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On the Growth of β-BaB_2O_4 (BBO) Single Crystals from High-Temperature Solutions

II. Physicochemical Properties of Barium Borate Solutions and Estimation of the Conditions of Stable Growth of BBO Crystals from Them

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The dynamic viscosity, density, and volumetric expansion coefficient of high-temperature solutions of the BaO–Na_2O–B_2O_3 system for the growth of β-BaB_2O_4 (BBO) single crystals have been determined. The data obtained are used for evaluation of the conditions of stable growth of BBO crystals by the TSSG technique. © 1992 Academic Press, Inc.

Introduction

The single crystals of β-BaB_2O_4 (BBO) are a new nonlinear optical material with an unusual combination of properties (*1–3*). Since BBO is a low-temperature phase, the most appropriate method of preparation of its crystals is the growth from high-temperature solutions, molten Na_2O being usually applied as a solvent (*4–6*). When the top-seeded solution technique (TSSG) without pulling is used, the crystals are found to grow quickly in the radial direction, whereas the growth perpendicular to the solution surface is very slow (*6*). As a result, crystals with the shapes of thin lenses are obtained. Their diameter is 5–10 times larger their thickness. This shape makes the use of the crystals for the production of optical elements inconvenient. In addition, it is established that when the crystal reaches a definite diameter, the smooth crystal/solution interface is disturbed and a large number of crystallites is formed, which evidences disturbance of the growth stability. It can be assumed that, above a certain diameter of the growing crystal, the free convection flow in the solution around the crystal in the direction from the crystal edge to its center is opposed by a counterflow of forced convection due to the rotation (with a constant rate) of the crystal. The interaction between the two convection flows below the crystal leads to a temperature instability and, hence, to disturbance of the growth stability.

In previous studies (*7, 8*), physical simulation of the hydrodynamics has been used to find a relationship between the physical and geometrical parameters of the crucible–melt–crystal system, which allows determination of the conditions under which the forced convection flow completely eliminates the free convection flow in the liquid below the crystal. This relationship is

$$N_{crit} = 3.18(g\beta\Delta t)^{0.44}D^{0.245}h^{0.155}\nu^{0.12}d^{-1.08}, \quad (1)$$

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where N_{crit} is the critical crystal rotation rate (rad/sec) at which the crystal/liquid interface becomes flat and is in contact with a forced convection flow only; D, the crucible diameter (cm); d, the crystal diameter (cm); h, the liquid layer height in the crucible (cm); ν, the kinematic viscosity of the liquid (cm^2/sec); g, the acceleration due to gravity (cm/sec^2); β, the volumetric expansion coefficient of the liquid (1/deg) and Δt, the temperature difference between the crucible wall and the interface (°C).

It was also shown (*9*) that a long time before the crystal rotation rate attains N_{crit}, forced convection instable in space and time arises in the liquid, and the interaction of its flow with the free convection flow leads to the appearance of significant temperature fluctuations at the crystal/liquid interface. Usually this is observed at rotation rates $N \sim 0.5N_{crit}$. Therefore, it should be expected that the disturbance of the stable growth of β-BaB_2O_4 would begin when

$$N \geq 1.59(g\beta\Delta t)^{0.44}D^{0.245}h^{0.155}\nu^{0.12}d^{-1.08}. \tag{2}$$

Obviously, the conditions of unstable growth can be estimated if the geometrical parameters and the temperature difference (which can be preset) are known and there are data on the kinematic viscosity (i.e., on the dynamic viscosity, μ, and the density, ρ) and the volumetric expansion coefficient of the corresponding high-temperature solution. In the literature there are no such data on the solutions used for the growth of BBO single crystals. Only in the paper of Feigelson *et al.* (*6*), an unpublished communication of D.-Y. Tang *et al.* is mentioned, according to which at 925°C a solution of 80 mol% BaB_2O_4 and 20 mol% Na_2O has a dynamic viscosity of about 300 cP.

The dynamic viscosity, density, and volumetric expansion coefficients of some high-temperature BaB_2O_4 solutions are measured in the present paper and, on the basis of the results obtained, it is attempted to estimate the stable regime conditions and their disturbance during the preparation of BBO single crystals.

Experimental

In a previous paper (*10*), the high temperature solvents for the growth of BBO from the BaO–Na_2O–B_2O_3 system have been investigated. It has been shown that the binary solvents with compositions (in molar parts) of $0.75Na_2O$–$0.25BaO$, $0.75Na_2O$–$0.25B_2O_3$, and $0.60Na_2O0.40B_2O_3$ have practically the same widths of concentration and temperature regions of crystallization of β-BaB_2O_4 as the width for the solvent of pure Na_2O used up to now. In addition, the latter two binary solvents containing B_2O_3 have the advantage that from their solutions crystals are grown whose shapes are more suitable for the preparation of optical elements.

In what follows, results from measurements on the dynamic viscosity, density, and volumetric expansion coefficients of solutions of BaB_2O_4 in Na_2O and in the above three binary solvents are presented. Each of the four solvents is used for the preparation of three solutions with a BaB_2O_4 concentration ensuring saturation temperatures of 825, 875, and 925°C. The investigations were carried out with 150–200 g of each solution placed in a platinum crucible with a diameter of 4.5 cm and a height of 5.0 cm. Under these conditions, the solution layer height in the crucible was 2.5–3.0 cm.

The viscosity and density of each of the 12 solutions were determined at three different temperatures: at the corresponding saturation temperature, t_s, at t_s + 25°C and at t_s + 50°C. The measurement of the dynamic viscosity was made by a device establishing the decrease in rotation rate of a platinum cylinder (with a 2-cm diameter and a 2-cm height) due to the resisting force of the solution. The viscometer was calibrated with glycerol–water solutions for ensuring μ val-

TABLE I

VISCOSITY, DENSITY AND VOLUMETRIC EXPANSION COEFFICIENT OF SOLUTIONS FOR THE GROWTH OF BBO SINGLE CRYSTALS

System A–M	C_a = 79.2 mol%, t_s = 925°C			C_a = 75.0 mol%, t_s = 875°C			C_a = 71.8 mol%, t_s = 825°C		
	t_s	$t_s + 25$	$t_s + 50$	t_s	$t_s + 25$	$t_s + 50$	t_s	$t_s + 25$	$t_s + 50$
μ(cP)	103	90	85	172	117	107	243	170	132
ρ(g/cm^3)	3.336	3.330	3.326	3.311	3.309	3.304	3.151	3.145	3.137
$\nu \times 10^2$ (cm^2/sec)	31	27	26	52	35	32	77	54	42
β(1/deg)		6.0×10^{-5}			4.2×10^{-5}			8.9×10^{-5}	
System A–R	C_a = 76.0 mol%, t_s = 925°C			C_a = 71.8 mol%, t_s = 875°C			C_a = 68.8 mol%, t_s = 825°C		
	t_s	$t_s + 25$	$t_s + 50$	t_s	$t_s + 25$	$t_s + 50$	t_s	$t_s + 25$	$t_s + 50$
μ(cP)	121	102	95	153	122	100	212	160	122
ρ(g/cm^3)	3.382	3.378	3.374	3.305	3.301	3.295	3.196	3.188	3.184
$\nu \times 10^2$ (cm^2/sec)	36	30	28	46	37	30	66	50	38
β(1/deg)		4.7×10^{-5}			6.1×10^{-5}			7.5×10^{-5}	
System A–T	C_a = 70.4 mol%, t_s = 925°C			C_a = 66.2 mol%, t_s = 875°C			C_a = 61.8 mol%, t_s = 825°C		
	t_s	$t_s + 25$	$t_s + 50$	t_s	$t_s + 25$	$t_s + 50$	t_s	$t_s + 25$	$t_s + 50$
μ(cP)	120	100	90	128	110	95	142	120	90
ρ(g/cm^3)	3.136	3.132	3.129	2.989	2.984	2.878	2.947	2.945	2.940
$\nu \times 10^2$ (cm^2/sec)	38	32	28	43	37	28	48	41	31
β(1/deg)		4.5×10^{-5}			6.7×10^{-5}			4.8×10^{-5}	
System A–V	C_a = 61.7 mol%, t_s = 925°C			C_a = 55.8 mol%, t_s = 875°C			C_a = 51.2 mol%, t_s = 825°C		
	t_s	$t_s + 25$	$t_s + 50$	t_s	$t_s + 25$	$t_s + 50$	t_s	$t_s + 25$	$t_s + 50$
μ(cP)	130	105	97	142	130	110	150	142	120
ρ(g/cm^3)	3.085	3.080	3.076	3.065	3.063	3.060	2.982	2.982	2.976
$\nu \times 10^2$ (cm^2/sec)	42	34	32	46	42	36	50	48	40
β(1/deg)		5.8×10^{-5}			3.3×10^{-5}			6.0×10^{-5}	

Note. $A = BaB_2O_4$; $M = Na_2O$; $R = 0.75Na_2O$–$0.25BaO$; $T = 0.75Na_2O$–$0.25B_2O_3$; $V = 0.60Na_2O$–$0.40B_2O_3$; C_a = concentration of BaB_2O_4)

ues within the range of 1–500 cP, and the data obtained were checked by measuring the viscosity of high-temperature solutions of the K_2O–TiO_2–P_2O_5 system, for which there are data in the literature (*11*). It was established that the measurement error for dynamic viscosities above 50 cP did not exceed 2%.

The solution densities were measured by the weight loss of a platinum body immersed into the corresponding solution. The error of these measurements was ±0.001 g/cm^3.

The volumetric expansion coefficient of the solutions was calculated using the data on the solution densities at temperatures t_s and t_s + 50°C.

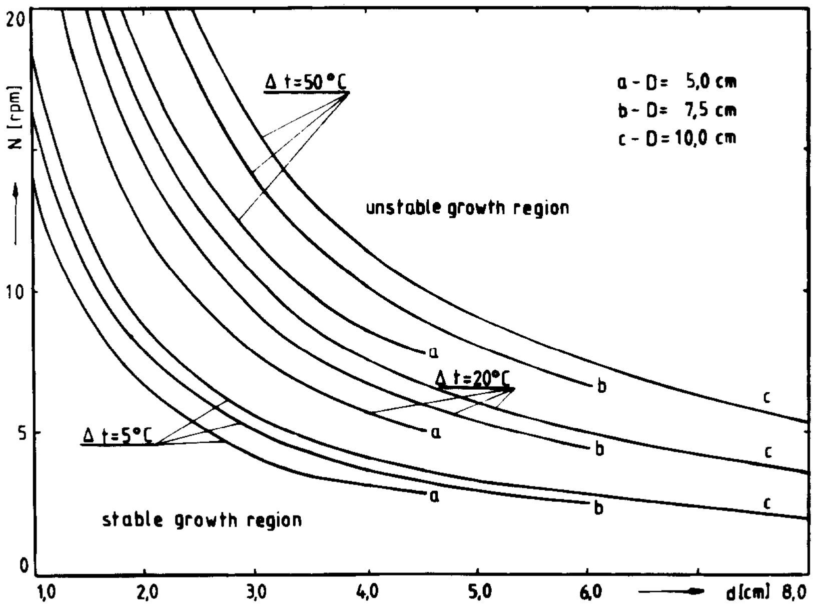

FIG. 1. Relationship between the diameter and the rotation rate of the β-BaB_2O_4 crystal, which determines the kind of convection regime for different D and Δt values when $h = 2/3D$.

The data obtained on the viscosity, density, and volumetric expansion coefficient of the solutions investigated are shown in Table I. It is evident that, depending on the composition, the dynamic viscosity of the saturated solutions varies between 103 and 243 cP. It is worth noting that with decreasing saturation temperature (with decrease in concentration of BaB_2O_4) the solutions in the different solvents exhibit differences in the increase of their viscosities. The largest differences are observed with Na_2O as a solvent, while the smallest difference (only 22 cP with a temperature drop from 925 to 825°C) corresponds to the solvent of $0.75Na_2O$–$0.25B_2O_3$. This is an additional advantage of the binary solvents of Na_2O–B_2O_3 in comparison with pure Na_2O, which is very important when BBO crystals are grown by the slow cooling technique.

The solution densities vary from about 3 to 3.4 g/cm^3 and gradually decrease when B_2O_3 is substituted for BaO. As to the volumetric expansion coefficients, which range from 3×10^{-5} to 9×10^{-5}, the experimental results obtained do not indicate a definite dependence on the solution composition.

The data obtained were used for estimating, by the dependence (2), the conditions of stable growth of β-BaB_2O_4 crystals. The evaluation was made for crucibles with three different diameters, $D = 5.0$, 7.5, and 10.0 cm, respectively, a liquid layer height, $h = 2/3D$, and three different radial temperature differences on the solution surface, $\Delta t = 5$, 20, and 50°C. On the basis of data in Table I, mean values of the kinematic viscosity ($\nu = 40 \times 10^{-2}$ cm^2/sec) and the volumetric expansion coefficient ($\beta = 6 \times 10^{-5}$ 1/deg) were used for the calculations. The results are presented in Fig. 1 as $N = f(d)$ dependences. Below each of the curves obtained for definite D, h, and Δt values, there is a region of stable regime, while above the curve the regime is unstable. Evidently, with a constant crystal rotation rate, the gradual increase in crystal diameter leads to a critical value above which the growth regime becomes unstable. When the crucible diameter and, especially, the temperature difference in the solution increase (with a constant N), the critical crystal diameter can also increase. The dependences obtained are qualitatively confirmed by the observations of Feigelson *et al.* (*6*). In their work these authors have used Na_2O as a solvent, a crucible with a diameter of 5.5 cm, and a solution layer height of 3.7 cm ($h = 2/3D$). Experiments have been performed with radial temperature difference values $\Delta t \sim 20$ and 50°C, the final diameter of the crystals having reached 4.5 cm. It has been established that a stable regime can be maintained when, along with the increase of the crystal diameter, the rate of crystal rotation decreases from 16 to 2 rev/min. It has also been established that a larger temperature difference ensures a more stable growth regime.

Conclusion

In the present paper it has been shown that on the basis of experimentally obtained data on the viscosity, density, and volumetric expansion coefficient of high-temperature solutions of BaB_2O_4, it is possible to estimate the optimum rotation rate of the β-BaB_2O_4 crystal which ensures its stable growth by the TSSG technique from crucibles with different sizes, at different radial temperature differences between the crucible wall and the crystal.

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