Reports

Transmission Electron Microscopy: Direct Observation of Crystal Structure in Refractory Ceramics

Abstract. *Using high-resolution multibeam interference techniques in the transmission electron microscope, images have been obtained that make possible a real-space structure analysis of a beryllium-silicon-nitrogen compound. The results illustrate the usefulness of lattice imaging in the analysis of local crystal structure in these technologically promising ceramic materials.*

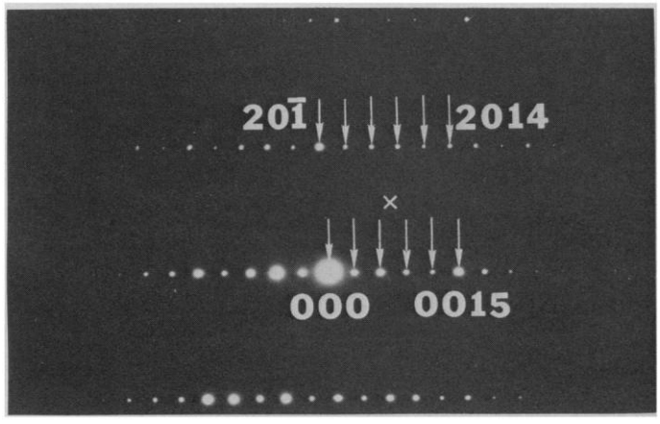
The improvement in resolution obtainable with transmission electron microscopes over the last decade, coupled with advances in the interpretation of image contrast through n-beam calculations (*1*), has made direct observation of crystal structures a useful technique for real-space structure determination. Comparison of experimental n-beam lattice images with calculated images has established the validity of the direct ("charge density") interpretation of multibeam images for thin crystals of a number of complex oxides at a resolution approaching the atomic level (*2*). The usefulness of this technique in confirming structures previously found by x-rays (*3*), determining new structures (*4*), and examining local atomic configurations in perfect and imperfect crystals (*5*) has been demonstrated. However, with only a few exceptions (*6, 7*), the technique of structure imaging has so far been applied only to crystals whose structures and lattice spacings are particularly suited for imaging in the 100-kV electron microscope; that is, open structures in which atoms or concentrations of atoms lie at least 3.5 Å apart. Most technologically important materials, however, have a much denser packing, with atoms 2 to 3 Å apart. The purpose of this report is to draw attention to the usefulness of imaging such densely packed but important ceramic materials, using direct high-resolution techniques in the electron microscope, and to show a real-space structure analysis of a complex Be-Si-N ceramic alloy.

Complex nitrogen ceramic alloys called sialons, based on Si_3N_4 with cation (for Si) and anion (for N) substitutions, have been investigated with a view to their use in high-temperature structural applications, as for advanced turbines and refractories (*8*). A large number of new and uncharacterized crystal structures have been found, including many polytypes that are not easily analyzed by x-ray methods. One example of such a polytype structure is that occurring near the Be_3N_2-rich composition range of the Be-Si-O-N system. These structures have two unit cell dimensions that remain constant while the third varies with composition. Each polytype phase occurs in the phase diagram along a tie line of constant metal : nonmetal atomic ratio (M : X). X-ray powder diffraction has identified these phases as being based on the wurtzite structure (*9*). The anions O and N form a close-packed lattice, and the metal atoms Be and Si occupy tetrahedral sites between the layers of these nonmetal atoms. From x-ray diffraction analyses, Thompson (*9*) proposed that each polytype could be described as a regular insertion of a cubic stacked layer into the basic hexagonally close-packed wurtzite structure. Possible tetrahedral sites for metal atoms in the cubic stacked layer then no longer share bases and can be fully occupied to give a composition M_2X. In the remainder of the structure the nonmetal atoms form a hexagonally close-packed lattice with half the tetrahedral sites occupied to give a composition MX. Varying the composition of the material then varies the spacing of the cubic stacked layers and hence the unit cell. For example, stacking of the close-packed layers in the $Be_9Si_3N_{10}$ (M_6X_5) 15R structure (*10*) in the three possible stacking positions A, B, and C follows the sequence

$$A^m_mC^mA^mC^mA^mC^m_mB_mC_mB_mC_mB^m_m$$
$$A^mB^mA^mB^mA^m_mC$$

in the notation of Thompson (*9*). A cubic stacked M_2X layer stacking sequence ACB, CBA, or BAC 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.

The aim of the work reported here was to test the correctness of this model by direct multibeam interference imaging. Samples of 15R $Be_9Si_3N_{10}$ were prepared by hot-pressing Si_3N_4 and Be_3N_2 powder mixes at 1800°C for 2 hours. Electron-transparent specimens were thinned from 0.02-mm sections of bulk material by using 5-kV argon ion beams incident on the surfaces at 15°. Thinned sections were coated on one side with a thin carbon film to avoid charging under the



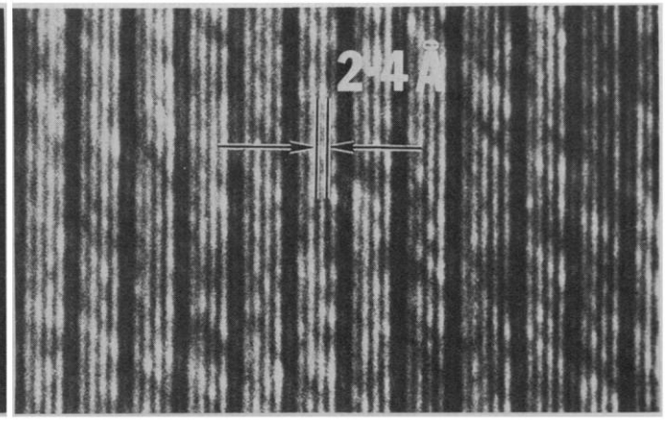


Fig. 1 (left). Selected area diffraction pattern from a region of 15R polytype structure. Arrows indicate the reflections used to form the image in Fig. 3a; the cross marks the position of the optic axis. Fig. 2 (right). Direct fringe image formed from the central row of reflections in Fig. 1 in which the close-packed planes (2.4 Å) can be seen. In this relatively perfect region a repeat block of five close-packed planes is seen.

0036-8075/78/1110-0625$00.50/0

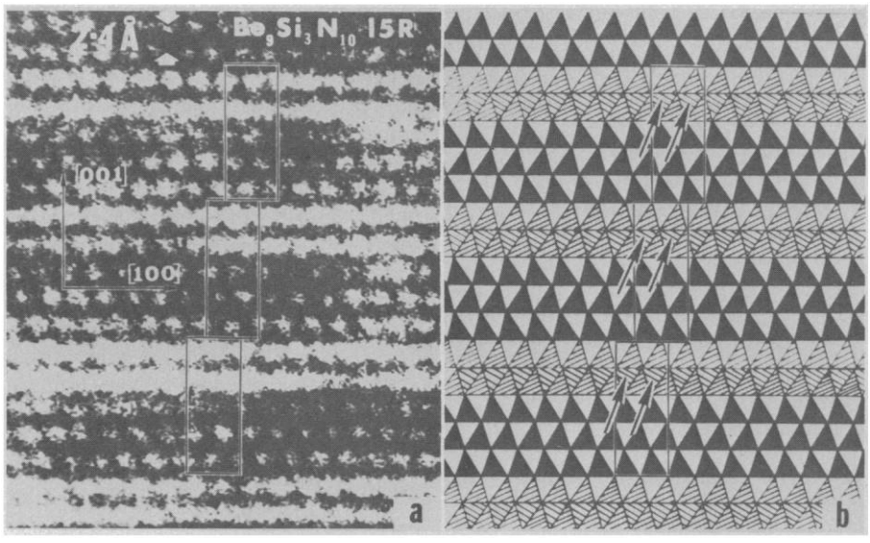


Fig. 3. Comparison of (a) a two-dimensional structure image, formed by using the reflections indicated in Fig. 1, and (b) a projection of the 15R structure in the same orientation. Rectangles enclose the three blocks of five close-packed planes each that make up the repeat stacking unit in the 15R structure. The arrows point to additional metal atom sites in the cubic close-packed layers.

electron beam of the 125-kV Siemens 102 electron microscope. This microscope was used with a double-tilt holder for accurate control of orientation.

Grains of polytype structure were oriented with the incident beam parallel to close-packed planes and parallel to one edge of the tetrahedron. In this orientation, stacking of the close-packed planes can be observed. The projected structure is relatively open, consisting of rows of nitrogen tetrahedra occupied by metal atoms and tunnels of vacant tetrahedral and octahedral sites. The selected area diffraction pattern from a region of 15R structure in this orientation is shown in Fig. 1.

Two approaches may be used to form a multibeam interference image from the diffraction information in Fig. 1. Lattice imaging along the systematic row containing the 15R periodicity reveals this periodicity directly (Fig. 2). However, this image is strictly one-dimensional and does not provide any further structural information. By imaging simultaneously with two rows of reflections, a two-dimensional lattice fringe image is obtained (Fig. 3a). To resolve the 2.4 Å periodicity directly it is necessary to tilt the main beam and to image preferentially with Bragg beams to one side of the transmitted beam. The projected charge density approximation therefore does not apply, but the stacking sequence of the close-packed planes may be inferred from the image as follows. The image is composed of blocks of identical contrast as outlined in Fig. 3a. Each block consists of five close-packed layers that have been directly imaged. Two of the five fringes have lighter contrast than the rest. This suggests that two of the five close-packed layers in each block have a stacking arrangement different from that of the remaining three. Each block of five layers is related to the adjacent one by a translation of $1/3\langle 100\rangle$. This gives rise to an overall repeat every 15 close-packed layers and a stacking sequence with rhombohedral symmetry; that is, the five layer blocks are stacked ABC, as opposed to ABAB for a hexagonal structure.

Examination of possible combinations of hexagonal and cubic stacking of the close-packed layers that could produce such an arrangement showed that only one stacking sequence fits these observations—the one deduced by Thompson from x-ray data. This stacking sequence is shown in Fig. 3b in the same orientation as the image. The black triangles represent rows of metal atom–occupied nitrogen tetrahedra in the hexagonal close-packed layers; the crosshatched triangles, rows of metal atom–occupied tetrahedra in the cubic stacked layers; and the unshaded triangles, rows of vacant tetrahedral and octahedral sites in the structure. Rows of nitrogen atoms lie at the corners of the triangles. The arrows point to additional tetrahedral sites in the cubic close-packed layers that do not share a common base with another site and so are capable of accommodating the excess of metal atoms in these composition-dependent polytypes. The resulting higher coordination of metal atom sites about nitrogen atoms in the cubic stacked layers makes these favorable sites for the lower-valence beryllium atoms to maintain local charge balance. Exclusive occupation of these sites by beryllium atoms produces a structure that is two close-packed layers thick and has the composition Be_3N_2 (one of the end members of the polytype series). The remainder of the structure has a hexagonal close-packed arrangement of nitrogen atoms with metal atom sites in the wurtzite configuration. If these sites are occupied, as for the other end member of the series, BeSiN[2] (ordered wurtzite structure), an overall composition $Be_9Si_3N_{10}$ is predicted for the 15R structure. In other words, the basic structural unit is composed of two layers of Be_3N_2 and three layers of $BeSiN_2$, as expected from the tie line connecting these phases at the $Be_9Si_3N_{10}$ composition. Thus, the 15R structure deduced from x-ray analysis is actually composed of three of these units translated with respect to each other by $1/3\langle 100\rangle$ (Fig. 3).

This example illustrates that local structural information can be obtained directly from close-packed structures by using the technique of lattice fringe imaging. Much of this information is unobtainable by any other direct method, and direct imaging at this level of resolution should prove a useful tool for structure determination in ceramic materials. Where a postulated structure has already been found by other methods, as in the example above, direct imaging can be used to confirm and refine the structure. For unknown structures more caution has to be exercised in direct interpretation of the image, but comparison of experimental and calculated images should make the technique very useful even here.

T. M. Shaw
G. Thomas

Department of Materials Science and Mineral Engineering, University of California, Berkeley 94720

References and Notes

1. J. G. Allpress and J. V. Sanders, *J. Appl. Crystallogr.* **6**, 165 (1973).
2. M. A. O'Keefe, *Acta Crystallogr. Sect. A* **29**, 389 (1973).
3. S. Iijima and J. G. Allpress, *J. Solid State Chem.* **7**, 94 (1973).
4. J. G. Allpress, S. Iijima, R. S. Roth, N. C. Stephenson, *ibid.*, p. 89.
5. S. Iijima, *Acta Crystallogr. Sect. A* **31**, 784 (1975).
6. O. L. Krivanek, S. Isoda, K. Kobayashi, *Philos. Mag.* **36**, 931 (1977).
7. N. Uyeda, T. Kobayashi, K. Ishizuka, Y. Fujiyoshi, K. Kobayashi, *Proc. 6th Eur. Congr. Electron Microsc.* **1**, 79 (1976).
8. K. H. Jack, *J. Mater. Sci.* **11**, 1377 (1976).
9. D. P. Thompson, *ibid.*, p. 1377.
10. Notation of L. S. Ramsdell, *Am. Mineral.* **32**, 64 (1947).
11. The samples were kindly provided by L. J. Gauckler, Max-Planck-Institut für Metallforschung, Stuttgart, West Germany. We acknowledge financial support from the National Science Foundation. We are especially grateful to D. R. Clarke for his help.

17 October 1977; revised 17 July 1978