A study of the growth kinetics and inclusions of beta -BaB$_2$O$_4$ crystals

LETTER TO THE EDITOR

A study of the growth kinetics and inclusions of β-BaB$_2$O$_4$ crystals

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**Abstract.** Single crystals of beta barium borate (β-BaB$_2$O$_4$ or BBO), an important new non-linear optical material, were grown by the flux method. Since the β-phase is the low-temperature phase, these crystals were grown using Na$_2$O solution to avoid the α–β phase transformation encountered when crystals are grown directly from the melt. The grown crystals were studied using scanning electron microscopy and the results are reported.

It is known that barium borate exists in two modifications, i.e. a high-temperature phase (α-BaB$_2$O$_4$) and a low-temperature phase (β-BaB$_2$O$_4$) [1]. The low-temperature form, β-BaB$_2$O$_4$, is a non-linear optical crystal which has been shown to be useful for harmonic generation in laser systems. Its important properties include phase matching from 410–3500 nm, optical transparency above 200 nm, large damage threshold and more efficient second-harmonic generation than potassium dihydrogen phosphate [2]. Fifth-harmonic generation of Nd:YAG laser light has been reported for β-BaB$_2$O$_4$ [3].

Barium borate melts congruently at 1095 °C, but the solid which crystallizes just below this temperature (the α-form) is a centro-symmetric crystal that does not exhibit non-linear optical properties [4]. This high-temperature form is an $R\bar{3}c$ structure [5] with $a = b = 0.7235$ nm and $c = 3.9192$ nm. The low-temperature β-form existing below a transition temperature of about 925 °C is a trigonal crystal determined by Liebertz and Stahr [6] to be an $R3c$ structure with $a = b = 1.2529$ nm and $c = 1.2731$ nm and six formula units per hexagonal cell. This structure has been confirmed by Frohlich [7] and Eimerl *et al* [8].

In this paper we report the experiments carried out in our laboratory in the growth and characterization of β-BaB$_2$O$_4$ crystals using different crucible materials. Striations in the grown crystals of β-BaB$_2$O$_4$ have been reported for the first time are and related to the temperature oscillations within the melt.

The experiments were carried out with Aldrich chemicals (BaCO$_3$, B$_2$O$_3$ and Na$_2$CO$_3$ of purity 99.9%) in the cylindrical muffle furnace fabricated by us. A programmable Eurotherm Controller (model 818P, UK) has been coupled to the furnace. The starting materials were prepared by the following solid state reactions:

$$BaCO_3 + B_2O_3 \rightarrow BaB_2O_4 + CO_2$$

$$BaB_2O_4 + Na_2CO_3 \rightarrow BaB_2O_4 \cdot Na_2O + CO_2.$$
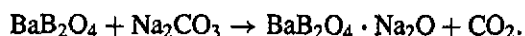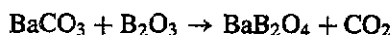
Stoichiometric amounts of BaCO$_3$ and B$_2$O$_3$ were weighed, mixed thoroughly and put into the platinum crucible. The charged crucible was placed into the furnace and was heated to 1200 °C at a rate of 100 °C h^{-1}. The crucible was kept at this temperature for 30 h

to let the solution melt completely and mix homogeneously. Then the melt was cooled to room temperature at a rate of 100 °C h^{-1}. The same procedure was repeated to synthesize the flux $BaB_2O_4 \cdot Na_2O$ from BaB_2O_4 and Na_2CO_3.

It can be seen from the binary phase diagram of BaB_2O_4–Na_2O [1], that β-BaB_2O_4 can be grown using 22–30 at.% Na_2O solution. In our growth experiments, 22 at.% Na_2O has been used as flux and a slow cooling process was adopted. The starting materials for this composition were weighed, mixed thoroughly and put into the platinum crucible. The charged crucible was placed into the furnace and was heated to 920 °C at a rate of 60 °C h^{-1}. After a soaking period of 10 h, the temperature was first decreased at a rate of 1 °C h^{-1} to 755 °C and then at a rate of 60 °C h^{-1} to room temperature. During growth the furnace was completely closed to the surrounding atmosphere. By this process needles of length 5–6 mm and platelets of size 7 × 5 mm were obtained.

Owing to the central vertical temperature distribution, the temperature at the crucible base is higher than at the melt surface, so spontaneous crystallization takes place first at the melt surface, or at the point where the melt surface meets the crucible wall. With the help of a focused light beam, initially fine crystallites were observed at the side wall of the platinum crucible. They grew into needles as the temperature decreased and crystallites were also observed in the melt surface. The crystallites which developed in the surface of the melt grew into platelets. Further, it was observed that the needles grew at a faster rate than the platelets.

When examined using SEM, striations were found in the needle crystals. A higher degree of entrapment of impurity (flux) occur during this needle growth, forming the bands (figure 1), when compared to the entrapment of impurities in the platelet crystal (figure 2).

Figure 1. SEM photograph showing the bands observed in an as-grown needle crystal. Bands are formed due to temperature oscillations within the melt. See text for discussion.

Generally, in a fluxed melt which does not contain seed crystals, nucleation occurs at relatively high supersaturation values. The initial growth is rapid and exhibits a dendritic character with tree-like formations spreading along the fast growth directions. The rapid dendritic growth which follows nucleation is invariably accompanied by a very high concentration of inclusions [9]. It has already been proved that the growth kinetics of a needle crystal have much in common with the dendrite tip and differ only by not producing side branches [10, 11]. On this basis, the observed needle growth can be understood.
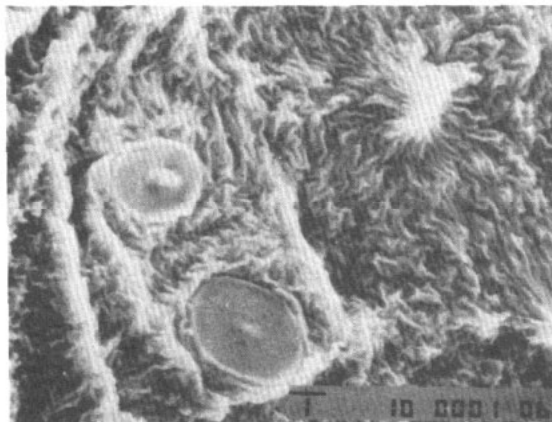
Figure 2. SEM photograph taken on the surface of an as-grown plate-like crystal reveals a void space and core area. Voids are formed due to the evolution of CO_2 gas which may be incorporated into the crystal during growth. The core area is due to the entrapment of the solvent phase.

The higher growth rate of needles can be explained as follows: due to the radial temperature gradient, the temperature near the wall of the platinum crucible is higher than that at the centre and consequently the supersaturation will be higher at the centre than near the wall of the crucible. As growth proceeds from the side wall of the crucible, the growth interface of the needle advances to the central region of the crucible, as observed. Since the latent heat of solidification can readily be transferred from the growth interface to the cooler surrounding liquid, growth of needles takes place at a faster rate. Needles were grown on the wall of the platinum crucible presumably at sites which favoured nucleation because of surface roughness. Nucleation in flux growth is usually heterogeneous, since it tends to occur at undissolved particles or on the surface of the platinum container. Hence the formation of crystallites at the surface of the melt may be due to the nucleation at undissolved particles present in the surface of the melt.

The higher growth rate of needles and the lower growth rate of platelets can be explained using the works of Liebertz [12]. The decisive factors are nucleation rate and growth velocity which are dependent on the supersaturation. Figure 3 demonstrates the principal behaviour of both these quantities in a viscous melt under spontaneous nucleation conditions. Borates will serve as typical examples for substances forming glassy melts due to their higher viscosity. It is reported that 80 at.% BaB_2O_4–20 at.% Na_2O solution viscosities rise rapidly from 300 cP at 925 °C as the solutions are cooled [13].

The original figure of Liebertz has been modified to suit the present case. Nucleation demands a certain degree of supersaturation. Therefore the curves of growth rate and nucleation rate start simultaneously below the melting temperature (T_m). Initially, the growth rate and the nucleation rate increase with increasing supersaturation. At higher supersaturation the nucleation rate and growth rate decrease due the rapidly increasing viscosity which reduces the atomic mobility in the melt. Glass-forming melts exhibit low maxima, because the viscosity is exceptionally high even at the melting point.

In the case of β-BaB_2O_4, nucleation initially starts on the wall of the platinum crucible. According to figure 3, this should be in the rising half of the nucleation curve. Since the growth rate in the rising half also corresponds to the nucleation curve, a higher growth rate
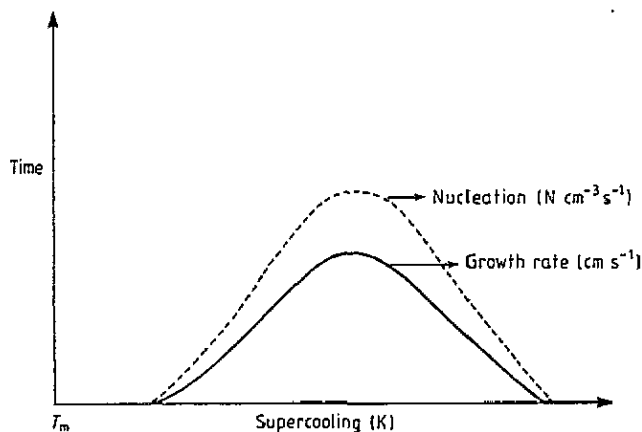
Figure 3. Principal behaviour of nucleation rate (N cm^{-3} s^{-1}) and growth rate (cm s^{-1}) in a highly viscous melt under spontaneous nucleation conditions. T^*—the temperature at which first nucleation is observed.

is favoured, which leads to the formation of needles. Nucleation in the surface of the melt occurs at a later stage (after the formation of needles), which may correspond to the falling half-cycle of the nucleation curve, and the growth rate should decrease as evidenced by the platelets of thickness 1–2 mm.

The formation of platelets can be explained on the basis of considering Ba^{3+} and $(B_3O_6)^{3-}$ as growth units. β-BaB$_2$O$_4$ has a layered structure, with layers made up of Ba^{3+} and $(B_2O_6)^{3-}$ rings which are nearly planar. The average distance between rings is 3.18 Å. This structure can easily account for the strong growth rate anisotropy (of platelet crystals) assuming $(B_3O_6)^{3-}$ as a growth unit. The dimensional increase along the a- or b-axis directions will be 4–5 times that along the c-axis when one $(B_3O_6)^{3-}$ has been added. Therefore, the c-axis was expected to be the slow growth direction, as observed, and this leads to the formation of platelets.

Bands (striations) parallel to the crystal faces usually represent compositional changes either in the major components of the crystal, or in amounts of impurity incorporated and are due to regular variations in the growth rate [14]. In studies on the growth of single garnet crystals, the characteristic imperfections in flux-grown YIG have been discussed by Lefever *et al* [15]. They observed that the impurity banding appeared to be the result of finely divided opaque materials. The periodicity of the banding in In$_2$O$_3$ was correlated with furnace temperature variations [16].

Timofeeva *et al* [17] observed banding in Y$_3$Al$_5$O$_{12}$. The origin of the striations has not been clearly established, although the examples quoted by Chase and Wilcox [16] were found to be due to imperfect furnace temperature regulation, leading to regular fluctuations. It is unlikely, however, that striations are invariably associated with imperfect temperature control since the period associated with the striations of Giess *et al* [18], about 30 min, does not correspond to any interval which might be expected to result from poor temperature control. In growth from the pure melt, striations have been clearly correlated with temperature oscillations due to convection within the melt [19, 20]. In solutions, convection may occur due to gradients either in temperature or in the solute concentration. The onset of stable or unstable convection may be described in terms of the Rayleigh number R and of a solute Rayleigh number R_s defined by

$$R_s = \left(\frac{g\beta L^3}{\psi_s \nu} \right) \Delta n$$

where β is the rate of change of density with concentration, L the length, ψ_s the solute diffusivity and Δ_n the solute concentration difference across the solution [9]. The solute diffusivity in the BaB_2O_4–Na_2O system is very low due to the very high viscosity of the melt. Since ψ_s is very much lower, R_s will be very high. R_s is a measure of free convection; a higher value implies temperature oscillations occur more readily in solutions than in pure melts. Further, the bands observed in β-BaB_2O_4 are not in correlation with the temperature of the furnace, since the temperature is decreased at a rate of 1 °C h^{-1}. Hence the formation of banding in β-BaB_2O_4 can be attributed to the temperature oscillations within the solution.

Figure 2 is the SEM photograph taken on the surface of the as-grown plate-like crystal and shows the presence of a flux inclusion. The inclusion was found to consist of a partial void space and core area. The major constituent of the core area is believed to be rich in sodium [21].

At present, the exact mechanism for the formation of solvent inclusions and voids is not known with any certainty. Possibilities include thermal fluctuation, insoluble particles in the melts, poisoning of the growth interface by impurities, evolution of dissolved gas at the growth interface etc. Feigelson and co-workers [13] suggest that more than one mechanism may exist in a fluxed melt.

In the case of β-BaB_2O_4, the presence of voids may be due to the evolution of undissolved CO_2 gas which may be incorporated in the crystals during growth. Since $BaCO_3$ and Na_2CO_3 were used as the starting materials the presence of CO_2 gas may be attributed to the trace amount of unreacted starting materials present in the melt. The flux inclusion is caused by small amounts of entrapped solvent phase. Similar trapping of inclusions has also been observed by Cheng *et al* [22].

In conclusion, β-BaB_2O_4 crystals have been grown using 22 at.% Na_2O as flux. A slow cooling method has been adopted to achieve supersaturation and thus growth of crystals. Striations have been observed in the grown needle crystals and are attributed to the temperature oscillations within the solution.

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