Sapphires

Sapphire (Greek: σάπφειρος; sappheiros, 'blue stone', which probably referred instead at the time to lapis lazuli) is a gemstone variety of the mineral corundum, an aluminium oxide (α-Al_2O_3). Trace amounts of other elements such as iron, titanium, chromium, copper, or magnesium can give corundum blue, yellow, purple, orange, or a greenish colour. Chromium impurities in corundum yield a pink or red tint, the latter being called a ruby. Commonly, sapphires are worn in jewellery. Sapphires may be found naturally, by searching through certain sediments (due to their resistance to being eroded compared to softer stones) or rock formations. They also may be manufactured for industrial or decorative purposes in large crystal boules. Because of the remarkable hardness of sapphires—nine on the Mohs scale—and of aluminium oxide in general, sapphires are used in some non-ornamental applications, including infrared optical components, such as in scientific instruments; high-durability windows; wristwatch crystals and movement bearings; and very thin electronic wafers, which are used as the insulating substrates of very special-purpose solid-state electronics (most of which are integrated circuits).

Natural sapphires

The sapphire is one of the three gem-varieties of corundum, the other two being ruby – defined as **corundum** in a shade of red—and padparadscha—a pinkish orange variety. Although blue is their most well-known colour, sapphires may also be colourless and they are found in many colours including shades of grey and black.
The cost of natural sapphires varies depending on their colour, clarity, size, cut, and overall quality – as well as their geographic origin. Significant sapphire deposits are found in Eastern Australia, Thailand, Sri Lanka, China (Shandong), Madagascar, East Africa, and in North America in a few locations, mostly in Montana. Sapphire and rubies are often found in the same geographic environment, but one of the gems is usually more abundant in any of the sites.

Blue sapphire

Colour in gemstones breaks down into three components: hue, saturation, and tone. Hue is most commonly understood as the "colour" of the gemstone. Saturation refers to the vividness or brightness of the hue, and tone is the lightness to darkness of the hue. Blue sapphire exists in various mixtures of its primary (blue) and secondary hues, various tonal levels (shades) and at various levels of saturation (vividness).

Blue sapphires are evaluated based upon the purity of their primary hue. Purple, violet, and green are the most common secondary hues found in blue sapphires. Violet and purple can contribute to the overall beauty of the colour, while green is considered to be distinctly negative. Blue sapphires with up to 15% violet or purple are generally said to be of fine quality. Blue sapphires with any amount of green as a secondary hue are not considered to be fine quality. Grey is the normal saturation modifier or mask found in blue sapphires. Grey reduces the saturation or brightness of the hue and therefore, has a distinctly negative effect.
The colour of fine blue sapphires may be described as a vivid medium dark violet to purplish blue where the primary blue hue is at least 85% and the secondary hue no more than 15%, without the least admixture of a green secondary hue or a grey mask.

Pink sapphire

Yellow and green sapphires are also commonly found. Pink sapphires deepen in colour as the quantity of chromium increases. The deeper the pink colour the higher their monetary value, as long as the colour is tending toward the red of rubies. In the United States, a minimum colour saturation must be met to be called a ruby, otherwise the stone will be called a pink sapphire.
Sapphires also occur in shades of orange and brown. Colourless sapphires are sometimes used as diamond substitutes in jewellery. Natural padparadscha (pinkish orange) sapphires often draw higher prices than many of even the finest blue sapphires. Recently, more sapphires of this colour have appeared on the market as a result of a new artificial treatment method that is called "lattice diffusion".

Padparadscha

Padparadscha is a delicate light to medium toned pink-orange to orange-pink hue corundum, originally found in Sri Lanka, but also found in deposits in Vietnam and parts of East Africa. Padparadscha sapphires are rare; the rarest of all is the totally natural variety, with no sign of artificial treatment.
The name is derived from the Sanskrit "padma raga" (padma = lotus; raga = colour), a colour akin to the lotus flower (Nelumbo nucifera 'Speciosa'

Star sapphire

A star sapphire is a type of sapphire that exhibits a star-like phenomenon known as asterism; red stones are known as "star rubies". Star sapphires contain intersecting needle-like inclusions following the underlying crystal structure that cause the appearance of a six-rayed "star"-shaped pattern when viewed with a single overhead light source. The inclusion is often the mineral rutile, a mineral composed primarily of titanium dioxide. The stones are cut en cabochon, typically with the centre of the star near the top of the dome.

Occasionally, twelve-rayed stars are found, typically because two different sets of inclusions are found within the same stone, such as a combination of fine needles of rutile with small platelets of hematite; the first results in a whitish star and the second results in a golden-coloured star. During crystallisation, the two types of inclusions become preferentially oriented in different directions within the crystal, thereby forming two six-rayed stars that are superimposed upon each other to form a twelve-rayed star. Misshapen stars or 12-rayed stars may also form as a result of twinning. The inclusions can alternatively produce a "cat's eye" effect if the 'face-up' direction of the cabochon's dome is oriented perpendicular to the crystal's c-axis rather than parallel to it. If the dome is oriented in between these two directions, an 'off-centre' star will be visible, offset away from the high point of the dome.
The Black Star of Queensland, the largest gem-quality star sapphire in the world, weighs 733 carats. The Star of India (weighing 563.4 carats) is thought to be the second-largest star sapphire (the largest blue), and is currently on display at the American Museum of Natural History in New York City. The 182-carat Star of Bombay, located in the National Museum of Natural History, in Washington, D.C., is another example of a large blue star sapphire. The value of a star sapphire depends not only on the weight of the stone, but also the body colour, visibility, and intensity of the asterism.

Colour change sapphire

A rare variety of natural sapphire, known as colour-change sapphire, exhibits different colours in different light. Colour change sapphires are blue in outdoor light and purple under incandescent indoor light. Some stones shift colour well and others only partially, in that some stones go from blue to bluish purple.
While colour change sapphires come from a variety of locations, the gem gravels of Tanzania is the main source.
Certain synthetic colour-change "sapphires" are sold as "lab" or "synthetic" alexandrite, which more accurately is called an alexandrite simulant (also called alexandrium) since the latter is a type of chrysoberyl— not sapphire, but an entirely different substance whose pleochroism is different and much more pronounced than colour-change corundum (sapphire).

Crystal structure of sapphire

Rubies are corundum which contain chromium impurities that absorb yellow-green light and result in deeper ruby red colour with increasing content. Purple sapphires contain trace amounts of vanadium and come in a variety of shades. Corundum that contains ~0.01% of titanium is colourless. If trace amounts of iron are present, a very pale yellow to green colour may be seen. If both titanium and iron impurities are present together, however, the result is a magnificent deep-blue colour.
Unlike localized ("intra-atomic") absorption of light which causes colour for chromium and vanadium impurities, blue colour in sapphires comes from intervalence charge transfer, which is the transfer of an electron from one

transition-metal ion to another via the conduction or valence band. The iron can take the form Fe^{2+} or Fe^{3+}, while titanium generally takes the form Ti^{4+}. If Fe^{2+} and Ti^{4+} ions are substituted for Al^{3+}, localized areas of charge imbalance are created. An electron transfer from Fe^{2+} and Ti^{4+} can cause a change in the valence state of both. Because of the valence change there is a specific change in energy for the electron, and electromagnetic energy is absorbed. The wavelength of the energy absorbed corresponds to yellow light. When this light is subtracted from incident white light, the complementary colour blue results. Sometimes when atomic spacing is different in different directions there is resulting blue-green dichroism.

Intervalence charge transfer is a process that produces a strong coloured appearance at a low percentage of impurity. While at least 1% chromium must be present in corundum before the deep red ruby colour is seen, sapphire blue is apparent with the presence of only 0.01% of titanium and iron.

Treatments

Sapphires may be treated by several methods to enhance and improve their clarity and colour.[16] It is common practice to heat natural sapphires to improve or enhance colour. This is done by heating the sapphires in furnaces to temperatures between 500 and 1800 °C for several hours, or by heating in a nitrogen-deficient atmosphere oven for seven days or more. Upon heating, the stone becomes more blue in colour, but loses some of the rutile inclusions (silk). When high temperatures are used, the stone loses all silk (inclusions) and it becomes clear under magnification.[17] The inclusions in natural stones are easily seen with a jeweler's loupe. Evidence of sapphire and other gemstones being subjected to heating goes back at least to Roman times.[18] Un-heated natural stones are somewhat rare and will often be sold accompanied by a certificate from an independent gemological laboratory attesting to "no evidence of heat treatment".

Yogo sapphire

Yogo sapphires sometimes do not need heat treating because their cornflower blue colouring is uniform and deep, they are generally free of the characteristic inclusions, and they have high uniform clarity. When Intergem Limited began marketing the Yogo in the 1980s as the world's only guaranteed untreated sapphire, heat treatment was not commonly disclosed; by 1982 the heat treatment became a major issue. At that time, 95% of all the world's sapphires were being heated to enhance their natural colour. Intergem's marketing of guaranteed untreated Yogos set them against many in the gem industry. This issue appeared as a front page story in the Wall Street Journal on August 29, 1984 in an article by Bill Richards, Carats and Schticks: Sapphire Marketer Upsets The Gem Industry.

Diffusion treatments are used to add impurities to the sapphire to enhance colour. Typically beryllium is diffused into a sapphire under very high heat, just below the melting point of the sapphire. Initially (c. 2000) orange sapphires were created, although now the process has been advanced and many colours of sapphire are often treated with beryllium. The coloured layer can be removed when stones chip or are repolished or refaceted, depending on the depth of the impurity layer. Treated padparadschas may be very difficult to detect, and many stones are certified by gemological labs (e.g., Gubelin, SSEF, AGTA).

According to United States Federal Trade Commission guidelines, disclosure is required of any mode of enhancement that has a significant effect on the gem's value.

Mining

Sapphires are mined from alluvial deposits or from primary underground workings. Commercial mining locations for sapphire and ruby include (but are not limited to) the following countries: Afghanistan, Australia, Myanmar/Burma, Cambodia, China, Colombia, India, Kenya, Laos, Madagascar, Malawi, Nepal, Nigeria, Pakistan, Sri Lanka, Tajikistan, Tanzania, Thailand, USA, and Vietnam.

The Logan sapphire, the Star of India, and the Star of Bombay originate from Sri Lankan mines. Madagascar is the world leader in sapphire production (as of 2007) specifically its deposits in and around the town of Ilakaka. Prior to the opening of the Ilakaka mines, Australia was the largest producer of sapphires (such as in 1987). In 1991 a new source of sapphires was discovered in Andranondambo, southern

Madagascar. That area has been exploited for its sapphires started in 1993, but it was practically abandoned just a few years later – because of the difficulties in recovering sapphires in their bedrock.
In North America, sapphires have been mined mostly from deposits in Montana: fancies along the Missouri River near Helena, Montana, Dry Cottonwood Creek near Missoula, Montana, and Rock Creek near Philipsburg, Montana. Fine blue Yogo sapphires are found at Yogo Gulch west of Lewistown, Montana. A few gem-grade sapphires and rubies have also been found in the area of Franklin, North Carolina.
The sapphire deposits of Kashmir are still well known in the gem industry, despite the fact that the peak production from this area mostly took place in a relatively short period at the end of the nineteenth and early twentieth centuries. At present, the world record price-per-carat for sapphire at auction was achieved by a sapphire from Kashmir in a ring, which sold for more than $175,000 per carat (more than $3.4 million in total) in May 2013.

Synthetic sapphire

In 1902 the French chemist Auguste Verneuil developed a process for producing synthetic sapphire crystals. In the Verneuil process, named for him, fine alumina powder is added to an oxyhydrogen flame, and this is directed downward against a mantle. The alumina in the flame is slowly deposited, creating a teardrop shaped "boule" of sapphire material. Chemical dopants can be added to create artificial versions of the ruby, and all the other natural colours of sapphire, and in addition, other colours never seen in geological samples.
Artificial sapphire material is identical to natural sapphire, except it can be made without the flaws that are found in natural stones. The disadvantage of Verneuil process is that the grown crystals have high internal strains. Many methods of manufacturing sapphire today are variations of the Czochralski process, which was invented in 1916. In this process a tiny sapphire seed crystal is dipped into a crucible made of the precious metal iridium or molybdenum,] containing molten alumina, and then slowly withdrawn upward at a rate of one to 100 mm per hour. The alumina crystallizes on the end, creating long carrot-shaped boules of large size up to 200 kg in mass.

Synthetic sapphire is industrially produced from agglomerated aluminium oxide, sintered and fused in an inert atmosphere (hot isostatic pressing for example), yielding a transparent polycrystalline product, slightly porous, or with more traditional methods such as Verneuil, Czochralski, flux method, etc., yielding a single crystal sapphire material which is non-porous and should be relieved of its internal stress.

In 2003 the world's production of synthetic sapphire was 250 tons (1.25 × 109 carats), mostly by the United States and Russia. The availability of cheap synthetic sapphire unlocked many industrial uses for this unique material:
The first laser was made with a rod of synthetic ruby. Titanium-sapphire lasers are popular due to their relatively rare capacity to be tuned to various wavelengths in the red and near-infrared region of the electromagnetic spectrum. They can also be easily mode-locked. In these lasers a synthetically produced sapphire crystal with chromium or titanium impurities is irradiated with intense light from a special lamp, or another laser, to create stimulated emission.

Transparency and hardness

One application of synthetic sapphire is sapphire glass. Here glass is a layman term which refers not to the amorphous state, but to the transparency. Sapphire is not only highly transparent to wavelengths of light between 150 nm (UV) and 5500 nm (IR) (the human eye can discern wavelengths from about 380 nm to 750 nm , but is also extraordinarily scratch-resistant.
Sapphire has a value of 9 on the Mohs scale of mineral hardness

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