Synthetic Sapphire: Extreme Performer

by Ian Doggett, Technical Specialist, Goodfellow Ceramic and Glass Division
c/o Goodfellow Corporation, Coraopolis, Pa.

Sapphire, the single crystal form of alumina (Al_2O_3), was first synthesized more than a century ago, but the most exciting advances associated with this versatile material are taking place today. Shaped by the dual forces of application demands and technological advances in the fabrication and finishing process, synthetic sapphire is often the material of choice for design engineers dealing with extreme conditions of high temperature, high pressure and harsh chemical environments.

An exceptional performance profile

Sapphire is second only to diamond in hardness and scratch resistance, having a rating of 9 on the Mohs scale. Its melting point of 2050˚C, physical strength, resistance to impact and corrosion, inertness, durability under extreme pressure, and the unusual combination of excellent thermal conductivity and high heat resistance further set sapphire apart from advanced ceramics and glasses. (See Table 1.) In addition, sapphire's optical properties are extraordinary: It is transparent to wavelengths of light between 150nm (UV) and 5500 nm (IR).

TABLE 1:
Typical properties of sapphire (Al_2O_3 99.9%)

Chemical Resistance	
Acids - concentrated	Good
Acids - dilute	Good
Alkalis	Good
Halogens	Good
Metals	Good
Electrical Properties	
Dielectric constant	7.5-11.5
Dielectric strength (kV mm^{-1})	15-50
Volume resistivity @25˚C (Ohm-cm)	$>10^{14}$
Mechanical Properties	
Compressive strength (MPa)	2100
Hardness - Knoop (kgf mm^{-2})	2000
Hardness - Vickers (kgf mm^{-2})	1600-1800
Tensile modulus (GPa)	350-390
Physical Properties	
Apparent porosity (%)	0
Density (g cm^{-3})	3.985
Refractive index	1.71-1.79
Useful optical transmission range (nm)	150-5500
Water absorption - saturation (%)	0
Thermal Properties	
Coefficient of thermal expansion @20-1000˚C ($\times10^{-6}$ K^{-1})	5.8
Melting point (˚C)	2050
Specific heat @25˚C (J K^{-1} kg^{-1})	750
Thermal conductivity @20˚C (W m^{-1} K^{-1})	35-40
Upper continuous use temperature (˚C)	1800-1950

Optimizing performance for specific applications

Applications are many and varied, from miniature bearings to large missile nose domes. Table 2 lists a sampling of typical applications. Optimizing performance for a particular application requires knowledge of not only the various sapphire crystal growth technologies, but also the effect of specific finishing techniques.

There are six main methods for producing sapphire and they all involve two basic steps: melting the raw material (alumina), then cooling and solidifying it in such a way that the crystals are aligned. Each crystal growth method has advantages and limitations. (See Table 3.) Given the variety of growth technologies, selecting a fabrication method is a challenge best met in collaboration with someone skilled in matching the fabrication technology and finishing process (shaping, slicing, grinding, polishing) to the intended application of the sapphire material or component. While some applications may demand sapphire's superb optical properties and scratch resistance, others may require the material's high operating temperature and mechanical durability. It is important to consider every physical and functional aspect of the proposed sapphire component in order to write specifications that result in a cost-effective (and feasible!) part.

As for finishing, how the sapphire crystal is cut can have a profound effect on performance. A sapphire crystal is a rhombohedral structure with three axes – R, A and C – and planes A, C, R, M and N. (See Figure 1.) As an anisotropic crystal of non-uniform dimensions, it displays properties that are specific to crystal orientation. These properties can be thermal, physical, optical or electrical. Although a specific crystal orientation may be unimportant for many applications, it is wise to consider its possible significance whenever specifying sapphire.

TABLE 2: Markets and applications

Semiconductor manufacturing
Substrates, wafers, plasma containment tubes, chamber viewports, lift pins, gas injectors

Optical
Laser applications; high-performance optical windows including UV, NIR, IR; NMR spectroscopy; windows, lenses, prisms, blanks

Military/Aerospace
Forward Looking Infrared (FLIR) windows, guidance systems, radiometry, missile nose domes, other general aerospace and marine applications

Industrial
Gas and chemical analysis, thermocouples, insulators for RF and microwave applications, medical instrumentation and implants, wear parts including rods, bearings, blanks, friction plates

TABLE 3: Sapphire crystal growth technologies

Method:	Verneuil	Czochralski	Kyropoulos
Date:	Late 19th century	1916	1926
Technique:	Flame-fusion (melt and drip)	Pull from the melt	Direct crystallization of the melt
Process:	In a Verneuil furnace, alumina powder is fused in a hydrogen-oxygen flame, then falls on the molten surface of an oriented seed crystal. As more fused powder falls on the resulting molten ball, the crystal enlarges.	Seed material is placed in a crucible and melted in a growth chamber. A thin seed of sapphire with precise orientation is dipped into the melt and withdrawn at a controlled rate while the crystal and crucible are rotated in opposite directions. The process is repeated continuously, with crystal layers being added during each cycle.	In a crucible, a seed crystal is mounted on a holder and the raw material is melted. Crystallization starts when the seed contacts the melt, with the crystal growing into the melt to form a hemisphere. When the crystal gets bigger and approaches the walls of the crucible, the seed crystal holder with the grown crystal rises and the growth continues until the crystal reaches the walls of the crucible again.
Advantages:	Still the least expensive way to make synthetic sapphire for some applications (e.g., synthetic sapphire gemstones, watch jewels, watch windows).	Sapphire made in this way has good optical properties suitable for lasers, IR and UV windows, transparent electronic substrates, high-temperature process windows, and other optical applications.	The size of the grown crystal is limited only by the size of the crucible, and the crystals are free of cracks and damage that can result from restricted containment. Also, resulting sapphire crystals are of very high optical quality, suitable for manufacturing ingots and substrates for LED and RF applications, windows, lenses and precision optics.
Limitations:	Limited size and shapes possible. Curved striations appear throughout the crystal, making it less suitable for optical applications.	This growth process can last up to eight weeks, requiring continuous power and monitoring.	As-grown Kyropoulos boules have circular traces around their side surface.

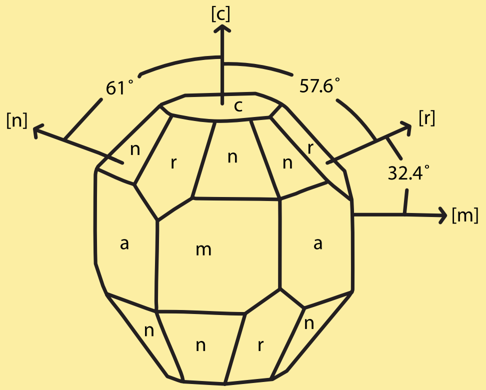
Method:	**Edge-defined Film-fed Growth (EFG) (Stepanov)**	**Heat Exchanger Method (HEM)**	**Horizontal Directional Solidification (HDS)**
Date:	1965	1967	1975
Technique:	Pull through the die	Inverted or modified Kyropoulos method	Horizontal slab growth
Process:	Alumina melted in a crucible wets the surface of a die and moves up by capillary attraction. A sapphire seed of specific crystalinity is dipped into the melt on top of the die and drawn out, solidifying into sapphire in the shape of the die.	A sapphire seed crystal is placed at the bottom of a crucible, which is then loaded with alumina crackle and placed in a furnace. Precise manipulation of heating and cooling causes the crystal to grow in three dimensions.	Crystals are grown from the melt in a horizontal container at a growth rate of 8-10mm per hour.
Advantages:	Sapphire crystals of any shape, including tubes, rods, sheets, ribbons and fibers can be produced, reducing machining and finishing costs. The crystals can have different crystallographic orientations (A, C, random).	Large boules can be created. Extended cooling process yields exceptional crystal quality.	Produces large slabs with nearly perfect edges of any crystal orientation. Enables the fabrication of very thick windows and components with excellent optical quality. Often used in blue LEDs.
Limitations:	Extra time and cost associated with producing the dies to create the shaped crystals. Low to medium optical quality limits use to mechanical, industrial and lesser grade optical applications.	Can be expensive due to the cost of replacing the molybdenum and tungsten crucibles often used in the process.	This process usually produces only thick material. As with HEM, cost may be an issue because of the use of molybdenum or tungsten boats.

What's ahead?

Recent advances in the ability to increase the size of sapphire parts – tubes up to 40 inches long, wafers approaching 12 inches in diameter, domes more than 8 inches in diameter – have opened the door to exciting design innovation. The move toward more near-net-shape crystal growth is also resulting in increased design flexibility. After more than 100 years, the story of synthetic sapphire is most definitely still being written.

For more information regarding synthetic sapphire, contact ian.doggett@goodfellowusa.com.

FIG. 1:



Crystallographic diagram of sapphire