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On the Growth of β-BaB_2O_4 (BBO) Single Crystals from High-Temperature Solutions: I. Study of Solvents of the BaO–Na_2O–B_2O_3 System

V. NIKOLOV AND P. PESHEV

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

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The concentration and temperature regions of crystallization of the β-BaB_2O_4 (BBO) phase are studied in 10 high-temperature solvents of the BaO–Na_2O–B_2O_3 system. It is shown that in this system there are, in addition to pure Na_2O used up to now as a solvent, also other solvents having a sufficiently high dissolving ability and ensuring practically the same concentration and temperature regions of crystallization of BBO as in the case of Na_2O. Some of the Na_2O and B_2O_3 containing solvents have the advantage of allowing the growth of crystals with commensurable dimensions in the directions of the three main axes.

Introduction

During the several past years, the single crystals of the low-temperature modification of barium borate, β-BaB_2O_4 (BBO), have been a subject of interest as a new nonlinear optical material. The data available show them to have an unusual combination of optical, chemical, and mechanical properties, which makes them more appropriate for many applications than some other well known oxide single crystals (*1–3*).

The fact that β-BaB_2O_4 is a low-temperature phase makes the application of the crystallization from its own melt difficult, and researchers have attempted to grow crystals from high-temperature solutions. In this case, the choice of a suitable solvent is very important. The use of an excess of BaO or B_2O_3 as a high-temperature solvent is not promising due to the narrow temperature and concentration regions of crystallization of β-BaB_2O_4 (*4*). There are publications on a series of other solvents, e.g., compounds of lithium (Li_2O, LiF and $LiBO_2$), sodium (Na_2O, $NaCl$, $NaBO_2$ and Na_2SO_4), potassium (KBO_2), calcium (CaF_2 and CaB_2O_4), strontium (SrB_2O_4), and barium (BaF_2, $BaCl_2$ and $BaSO_4$). The results from these investigations are discussed in the paper of Huang and Liang (*8*). The authors have noted that, due to some disadvantages, a large number of the solvents mentioned are either inapplicable (the compounds of Li, Ca, and Sr) or inappropriate (e.g., $NaCl$, owing to its volatility and $BaCl_2$, due to hydrolysis). Of the solvents used up to now, pure Na_2O seems to be most suitable. Irrespective of its advantages, the use of this solvent is accompanied with two serious problems during the crystal growth: the high viscosity of the solutions and the formation of nonisometric crystals, which makes the preparation of optical elements with suitable dimensions difficult (*4–6*).

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TABLE I

Composition of the Solvents Used (in Molar Parts)

No	BaO	Na_2O	B_2O_3	No	BaO	Na_2O	B_2O_3
1.	0.0	1.00	0.0	6.	0.0	0.75	0.25
2.	0.25	0.75	0.0	7.	0.0	0.60	0.40
3.	0.50	0.50	0.0	8.	0.0	0.50	0.50
4.	0.75	0.25	0.0	9.	0.0	0.25	0.75
5.	1.00	0.0	0.0	10.	0.0	0.0	1.00

The present paper contains the results from investigations on the determination of the concentration and temperature regions of crystallization of the β-BaB_2O_4 phase from solutions in solvents of the BaO–Na_2O–B_2O_3 system, two of its components being components of the phase in question. Special attention is paid to the relationship between the habit of the growing β-BaB_2O_4 crystals and the solvent composition.

Experimental

The investigations on the determination of the temperature and concentration regions of spontaneous crystallization of β-BaB_2O_4 were carried out using 10 solvents of the BaO–Na_2O–B_2O_3 system whose compositions are given in Table I. About 5–10 solutions with different barium borate concentrations were investigated using each of the above solvents. The solutions were obtained by subjecting mixtures of $BaCO_3$, Na_2CO_3, and H_3BO_3 with a purity higher than 99% taken in appropriate ratios, to decomposition and melting in a platinum crucible at a temperature above 1000°C. After homogenization, the saturation temperature of each solution was determined as described by Jiang *et al.* (*4*), but the cooling during the determination of the temperature of spontaneous crystallization and the heating when determining the saturation temperature were achieved with a rate of 2°C/h and not 6°C/h, and observations were made every 30 min. This change was necessary because the rate of 6°C/h proved to be insufficient to attain equilibrium in the system, especially when determining the saturation temperature. After the first determination, a certain amount of solvent was added to the corresponding solution until the concentration of BaB_2O_4 decreased by about 2 mol%. Another homogenization followed by determination of the new saturation temperature was performed, and the procedure was repeated until the appearance of a new phase differing from β-BaB_2O_4. The nature of the crystallizing phase was determined by X-ray phase analysis.

Figure 1 shows part of the phase diagram of BaO–Na_2O–B_2O_3 in which the concentration region of spontaneous crystallization of β-BaB_2O_4 is marked and the isotherms are plotted for temperatures of 800, 850, and 900°C. On one side this region has a common boundary with the region of α-BaB_2O_4 crystallization, and on the other with the regions where $Ba_3B_2O_6$, $BaNa_2B_2O_5$, $NaBO_2$, $Na_2B_4O_7$, and BaB_4O_7 crystallize. The concentration and temperature regions of crystallization of β-BaB_2O_4 have the smallest width in the case of BaO (beam 5), and B_2O_3 (beam 10) solvents. When Na_2O is added to BaO or B_2O_3, the regions become gradually broader and reach a considerable width with solvents of a composition ranging from 0.75 Na_2O : 0.25 BaO (beam 2) to 0.6 Na_2O : 0.4 B_2O_3 (beam 7).

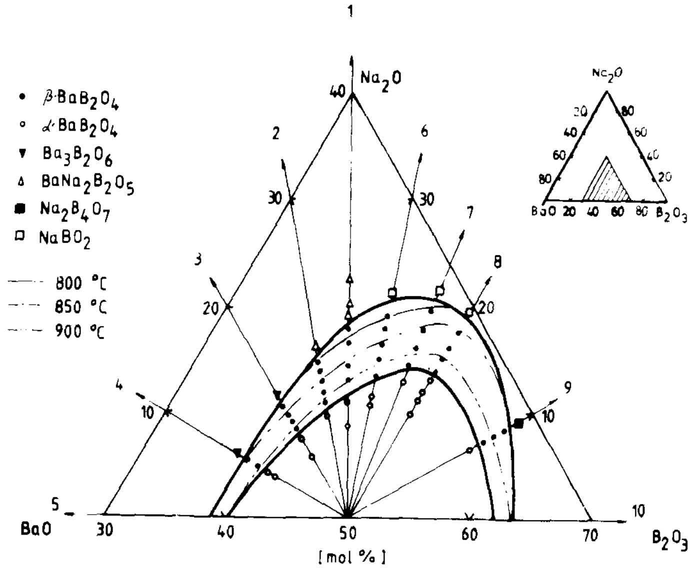

FIG. 1. Crystallization region of the β-BaB_2O_4 phase in the BaO–Na_2O–B_2O_3 system (symbols as in Table I).

The temperature dependences of the solubility of β-BaB_2O_4 in the solvents under consideration are presented in Fig. 2. Obviously, the maximum dissolving ability belongs to pure Na_2O, but in the other solvents the solubility of BBO is sufficiently high and suitable for the growth of single crystals. The narrower temperature and crystallization regions of the β-BaB_2O_4 phase in solvents 3, 4, 8, and 9, and especially 5 and 10, are inconvenient for the growth of crystals and for that reason we concentrated on the remaining solvents (1, 2, 6, 7). When these solvents are used, the concentration region has a width of 10–12 mol%, the temperature varying between 140 and 170°C. In addition, with decreasing temperature the solubility of BBO in these solvents decreases almost linearly (Fig. 2), while the calculated values of mean supersaturation per 100 g solution are very close (0.234, 0.240, 0.256, and 0.273 g/°C, respectively, for solutions in solvents 1, 2, 6, and 7). Hence, the suitability of the solvents can be estimated on the basis of other properties of importance for the growth of BBO crystals, e.g., the crystal habit, the solution viscosities, etc.

The effect of the solvent composition on the crystal habit was studied on solutions with solvents 1, 2, 6, and 7, the BBO concentration in them being 73, 70, 64, and 54 mol%, respectively, and the saturation temperature about 850°C. These solutions were

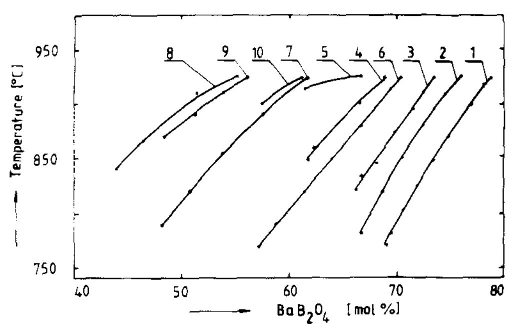

FIG. 2. Temperature dependences of the solubility of BaB_2O_4 in different solvents of the BaO–Na_2O–B_2O_3 system (symbols as in Table I).

TABLE II

SHAPES OF β-BaB_2O_4 CRYSTALS DEPENDING ON THE SOLVENT USED

No	Solvent composition $BaO : Na_2O : B_2O_3$ (molar parts)	BaB_2O_4 concentration in the solution (mol%)	Ratio of the dimensions along the main axes $a : b : c$
1.	0.00 : 1.00 : 0.00	73	1 : 1 : 4
2.	0.25 : 0.75 : 0.00	70	1 : 1 : 8
6.	0.00 : 0.75 : 0.25	64	1 : 2 : 2.5
7.	0.00 : 0.60 : 0.40	54	1 : 2 : 2

used for the growth of crystals by the slow cooling technique in platinum crucibles with diameters of 2.0 cm and heights of 4.0 cm. The experimental conditions used were: amount of solution, 10 g; solution layer height, 1.0 cm; radial temperature gradient on the solution surface, 5°C/cm; temperature gradient along the crucible axis, 5°C/cm; cooling rate, 1°C/h; and duration of cooling, 50 h.

The following procedure was used during the crystal growth: (i) preparation of the solution and its homogenization at 900°C for 12 h; (ii) cooling of the solution to 850°C with a rate of 10°C/h; (iii) maintaining a temperature of 850°C for 1 h followed by placing, on the solution surface, a crystal seed of β-BaB_2O_4 (size below 0.2 mm) heated previously at the same temperature; (iv) growth of the crystal on the solution surface, and (v) withdrawing the crystal above the solution and cooling with a rate of 50°C/h down to room temperature.

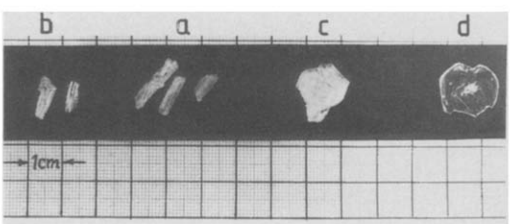

FIG. 3. BBO single crystals obtained from solutions in solvents 1 (a), 2 (b), 6 (c), and 7 (d) according to Table I.

The crystals obtained are shown in Fig. 3. Table II presents the average dimension ratios along the three main axes. Evidently, the solvent composition strongly affects the growth rate in the separate directions. In Na_2O or BaO–Na_2O solvents, crystals grow as needles which are strongly lengthened in the *c*-axis direction and become cylindrical in Na_2O–B_2O_3 solvents. In this case, the dimensions along the *a* and *b* axes are almost the same, while the dimension along the *c*-axis is commensurable with the other two dimensions.

Conclusion

The present investigation shows that when β-BaB_2O_4 single crystals are grown from high-temperature solutions, solvents containing 0.6–0.75 molar parts Na_2O and 0.4–0.25 molar parts B_2O_3 should be preferred to pure Na_2O, which has been used up to now. These solvents have a sufficiently high dissolving ability, and the widths of the temperature and concentration regions of crystallization of BBO are practically the same for these solvents and for Na_2O. The Na_2O–B_2O_3 solvents, however, allow the formation of crystals with close dimensions along the main axes.

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