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Investigation on the Li, Ba//BO_2, F ternary reciprocal system and growth of bulk β-BaB_2O_4 crystals

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ABSTRACT

Methods of spontaneous crystallization on a platinum loop, modified VPA method, solid phase synthesis, X-ray powder diffraction analysis and chemical analyses were used to study phase formation in the Li, Ba//BO_2, F ternary reciprocal system and the base of the BaO–B_2O_3–Li_2O prism of quaternary reciprocal system Ba, B, Li//O, F. In these systems the fields of primary crystallization of β-BaB_2O_4 were determined and a promising solvent for crystal growth was found. A series of experiments were carried out on the growth of bulk barium borate crystals in the system BaB_2O_4–LiF.

1. Introduction

Barium borate β-BaB_2O_4 (BBO) single crystals of low-temperature modification are important materials for nonlinear optics and are used for laser frequency conversion in the visible and UV regions. Radiation of YAG:Nd laser in β-BaB_2O_4 crystals converts into the 4th and 5th harmonic (213 nm). The melting point of barium borate is 1095 °C; temperature of α–β phase transition is 925 °C. The basic procedure for growing β-BaB_2O_4 crystals is solution-melt crystallization using the top-seeded solution growth technique [1,2].

The most common solvent used for growing β-BaB_2O_4 single crystals from solution-melt is Na_2O. We have grown high-quality β-BaB_2O_4 crystals in the BaB_2O_4–$NaBaBO_3$ system (k=1.69 g/kg °C, where k is the yield coefficient, i.e. weight of grown crystal at temperature decrease of 1° and initial load of growth crucible equal to 1 kg). Sodium fluoride is considered as a promising flux. The BaB_2O_4–NaF section and the BaO–B_2O_3–NaF system have a wide field of primary crystallization of β-BaB_2O_4 [3,4]. Our growth experiments showed that growth of β-BaB_2O_4 crystals with a high yield coefficient in the BaB_2O_4–NaF system is possible only in the first growth cycle (k=2.76 g/kg °C).

Absorption >500 ppm/cm at wavelength 532 nm was measured on β-BaB_2O_4 crystals [5]. Crystals with the absorption <100 ppm/cm are of great demand nowadays and therefore, a topical problem, which is actively being solved in the world, is the search for new solvents providing maximum yield coefficient and high optical quality of β-BaB_2O_4 crystals.

In this paper we have discussed results of systematic researches of phase equilibriums in the Li, Ba//BO_2, F ternary reciprocal system. To choose the optimal solvent in the fields under study, we had to analyze a great number of sections. Use of Li-bearing fluxes is assumed to reduce the viscosity of melt-solution. The ternary diagram BaO–B_2O_3–LiF has not been adequately studied so far. The narrow crystallization field of β-BaB_2O_4 along the BaB_2O_4–LiF section was reported in [6]. We have carried out systematic studies of phase formation and crystallization of the BaB_2O_4–LiF system. Applicability of BaB_2O_4–LiF section for growth of β-BaB_2O_4 single crystals is demonstrated.

Crystallization fields of β-BaB_2O_4 were studied considering that it belongs to the Ba, B, Li//O, F quaternary reciprocal system which can be presented as a trigonal prism based on oxide BaO–B_2O_3–Li_2O and fluoride BaF_2–BF_3–LiF concentration triangles. The BaO–B_2O_3–Li_2O phase diagram was studied in [7]. The compounds $2BaO \cdot B_2O_3$ on the BaO–B_2O_3 section, stated by the authors [7], were rejected earlier in [8]. It is also worth noting that triangulation in the system was conducted by the authors without considering the compound $LiBaBO_3$ discovered in [9]. Thus, the phase diagram BaO–B_2O_3–Li_2O in [7] is incorrect and requires substantial supplementation.

In this work results of studies of phase equilibriums in the Li, Ba//BO_2, F ternary reciprocal system and base of the BaO–B_2O_3–Li_2O prism of the Ba, B, Li//O, F quaternary reciprocal system and experimental results on growth of β-BaB_2O_4 crystals were reported.

2. Experiment

Phase equilibria in the Li, Ba//BO_2, F ternary reciprocal system were studied using the modified method of visual polythermal

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analysis, methods of spontaneous crystallization of melt, solid phase synthesis and X-ray powder diffraction analysis. As a starting substance we used high-purity $BaCO_3$, Li_2CO_3, H_3BO_3, BaF_2 and LiF.

2.1. Modified method of visual polythermal analysis (VPA)

The experiments were carried out in a precision heating furnace with a high symmetry and stability of heat field. A platinum crucible 40 mm in diameter was used for preparing 20 g of solution melt by gradually increasing the temperature to complete melting. The melt was observed through a quartz glass in the upper lid of the furnace. The melt was overheated and held for homogenization. Temperature in the furnace was decreased in steps by 5–10 °C. At each stage, after holding for 3–4 h, the surface of melt was touched with a platinum rod to remove supercooling. If the temperature of solution-melt corresponded to saturation point, primary spontaneous crystals were observed. From the established saturation temperatures for different concentrations the liquidus curves of systems were built.

2.2. Method of spontaneous crystallization on a platinum loop

Solution melt of 40 g was prepared in a platinum crucible 40 mm in diameter. Temperature was decreased in steps up to the appearance of first crystals and a platinum rod with a loop was placed in the central part of the melt surface. The temperature was decreased at a rate of 2 deg/day during a few days to produce spontaneous crystals suitable for identification of phases. To grow spontaneous crystals, the decrease in temperature was reduced to 0.2–0.5 deg/day. The time length was 15–20 days.

2.3. Solid phase synthesis

To determine the beginning of reaction, a mixture of initial components weighing 5 g was put into a platinum crucible and was annealed at predetermined temperature for a few days. During heat treatment, several intermediate grindings were carried out. The presence of additional phases in annealed samples along with initial components was controlled by the XRD (X-ray powder diffraction analysis) method. If the beginning of solid phase reaction did not take place, the temperature was increased. The XRD was performed on the DRON-3 diffractometer (CuKα-radiation).

3. Results and discussion

The arrangement of sections BaB_2O_4–LiF, BaB_2O_4–$LiBaF_3$ and BaB_2O_4–$LiBaBO_3$ in the quaternary reciprocal system Ba, B, Li//O, F is shown in Fig. 1.

Table 1 and Fig. 2 show results of study of the BaB_2O_4–LiF system by the method solid-phase synthesis. The criterion for the completion of the solid-state reactions was the constant ratio of peak intensities. The optimal experimentally established annealing time of samples was 3 days at 620 °C. It is worth noting that $LiBa_2B_5O_{10}$ is present in all X-ray diffraction patterns.

While studying the section BaB_2O_4–LiF by the method of solid-phase synthesis in the range from 5 to 85 mol% BaB_2O_4, it was shown that in the region of concentrations more than 83.3 mol% BaB_2O_4 a solid phase contains BaB_2O_4, $LiBa_2B_5O_{10}$ and BaF_2. At molar ratios 83.3 mol% BaB_2O_4 to 16.7 mol% LiF, BaB_2O_4 and LiF react completely to form $LiBa_2B_5O_{10}$ and BaF_2. In the region of concentrations from 83.3 mol% BaB_2O_4 to 76.9 mol% BaB_2O_4 a solid phase contains $LiBa_2B_5O_{10}$, $LiBaF_3$ and BaF_2. At molar ratios 76.9 mol% BaB_2O_4 to 23.1 mol% LiF, BaB_2O_4 and LiF react completely to form $LiBa_2B_5O_{10}$ and $LiBaF_3$. In the region of concentrations less than 76.9 mol% BaB_2O_4 the solid phase includes $LiBa_2B_5O_{10}$, $LiBaF_3$ and LiF. The presence of additional compounds on the X-ray diffraction patterns implies that the BaB_2O_4–LiF section is not quasibinary.

Using the modified VPA method, we studied the concentration range from 80 to 10 mol% BaB_2O_4. After determining the saturation temperature of initial melt, we changed the composition by adding the calculated amount of lithium fluoride. Concentration range 67.5–60 mol% BaB_2O_4 and 60–40 mol% BaB_2O_4 corresponds to the primary crystallization region of β-BaB_2O_4 and $LiBa_2B_5O_{10}$, respectively.

Fig. 3 shows the results of the study of the BaB_2O_4–LiF section by the modified VPA method and, for some compositions, with further crystallization on a platinum loop and X-ray powder diffraction analysis.

A spontaneous crystal of β-BaB_2O_4 of hexagonal shape with developed prism faces weighing 20 g was grown in the system BaB_2O_4–LiF from 80 g melt by the top-seeded solution growth technique. The temperature range of crystallization was 20° at a decreasing rate of 1 deg/day. In spite of the narrow crystallization range, LiF is a promising solvent for the growth of bulk BBO crystals owing to the high yield coefficient (k=12.5 g/kg °C) and melt stability.

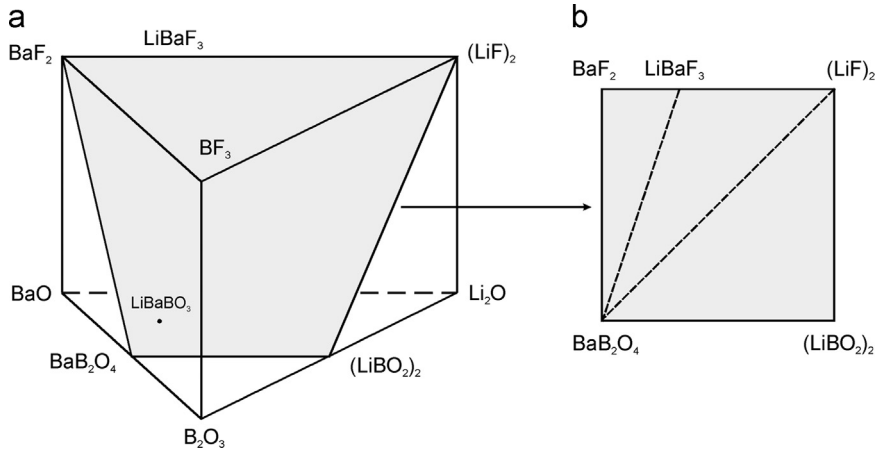

Fig. 1. Quaternary reciprocal system Ba, B, Li//O, F and the position of the ternary reciprocal system Li, Ba//BO_2, F (a); the ternary reciprocal system Li, Ba//BO_2, F (b).