LIGO-P030027-00-D

From *Proceedings of SPIE* Volume 5078 (2003)

Growth of 15-Inch Diameter Sapphire Boules

Chandra P. Khattak*, Paul J. Guggenheim and Frederick Schmid
Crystal Systems, Inc., 27 Congress Street, Salem, MA 01970

ABSTRACT

The world's largest sapphire boules up to 340-mm diameter are produced by the Heat Exchanger Method (HEM). In order to meet all applications, the highest purity crackle is used so the product has impurity levels very near the detectability limit of Glow Discharge Mass Spectroscopy (GDMS). The charge size of production 340-mm diameter sapphire boules was increased from 55-kg to 70-kg, and larger 380-mm diameter, 84-kg boules were produced. These boules were used to produce 315-mm diameter, 132-mm high sapphire cylinders to meet customer requirements. Efforts have been taken to produce a nearly flat top surface of HEM-grown boules with minimal undulations along the sidewalls to allow fabrication of larger sapphire pieces for production boules.

Keywords: crystal growth, sapphire, Heat Exchanger Method (HEM), optical properties, infrared materials

1. INTRODUCTION

Large aperture sapphire optical windows have been identified as a key element of new and/or upgraded airborne electro-optical systems. New advanced missile and reconnaissance systems place increasing emphasis on accuracy and precision resulting in very stringent demands on the optical window. A recent development in sensors is the advancement of visible-MWIR detector technology so that the requirement of far-infrared (FIR) radiation compatibility for window material is no longer necessary. It is also essential that the new high performance airborne optical reconnaissance systems operate in harsh environments. Therefore, the requirement of abrasion-resistant window material has increased substantially. The combination of development of new sensors and requirement of a high degree of accuracy has necessitated packaging of multiple sensors sharing a common aperture window. These developments demand robust, abrasion-resistant windows of high optical quality in sizes up to 500-mm diameter initially and eventual scale up to 750-mm diameter [1,2].

Sapphire has good optical properties in the 3-5μm wavelength range and the best resistance to erosion by rain and sand of any available window material. It also has excellent thermal shock resistance. The current state of technology for producing large sapphire windows is more developed than for any other window materials[3,4].

The world's largest sapphire boules up to 340-mm diameter are currently produced routinely[3,4] using the Heat Exchanger Method (HEM™). A program to extend HEM for growth of sapphire crystals up to 500-mm diameter was initiated at Crystal Systems[1,2,5]. It was demonstrated that larger crystals could be grown[6] but spurious nucleation in localized areas led to cracking of the boules due to anisotropic properties of sapphire. It was decided that intermediate size boules should be targeted prior to further concentration at the 500-mm diameter size. This decision was strengthened by demand for larger sapphire optical elements which could not be taken out of routine 340-mm diameter sapphire boules. This paper discusses growth of 380-mm diameter sapphire growth by HEM and comparison of the optical quality of these boules with the 340-mm diameter size.

2. LARGER OPTICAL ELEMENTS

In addition to very large windows for high performance airborne optical reconnaissance systems, there is a need for large sapphire masses for the Laser Interferometer Gravitational Wave Observatory (LIGO). There is a coordinated attempt by the international technical community to build a system to study astrophysical gravitational waves as well as their sources. A laser interferometer is used to measure with high precision the time taken by controlled laser light traveling between two suspended mirrors at 4 km apart[7]. Fused silica was used for test masses in the initial LIGO detector because of its excellent optical properties and maturity of production technology to deliver large test masses[8]. One of the critical research areas for the enhancement of the new LIGO detector is to reduce the thermal noise in the internal

*chandra@crystalsystems.com; phone 978 745-0088; fax 978 744-5059; crystalsystems.com

modes of the test mass. Single crystal materials such as sapphire are expected to reduce the thermal noise compared to fused silica. Sapphire crystals are transparent at visible and near-infrared wavelengths. Compared to the fused silica, sapphire's higher speed of sound, higher density and lower mechanical loss factor, or higher quality factor, would give a major improvement in the thermal noise due to internal modes. Low-loss sapphire crystals have been successfully developed as substrates in Fabry-Perot reference cavities[9]. Sapphire crystals are commercially available but there are also significant issues that need to be addressed for sapphire application in LIGO. Among these issues are size requirement of 314-mm diameter, 130-mm thickness, optical homogeneity of $<5 \times 10^{-7}$ and absorption of <20 ppm/cm at wavelength of 1.06 μm[10]. In addition, stringent purity and uniformity of properties dictate that it will be necessary to grow larger sapphire boules than the current production sizes. Therefore, emphasis was placed on growing 380-mm diameter sapphire boules.

Besides meeting the size requirements of LIGO, it is also important to measure properties as well as uniformity of boules for this application. Other criteria to be developed include suspending of test masses, handling of the large optical elements, polishing and coating of massive sapphire pieces, etc. Two full size sapphire pieces were produced, one of them from current production and from a larger boule. These masses were processed with standard optical polish (scratch/dig of 60/40 specification) for the large flat surfaces, and the cylindrical surface was polished on a best-effort basis. It is intended to use these pieces for characterization and development of processes to use them in the interferometer to develop sapphire specifications for LIGO application.

3. PURITY OF SAPPHIRE

In order to produce sapphire for a variety of high performance applications, high purity is essential. Different impurities can cause absorption bands, and the position of these absorption bands can change with the oxidation state of the impurities. The best recourse is to use the highest purity feedstock, minimize contamination during all steps of processing and use the process steps to minimize or reject impurities.

Sapphire produced by HEM uses sapphire crackle as feedstock for production; high purity alumina powder is used only for special applications when crackle use cannot meet specifications. Crackle is available in high purity form and gives a high packing density of the charge in the crucible. Titanium is a common impurity in most crackle. This impurity can cause several problems in high performance applications of sapphire. Some of the problems are:

- Ti^{3+} has an absorption band between 400 and 600 nm,
- Ti^{4+} has broad absorption bands centered at about 800 nm,
- solubility of Ti^{4+} in sapphire is low; hence, scattering centers can be formed,
- radiation between 0.4 and 0.6 μm can cause fluorescence,
- sapphire has a pink tinge and is no longer colorless.

Other impurities can cause similar or additional problems in application. Therefore, all sapphire crackle used for HEM growth is specified so that no intentional impurities are added during the crackle production. Prior to use for crystal growth, all crackle batches procured are analyzed by glow discharge mass spectroscopy (GDMS). Typical analysis of crackle is as follows[11] (all values in ppm): Na 2, Si 3, Fe 1, Ca 6, Mg 1, Ga 0.7, Cr 0.3, Ni 0.4, Ti <0.5, Mn 0.1, Cu 0.2, Mo <0.5, Li <1, Zn 1, Zr 0.5.

Crystal growth by HEM is carried out in a well-insulated furnace under vacuum. At this stage, it is important that no metal parts become hot and thereby contribute impurities to the charge. A schematic of the HEM furnace is shown in Figure 1. The graphite heat zone is designed with specified hard graphite interior parts backed by insulation with features to give uniformity in temperature within the heat zone while conserving energy. The entire heat zone is purified prior to use for crystal growth.

Sapphire boules are grown from the melt in molybdenum crucibles with growth initiating off a melted-back seed at the bottom center of the crucible and progressing three-dimensionally toward the top and sides of the crucible. This:

- promotes removal of volatile species from the melt surface,
- allows removal of gas expelled during solidification,
- exhausts reaction products with high vapor pressure from the heat zone.

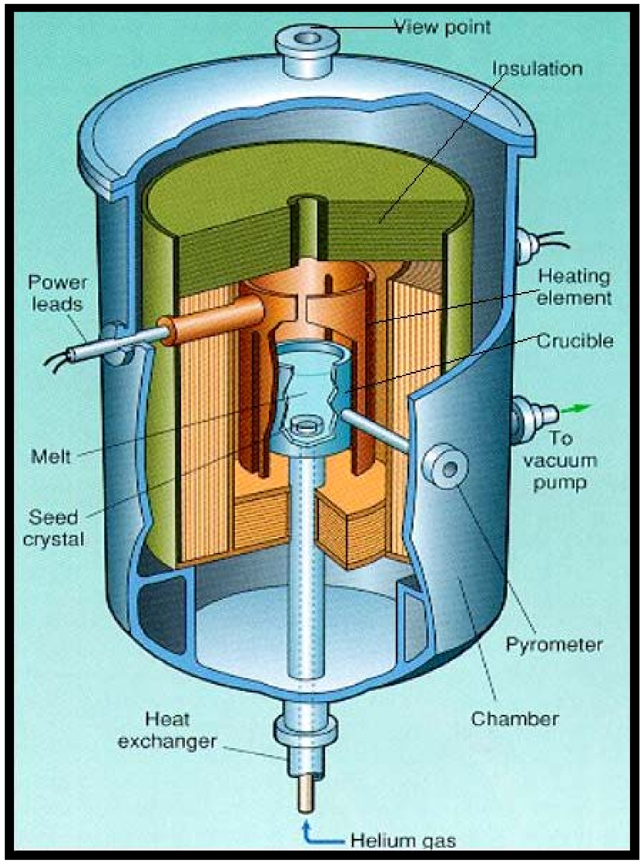

Figure 1. Schematic of HEM furnace used to grow world's largest sapphire boules.

In addition, most impurities have a low segregation coefficient in sapphire. Therefore, during solidification these impurities are rejected into the liquid in preference to being incorporated in the solid. As crystal growth progresses in HEM, this results in enrichment of impurities in the liquid phase until the impurities are finally dumped into the last material to solidify near the sidewalls of the crucible. Usually this contaminated layer is very thin, but for most applications the components are not taken from the outside surfaces of the boule. Glow Discharge Mass Spectroscopy (GDMS) analysis of HEM sapphire showed the following typical impurities (all values in ppm): Na 1, Si 4, Fe 0.6, Ca 2, Mg 2, Ga 2, Cr 0.2, Ni 0.3, Ti <0.3, Mn 0.5, Cu 0.1, Mo <0.5, Zn 1, Zr 1. Most of the impurities are close to the detectability limits of GDMS.

4. GROWTH OF LARGER SAPPHIRE BOULES

Even though very high purity sapphire boules up to 340-mm diameter sapphire boules are available, this material does not meet the requirements for some of the systems, e.g., reconnaissance systems, LIGO, etc. The anisotropic properties of sapphire put constraints on the availability of large pieces. During crystal growth, it is necessary to assure that there is no spurious nucleation as it can result in cracking of the boule during the cooldown cycle subsequent to crystal growth. Usually such spurious nucleation occurs during the seeding stage at the bottom of the boule for HEM growth. Even though only a small such grain is formed, the entire boule is shattered due to thermal stresses because of expansion variations for different orientations. Therefore, it is necessary to grow a completely single crystal sapphire to produce crack-free boules in reproducible production. This has been achieved for boule sizes up to 340-mm diameter, 55-kg size. For larger sizes, 500-mm diameter, spurious nucleation has resulted in cracking of the boules[6].

An initial requirement from LIGO was for sapphire cylinders, 315-mm diameter, 132-mm high. Even though the diameter could be taken out of 340-mm diameter boules, it was not desirable to use this approach as the edge of the cylinder would be too close to the outside surface of the boule. Moreover, any undulations in the diameter of the boule would further complicate extraction of the desired size pieces. In addition, similar restrictions would prevent getting the full height of the pieces from any boule because of the shape of the boule. Therefore, it was desired to produce 380-mm diameter sapphire boules and to see if taller 340-mm diameter boules could also be grown. Both approaches were pursued and the desired size pieces, 315-mm diameter, 132-mm high, were extracted from a 340-mm diameter, 70-kg boule and a 380-mm diameter, 84-kg boule.

One of the 380-mm diameter sapphire boules produced by HEM was #L-46, as shown in Figure 2. In the HEM, the submerged solid-liquid interface minimizes the thermal and mechanical perturbations reaching the growing interface. Therefore, uniformity is achieved during crystal growth without any requirement of rotating the crucible or the heat zone. However, when the growing solid-liquid interface reaches the surface, slight changes can affect the top shape of the surface and can result in undulations along the side wall. This can be seen in Figure 2 where the top surface shows that the solid-liquid interface was slightly convex when it approached the surface. The growth of material after that stage was affected by minor thermal perturbations in the heat zone. The side walls were similarly affected near the surface of the boule. A close-up view of the surface of a 340-mm diameter HEM-grown boule, #AJ-5 in Figure 3, shows that the top surface had a minimal convex curvature, whereas the sidewalls had minor undulations. These undulations were less than 2 mm. Such a boule could be used to produce the desired size pieces.

The pieces extracted from these boules were polished on the two flat surfaces with a scratch/dig specification of 60/40. The outside diameter was also hand polished. Figure 4 shows one of the finished pieces. These pieces have been delivered to the customer for detailed characterization for quality of sapphire so that specifications can be developed to meet the application.

Figure 2. An as-grown 380-mm diameter, 84-kg HEM sapphire boule (#L-46) after removal from crucible.

Figure 3. A taller 340-mm diameter, 70-kg sapphire boule (#AJ-5) with a nearly flat top surface.

Figure 4. One of the two 315-mm diameter, 132-mm high, 41-kg sapphire parts fabricated from each of the boules shown in Figures 2 and 3. The flat surfaces and the outside diameter were polished. These parts are undergoing detailed characterization.

5. GROWTH OF LARGER BOULES WITH MORE UNIFORMITY

As discussed earlier, it is recognized that subtle heat flow differences can change the shape of HEM–grown sapphire boules. When the solid-liquid interface reaches the surface of the melt, it is no longer protected by the surrounding liquid to minimize the mechanical and thermal perturbations. In some crystal growth processes, such as Czochralski, the mechanical and thermal perturbations are minimized by careful selection of heating element materials, design of the heaters, rotation of the crystal during growth, counter-rotation of the crucible, and raising the crucible as the crystal is pulled so that the liquid surface is maintained at the same position. These complexities are not necessary during HEM growth as the crucible and the heat zone are neither moved nor rotated. During crystal growth, the solid-liquid interface proceeds from the bottom center of the crucible three dimensionally toward the top surface of the melt and the wall of the crucible. Therefore, during most of the growth, the solid-liquid interface is protected by the surrounding liquid. However, toward the end of the growth cycle this protection is reduced. A proprietary approach has been developed which extends this protection of the solid-liquid interface from the thermal and mechanical perturbations in the heat zone. These procedures were used on a 340-mm diameter, 82-kg sapphire boule, and the result is shown in Figure 5. It can be seen that the top surface is nearly flat and the perturbations on the outside diameter are considerably reduced. This approach will allow fabrication of larger sapphire pieces from the production boules.

Figure 5. A 340-mm diameter, 82-kg sapphire boule (#R-57) produced in development showing symmetrical growth up to the surface of the boule. Such boules will allow fabrication of larger parts.

6. CONCLUSIONS

Sapphire boules are grown by HEM in production sizes up to 340-mm diameter, 55-kg. There are demands for even larger size sapphire boules with high optical quality in sizes up to 500-mm diameter initially, and eventual scale up to 750-mm diameter to meet optical window requirements of reconnaissance systems. Initial work on growing 500-mm diameter sapphire boules has shown that high quality sapphire can be grown by HEM, but spurious nucleation causes cracking of boules during cooldown because of expansion variations for different orientations. Larger sapphire test masses are also required for LIGO applications which cannot be produced from production boules. In addition to the size requirements, high optical quality and uniformity of properties are also necessary to meet LIGO requirements. The charge size of 340-mm diameter was increased to 70 kg and sapphire boules of 380-mm diameter, 84-kg were grown. Two sapphire cylinders of 315 mm diameter, 132 mm high, 40.9 kg were extracted from each of these boules. The cylinders were polished on the two flat surfaces with scratch/dig specification of 60/40 and the outside diameter was hand polished. These pieces have been delivered to the customer for detailed characterization for quality of sapphire. An approach has been developed so that boules with nearly flat top surface and minimal undulations of sidewalls are produced to allow fabrication of larger sapphire pieces. This procedure has been used on a 340-mm diameter, 82-kg sapphire boule. All sapphire boules produced by HEM utilize the highest purity sapphire crackle available and care is exercised in processing so that the final product is of highest quality.

ACKNOWLEDGEMENT

The LIGO material, in part, is based upon work supported by the National Science Foundation under the cooperative agreement with the California Institute of Technology, No. PHY-0107417.

REFERENCES

1. C. P. Khattak, D. M. Felt, F. Schmid, H. H. Rogers, J. Askinazi and R. Wientzen, *Development of Large Aperture Sapphire Windows*, Proc. 7th DoD Electromagnetic Windows Symposium, Applied Physics Laboratory, 26-34, 1998.
2. F. Schmid, H. H. Rogers, C. P. Khattak and D. M. Felt, *Growth of Very Large Sapphire Crystals for Optical Applications*, Proc. SPIE **3424** , 37-46, 1998.
3. F. Schmid, C. P. Khattak and D. M. Felt, *Producing Large Sapphire for Optical Applications*, Am. Ceramic Soc. Bull. **73**, [2] 39-44, 1994.
4. F. Schmid, C.P. Khattak and D. M. Felt, *Sapphire Sparkles in Many Optical Elements*, Laser Focus World, **32** [6] 167-174, 1996.
5. F. Schmid, C. P. Khattak, H. H. Rogers, D. M. Felt, J. Askinazi and R.V. Wientzen, *Current status of very large sapphire crystal growth for optical applications*, Proc. SPIE. **3705**, 70-76, 1999.
6. C. P. Khattak, P. J. Guggenheim, H. H. Rogers, D. M. Felt, F. Schmid, J. Askinazi and R. V. Wientzen, *Current Status of 20-Inch Diameter Sapphire Growth*, Proc. 8th DoD Electromagnetic Windows Symposium, U.S. Airforce Academy, 372-379, 2000.
7. A. Abramovici,, W. E. Althouse, R. W. P. Drever, Y. Gursel, S. Kawamura, F. J. Raab, D. Shoemaker, L. Sievers, R. Spero, K. Thorne, R. Vogt, R. Weiss, S. Whitcomb, and M. Zucker, *LIGO: The Laser Interferometer Gravitational-Wave Observatory*, Science **256**, 325–333, 1992.
8. P. Fritschel, *Second generation instruments for the Laser Interferometer*, Proc. SPIE, 4856 **39**, 282-291, 2002.
9. D. G. Blair, M. Notcutt, C. T. Taylor, E. K. Wong, C. Walsh and A. Leistner et al., *Development of Low-Loss Sapphire Mirror*, Appl. Optics, **36** [1] 337–341, 1997.
10. LIGO, *LIGO II Interferometer Reference Design*, www.ligo.caltech.edu/~ligo2/scripts/l2refdes.htm.
11. C.P. Khattak and F. Schmid, *Growth of the World's Largest Sapphire Crystals*, J. Crystal Growth **225**, 572-579, 2001.