the thin-crystal CBED pattern, since kinematical diffraction is more dominant in this case. The corresponding CBED pattern might reveal the symmetry of an apparent crystal potential dependent mainly on the silicon-atom arrangement, resulting in the space group $P6_3/m$ with the observation of a mirror symmetry. On the other hand, the intensity arising from such weak asymmetry is generally expected to increase with increase of crystal thickness as a result of the strong dynamical interaction for electron diffraction. Hence, the CBED pattern for a thick crystal shows the real crystal potential related to both silicon- and nitrogen-atom arrangements and reveals the true space group as $P6_3$.
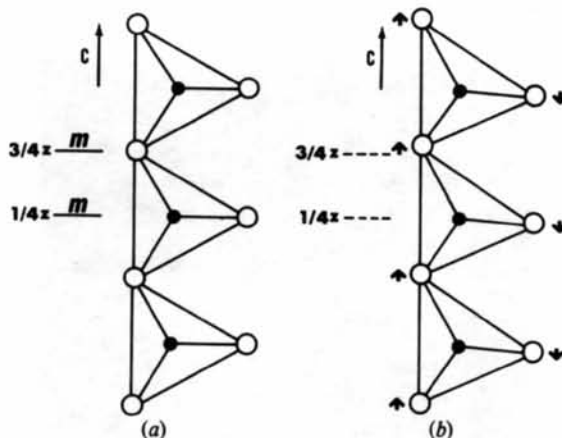

(a)   (b)

Fig. 4. One of the tetrahedral chains in β-Si$_3$N$_4$ with the space group (a) as $P6_3/m$, and (b) as $P6_3$. Trigonals show SiN$_4$ tetrahedra, in which dark and open circles indicate silicon and nitrogen atoms, respectively. Silicon and nitrogen atoms are located in the mirror planes ($z = \frac{1}{4}$ and $\frac{3}{4}$) in (a), while nitrogen atoms only are displaced from the mirror planes along the c axis as indicated by arrows in (b). The amount of the displacement is approximately 0·05 Å.

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The Structure of Potassium-Exchanged Heulandite at 293, 373 and 593 K

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Abstract

Single crystals of heulandite (Mossyrock Dam, Lewis County, Washington, USA) were potassium-exchanged to reach a chemical composition of $(Na_{0.10}K_{8.57}Ba_{0.04})(Al_{9.31}Si_{26.83})O_{72}.19.56H_2O$. Thermogravimetry up to 593 K of such single crystals was carried out concurrently with the X-ray diffraction measurements of one single crystal at 293, 373 and 593 K. At 593 K the sample was fully dehydrated. The crystal structures were refined by least squares to R_w values of 0·073 (293 K), 0·090 (373 K) and 0·112 (593 K). [Crystal data for the first structure (293 K): $C2/m$, $a = 17·767$ (7), $b = 17·958$ (7), $c = 7·431$ (1) Å, $\beta = 115·93$ (2)°.] The crystal structure at 593 K is essentially in agreement with that at 293 K of a single crystal previously heated to 573 K in an evacuated and sealed glass capillary. The process of dehydration is represented by these crystal structure determinations showing the change of the water molecules and the positions of the K^+ ions as well as the deformation of the silicate framework.

Introduction

It is a common practice to study the structures of dehydrated zeolites by sealing in glass capillaries crystals previously dehydrated in vacuum at high temperatures. The first aim of the present study is to check if any meaningful difference exists between the structure of a zeolite at 593 K and the structure of the same zeolite at 293 K after heating in vacuum at 573 K and sealing in a glass capillary. The second aim is to compare the hydrated structure at room temperature with the partially dehydrated structure at 373 K and the dehydrated structure at 593 K in order to detect which water molecule leaves first, and how cations change sites with increasing temperature.