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# Morphology of the polar twin structure in Czochralski grown α-$SrB_4O_7$ crystals

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ABSTRACT

The arrangement of a polar twin structure in Czochralski grown α-$SrB_4O_7$ crystals has been investigated. The transversal twin boundaries are stretched along [1 0 1] and [1 0 0] directions. The lateral twin boundaries are parallel to (0 1 0) plane. The twin structures have an extension up to centimeter size in all directions. Supposedly, they originate from polysynthetic polar microtwins revealed to form in (1 0 $\bar{1}$) and ($\bar{1}$ 0 $\bar{1}$) growth pyramids. The dimensions, planarity and thickness stability of each individual twin are favorable for organizing quasi-phase matching conditions for nonlinear optical doubling of high-aperture beams.



## 1. Introduction

Recently a number of investigations devoted to the creation of a regular polar twin structure in nonferroelectric crystals have appeared. The ability of such structures to obtain deep UV radiation by second harmonic generation (SHG) under quasi-phase matching (QPM) conditions has been shown in quartz and $Li_2B_4O_7$ (LB4) [1,2]. Orthorhombic α-$SrB_4O_7$ (SBO) crystals with a short fundamental edge close to 120 nm, high damage threshold, large thermal conductivity, chemical stability and sufficiently high optical nonlinearity [3–6] have been shown to be attractive candidates for the same role due to the spontaneous formation of growth twin structures [7–9].

This work is devoted to the investigation of the growth polar twin structure morphology in Czochralski grown SBO crystals.

Growth twinning was previously observed in several borate nonlinear optical (NLO) crystals such as LB4, β-$BaB_4O_7$ (BBO), and in SBO-isostuctural $PbB_4O_7$ (PBO). This phenomenon was considered an obstacle for high-quality growth and the approach to its investigation was determined mainly by this point of view [10–12]. Recently, however, another approach has emerged where growth twinning is considered in the context of the methods of periodic twin structure creation [13].

## 2. Experimental

First, it is necessary to mention that all 3 possible space groups for the SBO structure can be encountered in literature. We previously used the $Pnm2_1$ group according to [3]. In the present work, however, we change it to the standard $Pmn2_1$ group.

About a dozen of SBO crystals were grown in the course of the investigation. The charges were prepared from $SrCO_3$ ( > 99.5%) and $H_3BO_3$ ( > 99.8%) taken in stoichiometric ratio. In each growth run an average charge of 200–220 g was contained in platinum crucible 50 mm in diameter and 70 mm in height. The axial temperature gradient above melt surface was approximately 2 °C/cm. Seeds oriented along *a*-, *b*- and *c*-axes were used. The initial seeds were brought into a contact with the melt surface slightly overheated (2–3 °C) above SBO melting point so they were particularly melted (approximately 10–30% of initial diameter). Then the furnace temperature was decreased until equilibrium state was established. The growth of the crystals from *b*- and *c*-oriented seeds was done without pulling and with the steady temperature decreasing of 0.5 °C/day. The growth of the crystals from *a*-oriented seeds was done with pulling rate of 0.1 mm/h and with the same steady temperature decreasing so it was like in a typical Czochralski.

Single crystal X-ray diffraction data of the SBO crystals were collected with a SMART APEX II (Bruker AXS) Diffractometer, CCD-detector using the Mo$K_\alpha$ radiation at room temperature up to $2\theta_{max}=68°$. Corrections on X-ray absorption were made in accordance with the sample shape. The atom site locations were

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determined with an anisotropic approximation of the atomic temperature oscillations.

Twin structures in the grown crystals were revealed by grounding and polishing variously oriented cuts which then were etched with a 5% aqueous solution of nitric acid. The typical etching times were about 5–10 min, while the etchant temperature varied from 20 °C to 50 °C depending on the cut orientation.

Optical observations were carried out with a Carl Zeiss Axio Observer A1m inverted optical microscope and a Carl Zeiss Stemi 2000-C binocular microscope. An AxioCam MRc5 digital camera was used for the snapshots. The observations of the polished and etched cuts were done in the DIC mode, which proved urgent for the adequate representation of the surface morphology.

## 3. Results and discussion

In this work, we use conditional designation for the twinned areas of the polar cuts as was assumed in [7]. There, two types of etching behavior were emphasized for such areas. That is, some areas exhibited much higher etching rate than other ones, resulting in noticeably different etching patterns. Although the etching rates of the twinned areas also depended on the cut orientation, the relative etching rate difference still prevailed for any polar cut. We therefore designate the areas with the higher etching rate as positive, or "+", and the areas with the slower etching rate as negative, or "−".

The crystals grown from *b*- and *c*-oriented seeds had typical dimensions from $5\times5\times20$ mm to $5\times15\times20$ along the *a*-, *b*- and *c*-axes, respectively. The crystals grown from *a*-oriented seeds were from $15\times20\times20$ mm to $20\times30\times30$ mm. All grown crystals were colorless and transparent, with moderate gaseous inclusions localized around the initial seed. Faceting of the grown crystals was quite similar independently of the seed orientation; it included well-developed (1 0 0)-, (0 1 0)- and (1 0 1)-facets. (3 0 1)-facet was present on few crystals. We believe that it developed only when fitted well in the melting isotherm. (0 1 1)-facets were present only on one polar side of the grown crystals (namely, the side which exhibits a positive (1 0 1)-facet), so the crystals were asymmetrical relative to the polar direction. Such asymmetry was mentioned earlier for PBO [12]. However, the equilibrium shape given in [3] does not exhibit this asymmetry. In other respects our crystals match it quite well, however some facets present on the equilibrium shape usually didn't develop on our crystals. A shape of a typical crystal grown along *a*-direction is represented in Fig. 1. Stripes parallel to *a*-direction often formed on the as-grown crystal surface of (0 1 1)-less side of the crystal. We associate these stripes with the growth twins. No such stripes were observed on the opposite side.

XRD analysis of a non-twinned SBO sample was carried out. The sample was cut from (0 1 1)-faceted side of a SBO crystal and was ground to the shape of the plate with two opposite *c*-cuts. The dimensions of the sample came to $0.2\times0.2\times0.3$ mm. By the etching patterns the *c*-cuts were identified as positive and negative. The absolute structure of the sample in chosen crystallographic axes was established. The unit cell parameters are $a=10.6976(6)$ Å, $b=4.4210(2)$ Å, $c=4.2284(2)$ Å. The positive *c*-cut corresponds to the (0 0 1) plane, and negative *c*-cut corresponds to the (0 0 $\bar{1}$) plane. This correspondence is shown in Fig. 2.

Numerous cuts oriented along *c*- and (1 0 1)-planes were made on both sides of the crystals. On the cuts made through (0 1 1)-less sides of the crystals a specific areas were revealed. These areas anomalously differed from the rest of the crystal volume by their etching patterns, which didn't correspond with the etching patterns of both positive and negative planes. Anomalous areas occupied both (1 0 $\bar{1}$) and ($\bar{1}$ 0 $\bar{1}$) growth pyramids

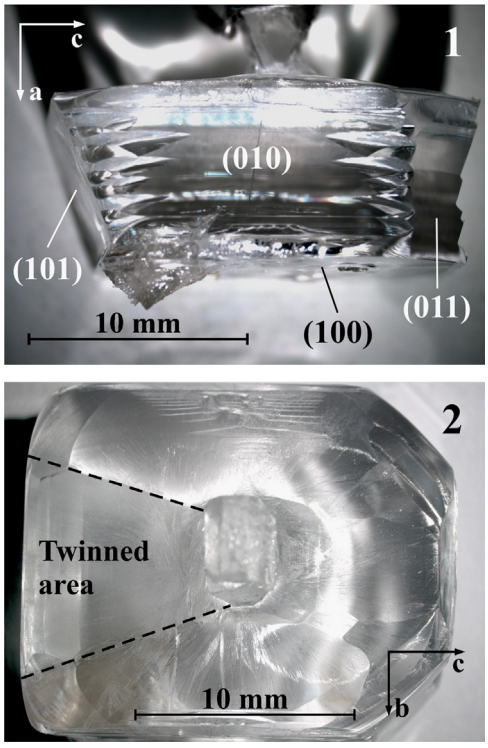


**Fig. 1.** Habit of SBO crystal grown in *a*-direction.

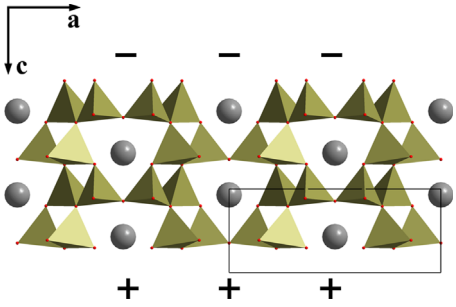


**Fig. 2.** Conformation between cut designation and SBO structure.

as shown in Fig. 3. Here the crystal grown in *c*-direction (Fig. 3.1) and its cross-section along *c*-plane (Fig. 3.2) are presented. These areas never formed on the opposite side of the crystals.

Closer investigation of the polished and etched *c*-cuts revealed that the anomalous areas contain numerous wavy stripes directed along the *a*-axis as given in Fig. 4.1.

On the *a*-cuts the anomalous growth areas exhibit basically the same interior pattern as on the *c*-cuts, however the stripes here are directed along *c*-axis and are much longer (see Fig. 4.2). A sample for XRD analysis was cut from the anomalous area. It was revealed that for 20% of the sample volume the direction of the polar axis is reversed relatively to that of the mother crystal. On the basis of this we speculate that the anomalous growth area is composed of small polysynthetic twins which are manifested on the polar cuts as abovementioned stripes. It is necessary to distinguish these new twins (henceforth microtwins) from those ones described in [7]. Contrary to the latter, the microtwins have uneven, wavy boundaries and more limited size: the typical microtwin dimensions are about several tens μm, 1–2 μm and several hundred μm along *a*-, *b*- and *c*-axes, respectively. The *a*- and *c*-dimensions depend greatly on the growth conditions while its *b*-dimension remains roughly constant through all grown crystals. Such morphologic distinctions between the twins and

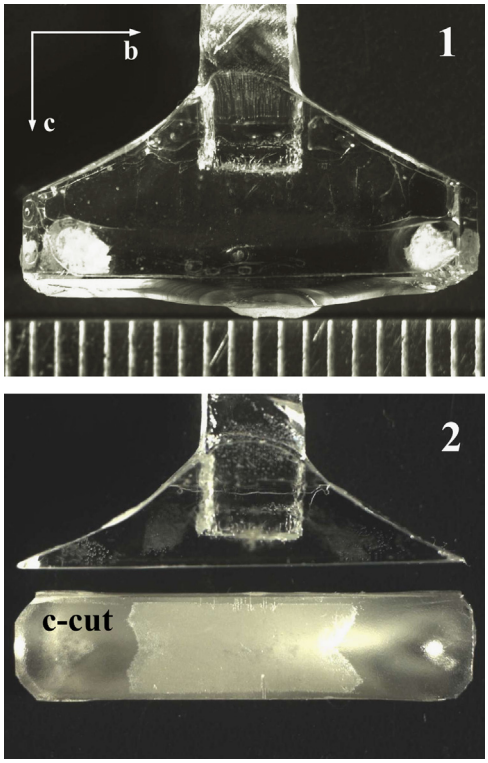


**Fig. 3.** SBO crystal grown in *c*-direction (1) and *c*-cut illustrating anomalous area localization (2).

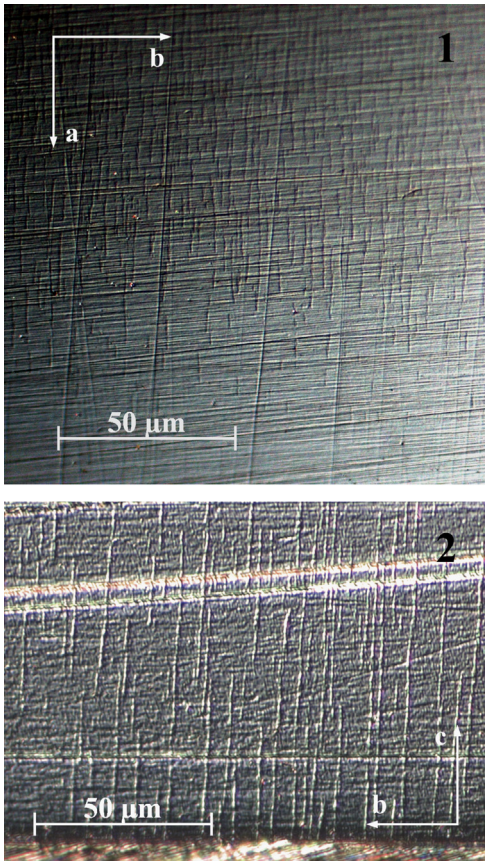


**Fig. 4.** Microtwins in anomalous area: *c*-cut (1) and *a*-cut (2).

the microtwins may indicate that they have quite different growth mechanisms. Fig. 5 illustrates twin propagation from microtwin-filled (1 0 $\bar{1}$) growth pyramid.

It was noted in [7] that the twin boundaries (referenced there as the domain walls) are parallel to *b*-plane. It is obvious that these "lateral" boundaries are insufficient to separate the twinned areas themselves, and there must be a set of boundaries transverse to *b*-plane to complete the separation. We investigated transversal twin boundaries located in the (1 0 0) growth pyramid by the following technique. *b*-cuts through separate plain twins of the suitable thickness were made. It was noticed that, despite the fact that the twinned areas shouldn't exhibit different etching patterns on *a*- and *b*-cuts, they actually may be different if a cut is finely ground or roughly polished and the etching is intensive enough. This peculiarity allowed us to visualize the twinned areas on the so-made *b*-cuts. The boundaries between the twins appeared as straight lines as depicted in Fig. 6. The nearly-horizontal lines are artifacts due to the cut being actually deflected from *b*-plane by up to 1° so that the cut intersects the lateral twin boundaries. The angle between the inclined lines, which are associated with the transversal boundary under study, and the direction of *a*-axis was measured to be around 21°. This angle agrees with that between *c*- and (1 0 1)-planes, so the transversal boundaries under investigation are assumed to run along [1 0 1]-direction.

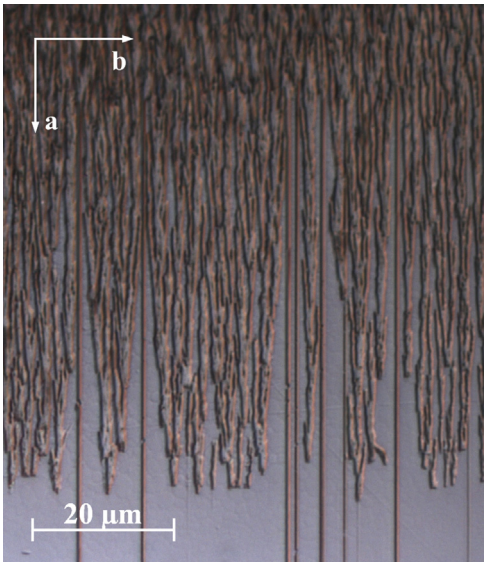


**Fig. 5.** Twins protruding from microtwin-filled (1 0 $\bar{1}$) growth pyramid.

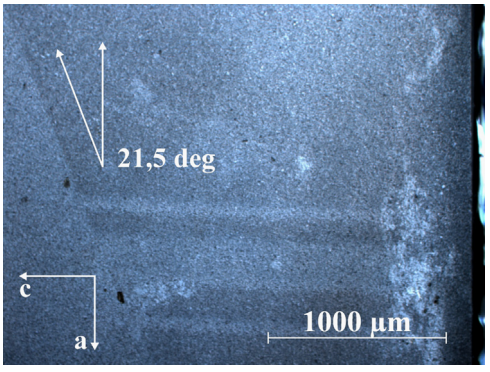


**Fig. 6.** Visualization of transversal twin boundary on *b*-cut.

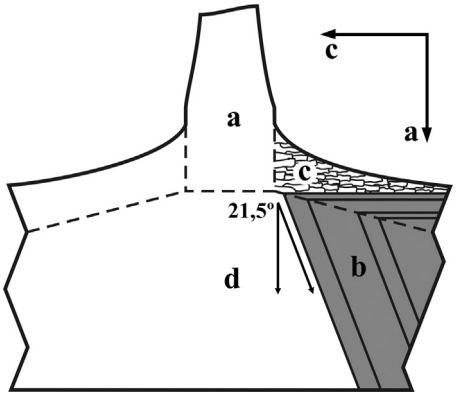


**Fig. 7.** Conformation of twins and microtwins in SBO crystals. (a) Initial seed, (b) twin structure, (c) array of microtwins in (1 0 $\bar{1}$) growth pyramid, (d) (1 0 0) growth pyramid.

This technique was supposed to be inadequate for the observations in the (1 0 $\bar{1}$) growth pyramid because the presence of the microtwins might render the transversal wall indistinct. Instead, a reference *a*-cut and several *c*-cuts across the crystal body were made. *c*-cuts were etched, so the twins propagated through the bulk of the crystal appeared on all cuts as stripes with one side ending somewhere on the given cut, another reaching the edge between the given cut and the reference *a*-cut. The distances from the stripe endpoints, which are associated with the transversal boundary, to the named edge were measured. For each twin the distances were equal on all cuts. From this we conclude that the investigated transversal boundaries in the (1 0 $\bar{1}$) growth pyramid stretch along [0 0 $\bar{1}$]-direction.

The described arrangement of the transversal twin boundaries implies that they start from the boundary between the (1 0 0) and (1 0 $\bar{1}$) growth pyramids. We believe that the twins originate from those microtwins which (under unknown circumstances) hit this boundary during the growth process. The conformation of the investigated twin boundaries and microtwins is shown in Fig. 7.

## 4. Conclusions

In this work we show that polar microtwins form in the (1 0 $\bar{1}$) growth pyramid of Szochralski-grown SBO crystals. These microtwins are assumed to be responsible for the origin of flat laminated twin structures. The flat twins propagate in the (1 0 $\bar{1}$) and (1 0 0) growth pyramids forming [0 0 $\bar{1}$]- and [1 0 1]-stretched boundaries, respectively. The described arrangement of the flat twin structures is advantageous for organizing QPM conditions. However, the arbitrary thickness of spontaneously forming twins enables organizing random QPM conditions only. Nonetheless, even randomized SBO twin structures can be effectively utilized for the doubling of tunable femtosecond pulses [14]. As an example, the generation of down to 121 nm VUV pulses was obtained in [15]. Still, the capability of growing regular twin structures would completely realize the SBO potential as a nonlinear optical material.

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