Growth of β-Ga_2O_3 by the Verneuil Technique

by A. B. CHASE

SINGLE crystals of transparent oxides that can incorporate transition metal ions, such as monoclinic β-Ga_2O_3, are of considerable interest for microwave and optical maser studies. The growth conditions for β-Ga_2O_3 by flux methods have been described,[1] and preliminary electron paramagnetic resonance (EPR) and optical absorption data on Cr^{3+} in crystals grown by this technique have been reported by Peter and Schawlow.[2] Because of the difficulties of obtaining large, high purity single crystals from the flux methods of crystal growth, the conditions for the growth of β-Ga_2O_3 by Verneuil techniques were investigated.

The crystal-growing furnace used in this work utilized a multiple-tube flame fusion burner* similar to the one used by Lefever and Clark[3] to grow C-type rare-earth sesquioxides. The powder hopper was equipped with a variable speed mechanism to control powder feed rates. The furnace consisted of two hollowed-out alumina bricks, which provided a crystal-growing chamber of approximately 1$^1/_2$ in. in diameter and 9 in. long with a viewing port $^1/_2$ by 3 in.

The feed powder used was Eagle-Picher Company electronic grade Ga_2O_3 (99.999% pure). The powder as delivered is the ϵ phase of Ga_2O_3.[4] This material was found to be unsuitable for crystal growth. The powder tended to flow poorly and to vaporize in the flame. The resulting crystals were filled with bubbles and were not suitable for optical studies. Subsequently, the ϵ-Ga_2O_3 was sintered at 1250°C for 18 to 24 hours to obtain β-Ga_2O_3. The melting point of pure β-Ga_2O_3 is about 1850°C (measured with an optical pyrometer uncorrected for emissivity). It is more stable in the flame than ϵ-Ga_2O_3 and does not volatilize as rapidly. In addition, the β-Ga_2O_3 powders flowed better, allowing improved control of powder feed.

The crystals were grown on pedestals of polycrystalline alumina rods. A sinter cone of Ga_2O_3 was deposited on the rod, and the tip of the cone was melted by raising the gas flow. Even though several crystallites were formed, the most favorably oriented crystallite rapidly outgrew the others, and a single crystal boule was obtained. The crystals were enlarged to the desired size by further increases of the gas flow and powder feed. In this manner, boules $^3/_8$ in. in diameter and 1 in. long were grown (Fig. 1). A slightly oxygen-rich flame composition was the most favorable for reproducible growth of pure β-Ga_2O_3 with typical flow rates of outer H_2 14 liters per m, inner O_2 1 liter per m, outer O_2 7.5 liters per m. It was found that a slightly H_2-rich flame is required for the growth of crystals doped with various transition metal ions.

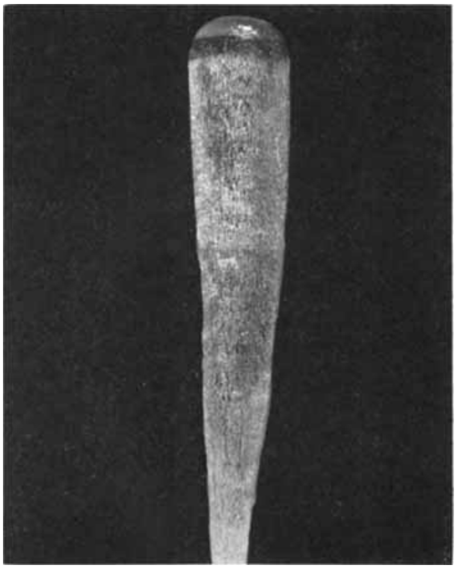

Fig. 1. Gallium oxide boule. (×2.)

The growth habits of β-Ga_2O_3 grown by this technique are such that the growth axis of the boule lies in the (100) plane. Frequently the growth axis was parallel to the crystallographic *b* axis but deviated by large angles in some boules. Crystals oriented in this manner gave rise to boules with elliptical rather than circular cross sections. The growth of boules on seed crystals oriented in a different manner proved to be extremely difficult and generally resulted in the development of polycrystalline boules.

The β-Ga_2O_3 has two cleavages, (100) and (001). The (100) cleavage is the better one, and thin slabs can be readily prepared by cleaving the crystals on this plane. In addition, the (100) is a twin plane in β-Ga_2O_3, and most of the crystals grown by the flame fusion technique exhibited fine laminar twinning. With careful control of the growth conditions, however, it is possible to produce crystals composed of four or five individual crystals. The largest untwinned crystal fragment produced to date had a cross section of 2 by 8 mm and was 20 mm long.

It has been found that β-Ga_2O_3 grown by this technique is easily doped with the trivalent transition metal ions. Detailed EPR and optical studies on Cr^{3+} have been completed by H. Tippins of this laboratory and will be published.

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[1] J. P. Remeika, "Growth of Single Crystals of Corundum and Gallium Oxide," U. S. Pat. 3,075,831, January 29, 1963; *Ceram. Abstr.*, **1963**, May, p. 148*a*.

[2] M. Peter and A. L. Schawlow, "Optical and Paramagnetic Resonance Spectra of Cr^{+++} in Ga_2O_3," *Bull. Am. Phys. Soc.*, **5**, 158 (1960).

* The burner is a vertical post-mix oxyhydrogen torch with a central tube carrying oxygen; the feed powder is surrounded by 20 tubes carrying hydrogen. Oxygen is also supplied in the interstices between the hydrogen tubes.

[3] R. A. Lefever and G. W. Clark, "Multiple-Tube Flame Fusion Burner for the Growth of Oxide Single Crystals," *Rev. Sci. Instr.*, **33**, 769–70 (1962).

[4] Rustum Roy, V. G. Hill, and E. F. Osborn, "Polymorphism of Ga_2O_3 and the System Ga_2O_3–H_2O," *J. Am. Chem. Soc.*, **74** [3] 719–22 (1952); *Ceram. Abstr.*, **1952**, October, p. 192*g*.