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RESEARCH NOTE
SRL-0116-RN

TECHNIQUES FOR THE FLUX GROWTH OF OPTICAL MATERIALS
(GROWTH OF BETA-BARIUM BORATE)

by

Janet B. Bedson, Robert W. Lawrence and Philip J. Picone

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SUMMARY

This report describes the method of flux growth of non-linear optical single crystals and the techniques required to determine the flux choice. This is illustrated by the crystal growth of beta barium borate. These techniques are applicable to other optical materials

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1. INTRODUCTION

The purpose of this report is to describe high temperature solution crystal growth techniques as applied to laser and non-linear optical materials. Many crystals used in laser applications and non-linear optics are commonly grown by the Czochralski technique [1]. With this technique large crystals are pulled directly from a congruent melt. These melts have the same composition as the growing crystal and thus the crystallisation temperature remains constant. However some crystals cannot be grown from congruent melts and it is necessary to use a solvent (called a flux) to grow these materials. In these situations the liquid comprising the flux (or solvent) and the composition from which the crystal will form is best referred to as a solution rather than a melt. The solvent is a compound which is a liquid (at the temperatures used) that dissolves the crystal to be grown. Fluxes are selected so that they do not contaminate the growing crystal. Considerable work is required to determine the most favourable flux. The crystal growth technique used is Top Seeded Solution Growth (TSSG), or a similar technique called High Temperature Solution growth (HTS) [2].

In this report, the flux growth of single crystals will be described, followed by a discussion on the crystal growth technique. The growth of beta-barium borate, flux selection, and phase diagram determination for this system will be described as an example of the technique.

2. FLUX GROWTH

In order to grow a crystal, the physical and chemical properties of the crystal and melt must be considered. Melt solutions comprise the chemical composition of the crystal to be grown with the addition of a flux which effectively dissolves the crystal at high temperatures. Lowering the temperature enables the crystal to nucleate in the solution, and then grow larger as the temperature decreases. In the flux growth techniques (TSSG and HTS) an attempt is made to control this process to produce high quality crystals. The variables under some control are:

1. The flux composition which affects the liquidus temperature, viscosity, growth range, and crystal yield.
2. The cooling rate which determines the growth rate which has a large bearing on the crystal quality.

When growing a crystal from a melt many different fluxes can be investigated. Each flux has different ranges of compositions and temperature over which growth is possible, and for which different growth morphology and melt characteristics occur for growing a particular crystal. Thus for each flux, a phase diagram is required which is a representation of all the possible phases of the compounds produced. A number of situations in which it is necessary to use flux growth will be described. This will be followed by a consideration of aspects of flux selection and a discussion on Differential Thermal Analysis (DTA).

2.1 High Temperature Phase

This situation is one in which the required material melts congruently, but at temperatures too high to be produced by the available furnace, or too high for the existence of a suitable crucible to contain the melt. Addition of a flux allows the required crystal to grow at a lower liquidus temperature because the melting point of the mixture is lower than that of the pure compound. This situation is represented by an ideal phase diagram using a simple eutectic system as an example (Figure 1). Crystals of A can be grown if the maximum temperature T_a can be obtained. If a lower growth temperature is required the addition of material B can make a mixture with a lower melting point. In this situation material B can be considered to be a flux. For example, at composition X the liquidus temperature is T_x where it is well below the melting point of phase A. As the solution is cooled, crystal phase A grows at the expense of the liquid phase, in which A becomes diluted with respect to B. As the liquid reaches the eutectic temperature T_e the remaining liquid solidifies to produce a eutectic mixture of A and B. The crystal growth must be halted before T_e is reached in order to remove the crystal before the remaining liquid completely solidifies. A characteristic of TSSG or HTS is that the crystallisation temperature varies as the crystal is grown. Similarly if crystals of B were required and temperature T_b was too high, A could be used as a flux.

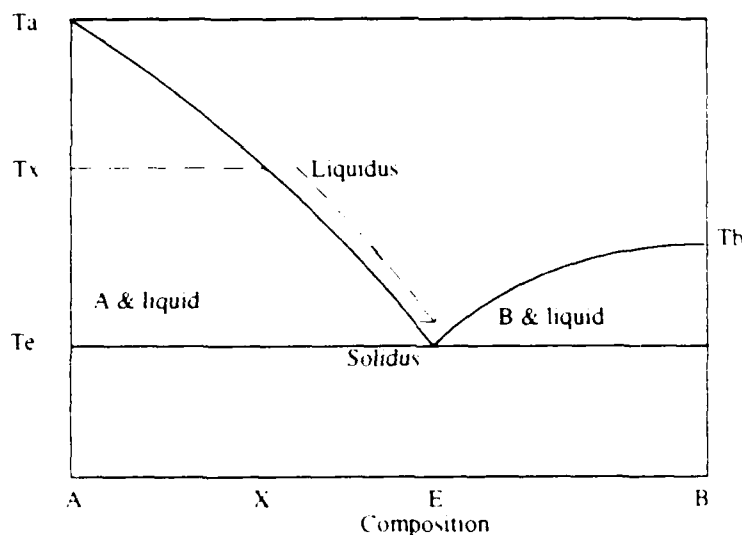


Figure 1. Ideal phase diagram of a simple eutectic system.

2.2 Phase Change

The second situation is that of a low temperature solid phase crystal structure (β) which transforms to the high temperature solid phase (α) at temperature T_x as shown in Figure 2. To enable the crystal growth of the low temperature phase, a flux (material B) can be used to reduce the liquidus temperature as the mixture has a lower melting point. This situation is similar to that of the high temperature growth discussed above, however in this case the flux is used to lower the liquidus temperature below the phase transition temperature (T_x). The low temperature phase (β) may be grown from liquid ranging in composition between X and E. At compositions between A and X, the high temperature phase (α) crystallises, while between E and B, compound B would crystallise.

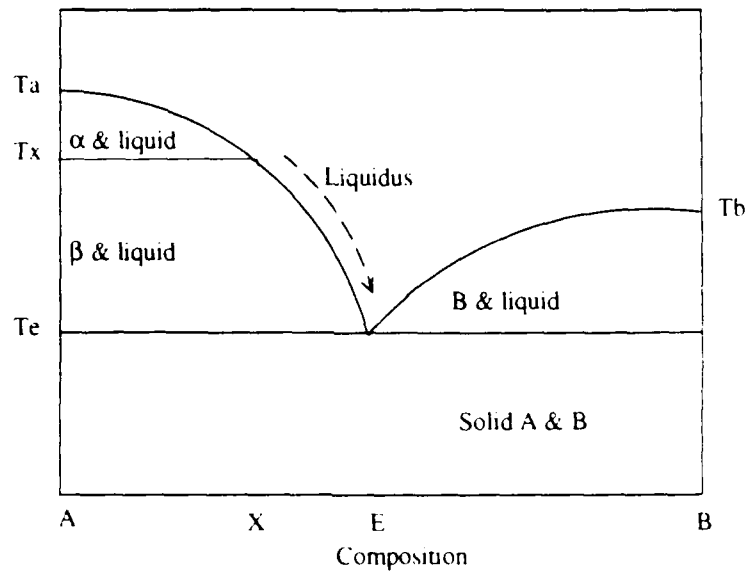


Figure 2. Idealised phase diagram showing the part of the liquidus (dashed arrow) over which the low temperature phase (β) may be grown.

2.3 Incongruent Melting

The third case is one in which the material of interest melts incongruently. The crystalline phase decomposes above the peritectic temperature, T_p , to form a second crystalline phase and a liquid (Figure 3). Addition of flux B enables a crystal of phase C to grow below the peritectic temperature T_p . Again the crystal can be grown to just above the eutectic temperature, T_e .

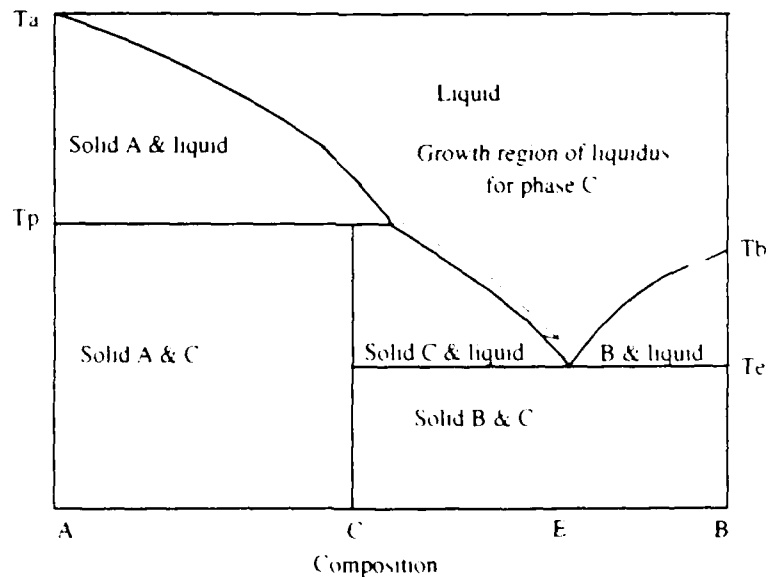


Figure 3. Idealised phase diagram showing the liquidus between the peritectic (T_p) and eutectic (T_e) temperatures over which phase C may be grown (dashed arrows).

2.4 Flux selection

Selection of a flux is difficult due to a variety of possible flux compositions, and the limited data on phase equilibria at high temperatures. In some situations the flux consists of a number of components, and phase relationships are generally not known. A flux needs to be a good solvent for the material of interest, and trial and error is often used with many flux compositions in finally selecting a suitable flux. Existing phase diagrams are used as a guide in the choice of fluxes to be tested. From these trials a phase diagram can be determined or its general properties estimated. If a phase diagram exists, the crystal yield can be calculated and values of crystal yields compared; the best flux will hopefully give the largest crystal yield. Further problems arise if the flux has a low viscosity. This results in melts becoming inhomogeneous, especially next to the growing surface of the crystal. To replenish nutrients at this surface it may be necessary to have a mixing process, in addition to diffusion of ions. This may be accomplished by causing convection currents within a high thermal gradient or using some form of mechanical agitation. Commonly the crystal is rotated during growth in order to establish uniform growth, but if the liquid is too viscous seeds may have a tendency to break off. It is also advantageous to use a flux which is non-volatile, to avoid evaporation and composition change when using an open crucible. Further the vapour could be hazardous or cause deterioration in the adjacent equipment.

General guidelines may be used to aid flux selection, and some of these are discussed below.

1. A preferred flux may be selected to have an ion in common with the composition of the crystal. This procedure reduces the possibility of lattice substitution of stable compounds.
2. If a flux has ions that are not in common with the crystal, then these ions may produce unwanted substitutional or interstitial impurities. In these cases the flux ions and crystal ions generally need to have a greatly different sizes, different valence states or different preferred coordination numbers, in order to prevent lattice substitution of impurities.
3. The flux should have a low melting point and be a good solvent.
4. The flux needs to have a low viscosity and have low volatility.

In general a flux often is a eutectic composition, particularly in a multi-component solution, which forms a stable solid phase. The eutectic composition also forms with a low melting point which may assist in the solubility of the crystal phase.

2.5 Differential Thermal Analysis

In practice many fluxes need to be investigated to find suitable ranges of temperature and composition in growing crystals of specified compositions. A phase diagram indicates a continuous range of crystal compositions and corresponding temperatures at which these compositions are produced. One method of determining a phase diagram is by using Differential Thermal Analysis (DTA) [3,4] coupled with x-ray analysis. In DTA, two thermocouples are used to measure the temperature difference between a sample

and a reference while the temperature is being scanned. Reactions and phase changes in the sample can be determined by monitoring this temperature difference. X-ray diffraction is used to determine the crystalline phases and relative amounts of constituents that result after the reactions. The DTA technique is fast and accurate in determining the temperatures of exothermic and endothermic reactions of the crystal and flux mixtures, thus allowing rapid and accurate determination of the temperature at which a phase change occurs. The main equipment consists of a small furnace, and two crucible supports which contain thermocouples (Figure 4). Heating elements produce a uniform temperature zone by being arranged cylindrically around the crucibles which are close together.

DTA involves measuring the difference in temperature between a small sample of the material of interest and a reference material in a uniform temperature zone while heat is being added at a constant rate so that the temperature is varied systematically. Sample size is optimised to maintain a uniform temperature, maximise the temperature response at a phase change and maintain a homogeneous mixture. Heating causes an increase or decrease in the temperature of the sample, when respectively an exothermic or endothermic reaction occurs. The heating rate is generally quite high (20 - 50 °C/min) to maximise any thermal difference that results. Each sample is sintered (ie formed at a temperature below its melting point) and x-rayed to confirm that the sample is a stable known composition and a single phase. The reference material is generally inert, but in some cases may have a phase change at a known temperature which is used in accurate temperature calibration. Alternatively standards such as pure gold or silver are used in the sample crucible. With the combination of data from x-ray analysis and the measurement of temperatures at which the reactions occur, a phase diagram may be drawn or inferred. Problems were identified with the DTA equipment and these are discussed in Appendix I(b).

Figure 5 is an example of a phase diagram which illustrates the DTA technique. Figure 6 illustrates the temperature changes which occur at specified temperatures and compositions indicated in Figure 5, which is the phase diagram of barium borate (BaB_2O_4 or BBO) and sodium barium borate ($\text{Na}_2\text{BaB}_2\text{O}_6$ or NBBO). Samples X1, X2 and X3 represent compositions of possible combinations of BBO and NBBO. A thermal analysis experiment for sample X1 would indicate exothermic (or endothermic) reactions at the eutectic temperature (T_e) where the sample begins to melt, at the $\alpha - \beta$ transition temperature (T_t) when the phase transition occurs, and at the liquidus-solidus temperature (point C) when the sample completely melts. The analysis for sample X2 has two reaction peaks, indicating a liquidus-solidus temperature (T_l) and the same eutectic temperature (T_e). Only a single large peak would be observed for sample X3 at the eutectic temperature. The size of the exothermic (or endothermic) reaction peaks is an indication of the relative amounts of a particular phase or the energetics of the transition. Thus the eutectic transition would have the largest peak for sample X3 as this is the eutectic composition, and progressively reduce in size and disappear at the end member (pure BBO or NBBO). The $\alpha - \beta$ transition will only be observed if the liquidus temperature is greater than T_t .

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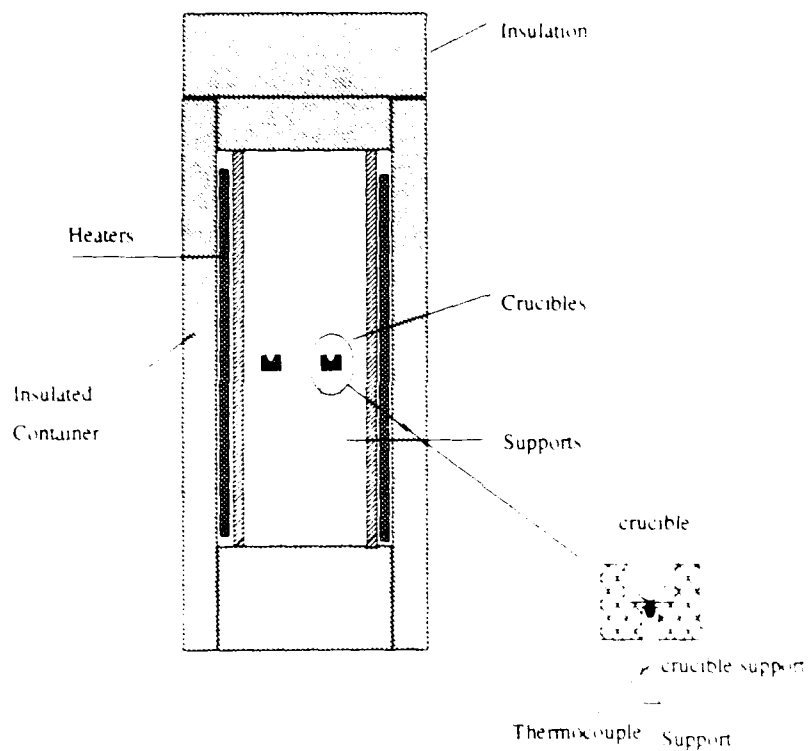
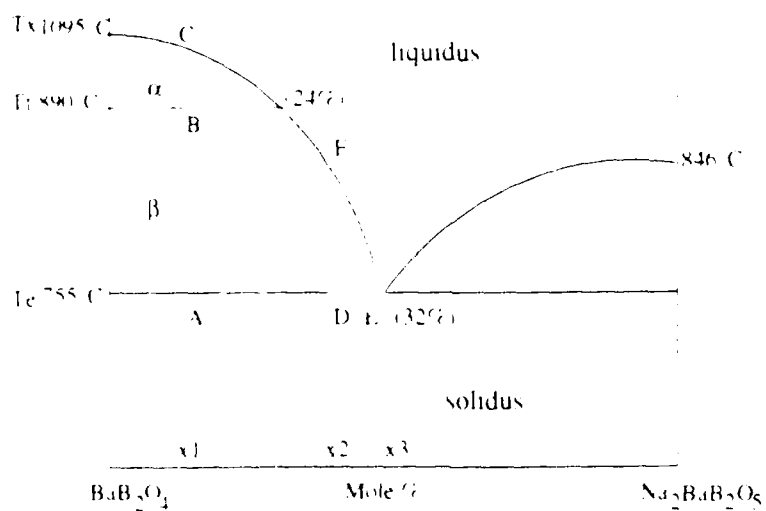


Figure 4. Differential Thermal Analysis Furnace.

Figure 5. Phase diagram of BaB_2O_4 - $\text{Na}_2\text{BaB}_2\text{O}_5$.

In summary, temperature differences between the sample and reference material would be observed at the eutectic temperature T_e for each composition (points A, D and E) and at the solidus and liquidus temperatures (points C and F for compositions X1 and X2 respectively). Further, a small temperature difference may occur at the α - β transition temperature T_t (point B) for sample X1.

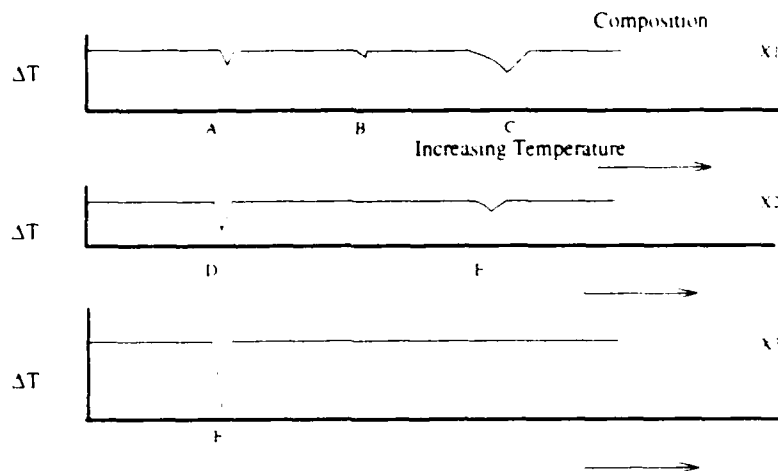


Figure 6. Graphical representation of data from DTA.

An example of the data obtained is given in Figure 7 which is a sample from the BBO - NBBO phase diagram at a composition of 24% NBBO, that is around the α - β transition at the liquidus. Delta temperature is the temperature difference between the reference and sample as a function of the reference temperature. The curve shows the eutectic temperature and a broad change of slope at the liquidus. The α - β transition may not be observed since its associated temperature change occurs over a comparatively small range of temperature which overlaps with the melting point. The rather broad change of slope in Figure 7 indicates that the liquidus and transition are probable occurring together. This could occur if the sample composition, nominally 24% NBBO, was such that the phase transition and the liquidus-solidus transition occurred at temperatures which were very close to each other. Alternatively the phase diagram may be slightly incorrect.

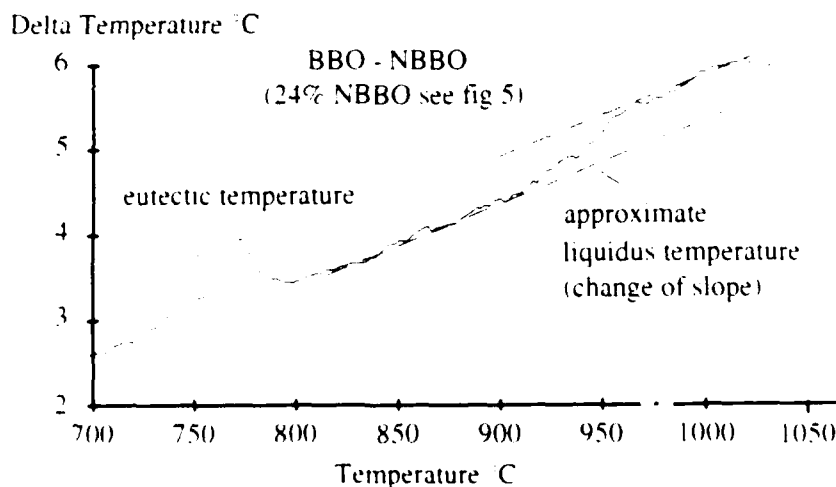


Figure 7. BBO - NBBO DTA data.

3. TOP SEEDED SOLUTION GROWTH

Top seeded solution growth (TSSG) is a general name for growing a crystal from a seed which has been lowered into a molten solution containing the crystal material. In general there is a very small thermal gradient normal to the melt surface, but crystal growth occurs virtually at thermal equilibrium with the melt. Growth on the seed crystal is achieved by slowly cooling the melt, in which case the crystallisation temperature varies with time.

3.1 TSSG Furnace

The TSSG furnace is approximately cylindrical in shape, and has resistive heated silicon carbide rod elements parallel to its axis (Figure 8). It is designed to have a uniform radial temperature profile. The silicon carbide elements have an operating temperature to 1500 °C and are arranged to be equidistant from the furnace axis. Concentric with the elements is an alumina pedestal on which the crucible is placed. Crucibles are usually made of thin-walled platinum or platinum/rhodium with a size range up to 50mm diameter and 70 mm deep. A vertical temperature gradient ensures that the melt surface is slightly cooler than the melt interior. The temperature gradient is also used to promote convective stirring within the melt as the bottom of the crucible is generally hotter and hot liquid will rise. When it reaches the top, the liquid cools, then sinks to the bottom. The resulting circulating stirring pattern homogenises the melt. If the surface of the melt is slightly cooler than the interior, nucleation and growth will occur at this surface. The circular heating elements and a hole in the top of the furnace are used to form the vertical temperature gradient. The hole size could be changed to vary this with a small hole resulting in an isothermal environment with very little stirring. A cooler spot to initiate growth is then achieved by using an air cooled seed rod to reduce the temperature of the seed crystal. The crucible is viewed through the hole in the top of the furnace in conjunction with a light source. A computerised lift and rotation seed rod is also placed through the hole. Temperature control of the crucible and the elements is continuously monitored by a computer which also controls the rate of cooling when growing a crystal.

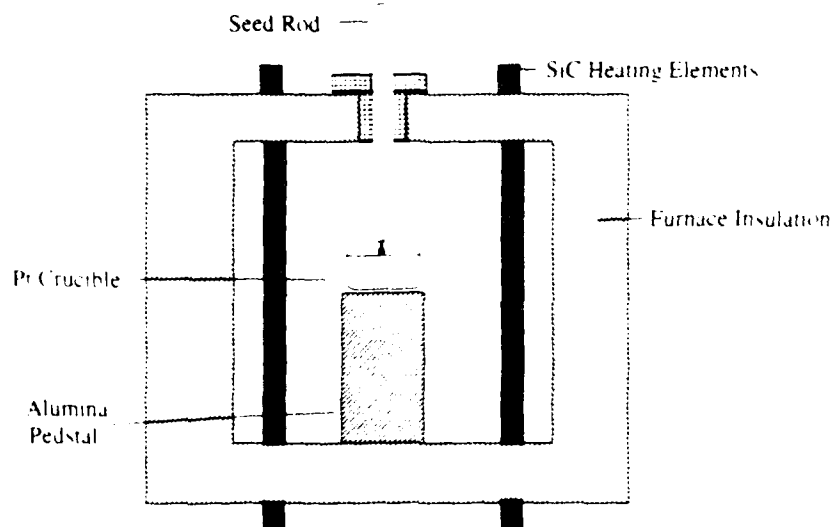


Figure 8. Schematic diagram of crystal growth furnace.

3.2 Crystal Growth

To initiate growth, the liquidus temperature of the melt must first be determined as this is the starting temperature for growth. As the melt is close to iso-thermal and there is minimal seed cooling, the correct liquidus temperature is required otherwise the seed will rapidly melt if the temperature is too high or there would be rapid growth if the temperature is too low. Rapid growth which should be avoided generally leads to poor crystal quality because of void formation and flux trapping. The occurrence of liquidus is determined by dropping a small piece of crystal into the solution. The solution is allowed to reach equilibrium over 24 hours, while the fragment is monitored for growth. If the fragment does not change size the small piece of crystal is in equilibrium with the melt and the liquidus has been found. The temperature is then increased slightly, typically 1 - 2 °C, to melt the small fragment, and the melt allowed to stabilise at this temperature.

Next a seed crystal is tied very securely to the alumina or platinum seed rod with some fine platinum wire (Figure 9) and attached to the furnaces lift and rotation stepper motors. The seed crystal is then lowered until the seed just breaks the surface of the solution, where a small amount will dissolve. A constant temperature is maintained for approximately 12 hours allowing thermal equilibrium to be established. Cooling of the solution then commences at very low rates (typically .01 - 0.05 °/hr). The seed is usually rotated very slowly to keep the layer around the seed homogenous which facilitates a uniform growth rate. The size of the crystal is monitored by observing through the top of the furnace with a light source directed at the seed. To increase its thickness, the crystal may be lifted at approximately 0.1 mm/hr while the crystal is allowed grow to the required dimension. Once the crystal has reached its required size or has been restricted by the cooling or crucible size, it is raised just above the melt. The crystal is then cooled slowly to minimise any thermal strain.

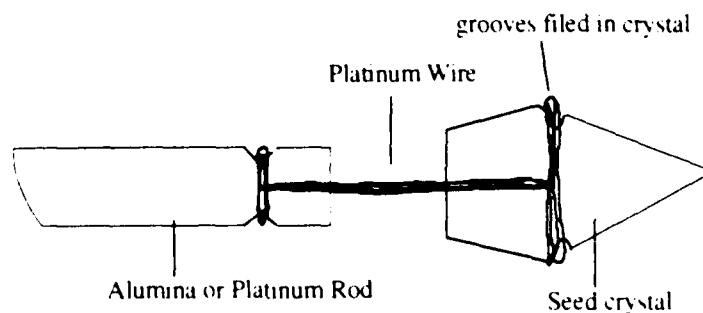


Figure 9. Seed crystal attached to seed rod.

3.3. Crystal growth of Beta-Barium Borate.

The crystal growth process is illustrated by the flux growth of beta Barium borate (B-BBO). Barium borate has a high temperature phase (α) with a melting point of around $1095 \pm 3^\circ\text{C}$ [5]. This phase transforms to the beta phase with a reported transition temperature between 890 and 925°C [5]. Thus in general B-BBO cannot be grown directly from a stoichiometric melt and a flux must be added to reduce

the liquidus by around 200°C. Recently the Czochralski growth of β -BBO from congruent melts [6] has been reported. Very large thermal gradients had to be applied with this method to produce large undercoolings to get the crystallisation temperature below the α - β transition temperature. Undercooling, or supercooling, occurs when a liquid is cooled below its freezing point. Very careful materials preparation and melt conditioning were required to allow the β phase to grow and prevent the transition to the α phase. This process may occur for BBO if the α - β transition is sluggish which has been reported [5]. Small fibres of BBO have also been grown with the Laser Heated Pedestal Growth technique [7]. Here a solvent was required to reduce the melting point below the transition temperature.

With the flux growth method, excess B_2O_3 reduces the melting point, but such melts are viscous and crystal growth is difficult to obtain. Sodium Oxide (Na_2O) reduces the melting point as seen from the phase diagram of BBO - $Na_2BaB_2O_5$ (NBBO) in Figure 5. Crystals of β -BBO can be grown from a composition of at least 24 mole % NBBO. However the range of composition over which crystals will grow is quite small, and only a small volume of crystal would result from a given melt volume. A study of the more complete system may indicate a composition that would allow a larger volume of the melt to crystallise as β -BBO. The phase diagram (Figure 5) of BBO - NBBO is only a partial diagram of a three component system as shown in Figure 10 where BaO, Na_2O and B_2O_3 are the three components of the phase diagram.

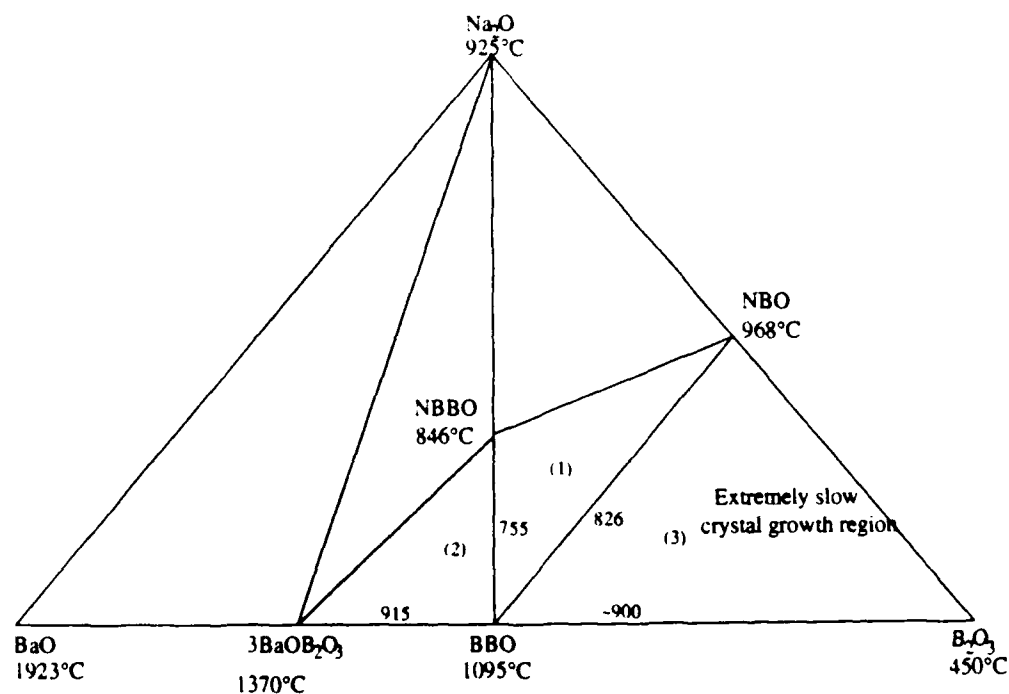


Figure 10. Full Phase diagram of BaO, Na_2O and B_2O_3 .

The temperatures indicated are the melting points of the materials at that point of the phase diagram. Also shown are the eutectic temperatures between BBO and other compounds in the phase diagram.

The region of interest for flux growth of BBO is indicated by the triangle shown as (1) in Figure 10. As the α - β transition temperature is around 925 °C, the lower the final crystallisation temperature (eutectic

temperature) and the larger the composition difference between the start and finish of growth, then the larger a fraction of the melt volume should crystallise. Region (1) encompasses the part of the phase diagram where BBO is most likely to grow from a flux with the lowest final temperature, thus giving a large growth range. Region (2) is also worth considering; however the higher melting point of $\beta\text{BaOB}_2\text{O}_3$ and the high eutectic temperature (915°C) eliminates this region for flux growth of BBO. Region (3) also has a high eutectic temperature ($\sim 900^\circ\text{C}$) and additionally melts rich in borate are generally very viscous, making this region difficult and slow for crystal growth. Generally β - BBO has been grown from a mixture of BBO and NBBO [5,11,12,13] along the phase line indicated and shown in the phase diagram (Figure 5). There has also been a report on growth from NaCl solutions [14].

The phase diagram of region (1), BBO - NBBO - $\text{Na}_2\text{B}_2\text{O}_4$ (NBO), has not been previously determined and was intensively studied by us. The phase diagram in Figure 11 is what is theoretically expected if no new phases form between the compounds. The dotted lines indicate possible eutectic iso-therms. If these should occur then there would exist a large growth range between the α - β transition and the central eutectic point, which should lead to the growth of the largest crystals from a given melt volume.

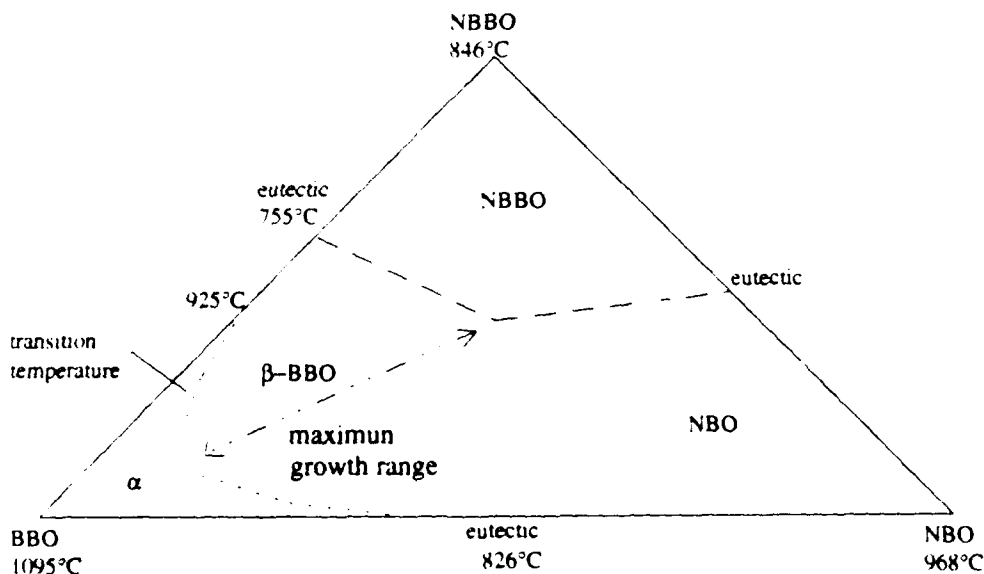


Figure 11. Theoretical Phase diagram of BBO - NBBO - NBO.

Using DTA and x-ray analysis of small melts, typically 1 -2 gm, the phase boundaries and temperatures were determined and the results are shown in schematic form in Figure 12. The x-ray analysis indicates the crystal phases that result when a particular composition is melted and slowly cooled while DTA only indicates phase temperatures. Identification of the crystal phases is required to determine the composition range of a compound in the phase diagram. Figure 12 indicates an unknown high temperature phase which forms above 900°C . Also shown is the approximate α - β transition isotherm. Appendix I(a) gives a summary of the lattice parameters of NBBO, which have not been reported, and a determination of the lattice parameters found for the unknown material. NBBO is needed to be characterised as it is used as one of the starting materials and a major component of the flux. The

presence of the unknown material has the effect of moving the eutectic towards the BBO compound on the ternary diagram. This reduces the composition growth range and there is little advantage to be gained from growing β - BBO within the ternary diagram.

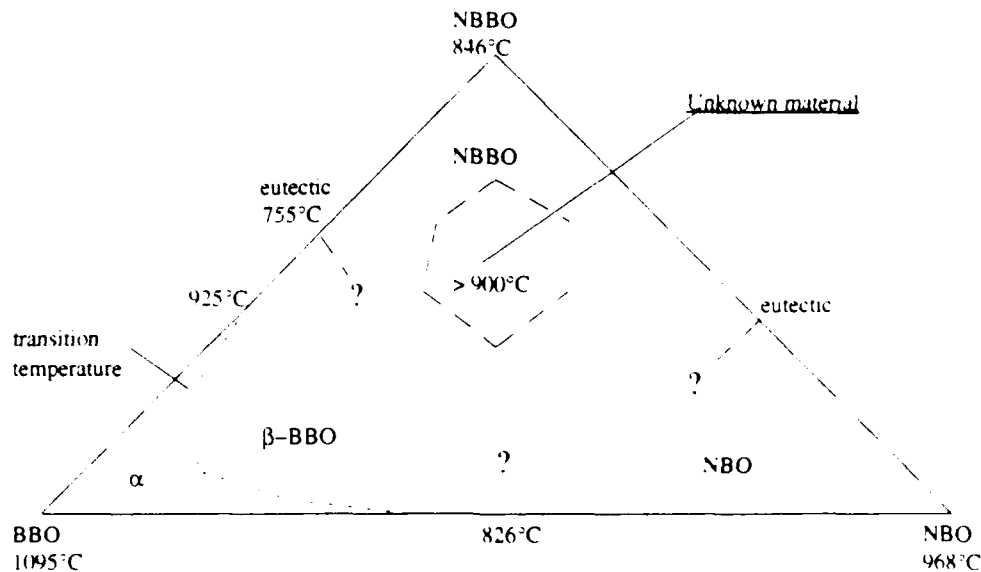


Figure 12. Schematic Phase diagram of BBO - NBBO - NBO.

4. SUMMARY.

The flux growth of crystals is an important technique for obtaining single crystal samples of many optical materials. The technique in itself is quite straight forward, however there are many subtleties that must be understood before high quality crystals can be grown. These subtleties vary for different materials and include flux selection, cooling rate, rotation rate and lift rate. The over-riding problem is flux selection, which is crucial for good quality crystal growth. This problem is generally solved by studying the phase diagram of the flux and crystal combination, and involves considerable trials and experimentation to optimise.

The example used to illustrate the technique, the growth of β -BBO from sodium borate fluxes, shows the importance of the phase diagram in top seeded solution growth. Sodium oxide is known to be a suitable flux with a range of liquidus temperatures less than the 925°C transition between high temperature (α) and low temperature (β) phases of BaB_2O_4 . In an attempt to extend the range of growth, this study was aimed at finding other lower temperature eutectic temperatures within the BaO , Na_2O , B_2O_3 system. It was evident from the known phase relationships that the subsystem BBO, NBBO, NBO provided the best potential.

A study of this system was attempted using a combination of differential thermal analysis, x-ray diffraction and visual observation of test materials in small crucibles with controlled temperature changes. A high temperature phase appeared to be present as indicated by the phase products and

transition temperatures found during the phase diagram study. This coincided with the observation of an unknown phase identified during XRD analysis. An attempt to determine lattice parameters of this material was unsuccessful because of its extreme hygroscopic nature causing the formation of multiple hydrated phases. The occurrence of this unknown phase severely restricts the growth range that can be obtained because of the shifting of the eutectic isotherm towards the α - β transition temperature. Consequently this reduces the composition difference between the phase transition and the eutectic composition. There is therefore very little advantage in using a flux from within this subsystem. Most of these studies were performed with materials having 99.9% or 99.99% purity. Impurities such as Ca within BaCO_3 , may possibly have been responsible for the new phase occurring, but this seems unlikely given the low concentration of impurities.

The crystal structure of $\text{Na}_2\text{O} \cdot \text{BaB}_2\text{O}_4$ (NBBO) was examined by x-ray diffraction. Mixtures of NBBO with substances of known lattice parameters were used for comparison and to calibrate the x-ray data. The results obtained for the two theta values (Appendix I(a)) are generally compatible with those in the literature. The crystal structure was found to be monoclinic as obtained from powder x-ray analysis.

5. ACKNOWLEDGEMENTS

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APPENDIX I(a)

LATTICE PARAMETERS OF NBBO AND UNKNOWN MATERIAL.

(a) Lattice Parameters of NBBO

NBBO is a major component of the BBO - NBBO - NBO system and while a table of 2θ (Bragg angle) vs line intensity has been reported⁸, the lattice parameters or crystal structure are unknown. A detailed knowledge of the lattice parameters (that is unit cell dimensions which define the crystal structure) is required for x-ray analysis and a more complete study of NBBO was undertaken. A large NBBO sample was prepared using BaCO_3 , B_2O_3 and Na_2CO_3 . After thoroughly mixing the chemicals the sample was placed in a platinum crucible and heated in a muffle furnace to 700°C . This is 55°C below the eutectic temperature between BBO and NBBO. The furnace was maintained at this temperature for 60 hours, then cooled to 460°C in 5 hours, and finally cooled rapidly to room temperature. X-ray diffraction showed that the sample was single phase with no evidence of the individual starting chemicals. It was found that NBBO is hygroscopic and would hydrate overnight if care was not taken to ensure that the prepared NBBO was kept in a dry environment.

Powder x-ray data were acquired on a standard x-ray diffractometer with the data electronically stored for latter analysis. Lorentzian line shape profiles were fitted to the data to determine the line position (2θ or d spacing), intensity and line broadening, where θ is the Bragg angle and d the interatomic spacing. The determined lattice spacings and the probable Miller indices, denoted by h , k and l are listed in Table I(a).2 along with the published results

Using the Unit Cell Refinement program of Visser [9], which determines the lattice parameters from x-ray powder patterns and assigns Miller indices, the measured d - spacings give consistent results for a monoclinic structure. This result is obtained with no assumptions about the crystal symmetry. Using the same conditions and the reported d - spacings [8] the results listed in Table I(a).1 are obtained. These data have also been refined using least squares analysis [10].

Table I(a).1. Calculated Lattice Parameters of $\text{Na}_2\text{BaB}_2\text{O}_5$.

Lattice Parameters	a (Å)	b (Å)	c (Å)	α ($^\circ$)	β ($^\circ$)	γ ($^\circ$)
Present data	9.576	5.570	6.190	90	98.88	90
Reference data [8]	9.573	5.565	6.185	90	98.92	90

(b) Lattice Parameters of Unknown Material

As indicated on the phase diagram, Figure 10, an unknown high temperature phase was found. Crystals of this material could be grown from the melt in the region indicated within the dashed lines. The exact composition range and temperatures were not determined. The material was extremely hygroscopic. Although this made analysis difficult, some x-ray data were obtained on freshly prepared samples. A table of 2θ s is shown in Table I(a).4 for one of the samples measured. Attempts to analyse these data with the Unit Cell Refinement program[9] were somewhat inconclusive and lattice parameters could

Table I(a).2. Measured x-ray data of $\text{Na}_2\text{BaB}_2\text{O}_5$.

2θ	I/I_0	d - spacing present data (Å)	d - spacing (reference) (Å)	h,k,l determined from Unit Cell Refinement
18.648	22	4.754	4.798	1 1 0
18.925	12	4.685	4.734	2 0 0
22.066	20	4.025	4.057	2 0 -1
22.777	37	3.901	3.929	1 1 -1
24.607	30	3.615	3.642	1 1 1
25.658	13	3.469	3.490	2 0 1
29.351	100	3.041	3.058	0 0 2
32.366	27	2.764	2.787, 2.773	0 2 0, 2 0 -2
32.756	69	2.732	2.746	3 1 0
33.633	17	2.663	2.676	3 1 -1
36.183	26	2.481	2.493	1 1 2
37.570	22	2.392	2.403	2 2 0
38.452	2	2.339	2.367	4 0 0
38.785	18	2.320	2.331	4 0 -1
39.366	25	2.287	2.296	2 2 -1
41.267	14	2.186	2.196	3 1 -2
41.634	22	2.168	2.176	2 2 1
43.204	7	2.092	2.100	4 0 1
44.105	9	2.052	2.059	0 2 2
44.793	23	2.022	2.027	4 0 -2
45.788	10	1.980	1.987	2 0 -3
46.360	15	1.957	1.964	2 2 -2
47.173	15	1.925	1.932	1 1 -3
47.527	11	1.912	1.918, 1.865	3 1 2
50.183	8	1.817	1.823	2 2 2
51.164	10	1.784	1.789, 1.772	4 2 -1
52.060	5	1.7553	1.759, 1.7445	1 3 -1
52.783	3	1.7329	1.7307	1 3 1
54.855	15	1.6723	1.6764	4 2 1, 4 0 -3
55.650	8	1.6503	1.6549	5 1 1, 5 1 -2
56.223	3	1.6348	1.6394	4 2 -2
57.049	6	1.6131	1.6164	2 2 -3
57.752	9	1.5951	1.5992	3 3 0
58.575	3	1.5746	1.5752	6 0 0

not be determined uniquely. A probable reason for this is the extreme hygroscopic nature of the material. For instance, samples left overnight would liquify causing confusion in interpretation of the x-ray data due to the appearance of a second phase associated with the hydration. However, a most probable structure was indicated. Using the lattice parameters determined in this way, data from four samples was least squares fitted. Of the 44 lines obtained in the investigation, only three weak lines were not indexed in the most probable structure. The results of this analysis are shown in Table I(a).3 and gave fairly consistent results for a monoclinic structure.

Table I(a).3. Calculated Lattice Parameters of Unknown Material.

Lattice Parameters	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
sample 1 (Table 4 data)	11.91	14.14	6.39	90	99.39	90
sample 2	11.96	14.22	6.42	90	99.27	90
sample 3	11.92	14.15	6.40	90	99.39	90
sample 4	11.90	14.15	6.38	90	99.16	90

Table I(a).4. Measured x-ray data of Unknown Material.

$2\theta^\circ$	I/I ₀	$2\theta^\circ$	I/I ₀
14.05	2	56.19	1
16.83	3	57.48	1
18.32	1	58.32	3
24.90	2	59.33	2
25.65	4	60.40	4
28.737	1	60.59	4
29.392	44	62.70	1
33.15	24	64.87	1
34.59	5	66.91	1
35.89	1	68.11	1
36.51	3	69.00	1
38.29	1	70.37	1
40.84	4	75.06	1
42.46	7	77.03	1
44.06	1	78.16	1
45.27	100	78.95	2
45.51	6	80.21	1
49.01	2	82.30	3
50.11	1	84.40	1
51.44	1	86.25	1
52.84	1	90.46	1
55.28	1	92.24	1

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APPENDIX I(b).
PROBLEMS IDENTIFIED.

Problems with the differential thermal analysis equipment were identified as follows and these should be addressed to improve the equipment.

(a) The differential thermal analysis equipment was designed and built in-house, and in particular made use of the Optoelectronics Division unique temperature control software developed for the Czochralski furnaces. On use it was discovered that to be effective the thermocouple wires (Pt/PtRh) needed to be thinner than those used. The wires used were 0.5 mm diameter, whereas 0.2 mm or less would be preferable. The thicker wire made the system less sensitive due to its higher thermal capacity and thermal conductance.

(b) Liquidus temperatures were difficult to determine with the existing equipment. The small sample crucibles were made of folded thin Pt foil. When the sample (which had been reduced in volume by prior melting and quenching) reached its solidus-liquidus temperature, some of the liquid separated from the solid due to its tendency to wet Pt. Thus the sample effectively changed composition during the measurement. An improved crucible design is needed, either to prevent the wetting effect or to enclose the sample totally.

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