Sapphire: Properties, Growth, and Applications

Sapphire has a high refractive index and a broad transmission band spanning the UV, visible, and IR bands. Sapphire also has a high hardness and melting point, and very good thermal conductivity, tensile strength, and thermal shock resistance (Table 1). The favorable combination of excellent optical and mechanical properties of sapphire, together with high chemical durability, makes it an attractive structural material for high-technology applications. Sapphire crystals are used in medicine and blood chemistry as they are resistant to human blood and body fluids, and are totally impervious to moisture and chemically inert. Frequently it is the combination of two, or more, of its properties that make sapphire the only material available to solve complex engineering design problems.

However, sapphire is difficult to shape owing to its high hardness and its physical properties are anisotropic since it possesses a hexagonal crystal structure. Nevertheless, there is a high demand for sapphire and it has been grown for a variety of applications by a number of techniques.

1. Bulk Crystals

1.1 Verneuil Method

One of the first techniques by which artificial sapphire was produced was the Verneuil method (Verneuil 1904), which is sometimes called the flame fusion method. In this technique, alumina powder to be crystallized is fused in a hydrogen–oxygen flame and falls on the molten upper surface of an oriented seed crystal placed in a furnace (Fig. 1(a)).

Since this is not a refined process, the material can contain voids and powder inclusions and is likely to be strained. However, crystals of up to 60 mm in diameter can be grown by this method. Figure 2 shows typical sapphire boules grown by the Verneuil technique.

1.2 Czochralski Growth

This technique originates from pioneering work by Czochralski (1917). Crystals grow from the meniscus formed on a free surface of the melt onto the seed crystal of the required crystallographic orientation. The pull rod is lifted and rotated, and crystallization onto the end of the seed occurs (Fig. 1(b)). Cockayne *et al.* (1967) reported on the pulling of single crystals of sapphire. The charge material is melted in an iridium crucible by induction in a flowing nitrogen–oxygen atmosphere. An after-heater is fitted above the crucible. Steep temperature gradients exist during crystal growth resulting in thermal stress, which can result in slip dislocations and low-angle grain boundaries, but major defects are avoided by careful high-temperature annealing.

Control of the diameter of the growing crystal has become the norm on all commercial equipment for production of large-scale, high-quality crystals. Sapphire crystals of high crystalline perfection up to

Table 1
Main properties of synthetic sapphire.

Physical
Chemical formula: α-Al_2O_3
Symmetry: $R\bar{3}c$; $a = 4.748\,Å$; $c = 12.957\,Å$
Melting point: 2053 °C
Density: 3.974 kg m^{-3}
Optical
Transmission: 0.17–6.5 μm
dn/dT: $13 \times 10^{-6}\,K^{-1}$
Refractive index at 0.589 μm: 1.760 ($\parallel c$-axis); 1.768 ($\perp$ c-axis)
Electrical
Dielectric constant at 300 K, 1 MHz: 10.6 ($\parallel c$-axis); 8.6 ($\perp$ c-axis)
Dielectric strength at 60 Hz: $48 \times 10^6\,V\,m^{-1}$
Mechanical
Hardness: Mohs 9; Knoop 2100 kg mm^{-2} ($\parallel c$-axis); 1800 kg mm^{-2} ($\perp$ c-axis)
Young's modulus at 300 K: 4.4×10^5 MPa
Tensile strength at 300 K: 190 MPa
Compressive strength at 300 K: 2100 MPa
Poisson's constant: 0.30
Thermal
Thermal expansion at 300 K: $5.3 \times 10^{-6}\,K^{-1}$ ($\parallel c$-axis); $4.5 \times 10^{-6}\,K^{-1}$ ($\perp$ c-axis)
Specific heat: 750 J kg^{-1} K^{-1}
Thermal conductivity (W m^{-1} K^{-1}): 10^4 at 30 K; 40 at 300 K; 4 at 1500 K
Maximum operating temperature: 2000 °C

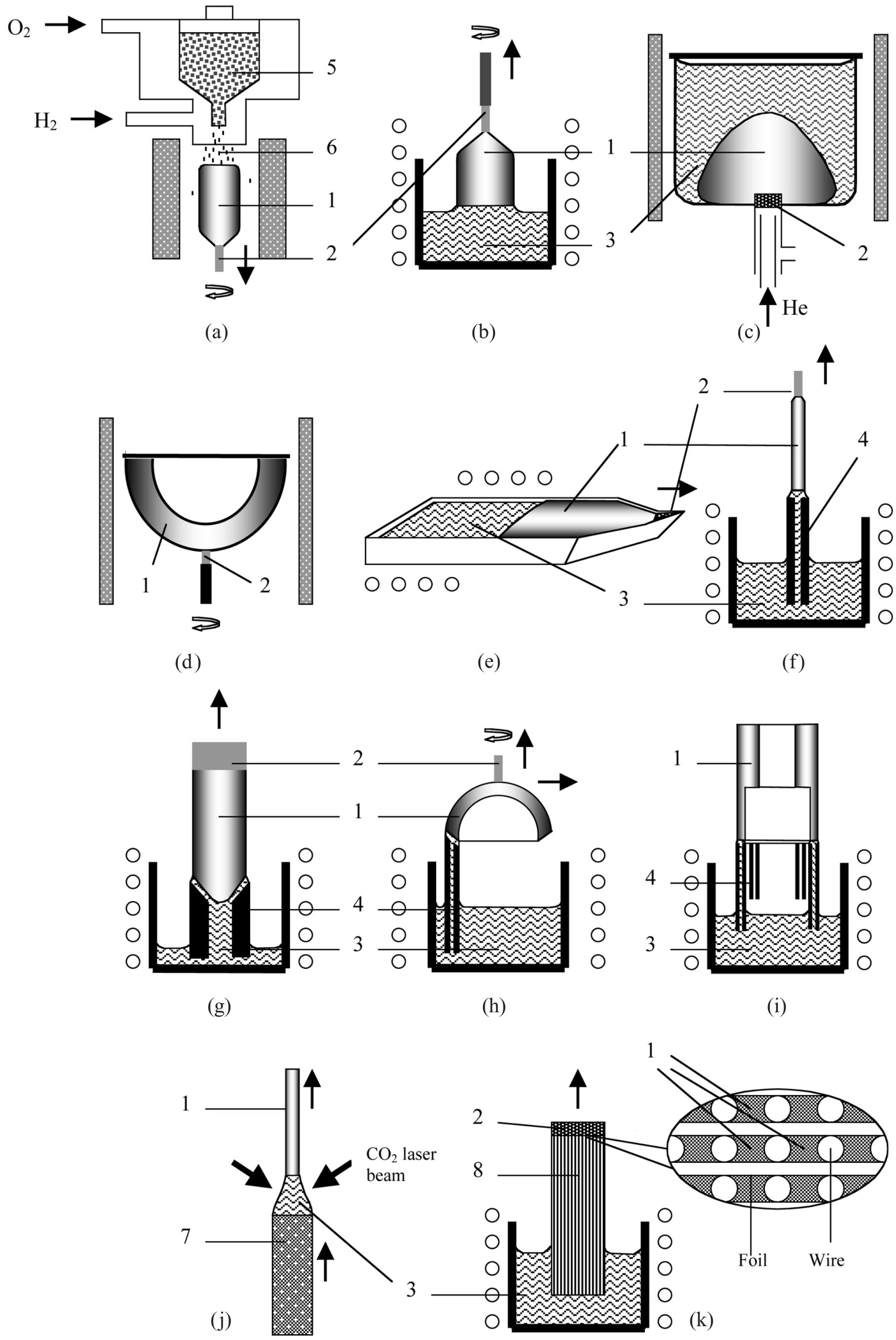

Figure 1
Schematic illustration of main sapphire growth techniques: (a) Verneuil, (b) Czochralski, (c) HEM, (d) GSM, (e) HDSM, (f) EFG, (g) NCS, (h) GES, (i) VST, (j) LHPG, and (k) ICM. 1, crystal; 2, seed; 3, melt; 4, die; 5, charge powder; 6, burning flame; 7, feed rod; 8, molybdenum matrix with fibers.

Figure 2
Sapphire crystals grown by the Verneuil technique (courtesy of RSA Le Rubis SA).

150 mm in diameter and 250 mm in length can be grown along the *c*-axis and along a direction 60° to the *c*-axis.

1.3 Heat Exchanger Method (HEM)

This method (Schmid and Viechnicki 1970) is a crystal growth process in which independent liquid and solid temperature gradients are controlled without movement of the crucible, heat zone, or crystal (Fig. 1(c)).

A distinguishing feature of the HEM, as compared to other crystal growth processes, is that the solid–liquid interface is submerged beneath the surface of the melt. Under these conditions, thermal and mechanical perturbations are damped out resulting in uniform temperature gradients at the interface. This promotes uniform growth that produces high crystal perfection and chemical homogeneity. As *in situ* annealing is part of the HEM solidification cycle, the defect density tends to be lower than that obtained with other methods.

This unique capability, combined with the ability to control cooling to room temperature, allows this method to be used to grow sapphire up to 32 cm in diameter (the largest yet achieved) and weighing about 50 kg, in many orientations including $(11\bar{2}0)$, $(1\bar{1}02)$, and $(10\bar{1}0)$. For zero birefringence optics, (0001) orientation is available in diameters up to 12 cm.

For production of near-net-shaped sapphire domes the HEM uses a double-wall preform immersed in a larger mass of molten sapphire. Crack-free, near-net-shaped (0001) orientation sapphire blanks of nearly hemispherical shape and 80 mm in diameter, with controlled outside and inside curvatures, have been produced directly from the melt by this method (Khattak and Schmid 1989).

1.4 Gradient Solidification Method (GSM)

This process was developed for the specific purpose of near-net-shape sapphire dome growth (Horowitz *et al.* 1993). The domes are grown in double-walled molybdenum crucibles (Fig. 1(d)), located at carefully designed thermal gradients and the growth is carried out via temperature lowering. The GSM is used to grow sapphire domes with different orientations, including the *c*-axis (zero birefringence) orientation, and with different geometry, including hemispherical. The process has the capability of growing near-net-shape domes as well as boules up to 150 mm in diameter with no grain boundaries and scattering centers.

1.5 Horizontal Directed Solidification Method (HDSM)

This method (Bagdasarov 1975) makes it possible to produce, using a simple procedure, a low-gradient temperature field for growing unstressed, large-scale sapphire crystals. The method can be understood as a modification of the horizontal Bridgman method. A molybdenum container (boat) is moved relative to a heater of rectangular cross-section (Fig. 1(e)). This economical method is used to grow plate crystals of different orientations with standard optical quality in sizes up to $250 \times 250 \times 25\,\mathrm{mm}^3$.

1.6 Applications

The main applications of sapphire bulk crystals are special windows, substrates, watch blanks, domes for relatively high-speed missiles, insulators, water and electrical meters, research and technological equipment, jewelry, etc.

2. Shaped Sapphire Crystals

Stepanov (1963) was the pioneer of the shaped crystal growth field. He formulated a crystal-shaping principle, namely that the shape or an element of shape is created in the liquid state, and then the shape or element is converted to the solid state by the use of appropriate crystallization conditions. The grown crystal has a shape close to that of the liquid column controlled by the shaper.

2.1 Edge-defined Film-fed Growth (EFG)

The first mention of EFG and its application to sapphire was by LaBelle and Mlavsky (1967). In the EFG technique, crystals are grown from a melt film formed on the top of a capillary die (Fig. 1(f)). The melt rises to the crystallization front within the capillary channel. It is ideal for producing crystals with a small square cross-section. Sapphire crystals can be grown in an automated way with weight control (Kurlov and Rossolenko 1997). Automated computer systems provide *in situ* crystal quality control as well as crystal shape control, which allow an increase in the output of high-quality crystals and the expansion of the areas of applications of sapphire crystals as constructive and optical material.

The technique of growing shaped sapphire crystals is well developed. Ribbons up to 150 mm in width, tubes up to 85 mm in diameter, fibers, near-net-shaped domes (up to 80 mm in diameter), rods of various cross-sections, rods with capillary channels, etc., have been grown by the EFG technique.

2.2 Noncapillary Shaping (NCS) Method

The main feature of the NCS technique is the delivery of the melt to the growth interface through a noncapillary channel via a wettable die (Kurlov 1997) (Fig. 1(g)). The melt column has negative pressure as in the EFG method. The word "noncapillary" indicates here that the diameter of the channel is greater than the value of the capillary constant.

The NCS method, as distinguished from the technique based on the traditional capillary feed, ensures the absence of microvoids, and gaseous and solid inclusions, which are formed in the regions with the minimal components of a melt velocity below the crystallization front. The dominant flow always moves from the center to periphery irrespective of crystal cross-section, thus enabling the growth of large sapphire crystals free of bulk inhomogeneities. The forming of the optimal interface surface and the hydrodynamic flows of the melt under the crystallization front are determined by the shape of the top surface of the die, by the velocity of growth, and by the size of the noncapillary channel.

Sapphire crystals of any predetermined cross-section, constant along the crystal length (rods of various cross-sections for optics, thick ribbons, and tubes with large wall thickness), and crystals with discretely changing cross-sectional configuration up to 80 mm in diameter (domes, boats, crucibles) can be grown by the NCS method.

2.3 Growth from an Element of Shape (GES)

The GES method consists of pulling a shaped crystal from a melt meniscus, which is only a small element of the whole transverse cross-section of the growing crystal (Antonov *et al.* 1985) (Fig. 1(h)). Actually, a comparatively small liquid volume displaced relative to the seed can result in crystals with complicated shapes. During the growth, the displacement may be applied to the seed or the die, or to both simultaneously. Crack-free sapphire domes (Théodore *et al.* 1999) and hollow cones without gas bubbles and grain boundaries in their volume have been obtained by the GES method.

2.4 Variable Shaping Technique (VST)

The technique of discrete variation of the dimensions and geometry of crystal cross-sections during growth was proposed by Kravetskii *et al.* (1980). The method was developed by Borodin *et al.* (1985) and was called the VST (Fig. 1(i)). In order to change the preset crystal shape during crystallization and to preserve the altered cross-sectional configuration during further growth, it is necessary to alter the geometry of the liquid meniscus. The VST may be treated as a consequence of the steady-state growth steps with different transition crystallization modes. During the transition, the base of the meniscus moves across the top surface of the die assembly from one edge to another, and the meniscus mass is altered.

Sapphire crucibles, boats, and other profiles with variable cross-sections up to 25 mm in diameter have been grown by the VST.

Figure 3 shows shaped sapphire crystals (tubes, ribbons, fibers, crucibles, boats, rods, hollow bodies, thread items, etc.) grown by various techniques (EFG, NCS, VST, and GES).

2.5 Applications of Shaped Sapphire Crystals

The main applications of shaped sapphire crystals are scanner windows, CVD reactors, arc envelopes for vapor lamps, domes for relatively high-speed missiles, watch windows, thermocouple sleeves, wear-resistant nozzles, insulators, high-pressure reactors, high-vacuum equipment, nuclear components, water and electrical meters, research and technological equipment, medical implants and instrumentation, etc.

3. Sapphire Fiber Crystal Growth

3.1 EFG Fibers

The first sapphire fibers were grown by EFG techniques (LaBelle and Mlavsky 1967) as structural reinforcement in composite materials. Flexible, continuous sapphire filaments of diameters in the range 100–500 μm, spooled up onto a rotating drum, can be obtained. The fibers are grown in *c*- and *a*-axis directions with very high growth rate (up to 20 cm min^{-1}) using a molybdenum die. Fibers show a high tensile strength some 5–10 times higher than Verneuil-

Figure 3
Shaped sapphire crystals grown by the EFG, NCS, VST, and GES techniques.

grown single crystals. Sapphire EFG fibers have a wide range of applications. However, the cost of fibers obtained by the EFG technique is too high for their use in structural applications.

3.2 Laser Heated Pedestal Growth (LHPG)

The first pedestal growth experiments were reported by Poplawsky (1962), who provided focused energy by an arc image furnace. The LHPG method was subsequently developed by Haggerty (1972) and Feigelson (1986). A tightly focused CO_2 laser is the heat source used to melt the refractory material. Growth proceeds by simultaneous upward (or downward) translation of the seed and source rods with the molten zone positioned between them (Fig. 1(j)). The laser focal spot, and consequently the zone height, remains fixed during fiber growth. Completely void-free sapphire fibers of various orientations have been obtained by the LHPG method for microlasers and other applications.

3.3 Internal Crystallization Method (ICM)

This method was originally developed to produce candidate materials for fiber reinforcement of metal matrices (Mileiko and Kazmin 1992). The crystallization of the sapphire fibers within a volume of an auxiliary matrix begins on an oriented (0001) seed located at the top of a molybdenum block with a system of internal channels and subsequent moving of the matrix to a cold zone of the furnace (Kurlov *et al.* 1999) (Fig. 1(k)). Extraction of the fibers after crystallization is achieved by dissolving the molybdenum matrix in acid mixtures. Sapphire fibers of homogeneous crystallographic orientation obtained by this method are shown in Fig. 4. The productivity rate of the process, which includes crystallizing a very large number of fibers at the same time, can be very high. The low energy input per unit mass of fiber is the main advantage of the process.

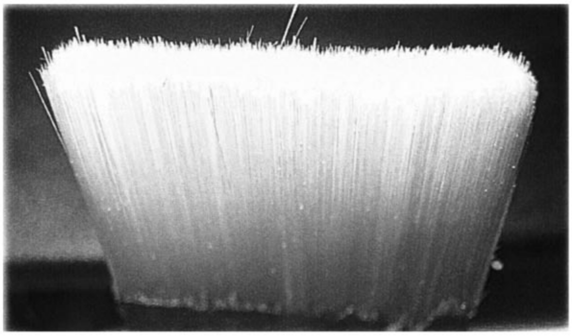

Figure 4
A bundle of sapphire fibers grown by the ICM.

The strength of ICM-grown sapphire fibers at room and elevated temperatures is sufficiently large for their use in metal-matrix, ceramic-matrix, and oxide-fiber/oxide-matrix composites.

3.4 Applications of Sapphire Fibers

The main applications of sapphire fibers are lasers, light guides, reinforcing fibers for composite materials, medical power delivery systems, sensors, etc.

4. *Concluding Remarks*

Sapphire has been produced commercially for many years and its unique properties make it an ideal material for hundreds of applications. Despite the fact that sapphire has been used for many years, it is still in a stage of development. Optimization of standard crystal growth technologies and development of new techniques are actively pursued in order to increase the dimensions of crystals, improve the crystal quality, reduce the cost of material, and to grow complex shapes. There are good reasons to believe that sapphire will not only strengthen its position in traditional markets, but will also be used in a number of new applications.

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