

# Replicating Nature's Treasures—Artificial Gemstones

Because gemstones are so beautiful, and so rare in nature, people have been trying to synthesize them since ancient times. The Romans learned how to culture pearls from oysters. The Egyptians created substitute gems out of soft, colored glass, which also became popular much later in Europe as imitations called "paste."

In the first recorded attempts at reproducing gems, wishful entrepreneurs planted natural gemstones in the ground in hopes they would either reproduce or grow larger. Alchemists spent long hours trying to create gemstones, but all such attempts were unsuccessful.

By 1800, chemists had recognized the basic composition of ruby and sapphire as aluminum oxide, though at first they believed the gems to include silicon oxide as well. Not until 1840 did chemist H. Rose discover that the silicon oxide portion actually came from the agate mortars used to grind the gemstones for analysis.

Marc Antoine Augustin Gaudin worked for 33 years on the problem of synthesizing red ruby, from 1837 to his last paper in 1870. He worked with ground alum in a crucible under an intense torch, adding chromium sulfate to provide the ruby red color. In 1857 he did succeed in producing small particles of ruby, but he didn't recognize them because they were milky and cracked easily—he thought he had merely created some kind of colored glass! Even so, Gaudin's rubies were still too small for any practical purposes.

Twenty-three years later, in 1878, Edmond Frémy and Charles Feil used a different process—fusing aluminum oxide and lead oxide—to produce ruby crystals from which gemstones (albeit small) could be cut.

French chemist August Victor Lewis Verneuil worked with Frémy and Feil, and took the position as Frémy's assistant when Charles Feil died in 1876. Verneuil and Frémy wrote three research papers on their work with the synthesis of ruby, and Frémy wrote a book on the subject in 1891. He retired the following year, and Verneuil moved on to become a professor of applied chemistry at the Museum of Natural History in Paris. However, he quietly contin-

ued his research.

In 1902, Verneuil surprised the world by announcing that he had reproduced ruby, not only in chemical composition and color, but also in crystals large enough to be cut as gems. He had apparently worked out all the details much earlier, between 1886 and 1892, because in 1891 he deposited a sealed note explaining his process in the Paris Academy of Sciences. In 1892 Verneuil added a second sealed note, describing how he had learned to make the crystals that would fracture less easily.

For some reason he waited a decade to make his announcement, and he did not write a detailed paper describing his method until 1904. The sealed documents, not opened until 1910, were published subsequently.

In his process, Verneuil first produced a boule, or a lump of alumina (aluminum oxide), with the same physical and chemical characteristics as corundum, the alpha form of aluminum oxide. To create the boule, Verneuil dropped finely ground alumina powder into the intense heat of an inverted oxy-hydrogen torch, which fused the material in a roughly cylindrical shape, sometimes reaching several inches in length.

The boule material has the characteristic atomic structure and physical properties of ruby, but it usually lacks crystal faces because of its rapid growth. With no coloring additive, the boule would be transparent, or known as a colorless sapphire. With only about 2 1/2% chromium oxide in the feed material, though, the crystal takes on a ruby color, growing deeper in hue as the percentage of chromium oxide is increased. Unfortunately, other impurities, such as iron, can make the color brown instead of red, or may even lead to fracturing of the boule.

Production of boules required exceedingly pure starting chemicals and gases. Verneuil purified his initial material by starting with ammonium alum dissolved in distilled hot water, which he then filtered to remove all insoluble matter. After he cooled the solution, crystals of alum formed, retaining only the soluble contaminants. Verneuil repeated the recrystalliza-

tion process several times until he had achieved the desired purity. He purified chromium alum (containing the chromium oxide necessary for the ruby color) the same way, then mixed the two alums inside a furnace operating at about 1100°C. There, the two alums combined in appropriate proportions of aluminum and chromium oxides. Other impurities (water, sulfur trioxide, and ammonium sulfate) vaporized in the furnace. After cooling, the oxide mixture was ground and sieved to create Verneuil's feed powder for synthetic rubies.

Verneuil's oxy-hydrogen furnace design remains essentially unchanged over nearly a century. The entire process is still used today with little modification for the manufacture of most synthetic gems, including ruby, sapphire, spinel, rutile, and strontium titanate (a gem not found in nature). Within three years of when Verneuil published a paper detailing his work, several manufacturers were already producing five million carats of synthetic ruby per year.

Oddly enough, another development occurred while Verneuil was still working on his process. In 1885 a Geneva gem dealer began selling quantities of high-quality rubies (worth \$1,000-2,500 per carat) as "genuine natural" stones. Studies conducted in 1886 found these "Geneva rubies" to have the same density, hardness, and optical properties as natural rubies, but microscopic round gas bubbles showed them to be of artificial origin. In fact, Verneuil himself was asked to perform some of the analytical experiments. (What he found led him to conclude that Gaudin's experiments reported decades previously had actually produced ruby and not merely red glass.)

The French Syndicate of Diamonds and Precious Stones ruled that such manmade stones could be sold not as "precious" gems, but only as "artificial" (worth only \$25-40 per carat); otherwise the sales would be considered fraudulent and punishable as a misdemeanor under the French penal code. All prior sales were ordered to be canceled and returned.

No inventor of the Geneva ruby process

ever came forward to claim fame, possibly because of the financial success from early marketing of the gems as "genuine natural" rubies. For a time, the story passed around that these were "reconstructed" or "reconstituted" rubies, made by fusing crushed fragments of natural ruby as the feed material (by a method similar to Verneuil's), although this has recently been brought into question.

George F. Kunz, working for Tiffany in New York, also analyzed the Geneva rubies and concluded for the New York Academy of Sciences: "There is little reason to fear that the true ruby will ever lose the place it has occupied for so many centuries. These stones show the triumph of modern science in chemistry, it is true; and although some may be willing to have the easily attainable, there are others who will [want] the unattainable. One will be nature's gem, and the other the gem made by man."

Creating synthetic emeralds involved a different process entirely. The 18th Century mineralogist R.J. Haiiy noted similarities in the crystal structure of emerald and beryl, and asked the chemist L.N. Vauquelin to analyze them both. Vauquelin found the two to be identical, and he also discovered a new element in beryl, which became known as beryllium. The green color in emerald comes from chromium and vanadium oxides.

In 1935, German chemists Jaeger and Espig of the I.G. Farben Co. announced the synthesis of emeralds by fusion and created crystals large enough to be cut into small gems. San Francisco chemist Carroll F. Chatham was the first to place synthetic emeralds on the market in 1940, but claimed to have produced them by his own technique even before the Germans in 1935. His secret process has never been divulged, and the Chatham company still produces a large amount of synthetic emeralds annually. Chatham's method apparently uses crushed beryl as a seed material in a tungsten or molybdate melt, and usable crystals may take up to a year to grow.

The most difficult gem to synthesize was also the most valuable—diamond. In 1891 E.G. Atchison produced carborundum, the second hardest crystal, while attempting to synthesize diamond. Several other experimenters claimed to have been



*The Von Hippel Award of the Materials Research Society is a single-crystal synthetic ruby. Pictured above is the Von Hippel Award as it was presented to Clarence Zener in 1982. The crystal is now mounted in lucite.*

successful, notably J.B. Hannay in England (1880), who heated organic matter with water in sealed glass tubes; Henri Moissan in France (1893), who dissolved carbon in molten iron in an electric furnace and then plunged the molten iron into a cold brine solution, where the sudden cooling and shrinking of the outside created terrific pressures in the still-molten inside, supposedly producing diamond crystals; and Sir William Crookes in England (1906), who exploded cordite containing excess carbon in a cylindrical chamber, which he claimed produced pressures of 100,000 pounds per square inch and a temperature of 5100°C.

Attempts to reproduce these processes have not been successful, although researchers have found microscopic crystals of metallic carbides that strongly resemble diamond, which could have been mistaken by the early experimenters. Not until February 1955 did the General Electric

Company in Schenectady, New York, announce the creation of the first synthetic diamonds. These crystals were not of gem quality or size, but two years later General Electric began producing and selling synthetic diamond grit as an industrial abrasive, to compete with natural diamond grit made by crushing low-grade diamond crystals. In 1970 Herbert M. Strong and Robert H. Wentdorf Jr., also of General Electric, succeeded in creating gem-quality stones weighing more than a carat.

Around 1920, industrial uses of synthetic gems began to supersede their value as purely decorative items. By 1935 synthetic gemstones had replaced natural jewels in U.S. and European industrial uses. Today, millions of carats of synthetic gems are produced annually for bearings in watches and meters...as well as for jewelry.

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