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Hydrothermal phase stability study of $Li_2B_4O_7$

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ABSTRACT

Growth of $Li_2B_4O_7$ by the hydrothermal method was attempted in 10^{-6} M LiOH, by both spontaneous nucleation and transport growth. $Li_2B_4O_7$ grew out of the first spontaneous nucleation reaction, while the seed dissolved and γ-$LiBO_2$ formed during the transport growth reactions. A species thermodynamic stability study showed that γ-$LiBO_2$ formed exclusively from 350 °C to 550 °C, and $Li_3B_5O_8(OH)_2$ was observed at 250 °C; $Li_2B_4O_7$ was not observed. A solubility study on $Li_2B_4O_7$ did not achieve equilibrium conditions, but did demonstrate that γ-$LiBO_2$ is significantly more thermodynamically stable than $Li_2B_4O_7$ under the tested conditions. Formation of $Li_2B_4O_7$ hydrothermally was shown to result from kinetic growth.

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1. Introduction

There has been increased use of $Li_2B_4O_7$ in recent years for very different practical applications. Among these are optical harmonic generation [1], piezo-electrics [2,3], gas detection [4], and thermoluminescence [5]. $Li_2B_4O_7$ has also been shown to have promise as a scintillator material, particularly for neutron detection owing to the density of lithium and boron, both of which possess isotopes with large thermal neutron capture cross-sections[6–9]. More than a scintillator material, however, Czochralski-grown $Li_2B_4O_7$ has been shown to both possess ohmic, albeit small, conductivity and act as a direct proportional neutron counter when biased at both 200 V and 300 V [10].

Large scale growth of $Li_2B_4O_7$ has occurred by the Czochralski [11–13] and Bridgman [14,15] methods. Unfortunately, these are not always optimal for growing lithium borates. A number of these compounds have been shown to melt incongruently, and are therefore unsuited to melt techniques [16], while flux growth methods can lead to undesirable inclusions as the flux cools and precipitates [17]. Borate melts may also have high viscosity, thereby forming glasses [16], which is detrimental to applications requiring long-range order. A further concern, particularly relevant to thermoluminescence and conductivity, is the incorporation of dopants within the system. Unfortunately, at least in the case of Bridgman growth, attempts to dope the crystal in bulk resulted in inhomogeneous dopant concentrations [18]. This is because the viscosity of the borate melts, noted above, acts as a barrier to homogeneous mixing of dopants into the melt for techniques reliant upon diffusion to achieve homogeneity. Such a barrier can be overcome in Czochralski growth, as shown by Tiwari et al. [19], who grew very clear tetraborate crystals; in related work, Rawat et al. illustrated that Czochralski-grown lithium tetraborate could effectively incorporate Cu and Ag dopants for use in both thermoluminescent and optically stimulated luminescent dosimetry [20]. It is further worth noting that the speed of growth had significant impact on the crystal quality and that the synthesis method may impact the dosimetric behavior of lithium tetraborate [19], making the exploration of hydrothermally grown $Li_2B_4O_7$ a worthwhile activity. Finally, Brant and Swinney both note that [21,22] the Czochralski method tends to form lithium and oxygen vacancies in the $Li_2B_4O_7$ lattice. Lithium vacancies are naturally contradictory to the goal of forming an efficient neutron detector, as they represent a decrease in the number of possible neutron interactions. Furthermore, vacancies in general are not desirable if one is to create a single-stage semiconductor neutron detector, as they impede current flow and therefore reduce the measurable signal.

Hydrothermal growth offers a promising method of overcoming the difficulties presented by other growth techniques, while providing high-quality crystals. The technique bypasses incongruent melting by dissolving the feedstock in an aqueous mineralizer solution. Moreover, the technique does not require the high temperatures involved in melt processes so that thermal strain and defect formation are reduced [23–25]. Additional advantages could arise if dopants can be adequately dissolved and subsequently incorporated into the lattice. Their complete mixing

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within the solution should give rise to a uniform distribution within the crystal, and consequently create a uniformly doped crystal. Byrappa made a limited exploration of hydrothermal $Li_2B_4O_7$ growth, with some success under subcritical conditions in dilute formic acid. Unfortunately, the study's product size was limited by the internal volume of the apparatus, and bulk growth was not demonstrated [26]. More recently, McMillen demonstrated the viability of growing γ-$LiBO_2$ hydrothermally. In particular, that author's work evinced solubility and growth rates at and above the supercritical point of water that approached those of quartz [27].

We propose that if growth rates comparable to those found for γ-$LiBO_2$ could be achieved with $Li_2B_4O_7$, hydrothermal growth would be competitive with Czochralski growth; it would also have the attendant advantages of lower-temperature formation. This study has therefore explored the possibilities of growing $Li_2B_4O_7$ in supercritical hydrothermal solution.

2. Experimental procedure

2.1. Spontaneous nucleation

The authors performed spontaneous nucleation (SN) reactions based on the work of McMillen et al. [28]. $Li_2B_4O_7$ powder (99.995%, metals basis, Alfa Aesar) and 10^{-6} M LiOH mineralizer solution were welded into a silver ampule 6.75 in long and of $\frac{3}{4}$ in outer diameter. The weak solution of LiOH was chosen to provide a small amount of excess lithium in the working fluid to minimize loss from the original crystal structure, without impacting the chemistry of the $Li_2B_4O_7$ dissolution and precipitation. The mineralizer was made immediately preceding its addition to the tube by dissolving LiOH powder (high-purity, 99.998%, metals basis, Alfa Aesar) in deionized water to form a 0.1 M solution, and then diluted. The ampule was welded shut and then agitated to disperse the feedstock powder into the fluid. It was then sealed in a 120 mL autoclave along with an appropriate counter-pressure water fill.

On that note, pressure does vary somewhat with each reaction, but the chief goal is to ensure that the internal ampule does not expand and form a friction-fit within the autoclave, or crush under an excessive load. Throughout the work, pressures measured on the external apparatus were in the range of 13–16 kpsi. For comparison, Laudise's commercially optimized hydrothermal growth conditions for quartz are quoted as ranging from 15 to 25 kpsi [29], indicating that pressure is a less significant factor in hydrothermal crystal growth, especially at this early stage of research.

Two temperature zones were maintained for the duration of the reaction by independently controlled external band heaters. Note that a greater temperature difference generally leads to smaller spontaneously nucleated crystals, but nonethless some gradient is necessary or the fluid in the tube will saturate, and the material precipitates out at some unknown temperature during cooling. Upon the completion of the reaction, the ampule was removed, and the reaction products flushed from it with deionized water in combination with a vacuum filtration apparatus.

2.2. Hydrothermal stability study

A hydrothermal stability study—an effort to isolate the most stable compound(s) for given conditions—was carried out using sealed 0.25 in outer diameter, 3 in long silver reaction ampules containing between 97.0 mg and 103.0 mg of $Li_2B_4O_7$ and 0.4 mL of 10^{-6} M LiOH. These were then sealed within Tuttle cold-cone seal autoclaves and heated using two external band heaters. The bottom was held at 25 °C hotter than the upper band heater in order to provide a thermodynamic precipitating thermal condition within the ampule. After three days, the autoclave was removed from the band heaters and insulation while at working temperature and cooled with flowing water, then opened. The total timeline from removal to rinsing of the crystals was dependent on the starting temperature to be reduced, but in no case it was longer than 15 min. The authors used single-crystal X-ray diffraction (SXRD) in order to perform fingerprint analysis on the crystals produced. For unit cell confirmation, anywhere between 12 and 540 images were analyzed. A full dataset and a solution were obtained for every phase reported.

2.3. Solubility study

A solubility study of $Li_2B_4O_7$ proved to be necessary, the conduct of which followed the outline set by Gelabert et al. [24]. Single $Li_2B_4O_7$ crystals were weighed and loaded into 0.25 in outer diameter, 3 in long Ag ampules with 0.4 mL of 10^{-6} M LiOH solution. Upon being welded shut, the ampules were loaded into small Tuttle cold-cone seal autoclaves. Two band heaters were clamped onto the autoclave and held at the same temperature. The band heaters would encompass the total length of the ampules to apply isothermal conditions to the samples. Target temperatures were held for 24 h to establish equilibrium within the system, after which time they were quenched. The crystals were then re-weighed and the solubility calculated as $\text{wt\%} = \Delta m/(m_{\text{Solution}} + \Delta m)$.

2.4. Transport growth

The authors conducted a transport growth reaction using a $Li_2B_4O_7$ seed crystal produced by the Czochralski method. It was 8.08 mm × 8.08 mm × 0.89 mm, facing the (110) plane. The crystal was drilled so that a wire could be threaded through it, and thereby suspended upon a silver support ladder. This ladder further included a baffle positioned approximately half-way along its length to reduce mixing and create two independent thermal zones for dissolution and precipitation. This ladder assembly was placed into a 0.75 in outer diameter by 10 in long Ag ampule after charging the lower half with 7.71 g of crystalline $Li_2B_4O_7$ feedstock, and then filled with 32.52 mL of 10^{-6} M LiOH solution. The ampule was welded shut and placed in a Bridgman autoclave, with upper and lower band heater temperatures of 495 °C and 535 °C, respectively. The system remained at temperature for eight days and was allowed to cool uncontrolled.

2.5. SXRD Characterization

The authors used a Rigaku XtaLAB Mini desktop SXRD apparatus for the principle characterization of all reaction products. For brief fingerprint analysis, 12 scans were taken, with $\phi = 0.0$ and 2θ from -60 °C to 106°, with a 15° step size and 1° precision. For a more thorough analysis, datasets were taken with $\phi = 0°$, 120°, and 240°, with 2θ from $-60°$ to 120° using a 1° interval. The X-rays were the Mo$K\alpha$ line, providing a resolution of 0.6 Å. For each reaction, three crystals out of every run were analyzed with SXRD; full crystal structures were solved as necessary.

3. Results and discussion

3.1. Spontaneous nucleation reaction

In the first reaction, 4.03 g of $Li_2B_4O_7$ powder and 16.38 mL of 10^{-6} M LiOH mineralizer solution were welded into a silver