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Direct Observation of the Polytype Periodicities in the Be-Si-O-N System

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A new class of polytypism, in which the unit cell is determined by the composition rather than by a periodicity of displacement faulting, has been reported to occur in the so-called "Sialon" ceramics (1). The purpose of this note is to present direct lattice fringe observations of polytypism in one such ceramic, the Be-Si-O-N system.

The polytypes were first reported to occur near the AlN corner of the Si-Al-O-N system (2), but structurally similar ones have since been found in the Be-Si-O-N, Mg-Si-Al-O-N, and Li-Si-Al-O-N systems.(3) In all these alloy systems there are a series of crystalline phases having narrow ranges of homogeneity extending along lines of constant metal:non-metal atom ratios, which have been interpretated on the basis of X-ray powder diffraction as wurtzite polytypes. In the Be-Si-O-N system, the polytypes are in the Be_3N_2 rich region. They occur for metal: non-metal atom ratios of $M_{m+1}X_m$ where the minimum value, m=2, corresponds to β-Be_3N_2 which has the polytype designation 4H (Ramsdell notation) and the maximum value m = ∞ (MX) corresponds to ordered wurtzite $BeSiN_2$. [1]

Polytypism in these systems is attributed to the insertion at regular intervals of a cubic stacked M_2X layer into the MX layer arrangement of the wurtzite structure. The spacing between these M_2X layers is determined by the overall composition. Using the notation of Thompson [1], the non-metal atom stacking in β-Be_3N_2 (M_3X_2) consists of a close packed layer sequence

$$A\,^{m}_{m}\,B\,^{m}\,C\,^{m}_{m}\,B\,^{m}\,A\,^{m}_{m}\,B\,^{m}\,C$$

with alternate M_2X and MX layers. Similiarly, the atom stacking in $Be_9\ Si_3\ N_{10}$, (M_6X_5) consists of a close packed layer sequence, 15R,

$$A\,^{m}_{m}\,C\,^{m}\,A\,^{m}\,C\,^{m}\,A\,^{m}\,C\,^{m}_{m}\,B\,^{m}\,C\,^{m}\,B\,^{m}\,C\,^{m}\,B\,^{m}_{m}\,A\,^{m}\,B\,^{m}\,A\,^{m}\,B\,^{m}\,A\,^{m}_{m}$$

in which the M_2X layer is inserted every fifth layer. The unit cell of this structure then consists of three rhombohedrally related blocks each of which contains five close-packed layers.

Using the technique of direct lattice fringe imaging in the transmission electron microscope we have been able directly to observe and confirm this structure. In Figure 1 the periodicity corresponding to the polytype block spacing 12.1Å has been imaged, and the selected area electron diffraction pattern of the same area is presented in Figure 2. The rhombohedral symmetry of this (01.0) diffraction pattern and the five regularly spaced spots between the transmitted beam and that corresponding to the close-packed spacing (marked 15) indicate that the area has the 15 R structure. The lattice fringe image of Figure 3, in which the individual close packed layers have been recorded, graphically confirms the suggestion of Thompson [1] that the unit cell consists of three symmetry related blocks each of five close-packed layers. Similar results have been found in the Mg-Si-Al-O-N System where the metal: non-metal atom ratios are $M_m X_{m+1}$.

Observing the close-packed planes also allows departures from the ideal polytype arrangement to be examined directly. An example of this is shown in Figure 4. Here, although the electron diffraction pattern again indicates an overall 15 R structure there are faults in the block structure and instead of comprising five planes some of the blocks have six and others only four. By incorporating such faults the local composition varies from the exact $Be_9 Si_3 N_{10}$ composition. Very large variations in composition may occur in this manner, and a later publication will present detailed evidence for the resulting structures.

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References

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2. K.H. Jack, J. Mater. Sci., 1976, vol. 11, p. 1135.
3. K.H. Jack, private communication.

Figure Captions

FIG. 1. Direct resolution of the block spacing (12·1Å) of the 15R polytype.

FIG. 2. Selected area electron diffraction pattern of the (01.0) reciprocal-lattice plase showing the h0.ℓ rows. The symmetry and spacing of the spots indicates that the area has the 15R structure.

FIG. 3. Direct lattice fringe image in which the individual close packed planes (2·4Å) can be seen. In this relatively perfect region each block consists of five close packed planes.

FIG. 4. An adjacent region to that of Figure 3. Departures from the ideal polytype arrangement are seen directly with some blocks comprising only four close-packed planes and other six.

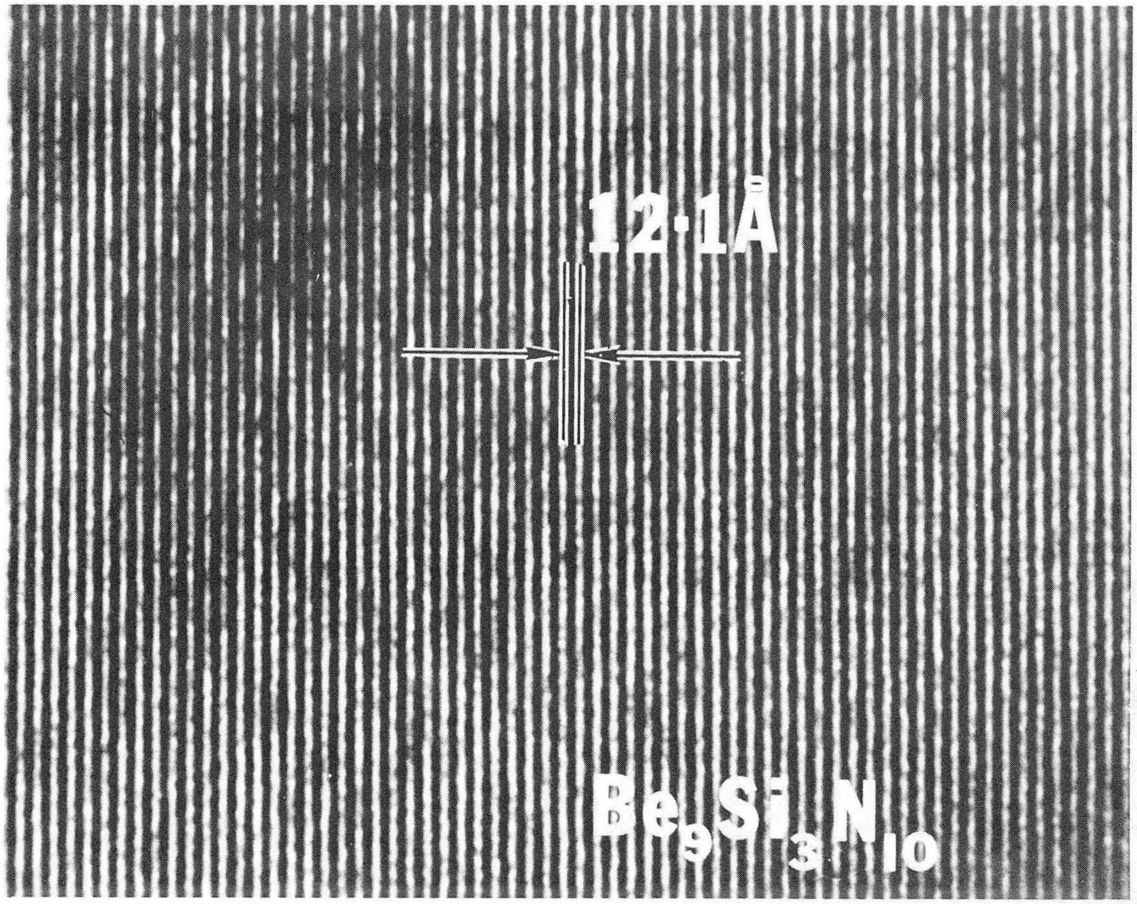

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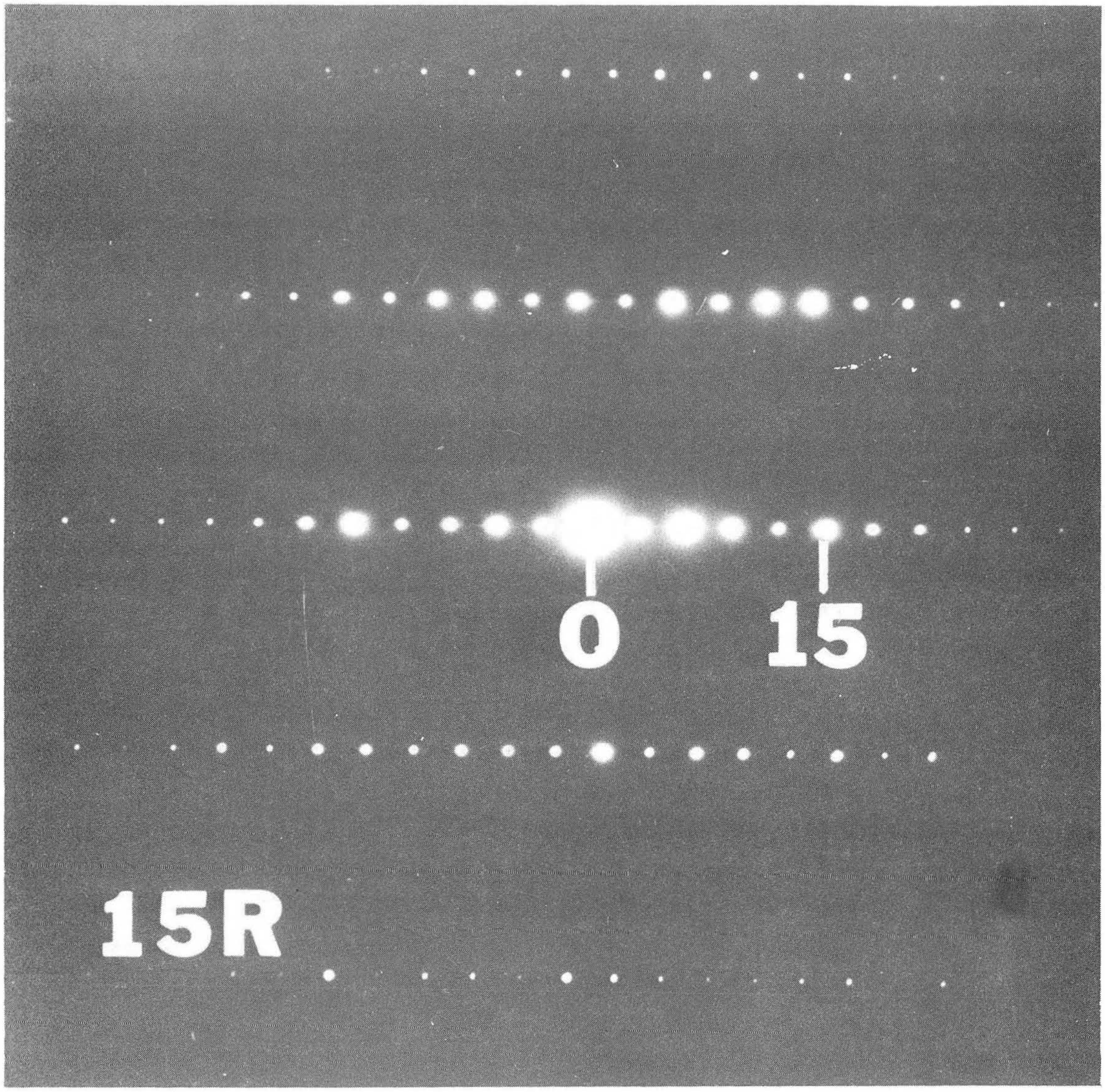
Fig. 1



XBB 771-598

Fig. 2

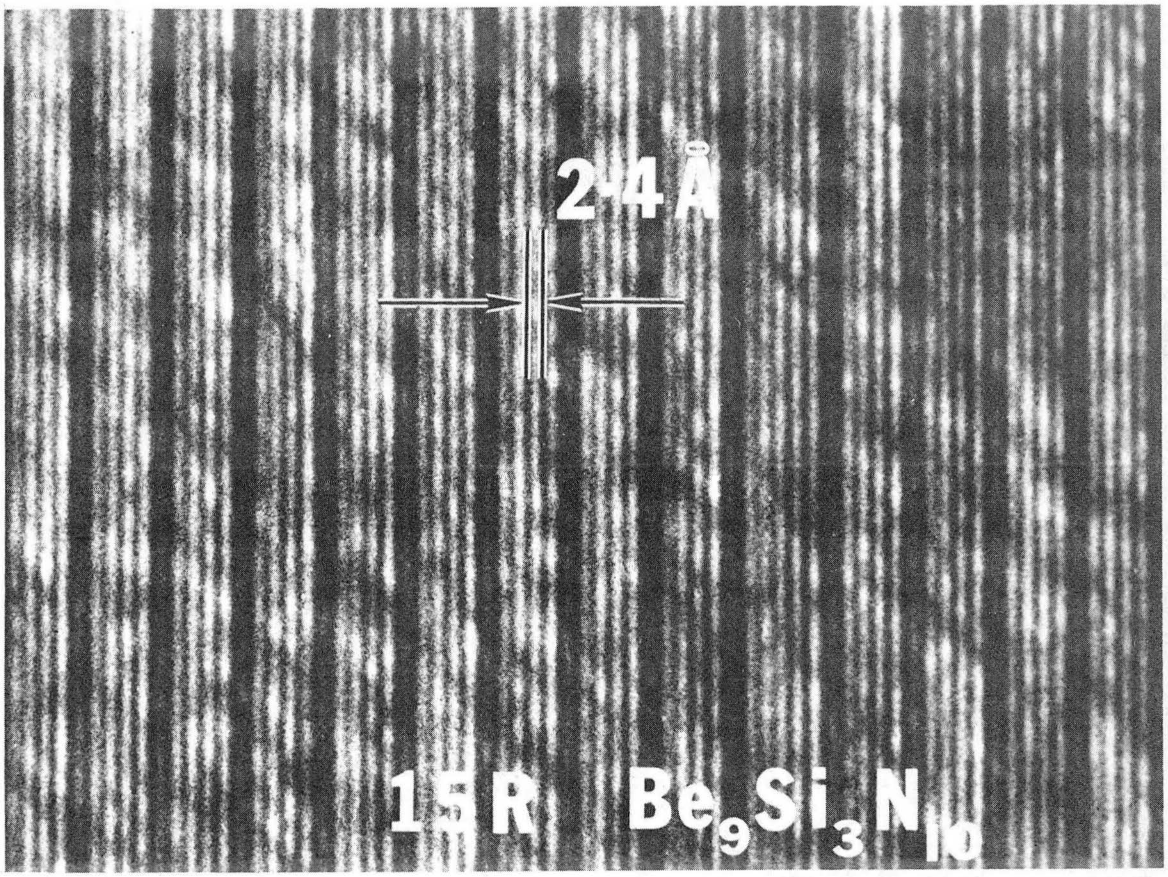


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Fig. 3

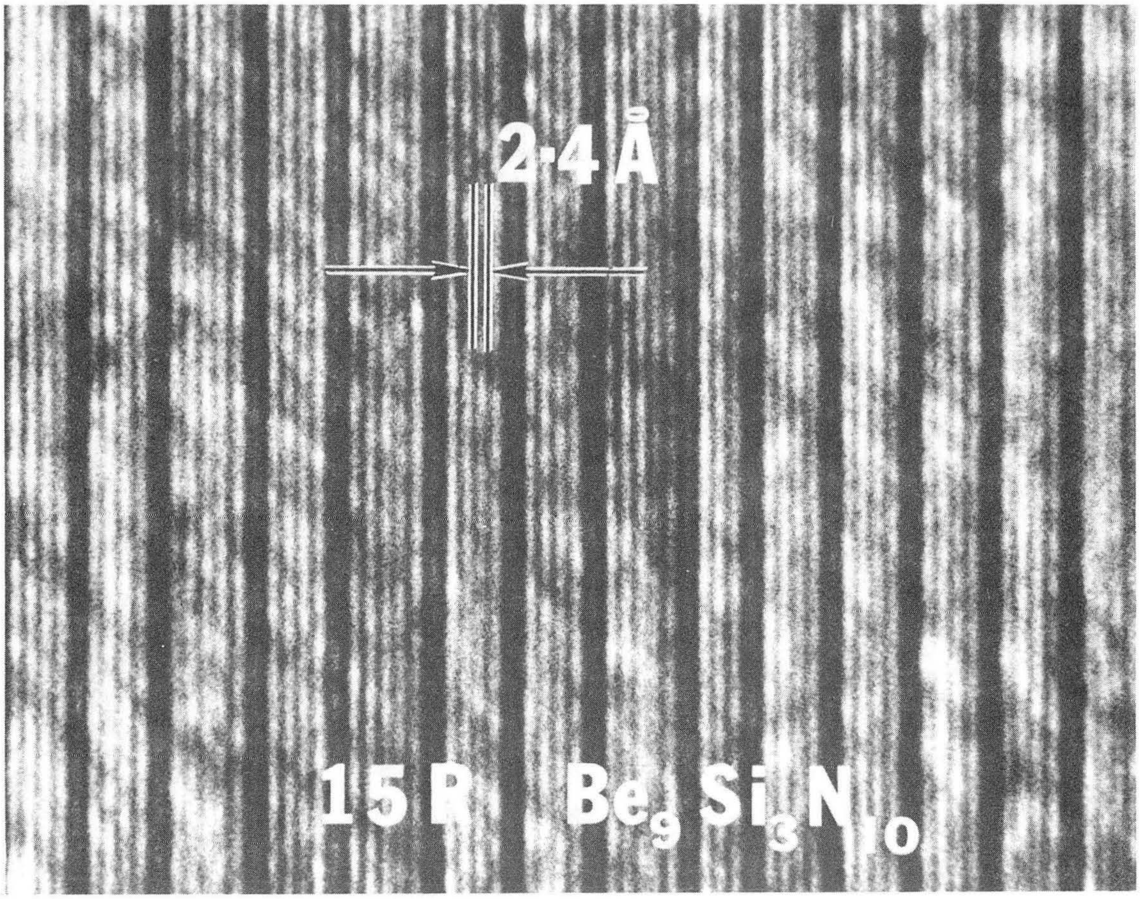

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Fig. 4

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