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Czochralski growth of α-BBO crystals under azimuthally anisotropic heating ☆

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ABSTRACT

Crystal growth of α-BBO in a modified low-gradient Czochralski furnace was performed. The distribution of temperature inside the furnace was described by a three-fold symmetry axis (L_3). The axial temperature gradient under the melt was ~2 K/cm, while that inside the melt was almost equal to zero. A 36 mm thick sample of the grown crystal shows extremely low 0.05 cm^{-1} absorption coefficient at wavelengths >220 nm.

1. Introduction

BaB_2O_4 (BBO) crystals are well known NLO materials due to β-modification existing below 925 °C [1]. But the structure of α-phase has a center of symmetry, which disables the nonlinear properties. On the other hand, a big transparency region (189–3500 nm) and high birefringence of α-phase crystals provide good materials to substitute calcite, TiO_2, $LiNbO_3$, etc.

Since BBO melts congruently, the easiest way for crystal growth seems to be a classical Czochralski method. Because of the high melt viscosity one should impose high gradients of temperature during crystal growth. Therefore crystallization from the stoichiometric melts often results in thermal stresses [2] and spontaneous α–β phase transition [3,4] in the grown crystals.

One of the ways to solve the problem of melt viscosity is the use of high temperature solutions. Addition of a solvent like Na_2O, PbO, etc. decreases both viscosity and crystallization temperature [2]. But solution growth of α-BBO results in the formation of micro-inclusions in the bulk. Therefore the main disadvantage of this technique is a low yield of the material.

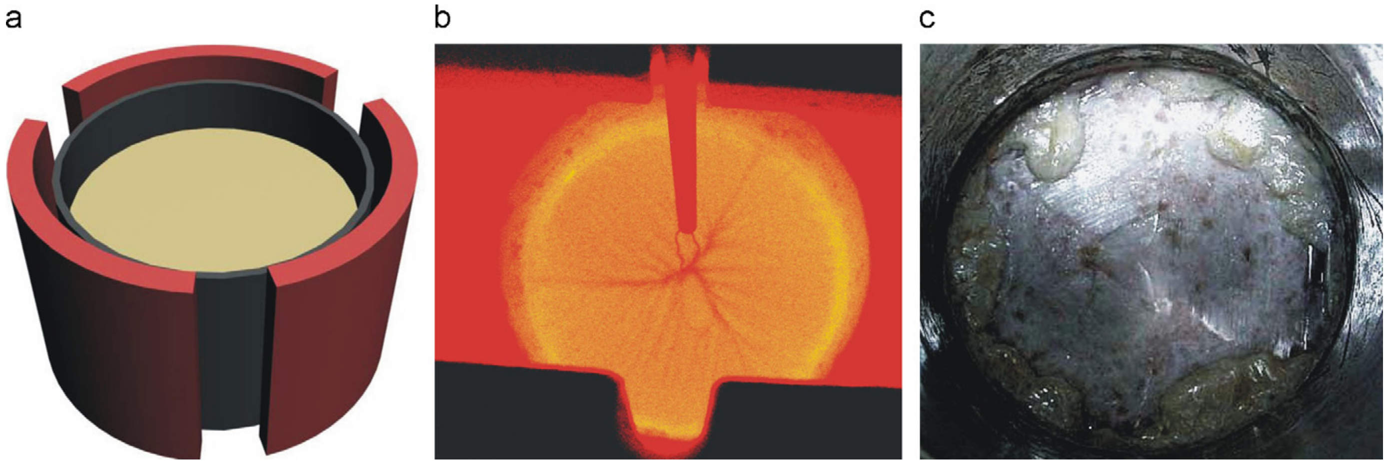

Fig. 1. Sketch of heater (a); flow pattern on surface of melt (b); and surface of frozen melt after growth experiment (c).

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2. Experimental details

A main modification of the Czochralski furnace consists of non-uniform heating of the crystallization medium. The heater framework is composed of an alumina pipe cut into three 100° sectors (Fig. 1a). Ceramic blocks are wrapped with a resistive wire and the sectors are connected serially outside the hot zone. Gaps among the sectors are in turn filled with caoline wool to increase the anisotropy of crucible heating.

In this way the crucible walls are heated by three "hot" areas giving rise to a specific pattern of natural convection (Fig. 1b). Observation of the melt surface reveals three dark rays indicating areas of more cold descending flows. Each ray begins at the corresponding "gap between heaters" and extends to the center of the crucible. Thus the convective structure inherits the symmetry of the heat field and is likely to be explained by the existence of three separate vortices positioned between the dark rays.

One of the features of the Czochralski method is a constantly decreasing melt level; so it is a problem to maintain the convective structure during the crystal growth. In this work a single crystal on the frozen surface is observed after every experiment (Fig. 1c). Orientation of the crystal marks the directions of the dark rays seen before the start of the experiment. Therefore the stability of convection is assumed to be sufficiently high.

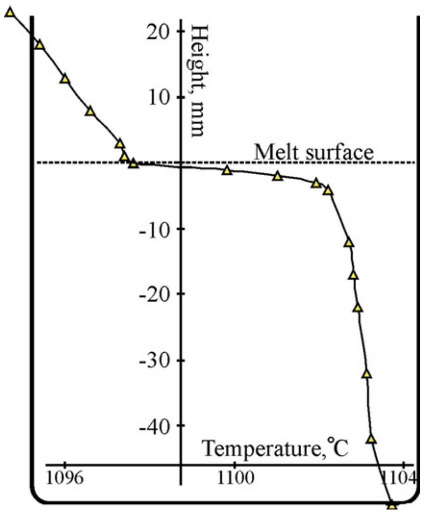

Fig. 2. Measured temperature distribution along central axis.

Fig. 2 shows the temperature distribution measured by an S-type thermocouple along the central axis. The temperature gradient above the melt surface is about 2 K/cm while that inside the melt is almost equal to zero except at the near-surface region. It should be noted that these thermal conditions are quite unusual for crystal growth from a viscous melt. For instance, the authors of Ref. [2] grew α-BBO crystals with a 70–80 °C temperature difference in the melt along the central axis.

3. Growth of α-BBO crystals

Crystal growth of α-BBO was performed in the modified low-gradient Czochralski furnace. Solid state synthesis of the charge was done at 800 °C from $BaCO_3$ (3 N) and HBO_2 (3 N). The stoichiometric charge was melted in Ø80 mm crucible. The furnace was put on the balance sensor in order to provide automatic control of crystal diameter with feedback ratio 0.8 °C per 1 g.

Other growth parameters were as follows: seed orientation—(0 0 0 1), crystal pulling—5 mm/day, and crystal rotation—4 rpm. The cooling rate after growth was 20 K/h.

Fig. 3a presents a photo of the as-grown crystal. The typical weight of the crystals is ~300 g. All crystals exhibit well-developed rhombohedra facets. The convex front of crystallization has a small plateau of the (0 0 0 1) plane at the center. Fig. 3b shows a slice of the α-BBO crystal polished perpendicular to the growth direction. The central part of the crystal demonstrates a defect region with the swirl structure (marked by the dash) but the other part of the crystal exhibits high optical quality. An absorption spectrum of the high-quality part of the 36 mm width sample is presented in Fig. 3c. The absorption coefficient at wavelengths >220 nm corresponds to an extremely low value of 0.05 cm^{-1}.

4. Conclusions

It was shown that growth of high-quality α-BBO crystals is possible under low temperature gradients. The temperature

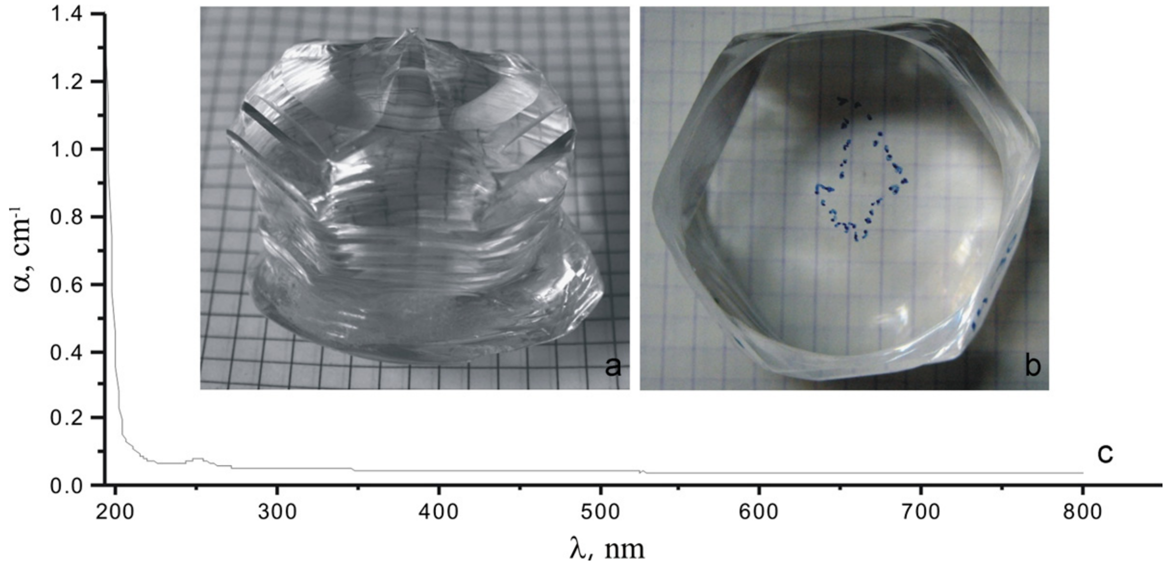

Fig. 3. As-grown α-BBO crystal (a) and polished slice (b) 36 mm in width, with cell size of 5×5 mm^2. (c) Absorption spectra of α-BBO sample at room temperature.

inhomogeneties imposed to the melt are supposed to play an important role in convection processes in the growing crystal. Hence the proposed technique seems to be promising for crystal growth from viscous melts.

Acknowledgement

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