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Abstract

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X-RAY DIFFRACTION STUDY OF STRUCTURAL FEATURES OF CRYSTALS OF CUBIC BORON NITRIDE

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All X-ray diffraction data published up to the present for cubic boron nitride have been obtained by powder methods and are limited to structural diagnosis of its lattice (structural type and unit-cell period) and to a qualitative assessment of the size of crystallites in synthesized blocks and in the granular product ([1–5]). No studies of the structure of individual crystals of cubic boron nitride by single-crystal X-ray methods have been reported in the literature; only information on their morphology has been published ([5–7]).

In the present work an attempt was made to study the structural features of individual crystals of cubic boron nitride by the Laue method. The following problems were posed:

1. Determination of the structural features of individual crystals: the degree of their perfection, and the presence in them of various defects and distortions.

2. Investigation of the monomineralic character of the crystal, detection and diagnosis of accessory phases, and determination of the nature of their distribution in the crystal lattice of cubic boron nitride.

3. Determination of the nature of twinning of the crystals.

X-ray photography was carried out in KROH-2 and RKV-86 cameras in copper radiation, with the tube operating at BSV-1, 35 kV, 10 mA. The exposure was 5 h at a specimen–film distance of about 40 mm. The orientation of the crystal $\langle 111 \rangle$ coinciding with the direction of the primary beam was adopted by analogy with the procedure for studying fine structural features in diamond crystals ([8], $p.24$). The crystal in the camera was fastened to a glass thread with BF-2 adhesive. Orientation of the crystals in the required direction was carried out with the aid of stereographic projections constructed from Laue diagrams of unoriented specimens.

The cubic boron nitride crystals studied (about 50 specimens) were black opaque pseudooctahedra of incomplete-faced form with unevenly developed faces, and also plates; crystals in the form of strongly distorted tetrahedra were sometimes encountered. The size of the crystals studied ranged from 200 to 500 μ.

The X-ray study showed that only some of the specimens proved to be true single crystals (Fig. 1a). All the others, including those specimens which on visual inspection could be assigned to single crystals, in reality are twins according to the spinel law, with varying degrees of development of the individuals (Fig. 1b).

From a number of isometric crystals 200-300 μ in size, Laue diagrams were obtained with point reflections, indicating the monolithic character of the specimen and the undistorted, nearly perfect, structure of its crystal lattice (Fig. 1). Evidently, these crystals nucleated and grew under the most equilibrium thermodynamic and concentration conditions.

Laue diagrams of platy crystals showed that the external appearance of the specimens (almost plane-parallel plates with dimensions $\sim 150 \times 250\times$

Fig. 1

Fig. 2

Fig. 3 **Fig. 4**

$\times 70\,\mu^3$) reflects their internal structure: the splitting of each 111 Laue spot in the radial direction into a series of separate reflections, connected with one another by weak continuous bands, indicates internal lamination of the crystal in the twinning direction [111] (Fig. 3). In the plate-like crystals studied, the total angle of mutual rotation of the {111} planes, calculated from the radial angular splitting of the entire Laue spot, is up to 2°. The rotation of neighboring plates relative to one another is about 0.5°. The lamination of cubic boron nitride crystals is associated with specific synthesis conditions.

Some crystals produced the following effects on Laue patterns. Intense local 111 Laue spots are accompanied by diffraction arcs attached to them, characteristic of the K_α- and K_β-radiation of copper from fine-crystalline cubic boron nitride, and by continuous bands of a peculiar shape crossing the Laue spots in the radial direction (Fig. 2a). The small azimuthal extent of the diffraction arcs ($\sim 10°$) indicates a high degree of texturing of the small cubic boron nitride crystals relative to the main crystal. The confinement of the continuous bands to the 111 Laue spots points to the existence in the crystal of considerable stresses caused by defects in the lattice, arranged in the $\langle 111 \rangle$ directions. It is possible that in this case the stresses arose as a result of intergrowth of the main crystal with small cubic boron nitride crystallites of close orientation. The formation of crystals of this kind is probably due to high concentration gradients of the components during synthesis and the simultaneous appearance of a large number of fine-crystalline nuclei near the {111} faces of the growing crystal.

For a large group of the crystals studied, with sizes of 300–500 μ, a special form

of Laue spots, different from those considered above, is characteristic: the 111 reflections are elongated in the radial direction and blurred in the azimuthal directions (Fig. 2b). The azimuthal blurring (2–3°) is due to mutual disorientation of the blocks making up the crystal. The asterism of the spots is caused by the nonparallelism of the {111} crystallographic planes as a result of internal defects and stresses in the crystal lattice. Such a micromosaic stressed structure is typical of crystals formed under conditions of rapid growth (dendritic character of crystallization), and indicates the presence of high temperature gradients during synthesis. Crystals of this group are also characterized by intergrowth with textured fine-crystalline cubic boron nitride.

In the Laue patterns of some crystals, weak second-order reflections from the flat {0001} nets of hexagonal boron nitride are observed in the form of arcs with an azimuthal extent of $\sim 25^\circ$, the arrangement of which follows the symmetry of the 111 reflections of one of the individuals of the crystal twin (Fig. 2b). The regularity of the orientation of hexagonal boron nitride α-BN relative to the matrix lattice of the cubic modification β-BN

Fig. 1. Laue patterns of cubic boron nitride crystals with a perfect structure: *a* –single crystal; *b* –twin according to the spinel law

Fig. 2. Laue patterns of cubic boron nitride crystals with a strained structure: *a* –intergrowth of a single crystal with a fine-crystalline aggregate, regularly oriented relative to the main crystal; *b* –twin according to the spinel law, individuals of different sizes; asterism and azimuthal blurring of Laue reflections; diffuse arcs –regularly oriented hexagonal boron nitride (indicated by an arrow)

Fig. 3. Laue pattern of a cubic boron nitride twin. Lamination in the [111] direction

Fig. 4. Laue pattern of a large cubic boron nitride crystal with overgrowths of smaller crystals. Debye ring from fine-crystalline magnesium oxide

$((0001)_{\alpha\text{-BN}} \parallel (111)_{\beta\text{-BN}})$ can be explained in two ways: either oriented crystallization of α-BN from vapors takes place during the growth of the cubic boron nitride crystal, or an ordered modification transition $\beta \rightarrow \alpha$ occurs (5, p. 48), by analogy with the graphitization of diamond crystals (9).

In almost all of the cubic boron nitride crystals studied, the presence of finely crystalline magnesium oxide was found (apparently in the form of periclase), distributed randomly throughout the volume of the crystal (Fig. 4). In individual crystals, small amounts of free boron were found, regularly oriented in the matrix lattice.

All the structural features of cubic boron nitride crystals listed above are revealed most effectively when X-rayed in the direction [111]. It may be assumed that the growth of cubic boron nitride crystals proceeds layer by layer in the

directions ⟨111⟩, since all distortions, defects, and secondary phases are concentrated in the crystals on the tetrahedron planes.

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