A century of sapphire crystal growth: Origin of the EFG method

Daniel C. Harris*
Naval Air Systems Command, 1900 N. Knox Rd., Stop 6303, China Lake CA 93555

With contributions from Harold LaBelle and M. I. Musatov

ABSTRACT

A. Verneuil developed flame fusion to grow sapphire and ruby on a commercial scale around 1890. Flame fusion was further perfected by Popov in the Soviet Union in the 1930s and by Linde Air Products Co. in the U.S. during World War II. Union Carbide Corp., the successor to Linde, developed Czochralski crystal growth for sapphire laser materials in the 1960s. Edge-Defined Film-Fed Growth (EFG) was invented by H. Labelle in the 1960s and the Heat Exchanger Method (HEM) was invented by F. Schmid and D. Viechnicki in 1967. Both methods were commercialized in the 1970s. Gradient solidification was invented in Israel in the 1970s by J. Makovsky. The Horizontal Directional Solidification Method (HDSM) was invented by Kh. S. Bagdasorov in the Soviet Union in the 1960s. Kyropoulos growth of sapphire, known as GOI crystal growth in the Soviet Union, was developed by M. Musatov at the State Optical Institute in St. Petersburg in the 1970s. Today, half of the world's sapphire is produced by the GOI method.

INTRODUCTION

The naturally occurring form of sapphire is the mineral corundum whose chemical composition is Al_2O_3. Precious forms of the mineral are red ruby (Cr^{3+}-doped Al_2O_3) and blue sapphire (Fe^{2+}/Ti^{4+}-doped Al_2O). Pure corundum melts at 2050°C and has a hardness of 9—second only to diamond on the mineralogical scale. Among common synthetic materials, only silicon carbide and boron nitride are harder than corundum.

Synthetic sapphire has been made for more than a century. Its most important commercial applications today are as a substrate for solid-state lighting (Figure 1) and for silicon-on-sapphire radio-frequency integrated circuits. Key requirements for substrates are crystalline perfection, high-temperature stability, and chemical inertness. The demand for substrates in 2008 was seven million 2-inch-equivalent substrates. Sapphire is laminated to the face of bar code scanner windows in retail stores to resist scratching by packages dragged across the window. Sapphire is used to make custom equipment for semiconductor processing and other kinds of manufacturing in which high-temperature stability in corrosive environments is required. Titanium-doped sapphire is an important solid-state laser material. Sapphire optical fibers are used in medicine to deliver light from Er:YAG lasers to sites in the body. Sapphire is used to make scalpels and prosthetic components for replacement of body parts. Sapphire windows and domes are used to protect infrared, visible, and ultraviolet sensors when durability is required. Sapphire fiber guides in the textile industry are used because sapphire is not rapidly worn out by passage of the fiber through the guide.

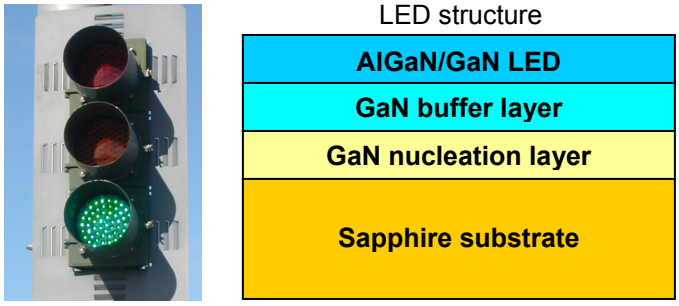

Figure 1. Sapphire substrates are found in aluminum gallium nitride light-emitting diodes (LEDs) for applications such as green traffic lights and white LED flashlights.

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Optical Materials and Structures Technologies IV, edited by Joseph L. Robichaud, William A. Goodman,
Proc. of SPIE Vol. 7425, 74250P · © 2009 SPIE · CCC code: 0277-786X/09/$18 · doi: 10.1117/12.824452

FLAME FUSION

Figure 2. Ruby grown by Verneuil method rests on alumina support. [Aram Dulyan, Natural History Museum, London]

The foundational science and technology for commercial production of sapphire and ruby date back to the work of Auguste Verneuil (1856-1913) at the Museum of Natural History in Paris around 1890.[1,2,3] Verneuil aimed a downward-pointing hydrocarbon-oxygen flame at the top of a pile of aluminum oxide (Al_2O_3, also called alumina) powder. The flame fused some of the powder, which solidified into a small crystal. Verneuil then sprinkled alumina powder through the flame. Particles of molten alumina landing on the surface of the small crystal fused with the crystal and caused it to grow. By adding chromium oxide to the alumina, beautiful crystals of red ruby (chromium-doped sapphire) could be grown (Figure 2). There was an immediate demand for synthetic ruby and sapphire for the jewelry industry and to make bearings for watches and precision instruments.

In the Soviet Union, S. K. Popov (1903-1953) began experiments with the Verneuil method in 1932.[4] By 1938 he had produced a semi-automatic growth apparatus which enabled long, thin rods to be manufactured for making jewels for watches and precision instruments. From 1938 until his death, Popov worked at the Institute of Crystallography of the Academy of Sciences of the USSR. In 1945-1950 he perfected equipment for making ruby rods, solving such problems as accurate supply of powder and uniform heating of the growing crystal. In 1951-1953 he developed a new use for sapphire as a durable fiber guide in the textile industry.

During World War II, America was cut off from European supplies of jewel bearings, so the government funded Linde Air Products Co. in Indiana beginning in 1942 to implement the Verneuil process. Linde was later acquired by Union Carbide Corp. After the war, the U.S. could not compete with Europe for economic sapphire production. The Linde plant in Indiana was closed in 1974.

CZOCHRALSKI SAPPHIRE

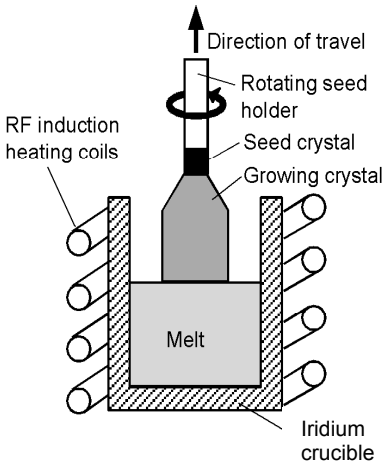


Figure 3. Czochralski crystal growth.

A resurgence of interest in ruby arose with the invention of the ruby laser in 1960 using a Verneuil boule grown by Union Carbide in 1959. It was quickly learned that the optical quality of Verneuil boules was not adequate for lasers. This dilemma led to the development of sapphire growth by the Czochralski method at Union Carbide in the 1960s. In Figure 3, alumina is melted in an iridium crucible in an atmosphere of 98% N_2 / 2% O_2. A seed crystal is then dipped into the liquid and withdrawn at a rate of 6-25 mm/h while rotating at a rate up to 30 revolutions/min. As the seed is withdrawn, alumina from the melt crystallizes onto the seed. The diameter of the boule is controlled by the rate of withdrawal of the seed. Diameters up to 11 cm can be obtained from a 15-cm-diameter crucible.

Union Carbide's Linde Crystal Products Division concentrated on Czochralski crystal growth in California and Washington State. In 1999 the Crystal Products Division was acquired by Bicron, a division of the French company, Saint-Gobain. In 2000 the division was renamed Saint-Gobain Crystals and Detectors. Saint-Gobain in Washington State and Crystar Research (a division of Johnson Matthey and later Honeywell) in Vancouver, Canada both produced sapphire by the Czochralski method. In 2008, Crystar was acquired by the Silian Instruments Group from China.

EDGE-DEFINED FILM-FED GROWTH (EFG)

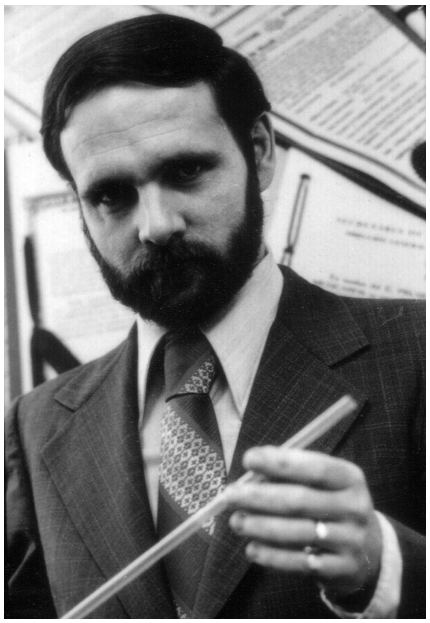


Figure 4. Harold Labelle, Jr. (1938–) in mid 1970s.

Harold LaBelle, Jr. (Figure 4) was born and raised in Brockton, Massachusetts in a low-income home. During high school, he worked as a meat cutter and never considered attending college. He joined the Navy reserves during high school and was ordered to active duty in 1956. Military aptitude tests showed that he was good at analyzing data, so the Navy sent him to a 16-week school to become an aerographer's mate—a weather man. For the first time in his life, Harry realized that he had talent beyond meat cutting. He applied himself to his studies and finished second in a class of 50.

Harry was assigned to work with the Air Force at White Sands Proving Ground in New Mexico. One of his jobs was to track objects released from a rocket to gauge the winds in the upper atmosphere. Although the only mathematics he took in high school was algebra, he had the interest and aptitude to take a class in calculus during his time at White Sands. When he left the Navy in 1960, he spent a semester at New Mexico State University as a physics major. He was married in 1957 and there was no possibility of going to college when he and his wife returned to Massachusetts.

Through the Massachusetts unemployment office, he found a job as a crystal growth technician at Raytheon in Waltham in 1961. Six months later, Raytheon cut its workforce and Harry lost his job. In 1962, he found a job at the Materials Research Laboratory—a small, busy company owned by Arthur Tyler. He found himself "swimming in a pool of PhDs" to whom he could address questions and from whom he learned a great deal. Allowed to do much on his own, he blossomed as he learned to grow semiconductor crystals by gradient freeze and "traveling solvent" methods, from which he gained an understanding of solid-liquid interface control.

After asking his boss, Ed Mlavsky for a project of his own, in 1965 Harry was given the lead role on an Air Force contract whose goal was to make sapphire fibers for reinforcement of metal matrix composites.[5,6,7] The cost goal for the fibers was <$200 per pound. Fibers needed to be strong, but there was no requirement for optical quality. By analogy with silicon growth at other laboratories, Harry found that if he plunged a cold tungsten rod into molten alumina, small, crystalline alumina dendrites grew from the tungsten, which served as a seed. However, the longest dendrites were only 3 mm, which was much shorter than required. In an attempt to improve temperature stability, he melted alumina in a tungsten boat in a vacuum evaporator. When a 0.25 mm tungsten wire was dipped into the melt and carefully lifted out, a sapphire crystal grew on the tungsten wire "seed". This process was essentially a Czochralski crystal growth that produced a carrot shaped sapphire crystal with the tapered tip attached to the last drop of molten alumina (Figure 5).

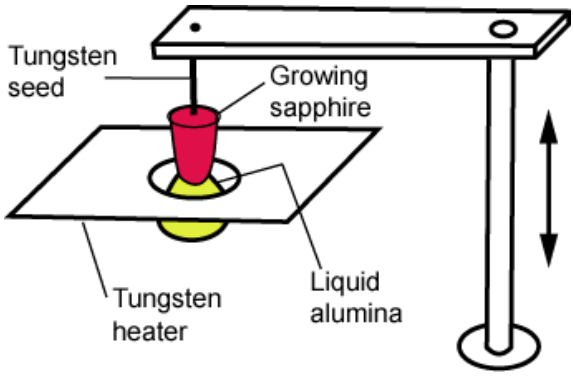


Figure 5. Czochralski-like growth of sapphire from molten alumina using tungsten wire as a "seed crystal". Redrawn from reference 6.

The final diameter of the sapphire depended on the diameter of the liquid drop remaining in Figure 5. Harry reasoned that a droplet of the right cross section would produce a filament of the desired cross section. A method was needed to feed liquid with a constant cross section from a reservoir so that long filaments could be produced. Therefore, he floated a molybdenum washer on top of molten alumina and drew a fiber by Czochralski-like growth through the orifice of the washer (Figure 6). Several 1-mm-diameter crystals up to 30 cm long were grown in this manner. These results were impressive enough to secure additional funding for the project.

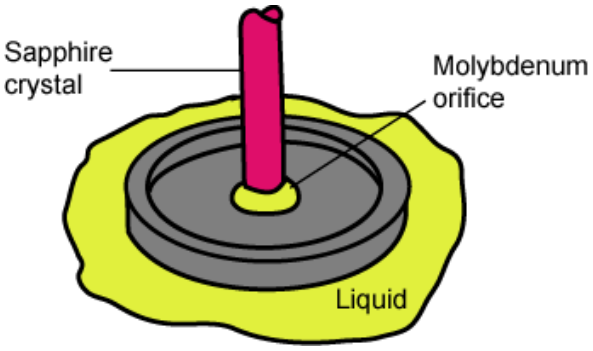


Figure 6. Sapphire crystal growth by the floating orifice technique in 1965. Redrawn from Ref. 6.

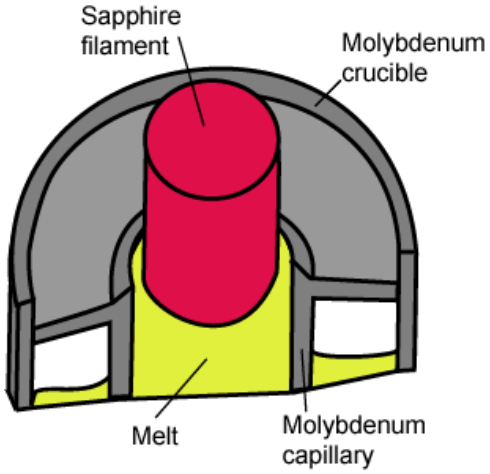


Figure 7. Self-filling capillary tube for filament growth in 1966. Redrawn from Ref. 6.

For several months, Harry grew crystals by this floating orifice technique. Eventually, he concluded that floating dense molybdenum on less dense alumina was too delicate for use in manufacturing. It then occurred to him that "a molybdenum capillary projecting out of the melt might yield the positive result that the floating orifice had, yet represent mechanical, and therefore, thermal stability as well."[6] The *self-filling tube* in Figure 8 provided filaments with more regular surfaces and 3 to 4 times as much strength as that of filaments grown earlier.[6,8] The capillary in Figure 8, made from concentric molybdenum tubes, produced the first sapphire tubes. Many tubes and ribbons were grown from self-filling tubes in 1967.

In a key observation, Harry noticed that sometimes the sapphire diameter grew larger than that of the orifice from which it was drawn. The difference depended on the angle of the upper surface of the orifice. He reasoned that, if the top surface of the molybdenum were flat, the liquid would spread to the edge and then stop. A crystal grown from such a capillary would be just as wide as the outer diameter of the molybdenum. Harry and his assistant, John Bailey, built the die in Figure 9, which easily produced a rod whose outer diameter was equal to the outer diameter of the molybdenum.

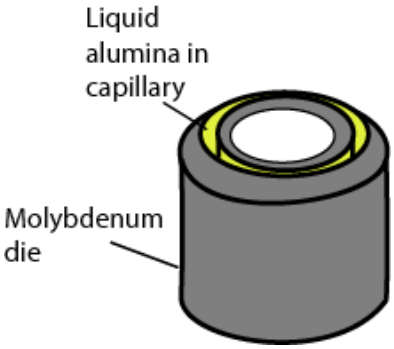


Figure 8. Self-filling capillary tube for tube growth in 1966. Redrawn from Ref. 6.

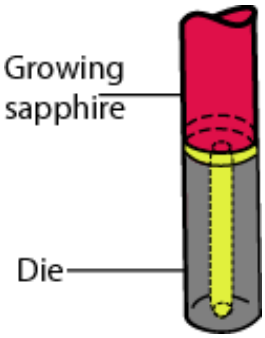


Figure 9. First edge-defined film-fed growth of a sapphire rod whose wall dimensions were equal to the dimensions of the molybdenum die (1966). Redrawn from Ref. 6.

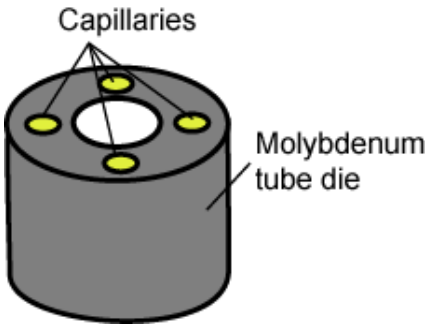
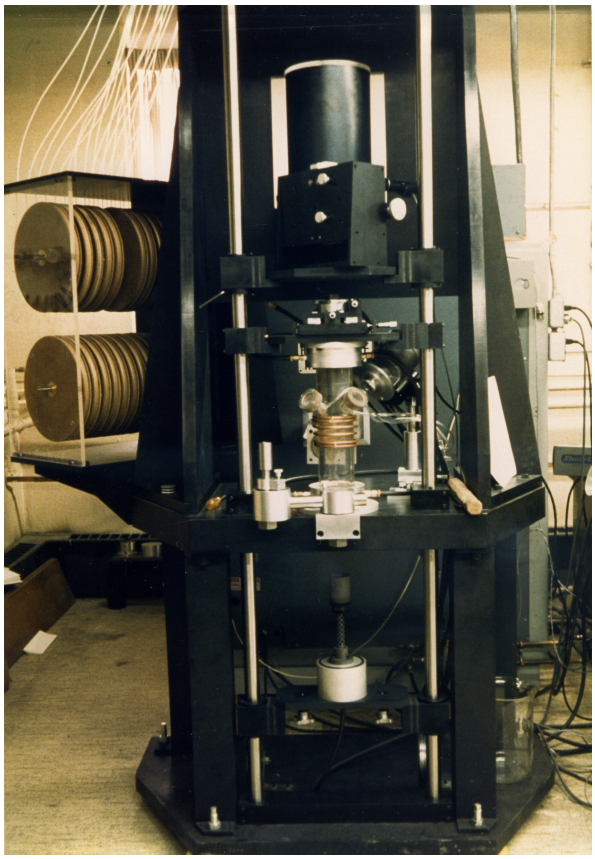


Figure 10. Die used in 1966 to prove that the edge of the molybdenum die defined the edge of the sapphire crystal. Redrawn from Ref. 6.



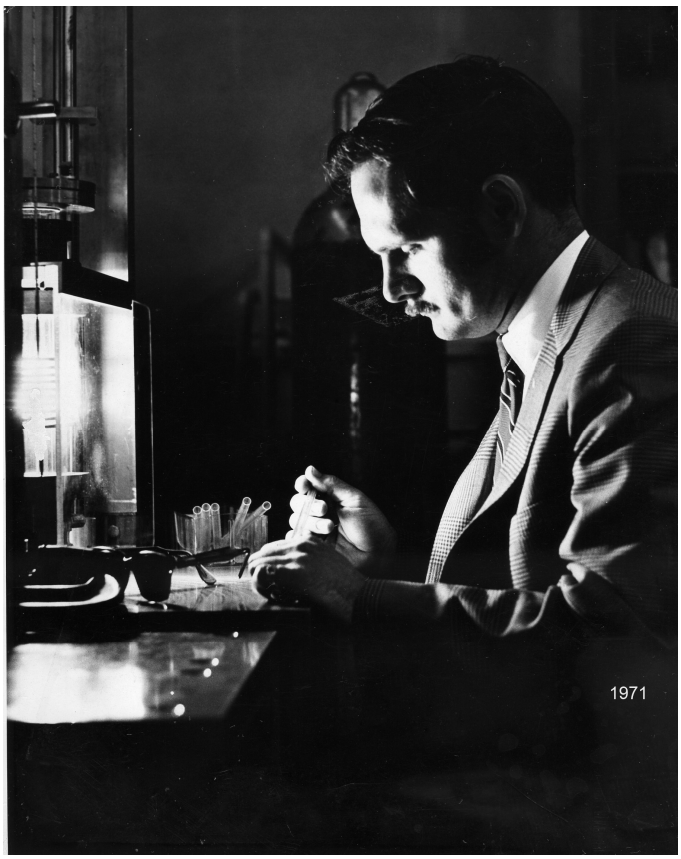


Figure 11. Sapphire multiple filament machine in 1971. **Figure 12.** Sapphire tube machine with Harry Labelle in 1971.

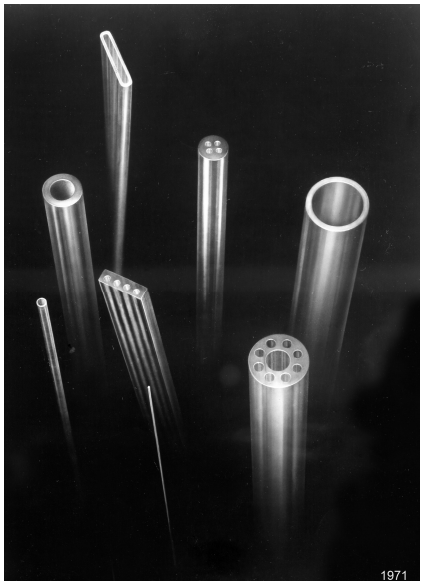


Figure 13. EFG sapphire shapes (1971).

Because the dimensions of the sapphire rod grown in Figure 9 were controlled by the molybdenum die, Ed Mlavsky coined the term "Edge-defined Film-fed Growth," or "EFG." To distinguish between edge-defined growth and self-filling tube growth, the die in Figure 10 was constructed. If the top surface of the molybdenum die controlled the shape of the crystal, then a uniform tube would grow from the liquid fed through the four capillaries. Sure enough, the die produced a tube with uniform walls. "The uniqueness of EFG in shaping was therefore established ... since the capillaries were of totally different cross-sectional shape than the growing crystal."[6]

The purpose of the Air Force contract at Tyco was to grow long filaments of sapphire. To accomplish this, Harry invented a mechanism to guide the growing fiber and to pull long lengths with a small machine. Harry's emphasis was on developing a useful manufacturing process, not just applied research. In a subsequent Air Force contract, Harry produced a puller that could make 25 sapphire filaments and wrap them onto separate spools in a continuous process (Figure 11). The strong sapphire fibers were in demand for research on the reinforcement of nickel-based alloys. With a properly designed die, sapphire tubes (Figure 12) and more complicated shapes (Figure 13) could be made. Harry filed a patent application for his crystal growth method in January 1968 and the patent was awarded in July 1971.[9] A paper describing the method was also published in 1971.[10]

The initial fibers grown for the Air Force were translucent and had no need for transparency. However, by the early 1970s, transparent sapphire could be grown in many shapes.[7,8,11] An early application of transparent EFG tubing was for sodium vapor lamps produced by Westinghouse. (Sapphire was eventually replaced by the less expensive General Electric Co. Lucalox alumina in this application.) Another significant market for transparent sapphire was 12.5 × 12.5 × 0.6 mm windows for erasable programmable read-only memory (EPROM) chips. By the late 1970s, *7.2 kilometers of sapphire ribbon per week* in 0.9-meter-long increments were being manufactured for EPROM windows with a unit price of $0.15. With its improved ultraviolet transmission, sapphire replaced translucent alumina in this application. Beginning in the mid 1970s, Saphikon was the leading manufacturer of sapphire-laminated bar code scanner windows, which it developed for and with IBM.

In the mid 1960s, Tyler's Materials Research Laboratory became Tyco Laboratories. Despite having no academic credentials, Harry LaBelle's noteworthy achievements led him to ask Tyco Vice President Ed Mlavsky for a promotion to Staff Scientist, which was agreeably granted. Mlavsky was both Harry's closest mentor and his boss. In 1970 Tyco created the Saphikon Division under the leadership of Harry LaBelle to manufacture sapphire by the EFG method. Later in his life, Harry described his assumption of the top management role in Saphikon as a mistake, because—despite his good business sense—he was better at developing new technology than he was at managing a company. In 1978, Harry moved Saphikon from Waltham to Milford, NH, where it is still located today in 2009.

In the 1970s and 1980s Saphikon received the bulk of its revenue by licensing its process to companies such as Kyocera, RCA, Corning, and Allied Signal, all of whom saw commercial potential for substrates for the newly developing silicon-on-sapphire electronics technology. Johnson & Johnson licensed the process to make transparent sapphire for dental braces. In 2009, Kyocera and another Japanese company, Namiki, are still major producers of EFG sapphire.

In 1982, Joseph Gaziano, the president of Tyco, died and John Fort became president. By 1985, Harry LaBelle was "burned out" as head of Saphikon. He gave Tyco 12 months' notice that he would retire from the hectic pace. With Harry about to leave, and with Saphikon revenues hovering only around $2M/year, John Fort sought to sell Saphikon, but no buyers emerged. Fort then invited Harry to "make an offer" to purchase the company. Harry and his wife considered that request carefully and, even though they wanted to retire, they offered "book value" for the company. That very low offer was accepted and Harry and his wife found themselves owners of Saphikon. They ran it successfully until health issues led them to sell the company to Cy Gregg at a nice profit in 1987 and truly retire. Gregg owned the company until 2000 when Saint-Gobain purchased Saphikon and the rights to make sheets, rods, tubes, and 3-dimensional shapes. The newly formed company Photran retained exclusive rights to manufacture sapphire fibers.

SHAPED CRYSTAL GROWTH BY THE STEPANOV METHOD

Alexander V. Stepanov (1908-1972) was raised in Leningrad (Saint Petersburg) and graduated from the Physical and Mechanical Faculty of Leningrad Polytechnic University in 1930.[12] His Ph.D. thesis submitted to the Leningrad Physical and Technical Institute of the USSR Academy of Sciences in 1937 dealt with the mechanism of plastic deformation in crystals. In 1939, he was awarded the degree of Doctor of Sciences, which is higher than the Ph.D. In 1938 he began his life's work pulling shaped materials from a melt. He made metal shapes by pulling solid metal from molten metal through shapers (guides) on the surface of the molten metal (Figure 14). Shapers were metal plates with holes to guide the metal being pulled.

Stepanov's application for a Soviet patent in 1940 was denied. One reviewer said that the method was already practiced for pulling glass sheets. The other reviewer stated that the viscosity of molten metals was too low for the method to possibly work. By 1959, Stepanov had given up hope of getting a patent and published his method for pulling aluminum shapes. Only in 1974 were his students able to convince the patent office of the validity of the original application. A posthumous patent with a priority of 1941 was finally awarded.

Stepanov spent much of his career at the Leningrad Physical and Technical Institute and he was also a professor of Physics at the Leningrad Teachers' Training College. He never married and was devoted to his work. His method was applied extensively to metals such as aluminum and to single crystals including germanium. By the late 1960s, 85% of

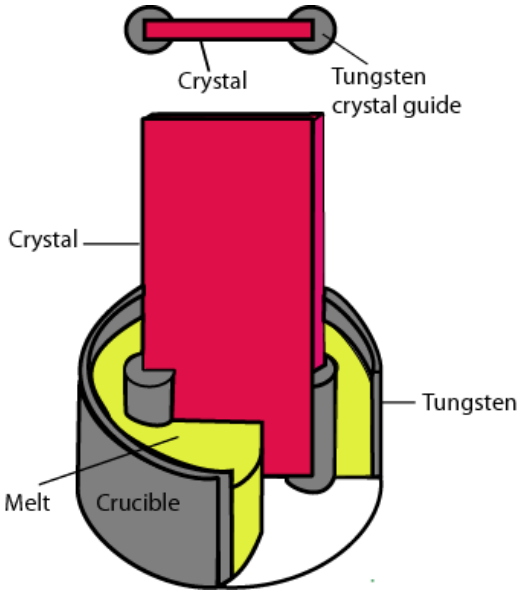


Figure 14. Stepanov growth of shaped crystal through guides.

germanium in the Soviet Union was grown by the Stepanov method, which was a state secret. For electronics, 26 10-mm-diameter cylinders of germanium were pulled at one time from one crucible and sliced into wafers.

RELATION OF STEPANOV AND EFG SAPPHIRE CRYSTAL GROWTH

The Stepanov method uses wettable or nonwettable aids to shape the melt column which, in turn, dictates the shape of the grown crystal (Figure 14).[11] By contrast, in edge-defined film-fed growth, the shape of the die, not the shape of the melt column, controls the shape of the crystal.

Nobody claims that sapphire was grown by Stepanov or his colleagues before Harry LaBelle's patent appeared and the EFG method was presented in 1971 by LaBelle at the Third International Conference on Crystal Growth in Marseille, France in July 1971.[13] Stepanov's associate P. I. Antonov was in the audience at the conference and LaBelle gave Antonov an 8-hole EFG sapphire tube as a gift.[14]

The organizers of the Third International Conference on Crystal Growth described the proceedings as follows in Ref. 13, page XVI (translated from French at Tyco Labs): "Undoubtedly the peak of 'savoir faire' (knowledgeability) on the subject of crystal growth was presented by a team from Tyco Laboratories. The principle of pulling monocrystals of well defined form through nozzles compares with the technique of the glassmakers, and in respect to crystals it dates back to Stepanov (1959) and Gol'tsman (1962). In the technique presented at ICCG-3 by H. E. LaBelle, Jr., the shape of the single crystal is not determined by the orifice in the die as was the case previously. Here the orifice serves only to bring, by capillarity, the liquid in the crucible to the top surface of the die across which it spreads. A seed put in contact with this film of liquid is pulled as a single crystal, the cross section of which is defined precisely by the full section of the die. These authors have played in a subtle manner with capillary forces. Hundreds of meters of refractory crystals of perfectly defined form, quite often a sophisticated one, can be pulled at speeds of several cm/sec. The audience was subdued by the apparent simplicity of the technique. There is no doubt that this work will have considerable echoes in industry, and definite repercussions in laboratories of research on crystal growth."

Stepanov's colleage and former student, V. Tatarchenko, described the Soviet reaction to the EFG technique:[12] "All variants of pulling techniques from the shaper were named Stepanov Techniques. Many laboratories in the former Soviet Union carried out many experiments in this field with different materials. The publication of the Edge Defined Film Fed Growth (EFG) patents changed the situation drastically. For Stepanov, it was a problem of his patent and the necessity of formulation: What does Stepanov's technique mean? At that time, he had some Russian patents…for concrete schemes for profile pulling, for instance, for germanium and aluminium, but his dream was to obtain a global patent. He asked me to help him. Unfortunately at that time, he changed his modest 1940 formulation and pretended to invent 'the Principle of shape formation from a melt, using capillary forces or some other actions (except of crucible walls) on the melt, of the cross section or an element of a cross section of solid profile its following crystallisation'. I tried to convince him that it was impossible to pretend with the 'umbrella' patent because it covered the Czochralski technique, the Verneuil technique, and the floating zone technique." In other words, after the EFG method was published, Stepanov sought to explain how the EFG method was a particular case of the more general Stepanov method.

A paper published in 1986 by Tatarchenko and his colleagues stated that "profiled sapphire crystals were first made in the early 1970s by Stepanov's method, which initiated a new stage in the use of this material."[15] The first two methods mentioned by Tatarchenko for growing shaped sapphire were two Saphikon patents from 1975. Soviet improvements to shaped sapphire growth are then described in publications from 1982 and 1983.

In summary, an argument could be made that the EFG method is a special case of the more general Stepanov method. However, the EFG method as described by LaBelle was not practiced prior to his invention, and shaped sapphire was not made in the Soviet Union prior to LaBelle's publications.

HEAT EXCHANGER METHOD

The Heat Exchanger Method (HEM) for growing large sapphire boules was invented by Fred Schmid and Dennis Viechnicki at the Army Materials Research Lab in Watertown, Massachusetts in 1967. The modern implementation of the heat-exchanger method at Crystal Systems in Salem, Massachusetts is shown in Figure 15. A sapphire seed crystal is placed at the bottom of a molybdenum crucible which is then loaded with pure alumina crackle, a byproduct of the Verneuil process. The furnace is evacuated and resistively heated to melt the crackle while keeping the seed just below its melting point by passing helium gas through the heat exchanger beneath the center of the crucible. Heat and vacuum help purify the alumina by vaporizing some impurities. After partial melting of the seed, helium flow is increased to cool the seed and initiate crystallization of alumina onto the seed. The furnace is held at constant temperature during growth of the crystal, which proceeds out from the seed in three dimensions. After crystallization is complete, the furnace temperature and the helium flow are decreased and the boule is slowly annealing *in situ*. The long slow cooldown produces sapphire of very high crystal quality. Boules with a diameter up to 38 cm and a mass of 82 kg are produced. In the heat-exchanger method, highest crystal quality is produced when the axis of the boule is the *a*-, *m*-, or *r*-axis of the crystal. Most often, the *a*-axis is the boule axis.

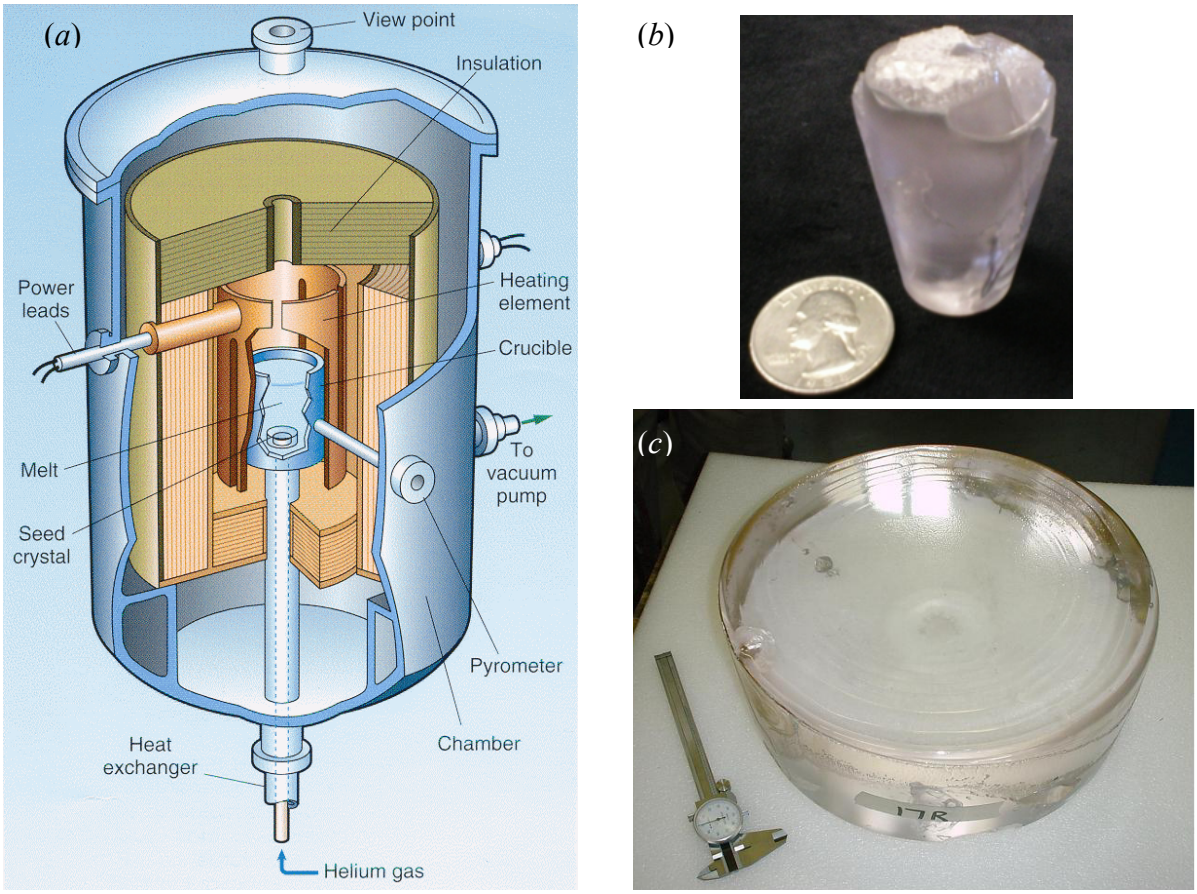


Figure 15. (*a*) Furnace used at Crystal Systems to grow sapphire by the Heat Exchanger Method. (*b*) The first sapphire boule grown in 1967. (*c*) Production-quality 34-cm-diameter sapphire boule. Courtesy Crystal Systems, Inc.

GRADIENT SOLIDIFICATION METHOD

Figure 16. Joseph Makovsky (1928–2004).

Joseph Makovsky (Figure 16) developed the gradient solidification method for growing sapphire in Israel in the 1970s. With further development by Atara Horowitz and her colleagues, this method is now used at Rotem Industries in Israel to make near-net-shape sapphire domes, as well as boules.[16,17] Alumina is loaded into a hemispheric molybdenum crucible with a sapphire seed at the bottom. The crucible is heated in vacuum to produce a gradient of temperature, with the highest temperature at the top. When the seed has partially melted, the temperature is lowered in a controlled manner so that crystallization proceeds out from the seed crystal.

BAGDASAROV HORIZONTAL DIRECTIONAL SOLIDIFICATION METHOD

The horizontal directional solidification method for growing sapphire, commonly called HDSM, was pioneered by Kh. S. Bagdasarov (1929–) in Moscow at the Institute of Crystallography, Russian Academy of Science in the early 1970s. In this process, raw aluminum oxide (crackle) is placed in the molybdenum boat in Figure 17.[18] A sapphire seed placed at the narrow nose of the boat nucleates crystal growth and determines the orientation of the growing crystal. The boat is translated to the right through the hot zone at a rate of ~8-10 mm/h. The narrow heating element melts aluminum oxide and evaporates many impurities. As molten material passes out of the hot zone, it solidifies on the growing crystal. Solid sapphire is denser than liquid alumina, so the volume of material decreases during crystal growth. If no crackle is added, the thickness of the crystal decreases from the nose at the right to the tail at the left in Figure 17. Alternatively, crackle can be added during growth to produce a more constant thickness. Impurities that are more soluble in the liquid than in the crystal tend to be concentrated in the tail of the crystal. Sapphire is grown in vacuum or in reducing mixtures of H_2, CO, and Ar. The atmosphere for growth and annealing affects the concentration of oxygen vacancies, the oxidation states of impurities such as titanium, the formation of 1- to 5-μm-diameter second-phase particles associated with anion vacancies, and ultraviolet transparency.

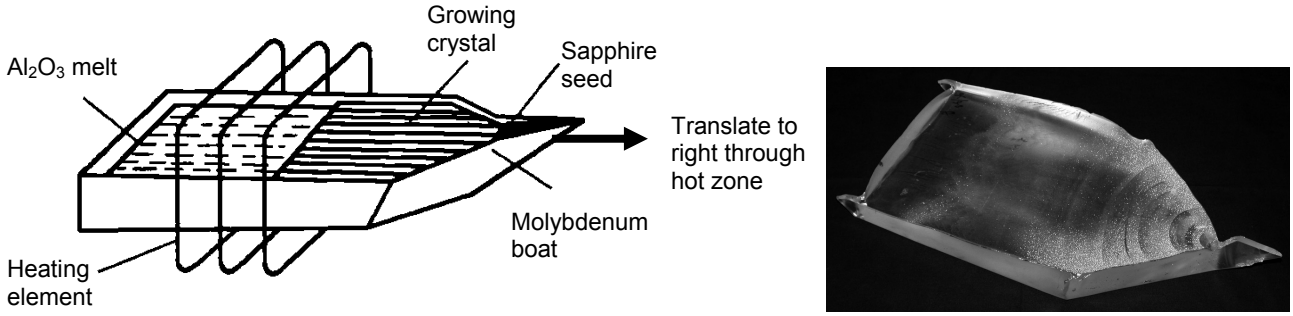


Figure 17. Horizontal directional solidification growth of sapphire, also known as the Bagdasarov method.[18] Photograph shows HDSM slab from Gavish (Omer, Israel).

GOI (KYROPOULOS) SAPPHIRE CRYSTAL GROWTH

M. I. Musatov (Figure 18) applied the Kyropoulos crystal growth method to sapphire at the State Optical Institute in St. Petersburg in the early 1970s. The method he developed is known in the Former Soviet Union as GOI, which is the abbreviation for State Optical Institute. Early boules of GOI material are shown in Figure 19.

Figure 18. M. I. Musatov (1930–) in 2009.

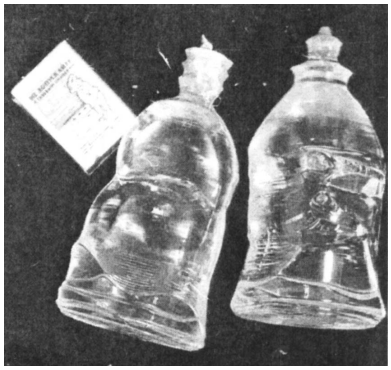


Figure 19. Sapphire grown by GOI method in fall of 1971. Crystal diameter up to 70 mm.

A schematic diagram of GOI (Kyropoulos) crystal growth is shown in Figure 20.[18] A sapphire seed crystal held on the end of a metal rod is dipped into the surface of high purity molten alumina at 2340 K in a molybdenum crucible. Heat is conducted away from the seed crystal by the metal rod. Initially, the seed crystal is lifted from the melt in a series of steps at 1 mm/h to allow the diameter of the growing crystal to increase and to prevent the growing crystal from touching the walls. After seeding, boule growth takes place with no further motion of the boule.

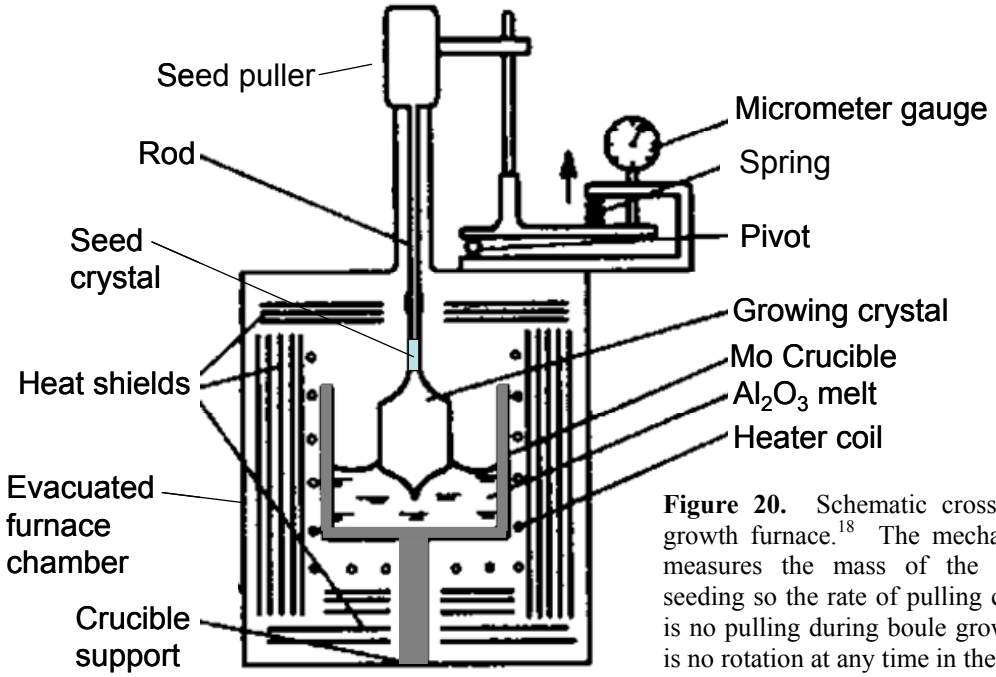
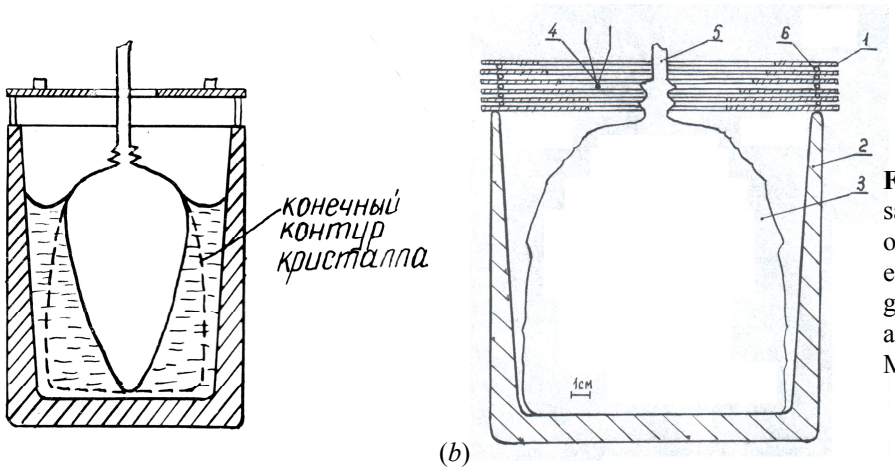


Figure 20. Schematic cross section of Kyropoulos growth furnace.[18] The mechanism at the upper right measures the mass of the growing crystal during seeding so the rate of pulling can be controlled. There is no pulling during boule growth after seeding. There is no rotation at any time in the growth.

Initial growth of the GOI crystal in Figure 21a, governed by Musatov's arrangement of heaters for the walls and floor of the crucible, produces an acute, convex front. The increase of crystal mass per unit time is faster than growth with a conventional, flat crystal front. At the end of the growth, the crystal fills the crucible, giving the shape in Figure 21b. Growth in a quiescent crucible with a very small temperature gradient gives exceptionally high crystal quality and few microscopic bubbles in comparison with sapphire grown by most other methods.



(*a*) (*b*)

Figure 21. Shape of GOI sapphire boule (a) in early part of crystal growth and (b) at the end of the growth run. Early growth is characterized by an acute, convex front. Courtesy M. I. Musatov.

Musatov's account of the early history of the GOI method is particularly interesting.[19] In the 1960s there was a great need for high quality sapphire for laser crystals. Verneuil sapphire had low optical quality, limited size, and high stress. When Bagdasarov developed horizontal directional solidification to make plates up to 200 mm across, the staff of the Institute of Crystallography of the Academy of Sciences was awarded the State Prize of the USSR in 1971. The problem of making high quality sapphire was officially considered to be "solved." The award effectively closed down funding for other work on growing sapphire. Unfortunately, horizontal directional solidification gave plates of limited thickness, poor ultraviolet transparency, a "block structure," high stress, and high cost.

Musatov was working at the State Optical Institute in St. Petersburg (GOI) on Czochralski crystal growth when he developed the GOI method. In the fall of 1971, a GOI sapphire crystal "accidentally fell into the hands" of L. V. Kondakova at the Scientific Research Institute of Applied Physics in Moscow. "After her first studies … she began to knock at all the doors of our ministry with a request—to immediately commit us to supply her with" GOI sapphire, which had high transparency and no internal stress. Her application was "special-purpose satellites," so GOI sapphire was given priority for development.

In the fall of 1972, Musatov was scheduled to give a report on the GOI method for the first time at a crystal growth conference in Armenia. "However, because there were foreign representatives…at the conference, I was advised not to give the report. Nevertheless, I hunted down two young people who were there from Zelenograd—my…report was given to them to review…. They did not believe what was written in the article."

"They later came to Leningrad, and I gave them one such crystal for testing. But what happened next was almost a joke. This crystal was examined with curiosity by higher and higher supervisors. At one of the first such demonstrations, the crystal accidentally fell to the floor. As the eye-witnesses recounted, everyone froze—the only crystal was now smashed!"

"Everyone had become accustomed to crystals grown by the Verneuil and HDC [horizontal directional solidification] methods, which have enormous internal stresses. But the crystal remained unbroken! Moreover, in further demonstrations even higher up the administrative ladder all the way to the minister, this crystal was always as it were accidentally dropped, and newcomers were again frightened and astonished by its extraordinary strength, caused by the absence of internal stresses."

"Since there was an enormous need for such crystals, despite the savage opposition of the Institute of Crystallography…, the GOI method was implemented in industrial scales...where it completely supplanted the earlier-organized, largest-in-the-world production of synthetic sapphire by the HDC method."

GOI crystals are shown in Figure 22. According to Musatov, in 2009 GOI accounts for almost half of world production of sapphire. Most is grown in Russia, with large and growing production in the U.S., China, Ukraine, and Israel.

Figure 22. GOI sapphire crystals grown by Musatov in 1978. Diameters are 80, 150, and 300 mm. Courtesy M. I. Musatov.

In 2009, the U.S. company Rubicon Technologies grew the world's largest GOI (Kyropoulos) sapphire boule, weighing 200 kg. Musatov notes that as the crystal size increases, the electric energy required per unit mass for GOI crystal growth decreases. He projects that a 520-mm-diameter crystal weighing 400 kg could be grown in 10 days with a maximum power of 140 kW.

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