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Correlation defects of macrostructure with morphology of BGO crystals grown by low thermal gradient Czochralski technique

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Abstract In the present work we consider morphological structure of the faces of BGO crystals grown by Czochralski technique under the conditions of low temperature gradient (0.1~1 deg/cm) and interconnection between the morphological features of faces at the crystallization front and the formation of defects within the crystal volume. It is demonstrated that the {112} faces retain stability while the growing surface deviates from the crystallographic (112) plane up to 1 degree. At larger deviation, the region of the stable facet growth passes either to the region of macrosteps or to the region of normal growth, depending on conditions.

Key words BGO, Low thermal gradient, Facet, Growth mechanisms, Inclusions

1. Introduction

Bismuth orthogermanate ($Bi_4Ge_3O_{12}$, BGO) is a known scintillation crystal that finds wide application in the physics of high energy, medical instrumentation and other areas. Bismuth orthogermanate exhibits a vividly expressed tendency to faceting that is explained by high crystallization entropy (according to Jackson criterion, the higher is crystallization entropy, the higher is tendency to layer growth). When BGO crystals are grown according to the traditional Czochralski technique under the conditions of high temperatrue gradient (50~200 deg/cm), the "face effect" is observed, which is typical for many crystals; this effect leads to the formation of core non-uniformities within the crystal volume. The formation of faces at the crystallization front is usually considered to be a deviation from the optimal growing conditions. Because of this, an increase of temperature gradients is usually applied in order to suppress the formation of faces; however, this leads to the enhancement of thermal strain in the growing crystal.

Some authors mention increase of the uniformity of material and decrease of the density of dislocations in the regions corresponding to layer (facet) growth [1, 2]. So, non-uniformity of the properties of a crystal is due not to facet growth itself but to coexistence of the normal and facet growth mechanisms differing in the dislocation density and concentration of impurities, which leads to the formation of a complicated relief of the surface and to the formation of inclusion on the surfaces of these regions.

The use of low-gradient Czochralski technique to grow BGO allows spreading facet growth over the whole crystallization front. A decrease of temperature gradients, increase of pulling rate and change of temperature profile allow one to avoid simultaneous formation of faceted and rounded regions. Stabilization of the facet growth is promoted by practically complete non-transparence of the melted bismuth orthogermanate for thermal radiation (absorption coefficient being $> 10^4\ m^{-1}$) and high transparence of the crystalline one (absorption coefficient $< 3\ m^{-1}$) [3]. Thus, unstable growth with the formation of inclusions is observed mainly at the stage of facet formation during the crystal growth from seeding to full diameter. After the facet crystallization front is completely formed, it is conserved practically till the end of growing process.

Under the low T gradient conditions, large-size BGO crystals with fully faceted crystallization front were obtained [4], their length being up to 450 mm, and cross section up to 130 mm; the size of frontal faces reached 100 cm^2. The morphology of the such large faces formed during the growth from melt is poorly investigated.

Investigation of the real structure of crystals grown under the described conditions shows that their main volume is nearly perfect. Half width (FWHM) of diffraction curves are less than 10 arc sec [5, 6].

The crystals exhibit unique optical uniformity (absorption length being up to 30 m for $\lambda = 480$ nm) and are highly stable to gamma-radiation.

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2. Experimental Procedure

Surfaces of faces were examined using the samples of polyhedral crystallization fronts both with visually flat faces and with different degrees of surface distortions. These samples were obtained by interrupting the growth process at different stages rapidly taking a crystal away from the melt (~100 mm/min). When a crystal is separated from melt in such a manner, the drop at the lower part of the polyhedral front is very small or it is not observed at all.

The relief of natural growth surfaces was measured using the fragments of fronts cut parallel to the crystallographic plane (112). Measurements were performed on a two-coordinate table. The thickness of the plate was measured with a micrometer scaled from 1 micrometer; the curvature radius of the probe was 0.25 mm.

Real structure of samples was investigated by means of X-ray topography and high-resolution X-ray diffraction.

Topographic images were obtained by using double-crystal X-ray spectrometer, Cu Kα_1 radiation, Si (004) monochromator (the (035) surface, asymmetric reflection, glancing angle ~3.5 deg.) with reflection geometry. 224 reflections were used for topographic imaging. Before measurements, the surfaces of natural growth faces were lapped to eliminate roughness and deviations from crystallographic plane. Lapping was performed with SiC grits of 40, 20 and 8 μm. In order to eliminate the stress induced in lapping process, the samples were etched in solution of HCl (3 M) for 5 min.

Diffraction curves were measured with a double-crystal diffractometer in Ni Kα_1 radiation, Ge (004) monochromator. The specimen crystal was oriented in the non-dispersive (+, −) configuration and symmetrical Bragg geometry (the (001) surface, symmetrical reflection).

3. Results and Discussion

The shapes of the crystallization front during the growth in the <111> direction are shown in Fig. 1.

The size of the faces under investigation is rather large (50~80 cm^2); surface regions may differ from each other in morphological structure. These shapes of the surface can be conditionally divided into 4 groups

- flat regions
- small macrosteps
- large macrosteps up to 1 cm long
- rounded surfaces.

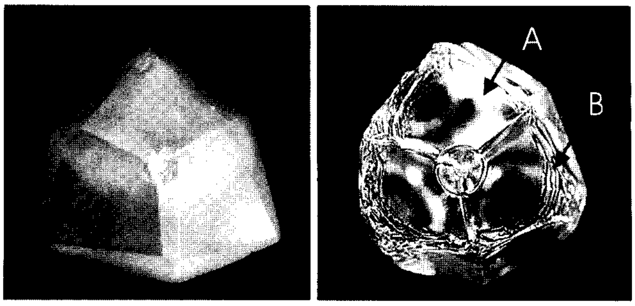

Fig. 1. Left: a typical BGO crystallization front formed by {112} faces; right: crystallization front with disrupted polyhedral shape (A - facet region; B - macrosteps).

A fragment of the defective facet incorporating regions of different morphology is shown in Fig. 2.

As we have already mentioned above, distortion of the stability of face, formation of macrosteps and coexistence of different growth mechanisms on crystallization front are accompanied by the formation of various inclusions in crystal volume.

At least 4 types of inclusions can be distinguished when looking at the crystal in laser beam or in an inten-

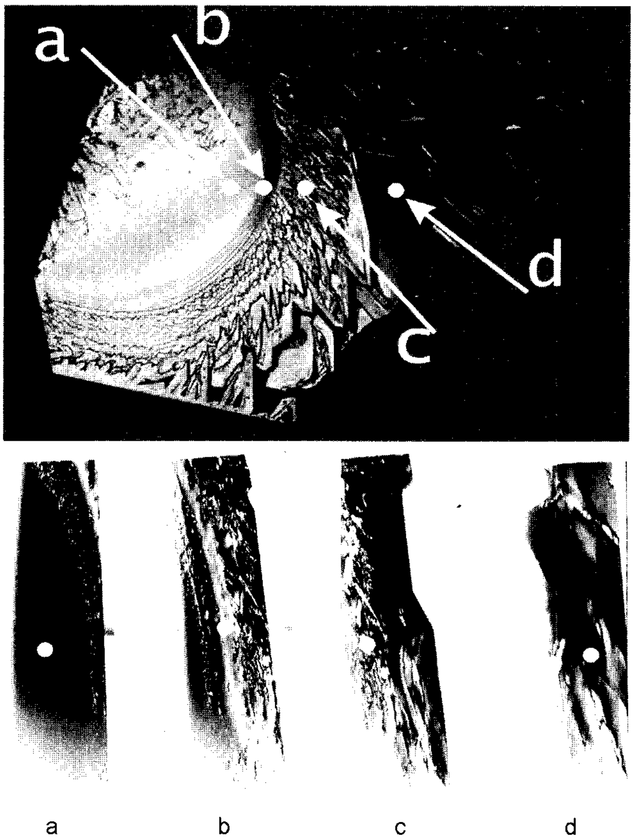

Fig. 2. A fragment of the 112 facet with (a) flat region, (b) transition region, (c) small macrosteps, and (d) large macrosteps. At the bottom the topographic images of corresponding regions are represented.

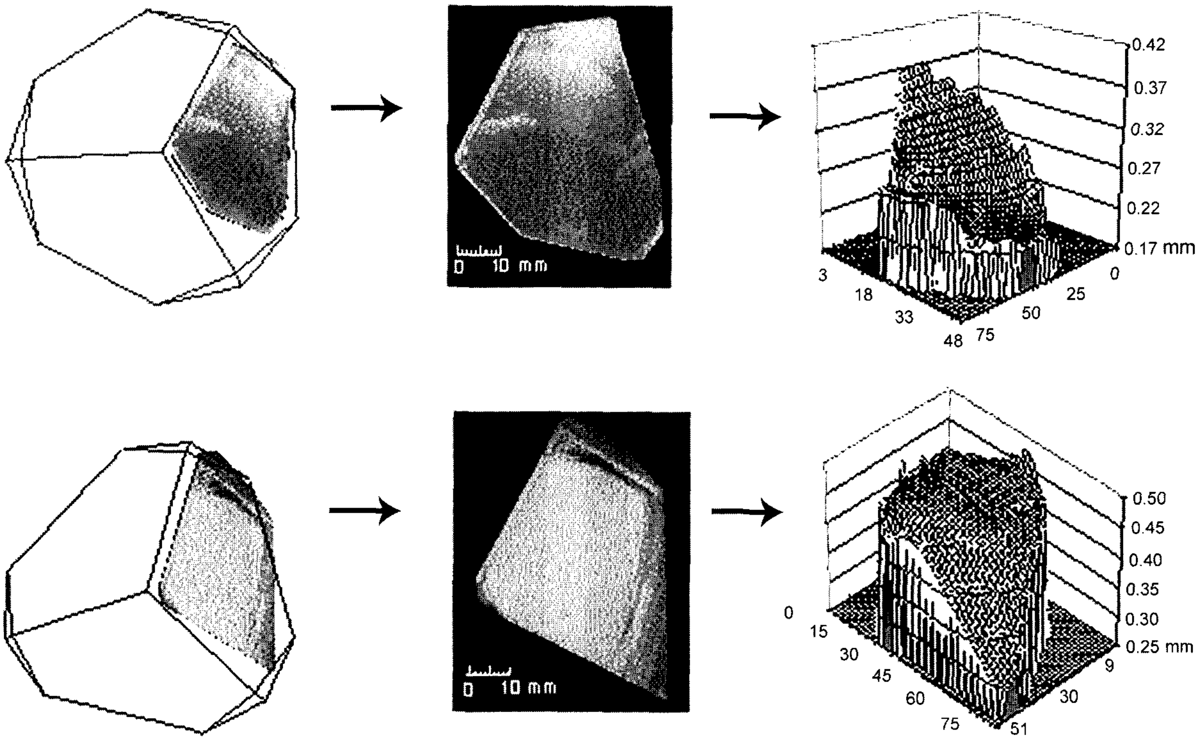

Fig. 3. Convex and concave relief of visually flat facets.

sive narrow directed beam of visible light:

- coarse inclusions up to several millimeters long;
- small uniformly spread light-scattering centers (fog);
- structured fog;
- gas bubbles up to millimeter in size.

The analysis of their positions in the regions of crystals adjacent to crystallization front reveals a connection of the distribution of inclusions with the surface relief.

A high-quality material (without inclusions) is mainly observed in regions formed by visually flat surfaces deviating from the (112) plane by no more than one degree. The topographic picture taking from such area exhibits high crystal perfection [Fig. 2(a)]. This is confirmed by the measurements of the half-width of diffraction curve (FWHM = 23 arc sec).

Figure 3 shows results of the measurements of the relief of visually flat faces, which nevertheless exhibit noticeable convexity, or concavity of the surface and the deviation of facet orientation from the crystallographic plane (112) by 0.5~0.7 degrees.

Small intermediate regions between stable faces and macrosteps, though remaining smooth, can deviate from the singular direction by one to three degrees. Small scattering centers (fog) appear in the adjacent volume of crystal (Fig. 4b). The length of such a intermediate region is usually not more than 2~3 mm (Fig. 2b), but sometimes it reaches 10~15 mm. In case of rather wide transient region, one can observe the appearance of non-uniformity in the distribution of scattering centers, the so-called structured fog (Fig. 4c).

This region is characterized by the formation of dislocations and the increase of their density till $100/cm^2$,

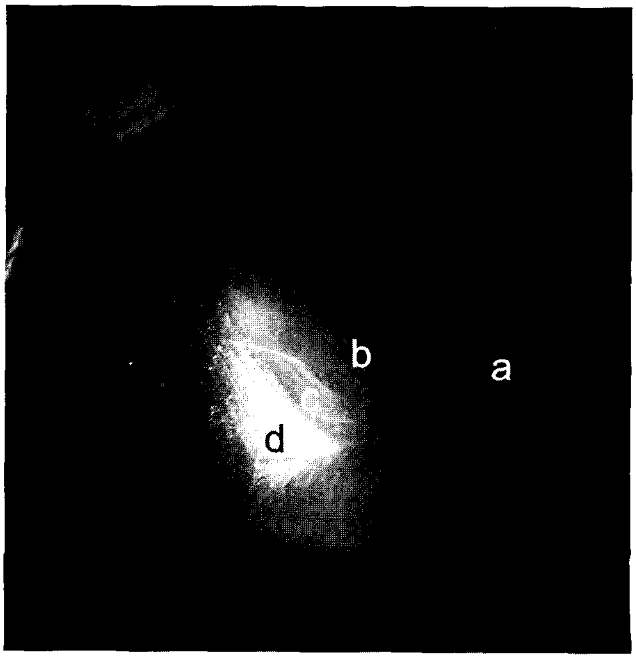

Fig. 4. Scattering of laser light beam in the region of a large inclusion. a - the region without inclusions; b - fog; c - structured fog; d - large inclusions.

with sequential transition to disordered grain structure, grain size being about 0.1~0.3 mm.

The intermediate region is followed by the region of small macrosteps that can develop and get larger as it is shown in Fig. 2. The measuring of the relief of flat parts in the region of macrosteps shows that these regions coincide within the measurement error with the crystallographic planes (112), while the averaged surface occupied by macrosteps can deviate from the (112) plane by 3~7 degrees.

Macrosteps seen in the crystallization front increase in area with increasing distance from the transient region. Step height also increases. In topograph, macrosteps are exhibited as subgrain having lattice distortions (Fig. 2d). Subgrain size increases and their mutual disorientation decreases with increasing distance from the transient region. Large flat regions in the area occupied by macrosteps are composed of large subgrains with lattice distortions and small number of small-angle boundaries. Mutual disorientation of blocks is 10~20 arc sec. Half-width of the diffraction curve taken from the largest flat region in the area occupied by macrosteps is 32 arc sec, which demonstrates rather good perfection degree of the formed subgrains.

It is essential to note that at definite growth conditions the angle between the growing surface and the (112) plane becomes more than 10 degrees; this is accompanied by a gradual transition to normal growth; the surface of the front becomes rounded.

Large inclusions of irregular shape are formed in the region of macrosteps. The occurrence of large inclusions is always preceded by the region with small scattering centers (fog).

4. Summary

Thus, the present work is a detailed investigation into specific features of the morphology of faceted fronts of BGO crystals formed during growing by low-gradient Czochralski technique. It is demonstrated that, depending on growing conditions, visually flat facets exhibit deviations of different sign from the corresponding crystallographic planes. An interconnection has been revealed between the positions of the defects of crystal structure and types of distortions of frontal faceting.

The obtained results are important for understanding of the mechanism of BGO crystals growth and can be useful for the optimization of growth process.

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