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ß-BaB_20_4, SINGLE CRYSTALS OBTAINED BY CZOCHRALSKI METHOD

ABSTRACT

Barium borate single crystals are known as a high temperature phase a BaB_20, and low temperature phase ß BaB_20,(BB0). Temperature transition is 925 °C. BBO single crystals are noncentrosymetric with trigonal structure and exhibit excellent nonlinear optical properties. In order to avoid formation of α - phase, ß - phase crystals have been obtained from the flux by top seeded solution growth.

It turn out possible to produce ß - phase BBO by Czochralski method without any flux. The growth is carried on from supercooled melt obtained from special prepared starting material BaB_20_4 examined befor melting by the X-ray difraction and by DTA analysis confirming existance ß - phase.

As a heater RF furnace was used. We measured axial temperature distribution and found suitable thermal conditions for growth of ß phase. Obtained BBO crystals were verified by second harmonic generation Nd : YAG laser system.

INTRODUCTION

Many inorganic crystals show strong nonlinear optical properties, and there still exists a need for new materials. One of them is barium borate existing in two modifications i.e. a high temperature phase α-BaB_2O_4 and low temperature phase ß-BaB_20_4. The ß-phase in single crystal form (BBO) belongs to trigonal structure and possess high nonlinearity. The α-phase crystals are centrosymetric and for nonlinear applications are not useful. Attractive fetures of BBO crystals are: large nonlinear optical coefficients about six times high, as compared with KDP, large birefringence, transmision range between 190 and 3500 nm, damage threshold as high as 10 GW/cm^2 measured with 100 ps pulses, low absorption, moisture insensitivity, and good mechanical and thermal properties. BBO crystals are used successfully for efficient generatio of ultraviolet Hght from visible light source. They are suitable for use with the most powerfull lasers for second and higher harmonic generation laser light and as an optial parametric amplifier (OPA) and optical parametric oscillator (OPO). Crystal structure of BBO has similarities with a molecular crystal structure and origin of its nonlinear properties is reminiscent of organic nonlinearity of organic crystals. The structure is built from B_30_6 rings packed up perpendicularly along the c-direction of hexagonal unit cell.

The low temperature phase is believed to be stabe below 920 °C, temperature transition is reported as 920-925 °C and the melt point is 1100 °C so first BBO crystals were obtained by flux technique [1,2]. High optical quality crystals, up to 80 mm in diameter and 15-18 mm in length have been grown by TSSG from sodium oxide flux with or without pulling. If pulling is used sutable pulling rate is about 0,5-1,0 mm/day. The cooling rate is usually 1-1,5 °C/day, and the growth temperature changes aproximately in range 900-860 °C. Consequently the growth time is 5 weeks or longer. The predominant defects found in BBO crystals grown by this method were flux inclusions. Fibrous sigle crystals of BBO have also been grown with heated pedestal growth (LHPG) [3].

It was found possible to grow BBO crystals without any flux by Czochralski technique [4,5]. This fact is explained by the relation of free energy for α-phase, ß-phase and liquid. The stable phase in given temperature is that with the lowest free energy, and equilibrium for α-phase

and liquid is at 1100 °C. It is possible to keep supercooled melt far below the melt point. At 1050 °C there is a point of equilibrium free energy for liquid and ß-phase. So carrying on growth near 1050 °C it should be possible to obtain BBO crystals by Czochralski growth. Another explanation is reported that interfacial energy $\sigma(ß)$ for ß-phase is sufficiently smaller than $\sigma(\alpha)$ for α-phase which makes the nucleations of ß-phase easier. It is also maintained that the melt for BBO growth ought to be obtained from startig material that is ß-phase.

EXPERIMENTAL

The starting material for the growth was prepared using carbonate method using the reaction:

$$BaCO_3 + 2H_3BO_3 \longrightarrow BaB_2O_4 + CO_2 + 3H_2O$$

The commercially available powder $BaCO_3$ and H_3BO_3 were mechanically mixed and held in platinum container at a temperature of 800 °C for 10 hours. Heating of synthetized ß-BBO above temperature transition 925 °C yielded the α-phase. Product was examined by the X-ray diffraction method and by DTA analysis shown in Fig.1. On DTA curve for ß-phase two endothermic peaks are observed. First of them at 925 °C relates with phase transformation ß to α and the second one at 1095-1100 °C is connected with melting. For α-phase barium borate powder peak at 925 °C is not observed.

The schematic drawing of employed RF furnace is shown in fig.2. As a container of the melt platinum crucible 40 mm in diameter and 40 mm in height was used. The growth was carried on in air atmosphere. First experiments were performed with platinum after-heater. The temperature gradient near the interface was adjusted by the crucible position inside the RF coil and also by changing afterheater position higher or lower above crucibie. In further research the afterheater was replaced by additional ceramic isolation. We found that the axial tempemture gradient in the vicinity of the melt surface ought to be kept 135-140 °C/cm and suitable temperature on the melt surface was 1045-1048 °C. Small changes of temperature on the melt surface in range 1-2 °C were observed.

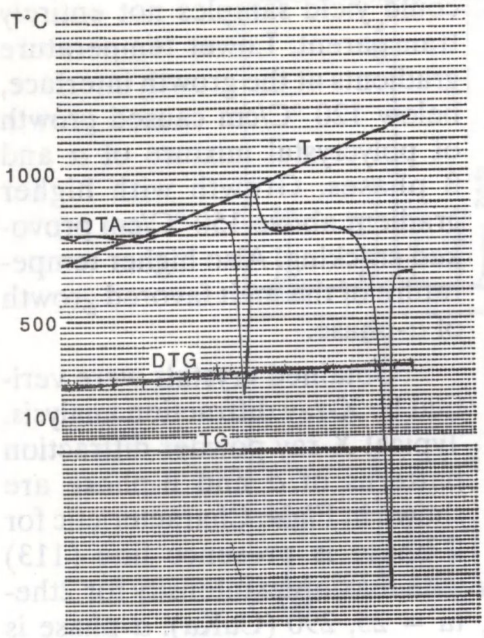

Fig.1
DTA analysis of starting material.

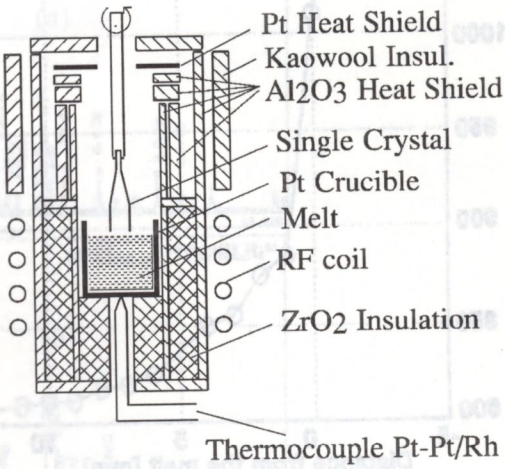

Fig.2
Schematic diagram of the growth apparatus.

Axial temperature distribution above crucible is given on Fig.3. In separate measurements we determined temperature relation between melt surface and the central point on the bottom under crucible. Measurments were performed without growing crystal. It made it possible to control the melt temperature with thermocouple attached under crucible. In first experiments platinum wire as cold finger was used.

RESULTS

High quality ß-barium metaborate single crystals up to 18 mm in diameter and 35-40 mm in length were grown. Diameter control during the growth was achieved by controlling the RF power and increase mass of the bulk in time. Samples grown on a platinum rod were used to cut seeds in [001] direction. We found that suitable pulling rate was 1-1,5 mm/h with-rotation 10-12 rpm. Growth with higher pulling above 3 mm/h

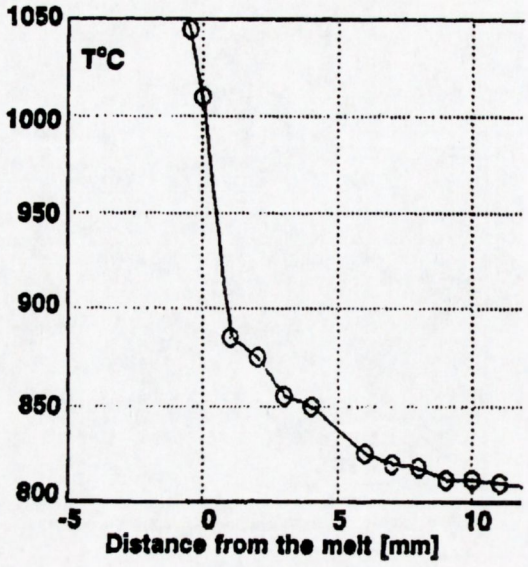

Fig.3
Axial temperature distribution above the melt.

could yield samples not entirely transparent. Lower temperature gradients at the growth interface, below 120 °C/cm caused growth of polycrystal mixture of α and ß phases. Growth with higher gradient above 150 °C/cm provoked cracking. Also higher temperature of the melt favored growth of α-phase.

Obtained crystals were verified by X-ray diffraction analysis. Typical X-ray powder diffraction patterns of α and ß-phase are shown in Fig.4. Characterictic for ß-phase is presence line (113) with maximum intensity for 2theta = 25, 290 (CuKa). α-phase is recognized by (1010) reflection peak for 2theta 26, 724 [6].

The samples 7x7x10 mm with phase matching angle 22 respect to optic axis C were cut for SHG test. The samples were irradiated with Nd :YAG beam and green light 530 nm was observed.

CONCLUSION

ß-BaB_2O_4 single crystals with good optial quality can be successfully obtained by Czochralski technique. The growth process is carried on from supercooled melt. The growth time is about 5 times shorter with compare to growth time by flux method.

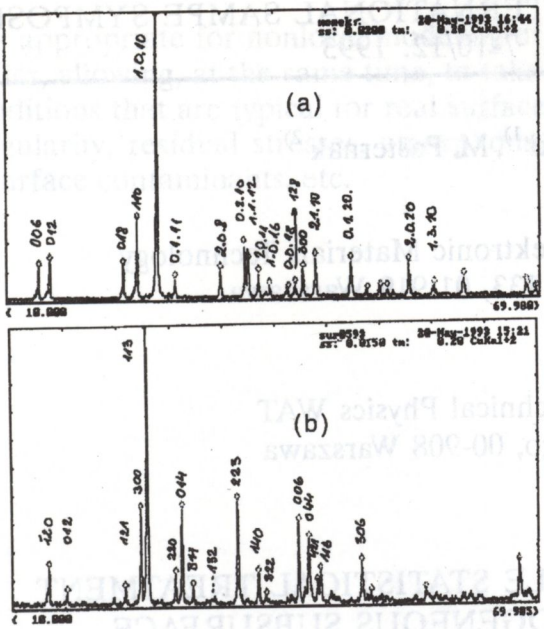

Fig.4
Diffraction patterns: (a) for α-phase, (b) for ß-phase .

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Materiał zaprezentowano na sesji referatów.
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AN ADAPTABLE STATISTICAL TREATMENT OF NONHOMOGENEOUS SUBSURFACE LAYER AS AN EFFECTIVE SUPPORT FOR HIGH FREQUENCY SAW

The topic of the paper is concerned with using high frequency surface acoustic waves (SAW) for nondestructive investigation of systems of distortion centres situated in the subsurface layer of substrate material. The considerations are focussed on a practically important case, when the layer undergoes a modification produced by in - diffused paraelastic impurities for the purpose of obtaining an effective SAW substrate of controllable parameters. The method involves analytical treatment of the lattice distortion as effected by impurities of the kind randomly distributed within the layer.

The treatment, formulated in terms of surface fluctuation waves is shown to be well adapted for interpreting data provided by sufficiently wide-band SAW NDE inspection, especially in the version with incorporated a WKB-type approach. The resulting analytical model scheme is flexible enough to accomodate a variety of physical situations, including

quasi-2D centres appropriate for nonlocal modeling of material subsurface characteristics, allowing, at the same time, to take into account the influence of conditions that are typical for real surfaces, involving their geometrical irregularity, residual stresses, amorphous nonhomogenous damage layers, surface contaminants, etc.

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Pełny tekst opublikowany będzie w materiałach konferencyjnych.