

## Preparation and characterization of boric oxide for single crystal growth of GaP and GaAs

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**Abstract.** Boric oxide, used as an encapsulant, prevents loss of volatile components in the growth of compound semiconductors. As the material readily absorbs moisture, and as moisture content has to be kept below a certain level, preparation and handling of this material becomes an involved process. In the present paper we report the process developed for preparing boric oxide from boric acid and growth of cylindrical rods of the desired diameter. The grown boric oxide is characterized by thermal analysis. Infrared characterization is also a powerful method and the advantages of this technique as well as the problems faced in taking the IR spectrum are discussed.

**Keywords.** Boric oxide; moisture control; crystal growth of electronic materials.

### 1. Introduction

The liquid encapsulated Czochralski technique has proven to be useful for the growth of III–V semiconductor crystals, especially GaP and GaAs (Metz *et al* 1962; Mullin *et al* 1965; Bass and Oliver 1968; De Kock 1980; Kirkpatrick *et al* 1985). To prevent evaporation of As or P, a molten layer of encapsulant is placed over the surface of GaAs or GaP and this layer, under the action of the external inert gas over pressure and the internal vapour pressure, acts as a sealing disc. Although many materials were tried for use as an encapsulant, boric oxide emerged as the most widely used because of its ideal properties (Weiner *et al* 1971) such as (i) low density (1.8 g/cc), (ii) low melting point (450°C) and low vapour pressure, (iii) immiscibility with the melt of III–V compounds and (iv) optical transparency. However, it is highly hygroscopic and the presence of water in the boric oxide is very deleterious. Large quantities of water lead to severe bubbling when boric oxide is heated resulting in a loss of up to 50% of the oxide which bubbles over the side of the crucible (Weiner *et al* 1971). Small quantities of water cause formation of bubbles which can bring up particles from the semiconductor melt, clouding the boric oxide and causing loss of visibility (Nygren *et al* 1971). Trace amounts of water appear to cause defect formation in the crystal and affect the electrical properties of the melt-grown semiconductor crystal. Water content present up to 1000 ppm in boric oxide does help crystal growth, especially if carried out in silica crucibles (Oliver *et al* 1981).

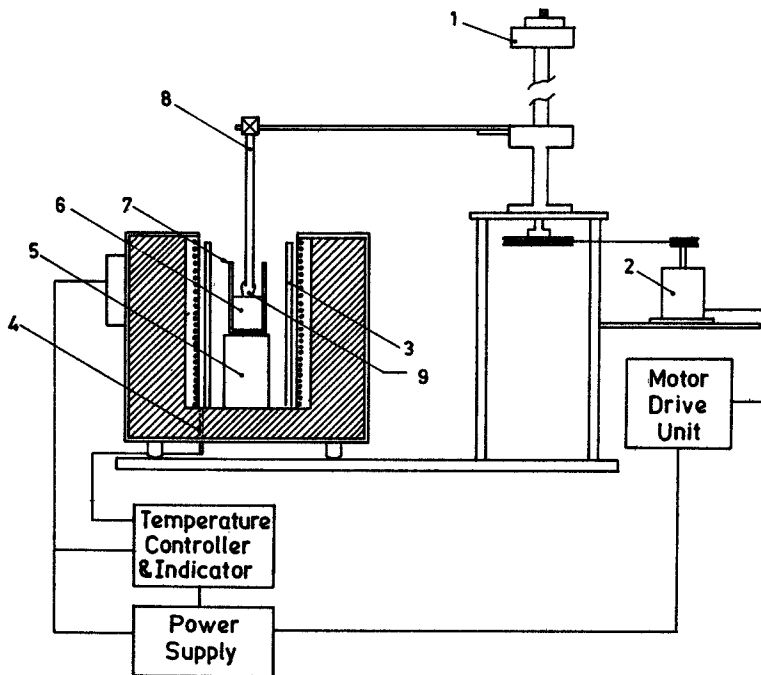
### 2. Experimental details

As boric oxide is not available in the country in the form useful for single crystal growth, a cylinder of the required length and specified moisture content is the most desirable form for use. In this paper we report a novel approach to produce boric

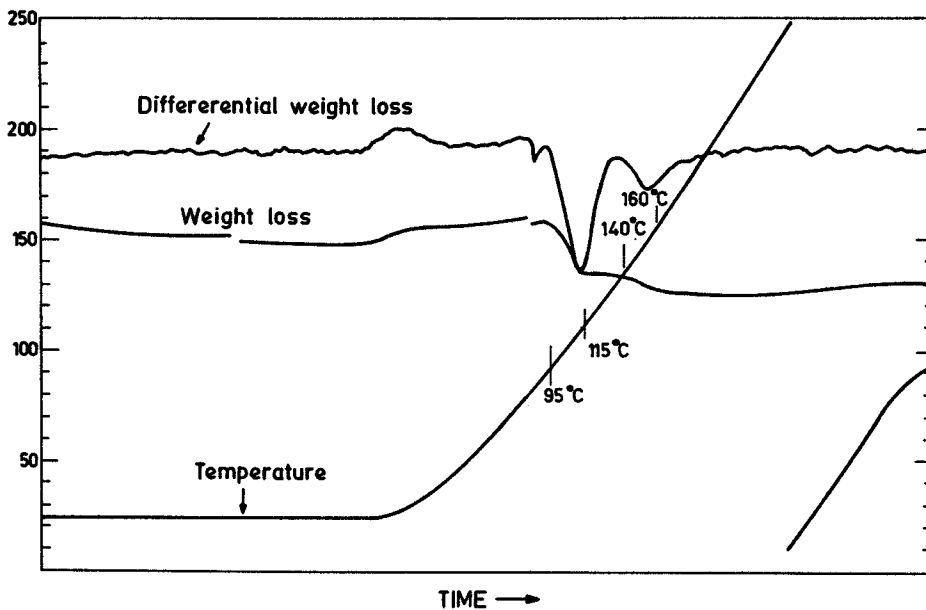
oxide rods starting from boric acid and its moisture control. This consists of employing crystal pulling methods for making cylindrical rods and growing  $B_2O_3$  cylinders in the final form needed. In other words, the boric oxide rods need not be separated from any crucible. Also, shaped pulling is possible by this method. Boric oxide was prepared from boric acid in a crucible and the rods were pulled from the melt using standard crystal pulling methods. A puller was designed for making cylindrical rods of clear boric oxide in the required diameter from the molten boric oxide. Nichrome wire wound resistance furnace with a temperature controller was used. Since silica crucibles could be used only once as they cracked, stainless steel crucibles were used. Weiner *et al* (1971) used platinum crucible but found it difficult to remove the solid oxide from the crucible later. Instead, the platinum crucible containing the boric oxide was kept upside down in the crystal puller and the heat from the crystal puller was used to melt the boric oxide. Once boric oxide melts, it pours over the charge. The technique, although used for GaAs, will pose severe problems when used for GaP. The starting material is the readily available boric acid ( $H_3BO_3$ ). Boric acid was heated in air slowly upto  $1000^\circ C$  and held at that temperature for several hours. Care was taken to avoid excessive bubbling due to moisture liberation. After the melt became clear of moisture bubbles the temperature was reduced to  $500^\circ C$ . A stepper motor was used to drive a pulley which in turn drove a lead screw up and down. A copper rod attached to the lead screw was used for pulling boric oxide rod from the melt. A stepper motor driving unit was used for varying the speed of the motor so that the diameter of the boric oxide rod coming out of the melt could be varied. The transparent, moisture-free rods of  $B_2O_3$  were immediately transferred to a vacuum desiccator. For preparing a rod of diameter 10 mm the pulling speed was set at 9 mm/min and the melt temperature was fixed at  $500^\circ C$ . The layout of the apparatus is shown schematically in figure 1.

### 3. Results and discussion

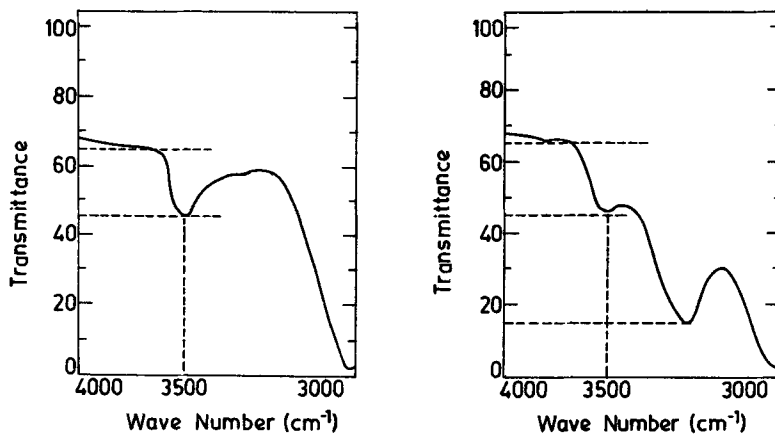
The moisture content in freshly prepared boric oxide could be determined using thermogravimetric analysis and is given by 100 weight loss/weight of the sample. Freshly prepared boric oxide exposed to air gets saturated with 3 wt% water, partly on the surface and the rest in the bulk. Figure 2 is a typical thermogravimetric chart and shows that the surface moisture is released at  $105^\circ C$  and the bulk at  $150^\circ C$ . Infrared absorption spectrum of boric oxide shows two broad bands centred around  $2.85 \mu$  and  $3.13 \mu$  and these are due to the presence of bulk and surface moisture respectively. Taking the IR absorption spectrum of freshly prepared boric oxide poses a major problem. As can be seen from figure 3, the IR spectrum of freshly prepared boric oxide shows the prominent bulk moisture band, while the surface moisture band is just discernable. Just two minutes of exposure to air increases the surface moisture band absorption drastically. The moisture content can be calculated from the relative intensities of the band if the molar extinction coefficient of boric oxide is known (Franz 1965; Hunter *et al* 1984; JMC product leaflet 1987). The success of the technique depends on the ability to perform measurements by deflecting the IR beam on boric oxide which is housed in an inert atmosphere (Ostrogorsky *et al* 1987). In this report, the sample had to be transported in a desiccator to the infrared spectrometer and the spectrum taken in air. A large absorption band resulted and the moisture levels were estimated to be around



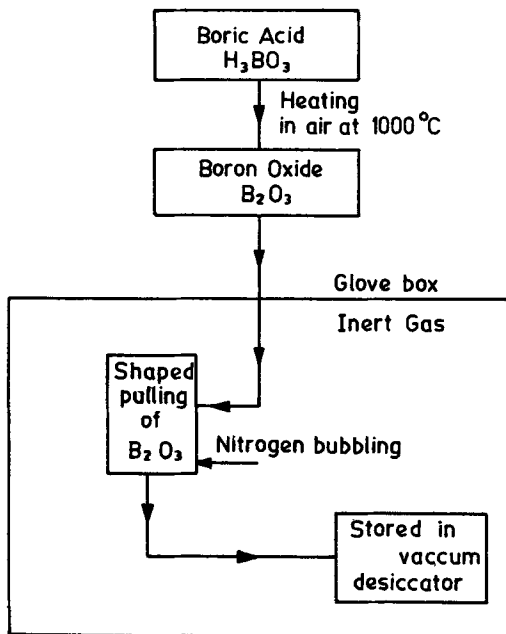
**Figure 1.** Schematic of the boric oxide puller. 1. Lead screw drive 2. motor 3. ceramic shield 4. thermocouple 5. ceramic pedestal 6. boric oxide melt 7. silica crucible 8. copper rod 9. growing boric oxide rod.



**Figure 2.** Thermogravimetric analysis of boric oxide exposed to air. The moisture evolution in the range 95–115°C and 140–160°C are for surface and bulk moisture evolution respectively.



**Figure 3.** Infrared transmittance spectrum of boric oxide reproduced from the Johnson Matthey product information leaflet. The top curve is for freshly prepared boric oxide and the bottom curve is for the same sample after 2 min exposure to air.



**Figure 4.** Preparation of boric oxide rods with moisture control.

0.5 wt% (5000 ppm). In other words, to take the IR spectrum of boric oxide at room temperature, its preparation must be carried out in an inerted glove box and the spectrum taken either with the spectrometer housed inside or with a suitable deflection of the infrared beam, if the spectrometer is to be stationed outside. Methods like coating the sample with a lacquer to prevent moisture attack were not successful. However, a systematic method for preparation of boric oxide cylindrical rods, to perform the entire operation in a glove box was identified and is shown in figure 4. The procedure utilizes a standard glove box in which an inert gas

atmosphere with a moisture content as low as 10 ppm can be ensured. It is possible to use shaped dies to get cylindrical rods of any desired diameter. Thus the boric oxide rods produced can be stored in the glove box and quickly transferred before the crystal growth. It is interesting to note that bubbling of dry nitrogen through molten boric oxide enhances efficient drying of the melt (Chang and Wilcox 1971). It is proposed to undertake a detailed IR characterization by a suitable beam design.

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