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Crystal structure of $Si_3N_4 \cdot Y_2O_3$ examined by a 1 MV high-resolution electron microscope

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The crystal structure of $Si_3N_4 \cdot Y_2O_3$ prepared by a hot-press is examined in a 1 MV high-resolution electron microscope. The image contrast reveals that it is isostructural with one of the layered silicates, Akermanite, in accordance with the previous estimation by means of powder X-ray diffraction. The crystal growth from a glass phase is discussed briefly.

1. Introduction

The silicon nitride hot-pressed with Y_2O_3 shows an excellent high-temperature strength [1]. In the preparation a liquid phase is first formed at the grain boundary which causes rapid sintering. At higher temperature the phase further reacts with the matrix silicon nitride to produce a highly refractory phase, $Si_3N_4 \cdot Y_2O_3$ [2, 3].

According to powder X-ray diffraction [3], $Si_3N_4 \cdot Y_2O_3$ has been considered to be isostructural with Akermanite, $Ca_2MgSi_2O_7$, which is a member of the Melilite silicates. The structure is schematically described in Fig. 1. Si–O tetrahedra form the layers normal to the *c*-axis. The sites of large cations between the layers, marked by circles, are occupied by Ca ions. In $Si_3N_4 \cdot Y_2O_3$, Y ions are considered to replace these sites and nitrogens partly substitute for oxygens. Other workers, however, have reported different intensities of X-ray diffraction [2, 4]. The difference may be due to the preferential orientation of specimen powders. Since the phase coexists with a glass phase, accurate X-ray analysis is impossible. In the present paper we try to solve the problem by examining the structure in a 1 MV high-resolution electron microscope.

One of the important applications of a high-resolution, high-voltage electron microscope is to determine the crystal structure [5]. Our 1 MV electron microscope has a resolution limit due to chromatic aberration of 2.3 Å [6]. A greater proportion of the scattered waves can then be used for imaging as compared to the 100 kV class of electron microscopes. Accordingly, it has so far been possible to obtain the so-called structure images, from which atom positions are directly read out, from several oxides [7].

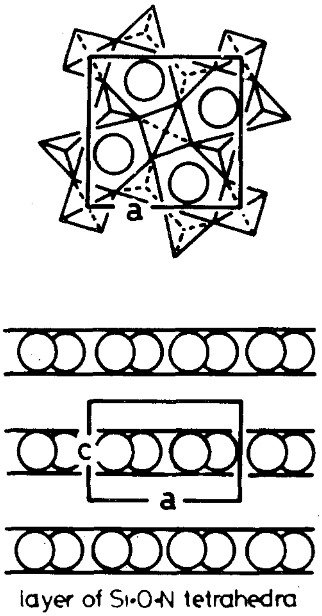

Figure 1 Projections of the crystal structure of $Si_3N_4 \cdot Y_2O_3$, suggested by a powder X-ray diffraction, along the *c* and *a* axes. It is isostructural with Akermanite, $Ca_2MgSi_2O_7$. The symmetry is tetragonal; $a = 7.60$ and $c = 4.91$ Å.

2. Experimental procedure

Powders of Si_3N_4 (mainly of α type) and Y_2O_3 were mixed and hot-pressed at 1750° C under a

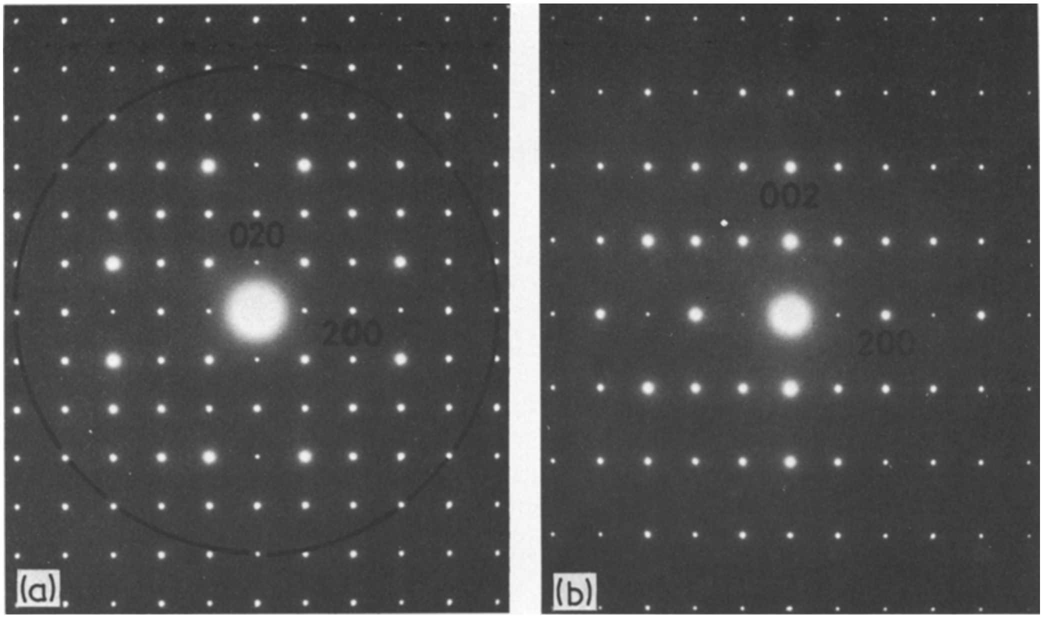

Figure 2 Electron diffraction patterns taken from $Si_3N_4 \cdot Y_2O_3$. The electron beam is incident paralled to the [0 0 1] and [0 1 0] direction in (a) and (b), respectively. $2n + 1\,0\,0$ spots are excited by a double diffraction and disappear when the crystal is tilted.

pressure of 200 kg cm^{-2} for 1 h. The purity of the starting powders was better than 96.5 and 99.9 wt %, respectively. The peak profile in an X-ray diffractometer chart taken from the product coincided well with that reported previously [2]. A block of the product was lightly crushed in an agate mortar. The fragments were then examined in the high-voltage electron microscope operated in 1 MV. The adjustment and operation of the microscope were as reported previously [8]. Images were taken at an underfocus of about 700 Å, where heavy cations are resolved separately as dark spots [6].

3. Results and interpretation

The fragments often consists of two phases, which are divided by a planar boundary, as in an example shown later. One phase gives a clear diffraction-spot pattern, while the other a halo pattern. Many patterns were taken from the crystalline phase on tilting the specimen, two of which are shown in Fig. 2. The size of the objective aperture used is shown by a circle in Fig. 2a. It is known from the patterns that the crystal has a tetragonal system with lattice parameters, $a = 7.60$ and $c = 4.91$ Å, in accordance with the X-ray diffractometer data. The extinction of the spots occurs for $2n + 1\,0\,0$ reflexions, where n is an integer. Possible space groups are therefore $P\bar{4}2_1m$ (centrosymmetric) or $P\bar{4}2c$ (non-centrosymmetric).

Fig. 3 is a 1 MV high-resolution electron microscope image of a very thin part of the crystal taken with an incident beam parallel to the c-axis. The contrast is interpretable with reference to the structure model in Fig. 1; a bright spot represents a Si–O–N tetrahedron whose two edges are parallel to (0 0 1). Dark spots correspond to the sites of individual Y ions. That is, the image contrast approximately reflects the projected potential of the crystal, in accordance with the theory of electron optics [9, 10].

Fig. 4 is another high-resolution image, for which the electron beam is incident parallel to the a-axis. It is clear on comparing this to Fig. 1 that the site of two neighbouring Y ions is imaged as a dark spot in the bright matrix of the layers of Si–O–N tetrahedra.

The crystal point group can be determined by a method recently developed under the consideration of dynamical scattering of electrons [11]; Fig. 5 shows an image of the thicker region, taken in the same film as Fig. 3. Only the sites of Si–O–N tetrahedra whose two edges are parallel to (0 0 1) are imaged as bright spots, while the site of Y ions is no longer defined. The two mirror planes normal to [1 1 0] and [1 $\bar{1}$ 0] are however

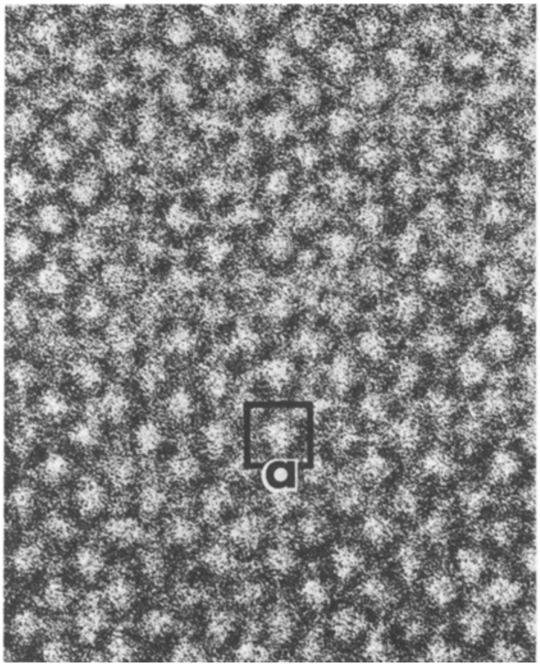

Figure 3 A structure image of $Si_3N_4 \cdot Y_2O_3$ taken by a 1 MV high-resolution electron microscope with the incident beam parallel to the *c*-axis. A bright spot corresponds to the Si–O–N tetrahedron, whose two edges are parallel to (0 0 1), while the dark spot corresponds to a Y ion.

still noticed. This means that $F(h', k') = F(h', \bar{k}') = F(\bar{h}', k') = F(\bar{h}', \bar{k}')$ independently of the crystal thickness, where F is the dynamical structure factor and the principal axes of the reciprocal lattice are taken parallel to [1 1 0] and $[1\,\bar{1}\,0]$. The present crystal must therefore be centrosymmetric.

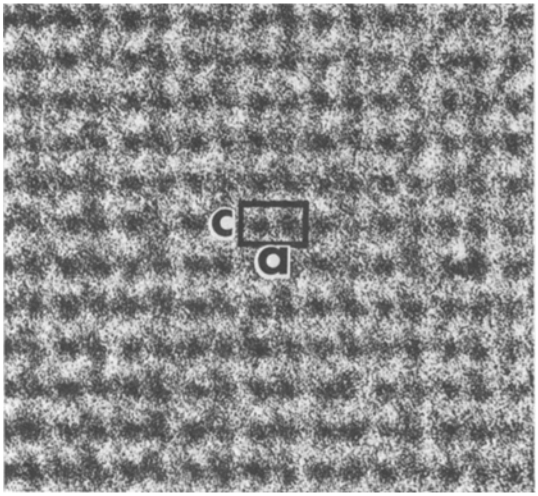

Figure 4 1 MV high-resolution electron micrograph of $Si_3N_4 \cdot Y_2O_3$ taken with the incident beam parallel to the *a*-axis. Dark spots correspond to the two neighbouring Y ions; $a = 7.60$ and $c = 4.91$ Å.

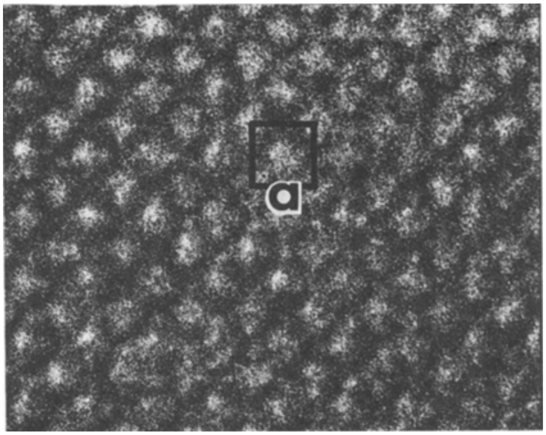

Figure 5 An image of the thick region taken on the same film as Fig. 3. Although the resolution is poor, the mirror symmetry relation seen in Fig. 3 is retained, showing that the crystal structure is centrosymmetric. $a = 7.60$ Å.

According to these results it may be concluded that $Si_3N_4 \cdot Y_2O_3$ has the same structure as that of Akermanite.

4. Discussion

A glass phase often coexists with the $Si_3N_4 \cdot Y_2O_3$ crystalline phase in the present specimen fragments. Fig. 6 shows an example. The upper left of the figure is $Si_3N_4 \cdot Y_2O_3$, which is so oriented that the *c*-axis is almost parallel to the incident beam. The Si–O–N tetrahedron whose two edges are parallel to (0 0 1) is noticed as a bright spot. The boundary between two phases runs almost parallel to (1 1 0). Some steps are observed at the parts marked by arrows. Each of them has a height of about 5 Å. It seems likely that they move in the $[1\,\bar{1}\,0]$ direction to cause the growth of the crystalline phase. It is interesting to note that the image contrast of the glass phase is quite different from that of amorphous carbon formed at the edge of the fragment as a contamination during observation. This may suggest that some short-range orders exist in the glass phase. Detailed analysis of the contrast will be reported elsewhere.

In Figs. 3 and 4 the sites of Y ions are separately resolved. As far as we know, these are the first case, where the structure image is obtained from the crystal with a relatively small unit cell under the Scherzer's optimum imaging condition. When we used a 100 kV electron microscope, only

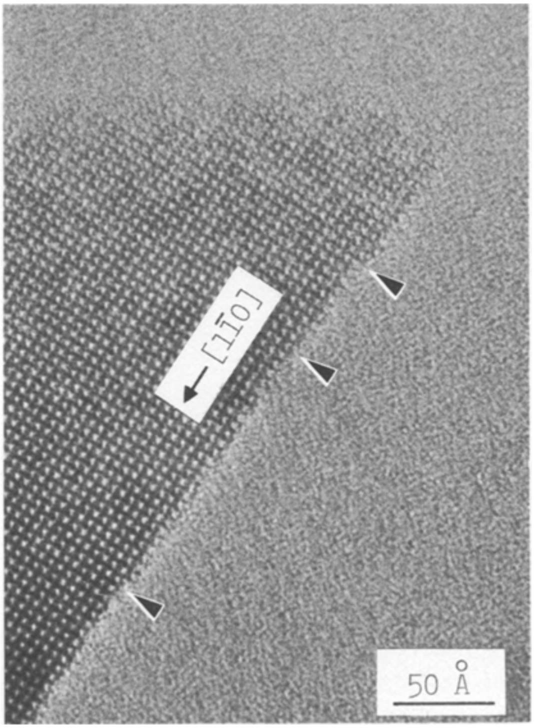

Figure 6 An electron micrograph showing the boundary region between a $Si_3N_4 \cdot Y_2O_3$ phase (left) and a glass phase (right). The former grows at the expense of the latter. At the upper edge of the fragment a carbon contamination film is seen.

the lattice fringes appeared. Dark spots in Fig. 3 are not so sharp as compared to those in the previous observations on some oxides [6, 7]. This must be due to that the scattered waves contributing to imaging are still small in number even for the present 1 MV electron microscope.

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