

# A peek into the history of sapphire crystal growth

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## ABSTRACT

After the chemical compositions of sapphire and ruby were unraveled in the middle of the 19<sup>th</sup> century, chemists set out to grow artificial crystals of these valuable gemstones. In 1885 a dealer in Geneva began to sell ruby that is now believed to have been created by flame fusion. Gemologists rapidly concluded that the stones were artificial, but the Geneva ruby stimulated A. V. L. Verneuil in Paris to develop a flame fusion process to produce higher quality ruby and sapphire. By 1900 there was brisk demand for ruby manufactured by Verneuil's method, even though Verneuil did not publicly announce his work until 1902 and did not publish details until 1904. The Verneuil process was used with little alteration for the next 50 years. From 1932-1953, S. K. Popov in the Soviet Union established a capability for manufacturing high quality sapphire by the Verneuil process. In the U.S., under government contract, Linde Air Products Co. implemented the Verneuil process for ruby and sapphire when European sources were cut off during World War II. These materials were essential to the war effort for jewel bearings in precision instruments. In the 1960s and 1970s, the Czochralski process was implemented by Linde and its successor, Union Carbide, to make higher crystal quality material for ruby lasers. Stimulated by a government contract for structural fibers in 1966, H. LaBelle invented edge-defined film-fed growth (EFG). The Saphikon company, which is currently owned by Saint-Gobain, evolved from this effort. Independently and simultaneously, Stepanov developed edge-defined film-fed growth in the Soviet Union. In 1967 F. Schmid and D. Viechnicki at the Army Materials Research Lab grew sapphire by the heat exchanger method (HEM). Schmid went on to establish Crystal Systems, Inc. around this technology. Rotem Industries, founded in Israel in 1969, perfected the growth of sapphire hemispheres and near-net-shape domes by gradient solidification. In the U.S., growth of near-net-shape sapphire domes was demonstrated by both the EFG and HEM methods in the 1980s under government contract, but neither method entered commercial production. Today, domes in the U.S. are made by "scooping" sapphire boules with diamond-impregnated cutting tools. Commercial markets for sapphire, especially in the semiconductor industry, are healthy and growing at the dawn of the 21<sup>st</sup> century.

**Keywords:** Sapphire, crystal growth, Verneuil, EFG crystal growth, HEM crystal growth, gradient solidification, dome

## 1. INTRODUCTION AND PREHISTORY

Commercial production of synthetic sapphire is now 100 years old.<sup>1</sup> Sapphire is a readily available crystal product used as an optical window for industrial and military applications in which the window must withstand extreme environments. Sapphire transmits from the ultraviolet through the visible and into the midwave (3-5  $\mu\text{m}$ ) infrared regions. It withstands high temperature, rapid heating and cooling, high pressure, and resists chemical corrosion. Sapphire is the abrasion-resistant window in bar code scanners and the scratch-proof crystal face of expensive wristwatches. The high crystal perfection, low reactivity, and appropriate unit cell size make sapphire an excellent substrate in the semiconductor industry for blue light-emitting diodes and diode lasers. Sapphire is also used for equipment to manipulate semiconductor wafers during processing in extreme environments. Sapphire and its cousin, ruby, are employed as jewel bearings in precision mechanical instruments.

Sapphire is also known as corundum, the natural crystal of aluminum oxide,  $\text{Al}_2\text{O}_3$  (Figure 1). It is stable up to its melting temperature of 2050°C. Its hardness of 9 on the Mohs mineral scale is second only to that of diamond. The crystal has trigonal

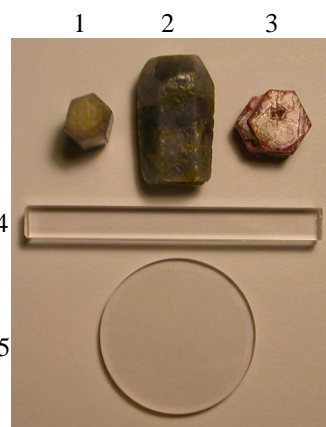


Figure 1: Natural sapphire (1, 2), natural ruby (3), and synthetic sapphire (4, 5).

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symmetry. The 3-fold symmetry axis, designated  $c$ , is also called the optical axis. Two-fold symmetry axes designated  $a$  and  $m$  are found perpendicular to the 3-fold axis. Pure corundum is clear and colorless. Natural sapphire has a variety of colors. Blue sapphire contains iron and titanium impurities whose charge transfer transition ( $\text{Fe}^{2+}, \text{Ti}^{4+} \rightarrow \text{Fe}^{3+}, \text{Ti}^{3+}$ ) absorbs red light and imparts blue color to the crystal.<sup>2</sup> The red color of ruby comes from  $\text{Cr}^{3+}$  impurities in corundum, which gives rise to electronic transitions that absorb visible light.

Early in the 19<sup>th</sup> century, it was thought that sapphire and ruby were oxides of aluminum and silicon.<sup>1</sup> In 1817, J. L. Gay-Lussac found that pure aluminum oxide (also called alumina) could be prepared by thermal decomposition of ammonium alum,  $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . Alumina prepared by this route remains as the raw material for sapphire today. In 1840 H. Rose showed that silicon observed in sapphire was an impurity introduced from the agate mortars used to grind sapphire for chemical analysis. Once the true composition of sapphire was known, many chemists sought to make the valuable crystal. In the period 1837-1840, H. Gaudin conducted noteworthy investigations. He used a torch to fuse alumina prepared from ammonium alum to prepare small hexagonal platelets of corundum. Mixing alum with chromium salts prior to fusion produced small, strained, hard red particles whose density was less than that of natural ruby because of trapped gas. Gaudin believed he had made a glass, but modern work suggests that he made crystalline ruby.<sup>1</sup> In 1851, H. Senarmont made microscopic rhombohedral crystals by heating solutions of aluminum chloride to over  $350^\circ\text{C}$  in sealed tubes. In 1848, J. J. Ebelman prepared ruby by fusing alumina and boric acid with chromium oxide. Ebelman and F. Parmentier prepared crystals from alumina dissolved in fused salts at high temperature. Other investigations were carried out by Boettger, Bruhns, Brun, Debray, Deville, Caron, Daubré, Doelter, Elsner, Friedel, Grandeau, Hautefeuille, Houdard, Loyer, Mallet, Medanich, Meunier, Moissan, Morozewicz, Oetling, Perrey, Schuch, and Weinschenk.<sup>1,3,4</sup> None of this work produced more than microscopic crystals.

More successful investigations were led by Edmond Frémy (1814-1894) at the Museum of Natural History in Paris.<sup>1</sup> Frémy and his assistant, Charles Feil, published a paper in 1877 in which they obtained small, clear, red ruby crystals. Fireclay crucibles with 20-kg charges were held at red heat for periods up to 20 days. Lead oxide ( $\text{Pb}_3\text{O}_4$ ) was converted to lead aluminate, which reacted with silica to give lead silicate plus corundum crystals. Ruby was obtained by adding 2-3 wt% potassium dichromate to the reaction. After Feil died in 1876, Frémy's new assistant was Auguste V. L. Verneuil (1856-1913), who had applied to work with Frémy at the age of 17. Clear ruby crystals up to 3 mm in diameter and 0.3 carat in mass (1 carat = 0.2 grams) were grown from alumina in a potassium hydroxide/barium fluoride flux in a ceramic crucible at  $1500^\circ\text{C}$ . In unsuccessful attempts to increase the size of the ruby crystals, flux growth was scaled up at the Saint-Gobain glass factory and then in 50-liter crucibles at the Appert glass factory. Although Frémy thought he was crystallizing alumina from the flux, Kurt Nassau<sup>1</sup> suggests that alumina and barium fluoride give gaseous aluminum fluoride. Aluminum fluoride reacts with water vapor that diffuses through the porous crucible to give alumina, which crystallizes in many locations with little chance to grow into larger crystals. Frémy summarized his investigations in a book in 1891.<sup>5</sup> He retired in 1892 and died in 1894. Figure 2, reproduced from Nassau,<sup>6</sup> was taken from Frémy's book.

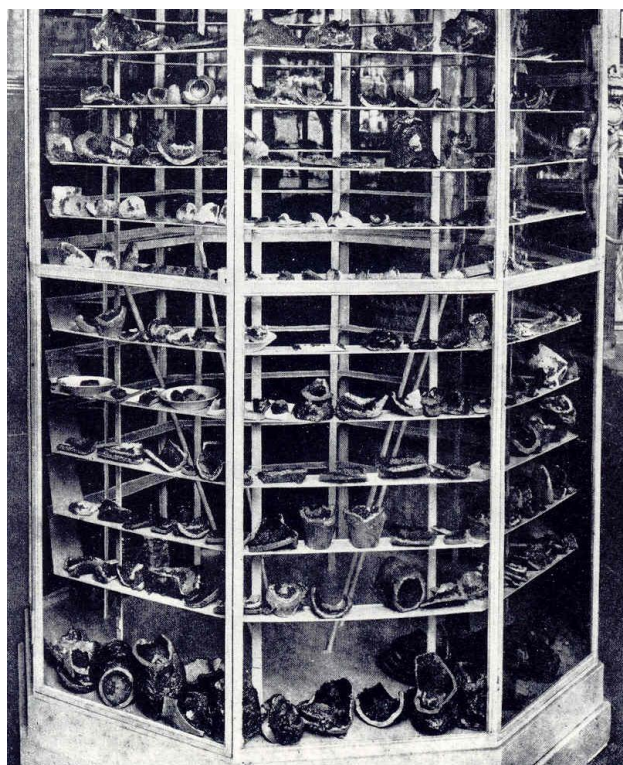


Figure 2: Crystal growth storage cabinet from Frémy's lab.<sup>5,6</sup>

## 2. FLAME FUSION AND THE VERNEUIL PROCESS

In 1885 rubies selling for \$1000-2500 per carat from an unknown source appeared in Geneva and were purported to be natural gems.<sup>1</sup> Investigation of the crystals at the Sorbonne in Paris and at Tiffany in New York found microscopic gas bubbles suggestive of a high-temperature synthetic process. The French Syndicate of Diamonds and Precious Stones ruled that the crystals had to be marketed as “artificial,” which dropped their price to \$25-40 per carat. Modern investigation of “Geneva” rubies by Nassau suggests a 3-stage flame fusion synthetic process.<sup>1</sup> In the first stage, alumina plus a chromium salt are fused on a ceramic support to form a tiny crystalline ball. The ball is then turned upside down and growth of a larger crystalline ball is continued by adding fresh material to the flame. The final stage appears to require 2 torches to enlarge the growing crystal to its final dimensions. The proposed mechanism is supported by 2 discontinuities in chromium concentration inside “Geneva” rubies. One of the people who examined “Geneva” ruby in 1886 was the mineralogist, P. M. E. Jannettaz at the Museum of Natural History in Paris. He concluded that fusion was involved in the creation of the “Geneva” ruby and he discussed his findings with his colleague, Verneuil.

While working with Frémy, Verneuil had earned his bachelor, masters, and doctoral degrees. When Frémy retired in 1892, Verneuil became professor of applied chemistry at the Museum of Natural History in Paris. In 1886, following his introduction to the “Geneva” ruby by Jannettaz, Verneuil and G. A. Terreil used a hydrogen-oxygen torch to fuse alumina powder with some added chromium salt. They obtained tiny particles, which Jannettaz identified as ruby. From this experiment, Verneuil began in earnest in 1888 to develop flame fusion growth of ruby.

Working with his student, Marc Paquier, Verneuil developed the flame fusion process well enough to write the details in a sealed report that he deposited at the Paris Academy of Science in 1891. After further improvement in decreasing growth stress, Verneuil deposited a second sealed document at the Academy of Science in 1892. Marc Paquier, presumably the same person who assisted Verneuil, displayed ruby crystals at the World Fair in Paris in 1900. The crystals, for which there was brisk demand, appear to have been made by the Verneuil process, not the Geneva process, and commercial production had already begun by 1900. In 1902, Verneuil announced that he had developed a flame fusion process for making ruby and he published full details in 1904.<sup>7</sup>

Figure 3 is taken from one of Verneuil’s two U.S. patents. To make feed powder, ammonium aluminum sulfate and ammonium chromium sulfate were each recrystallized 4-5 times and a mixture of the two was calcined at 1000-1200°C to give a mixture of the oxides. Ground powder was placed in container B in Figure 3 and delivered into tube K by the tapping hammer D. Oxygen was also delivered through tube K and illuminating gas was delivered through tube S. The flame burned inside the ceramic muffle insulator M whose inside diameter was 25 mm and whose inside height was 105 mm. An alumina pedestal L held by a platinum tube could be lowered away from the flame by crank P as the crystal grew on the pedestal. A mica window covered by a steel shutter, neither of which is shown in Figure 3, enabled the operator to view the growing crystal inside the muffle.

The crystal growth process described in Verneuil’s patent is shown in Figure 4. Powder falling through the flame was heated just below its melting point. The initial powder built up a conical pile in which the hot particles sintered together to make a rigid “sinter cone.” The upper tip of the cone became molten when the cone got sharp enough. Fresh powder landing on the molten ball would melt and enlarge the crystal. Only the uppermost skin of the growing crystal was molten. As the crystal grew in a vertical direction, the pedestal was lowered to keep the top of the crystal at the correct location in the flame. Flame temperature during crystal growth was regulated by controlling the flow of oxygen. At the end of a growth run, the flame was shut and, if there was not too much strain, the crystal would not shatter. Even so, crystals had so much strain that a light tap at the end would split the crystal lengthwise into two halves. A typical growth time of 2 hours produced a 15 carat cylinder with a diameter of 6 mm and length of 25 mm.

In 1909 Verneuil was appointed chief chemist at the Paris laboratory of the New York jewelry company, L. Heller and Sons. His charge was to grow blue sapphire for jewelry. The origin of the blue color was not known until chemical analyses by Verneuil showed that natural blue sapphire always contained both iron and titanium. Armed with this knowledge, Verneuil was able to grow deliberately doped blue sapphire. The Paris laboratory was closed in 1911 with the successful completion of the project.

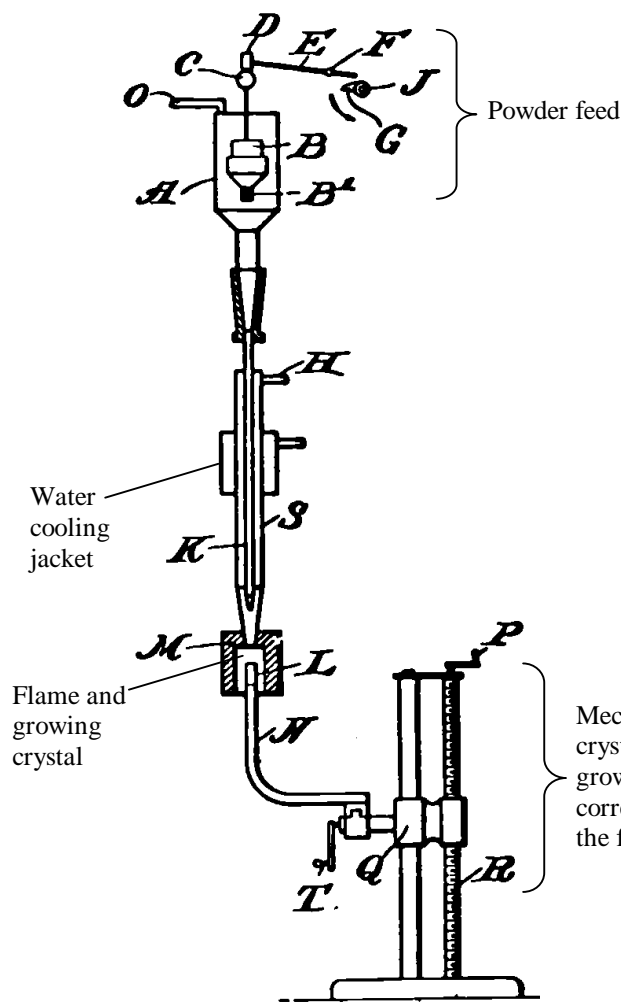


Figure 3: Diagram of Verneuil's apparatus for growing sapphire. From U.S. Patent 1,004,505, September 26, 1911.

- B. container of feed powder
- D. hammer
- G. rotating cam
- O. oxygen feed tube
- H. illuminating gas feed tube
- K. inner tube carries oxygen
- S. outer tube carries illuminating gas
- M. muffle (insulation) surrounding downward-pointing flame
- L. ceramic pedestal
- P. crank for lowering pedestal to keep crystal at correct

Water cooling jacket

Flame and growing crystal

Mechanism to lower crystal to keep growth surface at correct elevation in the flame

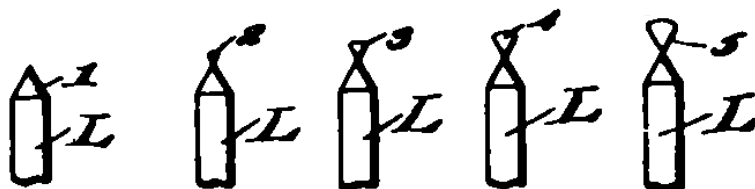


Figure 4: Method of growing sapphire described in Verneuil's U.S. Patent 1,004,505.

Ruby and sapphire manufacturing by the Verneuil process had begun in Europe prior to Verneuil's publication of 1904.<sup>1</sup> One of the largest Verneuil operations was that of Industrie de Piéres Scientifiques, Hrand Djévahirdjian in France and Switzerland. The company had a room with approximately 100 Verneuil torches operating around 1920. Heller Company had planned to manufacture blue sapphire in the U.S. but found that labor costs were too high to compete with European manufacturing. Blue sapphire was grown for Heller by Baikovsky Brothers in France. Baikovsky had 3 torches in 1903, 80 in 1914, 400 in 1919, and 1600 torches in 1980. By 1980 there were approximately six large Verneuil manufacturers with a total capacity of  $10^9$  carats/yr. Most sapphire was cut into jewel bearings for watches and precision instruments. The process of cutting jewels wastes approximately 99% of the as-grown boule.

In the Soviet Union, S. K. Popov (1903-1953) began experiments with the Verneuil method in 1932.<sup>4</sup> By 1938 he had produced a semi-automatic growth apparatus which enabled the manufacturing of long thin rods suitable for making jewels for watches and instruments. From 1938 until his death, Popov worked at the Institute of Crystallography of the Academy of Sciences of the USSR. In 1945-50 he improved the equipment for making ruby rods, solving such problems as accurate supply of powder and uniform heating of the growing crystal. In 1951-53 he developed a new use for sapphire as a durable fiber guide in the textile industry. He also devised equipment for bending corundum rods into shapes. A commentary written by N. N. Sheftal' in 1959 stated that Popov's equipment was more advanced than that of Western Europe and that the crystal quality produced in the Soviet Union was higher than that available elsewhere.<sup>4</sup>

### 3. BIRTH OF THE SAPPHIRE INDUSTRY IN THE UNITED STATES

Prior to the publication by Verneuil in 1904, industrial production of ruby began in the town of Hoquiam, Washington in the period 1903-1904. The story pieced together by Nassau<sup>1</sup> states that two entrepreneurs, Polson and Ninemire, who had accumulated wealth in the lumber industry, hired an assistant of Verneuil to establish a flame fusion facility to grow ruby for jewelry. It was necessary to send boules to New York for cutting and the venture as a whole was not economical. The arrival of less expensive Verneuil ruby from Europe ended any hope of American production.

There was no further U.S. production of ruby or sapphire until America was cut off from European supplies of jewel bearings in World War II. The U.S. government issued development contracts which led to production by Linde Air Products Co. in Indiana in 1942. One advantage that Linde had for sapphire production was that Linde was a major supplier of industrial gases, including those used for the Verneuil torch. Linde was later acquired by Union Carbide Corp. After the war, the U.S., again, could not compete with Europe for economy in sapphire production. In the late 1940s Linde developed a process for making star sapphire and star ruby, which contain needles of titanium dioxide, for jewelry. Another market for sapphire was fiber guides in the textile industry. The Linde plant in Indiana was closed in 1974 and 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 Bicon, a division of the French company, Saint-Gobain. In 2000 the division was renamed "Saint-Gobain Crystals and Detectors".

### 4. INVENTION OF NEW METHODS FOR GROWING SAPPHIRE

Verneuil's flame fusion process, perfected in 1892, hardly changed in the 70 years in which it was the only significant commercial production method for sapphire. There is still demand for Verneuil material at the dawn of the 21<sup>st</sup> century because the method is the least expensive way to make sapphire and ruby whose quality is adequate for many applications. However, higher crystal quality demanded by electronic and optical applications, and the need for sizes and shapes that cannot be made by flame fusion, sparked the development of other ways to make sapphire after 1960.

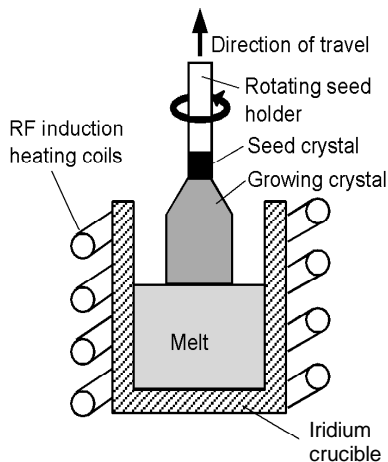


Figure 5: Czochralski crystal growth.

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 discovered 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 this process, alumina is melted in an iridium crucible in an atmosphere of 98% N<sub>2</sub> / 2% O<sub>2</sub>. 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 rpm. As the seed is withdrawn, alumina from the melt crystallizes onto the seed. The diameter of the boule could be controlled by the rate of withdrawal of the seed. Boule diameters up to 11 cm could be obtained from a 15-cm-diameter crucible. Saint-Gobain in Washington State and Crystar Research (a division of Johnson Matthey) in Vancouver, Canada both produce sapphire today by the Czochralski method.

In addition to Czochralski crystal growth, three other methods to grow sapphire were introduced in the 1960s. Edge-defined film-fed growth was developed independently in the U.S and the U.S.S.R. The heat exchanger method was developed in the U.S. and

gradient solidification was introduced in Israel.

Edge-defined film-fed growth (EFG) was invented by Harold LaBelle at Tyler Laboratories in Waltham, Massachusetts and patented in 1971. Tyler was a small laboratory that received a contract from the Air Force in 1965 to make fibers for reinforcement of metal matrix composites.<sup>8,9,10</sup> LaBelle showed that molten alumina could wet the surface of a molybdenum die which could be used as a wick to deliver molten material to a growing crystal. Figure 6 shows a sapphire seed crystal in contact with molten alumina at the top of the die. As the seed is withdrawn, liquid crystallizes near the interface of the die and the seed. Dies of different shape can create crystals that match the shape of the die. Fibers would be drawn from a narrow-diameter die with a hole through the middle. Tubes could be drawn from the die shown at the right in Figure 6. Fibers grown in the Air Force program in 1965-66 were nearly opaque and there was no demand for the product. In the 1980s, EFG growth of transparent sapphire optical fibers for high temperature environments was initially funded by the Department of Energy. Concurrent with the work of LaBelle in the 1960s, Stepanov independently invented edge-defined film-fed sapphire growth in the Soviet Union.<sup>11,12</sup>

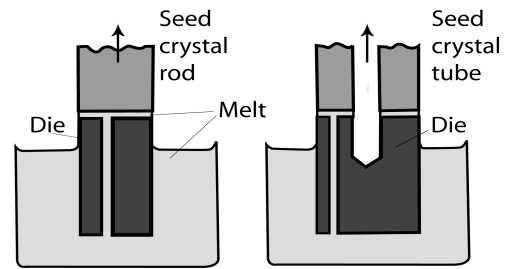


Figure 6: Edge-defined Film-fed Growth (EFG) of sapphire from molybdenum dies.

Tyler and other small companies were acquired by a single owner who changed the name to Tyco Laboratories. In 1970 Tyco created the Saphikon Division to produce EFG sapphire in Waltham. Around 1979 the Saphikon Division moved to Milford, New Hampshire. In the 1970s and 1980s Saphikon received the bulk of its revenue by licensing the EFG process to companies such as Kyocera, RCA, Corning, and Allied Signal, all of whom saw commercial potential for sapphire substrates for the newly developing silicon-on-sapphire electronics technology. In the mid 1980s the owner of Tyco died. With less than two million dollars per year in sapphire revenue at that time, the new owner unsuccessfully sought a buyer for the Saphikon Division. Eventually he made a deal with LaBelle that was “too good to refuse”. LaBelle purchased Saphikon in 1985 and resold it at a profit in 1987. Saphikon remained independent until 2000 when Saint-Gobain purchased the company and the rights to make sheets, rods, tubes, and 3-dimensional shapes. The newly formed, independent company Photran retained exclusive rights to manufacture sapphire fibers.

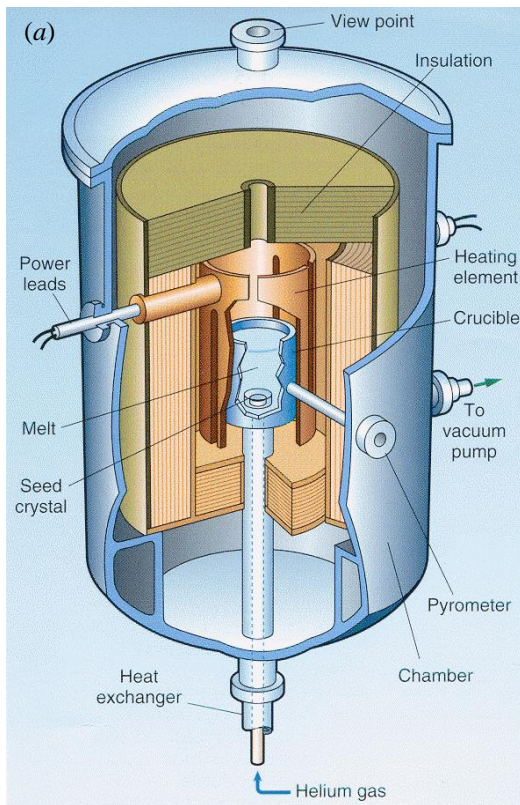
Kyocera in Japan acquired EFG technology from Saphikon and further developed the process. Kyocera sells *r*-, *a*-, or *c*-plane sheets up to 20 cm wide x 30 cm long x 0.02-2 cm thick. Kyocera also sells *c*-axis rods and tubes.

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.<sup>13,14</sup> Fresh out of college in the early 1960s, Schmid worked in manufacturing at the Watertown Arsenal, where he gained experience in the directional solidification of metals and with a helium-cooled arc furnace for casting titanium. He then went to graduate school at Northeastern University to earn a masters degree in materials science. Returning to the Watertown Lab in 1967, Schmid set to work with Viechnicki on directional solidification of an alumina melt onto a sapphire seed crystal.

The modern implementation of Schmid and Viechnicki’s heat-exchanger method at Crystal Systems in Salem, Massachusetts is shown in Figure 7. 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 3 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 the highest crystal quality. Boules with a diameter of 34 cm and a mass of 65 kg are routinely produced and boules up to 38 cm have been grown.

Single crystals of sapphire were grown in an 18-mm-diameter crucible in 1967 at Watertown. By 1969, after about 50 attempts, crack-free sapphire with a diameter of 76 mm was grown. By 1971 the diameter was up to 152 mm. The

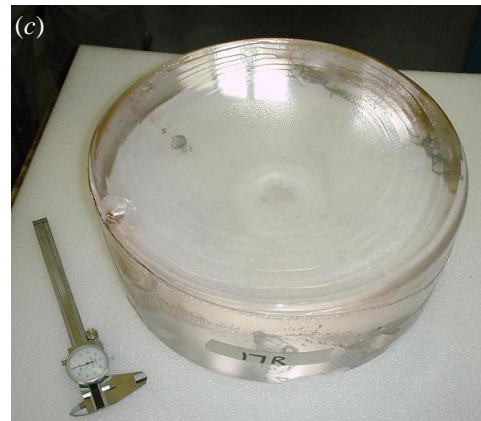




(b)



Figure 7: (a) Furnace used at Crystal Systems to grow sapphire by the Heat Exchanger Method. (b) The first sapphire boule grown at Watertown in 1967. (c) Production-quality 34-cm-diameter sapphire boule. Courtesy Crystal Systems, Inc.



first patent for the process, which was then known as the Schmid-Viechnicki technique, was issued in 1969.

By early 1971, Schmid was convinced that the new method was a breakthrough and wanted to find a commercial market for the product. He found interest at Inselec and Insaco in obtaining sapphire wafers for silicon-on-sapphire electronics. Schmid persuaded a sailing buddy and an accountant to invest in creating the company, Crystal Systems, of which Schmid would own 51%. The company was incorporated in August 1971 after Schmid had purchased a scrapped furnace from Raytheon in July. He began refurbishing the furnace in his garage and soon moved the operation to Shetland Industrial Park in Salem. For the first year of the company, Schmid held his old job at Watertown and worked on the furnace at night. By July 1972 he grew his first 152-mm-diameter boule, from which 51-mm cores were drilled for silicon-on-sapphire substrate wafers. In September 1972 Schmid resigned from Watertown to devote full attention to Crystal Systems. He hired his first helper (who was “just getting out of high school”) and his wife handled advertising. First-year sales were less than fifty thousand dollars. Shortly after the first advertising went out in 1974, Schmid received a letter from Union Carbide indicating that Crystal Systems was infringing on their patent and offering to license Union Carbide technology. This claim led Schmid to clarify the difference between the processes and to obtain a patent for his technique, whose name he changed to “heat-exchanger method” because of its unique, controllable heat exchanger.

In the mid 1970s Crystal Systems began to hire full-time employees. Schmid developed a fixed-abrasive slicing technique using a diamond-impregnated blade or wire to slice wafers from a cylinder with minimal loss of material. The National Aeronautics and Space Administration selected HEM sapphire for use in satellites because of its extremely low optical scatter. In 1978 the company moved to its current, larger quarters in the same industrial park. In 1979 Crystal Systems received a contract to grow laser-quality ruby in one of the first actions of the government’s new Small Business Innovative Research program. In 1987-89, titanium-doped sapphire for lasers was commercialized. Military and commercial markets for sapphire expanded greatly in the 1980s. In 1974 Crystal Systems got its first government contract to grow silicon and in 1977 Chandra Khattak at Crystal Systems used the heat-exchanger method to grow crack-free polycrystalline silicon ingots in high purity silica crucibles for the first time.

HEM silicon for photovoltaics and equipment for growing silicon are currently major products of Crystal Systems, in addition to sapphire and crystal slicing equipment. HEM silicon ingots weighing 240 kg with a cross section of 69 × 69 cm are routinely produced.

## 5. SAPPHIRE DOMES

One of the most demanding applications for an infrared window material is the seeker dome on an infrared-guided missile. The dome must withstand stress from very rapid heating and it must survive collisions with raindrops, sand particles, and insects in the air. Among the infrared-transparent materials available in the 1980s, sapphire was clearly the most durable with respect to thermal stress and particle impact. However, the cost of growing sapphire was high and the cost of fabricating it into an optically polished hemisphere was even higher. To decrease the cost, the government invested in two efforts to grow near-net-shape domes which would require relatively little machining after growth.

One Navy-funded effort at Saphikon led to a Manufacturing Technology contract in 1989-92. A curved sapphire seed crystal was placed in contact with a curved slit at the top of a molybdenum die for EFG growth. The seed was slowly withdrawn in a path that traced an arc in space. The result was an as-grown dome such as that in Figure 8. The sapphire at the right of the figure could be machined into a dome shape. However, the crystal quality was not as high as desired and the manufacturing process was never optimized.<sup>15,16</sup>

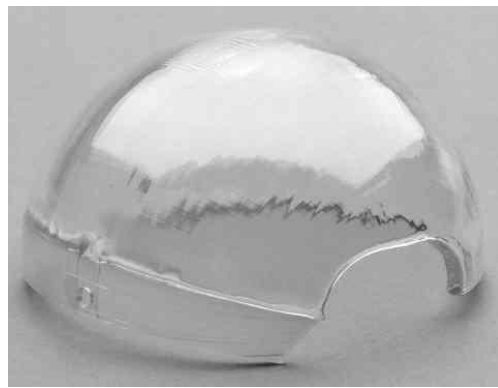


Figure 8:  
As-grown EFG  
sapphire  
produced by  
Saphikon.<sup>15,16</sup>

Another Navy Small Business Innovative Research contract was conducted at Crystal Systems. Work done in the mid to late 1980s used the apparatus shown at the left in Figure 9 to grow the near-net-shape domes at the right.<sup>17-19</sup> Two hemispheric molybdenum mandrels were inserted into the crucible in which sapphire was grown. After a boule was grown and cracked apart, sapphire that crystallized in the volume between the two mandrels had a hemispheric shape. This method suffered from cracks extending into the boule and it was never taken beyond an initial demonstration.

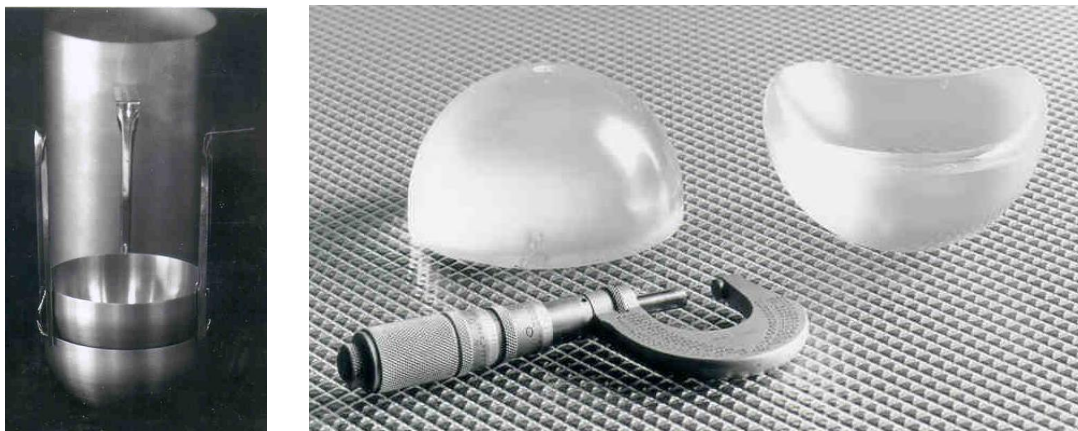


Figure 9: Molybdenum apparatus at left was used at Crystal Systems to grow near-net-shape sapphire domes at right.<sup>17-19</sup> Photos courtesy Crystal Systems.



Domes were formerly produced from sapphire boules by machining each dome out of a cylindrical piece of material, as shown at the left in Figure 10. This process wastes valuable material and requires a great deal of machining. A cost effective method for making domes—the process used today in the U.S.—is called *scooping*. Shown at the middle of Figure 10, 7 nested domes could be taken from the same volume of material that produced 3 domes by conventional machining. Diamond-impregnated cutting tools shown at the right of Figure 10 are used to cut out first the inner surface and then the outer surface of consecutive domes. In the cutting process, the sapphire is rotated in one direction while the tool is rotated against it in the opposite direction. At the end of the scooping, neighboring domes are connected by a small cylinder of material at the apex. The domes are broken apart by tapping and then they are ground and polished to their final finish.

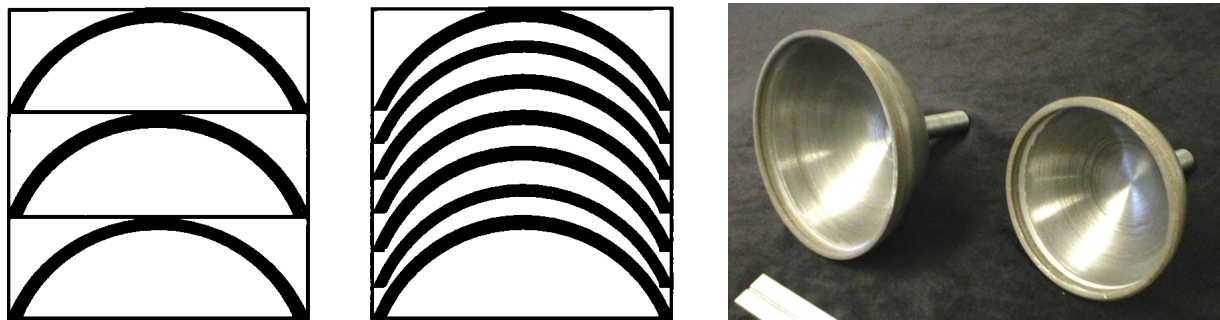
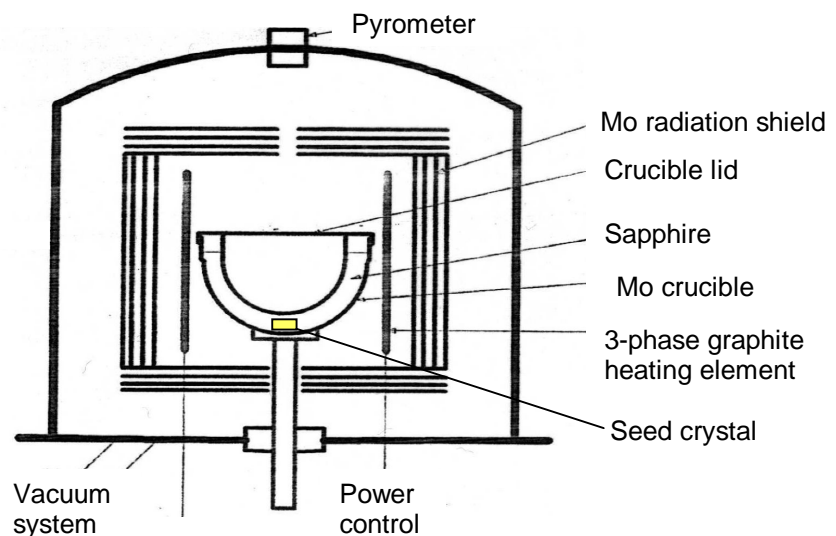


Figure 10: Line drawings compare conventional use of a boule to make 3 domes and scooping to make 7 domes from the same volume. Photograph shows diamond-impregnated scooping tools used at Crystal Systems for scooping sapphire. Photo courtesy Crystal Systems.

Rotem Industries, which was founded in 1969, provides sapphire products for defense applications. The gradient solidification method for sapphire growth was developed at Rotem to produce high quality, near-net-shape domes.<sup>20-24</sup> In Figure 11, alumina is loaded into a hemispheric molybdenum crucible containing 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 carefully controlled manner so that crystallization proceeds out from the seed crystal. An as-grown hemispheric dome and a solid hemisphere are shown in Figure 12.

Figure 11: Apparatus used to grow sapphire by gradient solidification at Rotem Industries in Israel.



In the heat-exchanger method, highest crystal quality is produced when growth takes place along the  $a$ -axis of the crystal. For the boule in Figure 7(c), the  $a$ -axis is the cylindrical axis. The optical axis of sapphire (the  $c$ -axis) is perpendicular to  $a$  and comes out the curved side of the boule. To make  $c$ -axis domes, a cylindrical core is drilled from the side of the boule and domes are scooped out from the core. In Rotem's gradient solidification method, the thermal mass is low enough to permit the growth of good quality  $c$ -axis boules and domes, as well as  $a$ -axis material.

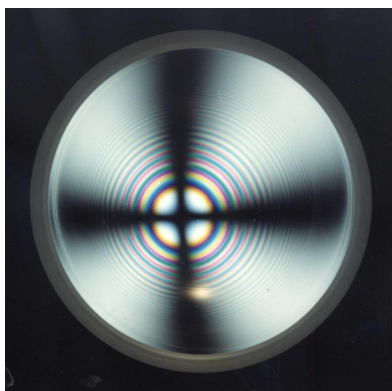
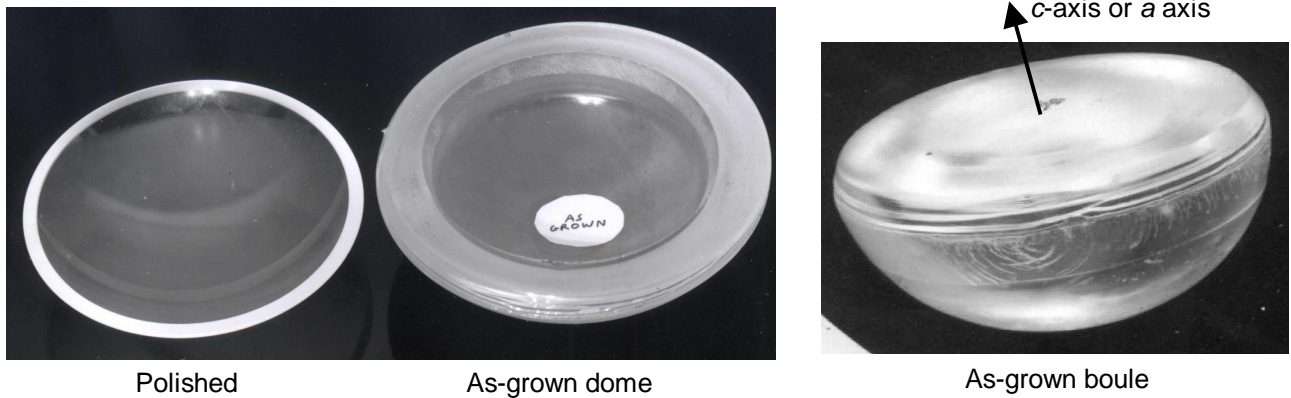


Figure 12: Sapphire produced at Rotem Industries by gradient solidification. When a  $c$ -axis flat or dome is viewed through crossed polarizers, as shown at the left, crystal imperfections and grain boundaries appear as irregularities in the circular fringes and characteristic cross. The symmetry of the pattern in the photo at the left is evidence of high crystal quality. Each line of the black cross, referred to in optics as an isogyre, is parallel or perpendicular to the direction of a polarizer, and occurs from extinction of either  $p$ - or  $s$ -polarized light when only light of that polarization is incident on the crystal. Photos courtesy Atara Horowitz.

Dome viewed through crossed polarizers

## 6. OUTLOOK

Current issues for sapphire production for windows and domes include: (1) The cost of sapphire is high. Much of the cost is in machining and polishing. (2) There is a need for larger area windows. The EFG method can make inherently large windows. The Heat Exchanger method has been scaled up to 38-cm-diameter, but larger sizes would be desirable. Materials Systems, Inc. has demonstrated a way to bond sapphire panes to each other to make large windows, but the bond lines are not as strong as sapphire and they provide an optical discontinuity.<sup>25</sup> (3) Optical fabrication is not well enough controlled to give reproducible mechanical properties. It is virtually impossible to know the mechanical strength of a particular sapphire part unless it is proof tested. In the absence of proof testing, designs must be conservative to be reliable.

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