Synthesis and Characterization of Large Optical Grade Sapphire Windows Produced from a Horizontal Growth Process

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Abstract

Several prototypes have been synthesized up to 1.75 inches thick, 14 inches wide and 20 inches long.

As sensor technology and applications have advanced over the years, the size of sensor windows has grown substantially to satisfy current and future demands. Rubicon Technology, with their strong history in scaling sapphire crystal growth and large scale production processes, has successfully produced large sapphire blanks using a highly modified horizontal directional solidification process. Several prototypes have been synthesized up to 1.75 inches thick, 14 inches wide and 20 inches long. Crystal properties and optical characteristics such as transmission and refractive index homogeneity will be presented on several polished bubble-free windows with excellent results. This research sets the standard for high quality monolithic sapphire sheets large enough for use as seamless integrated optical windows in both military and civilian applications.

Keywords: Sapphire, crystal growth, index homogeneity, optical windows, Infrared, transmission, X-ray rocking curve

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1.0 Introduction

1.1 Sapphire

Rubicon's method, termed the Large-Area Net-shape Crystal Extraction (LANCE) system is currently able to produce crystals of several different orientations weighing up to 50 kg with plans to expand the process to larger 100 kg sapphire crystals.

Sapphire is a remarkable material owing to its high hardness and strength, transparency in the visible and Infrared (IR) spectrum, thermal conductivity, thermal shock resistance, abrasion resistance, high melting point, and chemical inertness.1-3 As a result, sapphire is particularly suited for IR windows in extreme environments where material durability is just as much a requirement as optical clarity. Thus, there is ample demand for a crystal growth production process tailored to produce large sapphire windows in high volume.

Despite the numerous advantages of sapphire, the difficulty of producing high quality material has often been viewed as a drawback. The necessity for temperatures exceeding 2000 °C and a nonreactive atmosphere has historically led to slow development in the sapphire industry. However, Rubicon Technology, with their extensive experience in scaling up sapphire growth processes, has in a little over 10 years increased the boule size from 3 kg to 200 kg using a modified Kyropoulos technique called ES2 (Figure 1). Similar goals, to produce the world's largest near-net shape slab, were set using a modified process based on yet another technique, the Horizontal Directional Solidification (HDS) method. Rubicon's method, termed the Large-Area Net-shape Crystal Extraction (LANCE) system is currently able to produce crystals of several different orientations weighing up to 50 kg with plans to expand the process to larger 100 kg sapphire crystals.

1.2 Horizontal Directional Solidification

During the 1960's Kh. S. Bagdasarov pioneered the use of a horizontal hot zone compared to the more conventional vertical hot zones at that time.4 The HDS method, as it is known, relies on moving a boat containing aluminum oxide through a heater surrounded by thermal insulation. The raw material melts once it enters the vicinity of the heater and slowly crystallizes as it is exits out the other side. This method is advantageous because of the relatively small heater needed for the process compared to the Kyropoulos or Heat Exchanger methods (HEM) that require a heater large enough to melt the entire charge prior to crystallization. The HDS method also produces plates compared to Czochralski, Kyropoulos, and HEM processes that produce cylindrical boules.

Figure 1. Sapphire boules grown by Rubicon Technology. Crystal sizes depicted include 3 kg, 31 kg, 83 kg, and 200 kg. A 12-inch ruler is included for scale.

Growth of plates is particularly advantageous if one desires large windows for the final product because the near-net shape drastically limits machining and associated costs. Additionally, since the melt is horizontal, capillary forces play a minimal role during growth and the crystal is not limited in size or thickness compared to Edge-defined film-fed growth (EFG) crystals. An alternative to producing large sapphire windows from individual crystals utilizes bonding technology to join small sapphire pieces together to create one large panel. This approach is time consuming and has the disadvantage of introducing inhomogeneities and defects at the bond interface, significantly reducing the strength of the panel. Gentilman, et al. reported how to create a bonded sapphire panel 12.6" wide and 16.1" long from 4 smaller pieces using 3 separate steps. The final piece had a nominal bond strength of 130 MPa, less than half of single crystalline sapphire with a value of 284 MPa.5 These drawbacks eliminate sapphire bonding as a feasible approach for creating large sapphire windows for use in extreme environments.

A concern for the end user when utilizing sapphire crystals produced from various methods is the potential for dissimilar optical and mechanical properties (such as internal stress, optical transmission, dislocation density, etc.). Arakawa, et al. recently published a study on acoustic measurements of sapphire produced by both HDS and Kyropoulos methods.6 They observed no significant differences for the bulk-wave velocities (longitudinal and shear) and elastic constants for the crystals grown by each method. Both properties correlate well with shear strength and hardness.7,8 The study confirms that HDS is a viable approach for producing high quality sapphire windows. Additionally, optical grade sapphire crystals 10" long and 4" wide have been grown by the HDS method with a dislocation density of only 103 cm-1, confirming the high quality nature of HDS sapphire.9

2.0 Experimental setup

2.1 Furnace Design

Crystal orientation in the LANCE system is determined by a sapphire seed placed at the front of the boat with the designated orientation parallel to the largest crystal face. Changing orientations from r-plane, to a-plane, to c-plane between runs requires nothing more than using the specifically oriented seed; no modifications to the furnace or hot zone are required. As previously stated, the crystals are grown by pulling the sapphire-containing boat through a heater allowing for controlled crystallization (Figure 2). As the boat passes under the heater the sapphire melts and then slowly solidifies, creating a single crystal. The seeding process is controlled visually through a viewport and the solid-liquid interface is observed for the entire growth. Crystal quality is determined by a combination of factors including pulling rate, cooling rate, and heater design. The pulling speed and heater power are computer controlled using preset rates determined by the operator but can be adjusted manually as needed during the process. The thermal insulation surrounding the hot zone plays an equally important role to achieve the optimal thermal gradient for high quality crystals free of cracks, bubbles, and grain boundaries.

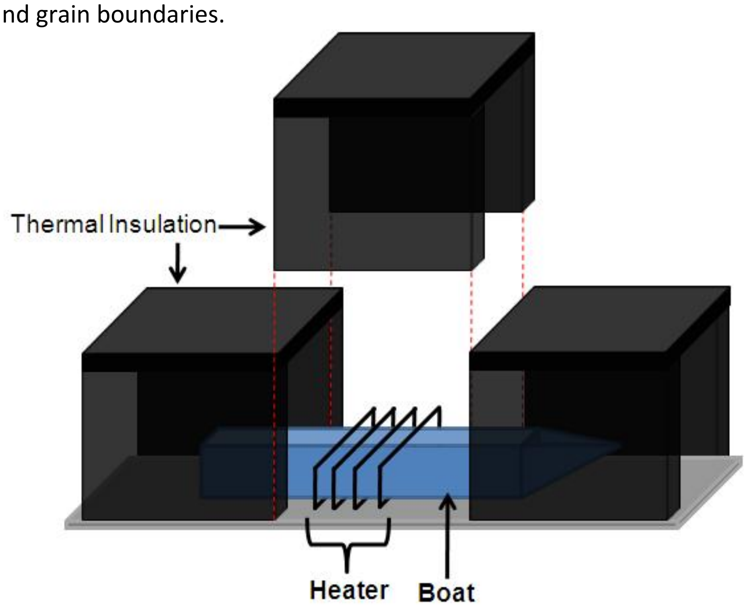

Figure 2. Schematic for sapphire crystal growth with the LANCE system.

Crystals were grown such that the largest face was parallel to either the r $(1\bar{1}02)$, a $(11\bar{2}0)$, or c (0001) planes. Several crystals are shown in Figure 3. The large as-grown slab is oriented with respect to r-plane (the largest face) and is approximately 14” wide x 37” long x 1.5” thick. The as-grown crystals often contain metal deposits just below the crystal surface, as seen in figure 3, however, these deposits are removed during grinding. Rubicon Technology has thus demonstrated expertise in both equipment design and growth process design for synthesizing these large sapphire slabs. This basic platform is designed to be fully scalable to manufacture ever larger sapphire crystals on a commercial scale.

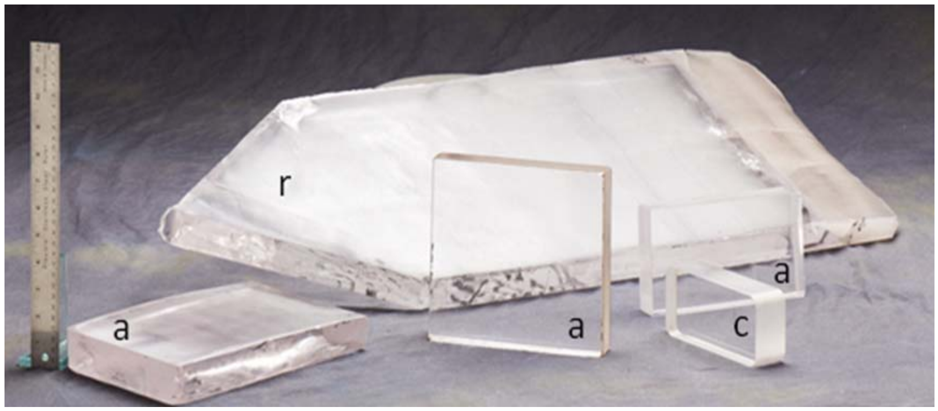

Figure 3. Photo containing a selection of as-grown and polished LANCE sapphire crystals with the crystallographic orientation shown on the corresponding face; r-plane, a-plane, & c-plane. A standard 12” ruler is included to show scale.

3.0 Results

3.1 X-ray Rocking Curves

Several small sections of a- and c-plane crystals were cut and polished in order to confirm the material’s quality. Crystalline quality was determined via X-ray rocking curves measured at the Advanced Photon Source at Argonne National Laboratory. Data was collected on beamline 1-BM-C using a beam energy of 8.0 keV and a Si(111) double crystal monochromator. The polished LANCE c-plane window measuring 5.76” x 2.69” x 1.47” exhibited a full width at half maximum (FWHM) of 25.5 arc seconds. For comparison, Rubicon’s standard epitaxial-grade ES2 c-plane wafers, 1 mm thick, possess a FWHM of 10.3 arc seconds when measured on the same system. Both FWHM values are indicative of the high crystalline quality of Rubicon’s sapphire material.

3.2 Optical Transmission

As sapphire windows are often used in IR targeting systems, optical quality of the grown crystals is of the utmost importance. Index homogeneity and optical transmission experiments were therefore performed on these crystals. Transmission data was collected on a polished a-plane window between 500 nm and 6000 nm at Exotic Electro-Optics (Figure 4). The blue line represents the average transmission in each of the 4 corners of the window. The red line represents the theoretical transmission for a sapphire window with an equivalent thickness. The discontinuities in the blue line (indicated by the black circles) are artifacts of the spectrophotometers used and are not indicative of material quality. The results confirm that LANCE sapphire exceeds the standard transmission expectations, approaching 90% transmission in the near and mid-IR regions, for an uncoated window.

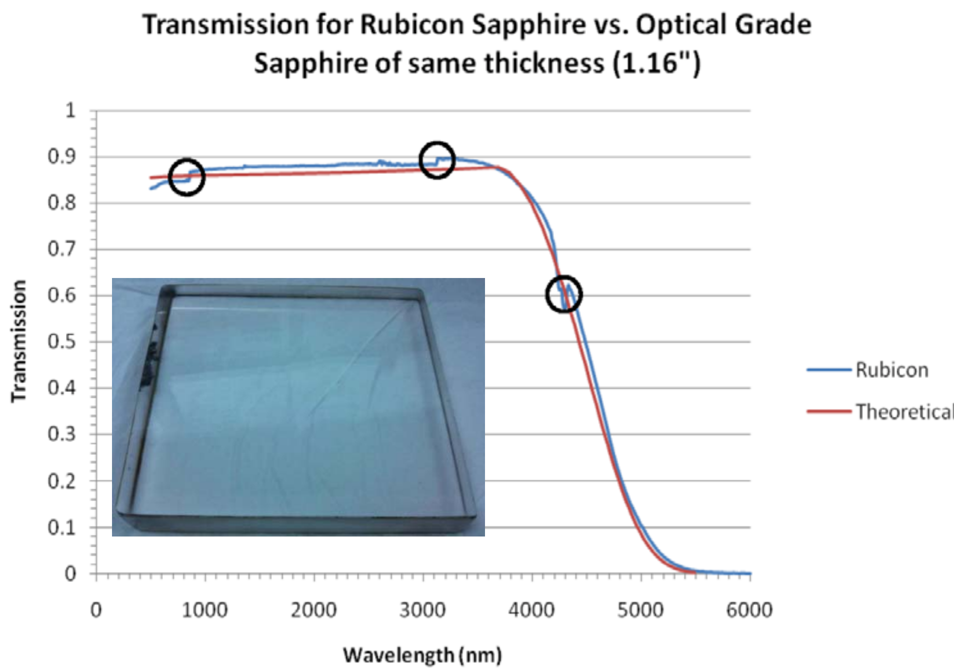

Figure 4. Transmission data for a-plane LANCE sapphire (blue) and theoretical transmission data for an equivalently thick sapphire specimen.

3.3 Refractive Index Homogeneity

Index homogeneity measurements were performed on both a- and c-plane sapphire by the Intelligence, Surveillance, and Reconnaissance (ISR) Systems division at UTC Aerospace Systems (formerly Goodrich Corporation). Prior to testing, the samples were also polished by the ISR group. Homogeneity is a measurement of the variation in the index of refraction throughout a sample. The measurement is designed to remove any surface effects and is therefore an indicator of bulk optical quality. To calculate homogeneity, the transmitted wavefront of a test window is measured and the distortions of the two surfaces are subtracted. The net distortion yields the bulk homogeneity and is calculated by the following formula:

$$\Delta n = \frac{n(T - C) - (n - 1)(S_2 - S_1)}{t}$$

where n is the refractive index of the material, t is the part thickness, and T, C, S1, and S2 are the measurement results for transmission through the part, the empty cavity, surface 1, and surface 2, respectively. The polished c-plane window, 1.47” thick, has an index homogeneity of 3.67 ppm rms (Figure 5) and the a-plane window, 1.13” thick, possesses a homogeneity of 1.8 ppm rms. These values confirm the high quality of Rubicon’s LANCE sapphire.

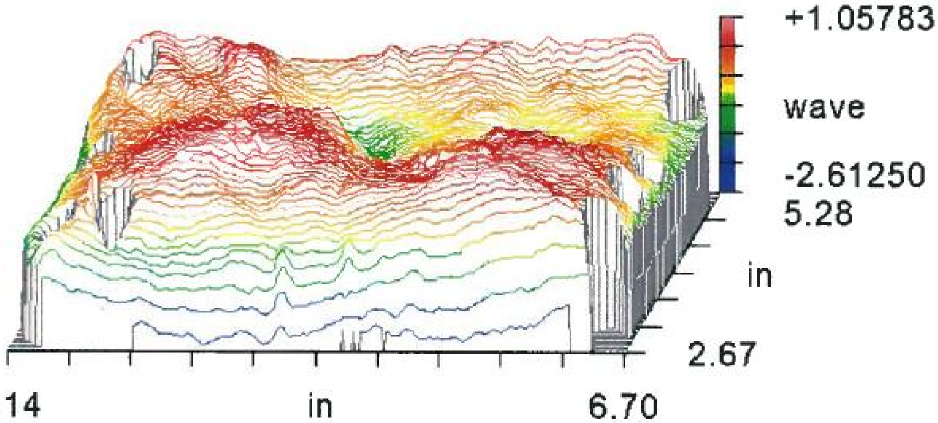

Figure 5. Interferogram for a polished c-plane sapphire crystal 1.47" thick. The index of refraction homogeneity was measured through the opposing polished faces and has a value of 3.67 ppm rms.

4.0 Conclusions

Large sapphire crystals were grown by Rubicon Technology using the newly developed LANCE system. Crystals were grown oriented with respect to r-, a-, and c- planes. X-ray rocking curves, index homogeneity measurements, and optical transmission experiments confirm that the quality of the material meets or exceeds the requirements for next generation, high performance windows.

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