Crystal structure of Si$_3$N$_4$·Y$_2$O$_3$ examined by a 1 MV high-resolution electron microscope

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The crystal structure of Si$_3$N$_4$·Y$_2$O$_3$ 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$_2$O$_3$ 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$_3$N$_4$·Y$_2$O$_3$ [2, 3].

According to powder X-ray diffraction [3], Si$_3$N$_4$·Y$_2$O$_3$ has been considered to be isostructural with Akermanite, Ca$_2$MgSi$_2$O$_7$, 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$_3$N$_4$·Y$_2$O$_3$, 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].

2. Experimental procedure

Powders of Si$_3$N$_4$ (mainly of α type) and Y$_2$O$_3$ were mixed and hot-pressed at 1750°C under a
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 consist 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 \(2n + 1\) 00 reflexions, where \(n\) is an integer. Possible space groups are therefore \(P\overline{4}2_1m\) (centrosymmetric) or \(P\overline{4}2c\) (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 (001). 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 (001) are imaged as bright spots, while the site of Y ions is no longer defined. The two mirror planes normal to [110] and [1\(\overline{1}\)0] are however