

A brief overview of gem materials: Natural and synthetic

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A variety of synthetic and natural gem materials are discussed in this article. Their preparation techniques, properties and the origin of their colour are briefly covered. The article represents a broad overview of the subject of synthetic and natural gem materials.

Introduction

What makes a material worthy of being considered as a precious gemstone? From the point of view of the laity it is the visual appeal, colour, shape, brilliance, or some special optical effect associated with the material. A scientific approach lays down certain criteria for a material to qualify as a gem. These are high refractive index, dispersion, colour and hardness (see Table 1). Only materials with a high refractive index, when cut properly, can be brilliant. Dispersion is the ability to split different colours which makes a well-cut gem sparkle (or exhibit 'fire'). Hardness and toughness enhance wear resistance and durability. Among gemstones diamond reigns as the monarch of all, for it superbly meets all the above requirements. Further, its rarity of occurrence and centuries of lore on it have accorded diamond the top place and value.

Having met some of the properties mentioned above, gemstones have to be cut and shaped to maximize their appeal (Figure 1). Historically, gem cutting and shaping techniques have been perfected with diamond and the so-called brilliant cut with $57 + 1$ facets has become the standard. The facetting and angle of cut is chosen, taking into account the refractive index and dispersion (Figure 2). Larger stones over a few carats (carat = 200 mg) in size are often fashioned in different geometric shapes. With very large gemstones, the shape and cut are determined by the consideration to save the largest size possible out of the uncut stone, avoiding however defects that might be present in the original material. Diamonds can be cut, shaped and polished only with diamonds and the technology and tools for this purpose have been perfected. Presently, brilliant cut diamonds as small as a few hundredths of a carat (carat = 100 points) are available in the market. Multiple-stoned jewellery made from assemblies of small

diamonds of a few points each has a brilliant sparkle and is affordable. Hence, it has gained much popularity.

The price of diamonds, or any gemstone for that matter, depends upon the four Cs; carat, clarity, colour and cut. A one carat brilliant cut diamond weighing 200 mg is 6.5 mm in diameter when viewed from the front and may cost anywhere from 2000 to 10,000 dollars, depending on its clarity and colour. For smaller stones, e.g. 10 point stones, the price per carat drops by a factor of 5 to 10. The larger the stone the higher is the price; the price variation is not linear, but goes up with size by a power law.

Ruby, sapphire and emerald are often shaped differently from diamond, although in small sizes brilliant-cut stones are common. The star rubies and sapphires are

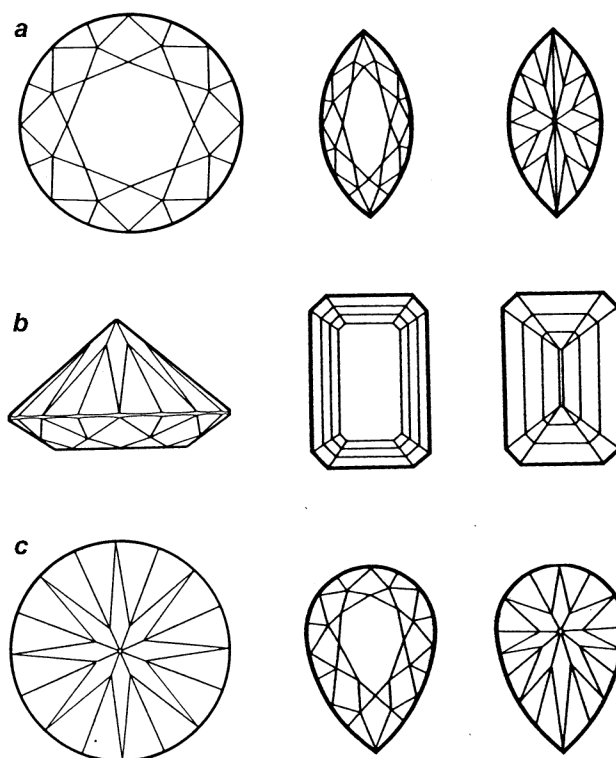


Figure 1. Some popular gemstone cuts. First column shows three different views of the brilliant cut, with 57 facets. *a*, Crown with 32 facets, plus the large Table facet; *b*, Side view; and *c*, pavilion with 16 lower girdle and 8 pavilion facets. If there is a culet facet, the total will be 58 facets. To the right are shown the crown and pavilion views for the Marquise (top), emerald (middle), and pear-shaped (bottom) cuts.

Table 1. Select physical properties for some important gem materials

Material	Composition	Crystal structure	Specific gravity	Refractive index	Dispersion Moh's scale	Hardness
Diamond	C	Cubic	3.52	2.417	0.044	10.00
Moissanite	SiC	Hexagonal	3.22	2.67	0.104	9.25
Sapphire	Al ₂ O ₃	Trigonal	4.05	1.77	0.018	9.00
Alexandrite	BeAl ₂ O ₄	Orthorhombic	3.73	1.75		8.50
YAG	Y ₃ Al ₅ O ₁₂	Cubic	4.55	1.83	0.028	8.25
CZ	ZrO ₂	Cubic	5.80	2.16	0.060	8.25
Spinel	MgAl ₂ O ₄	Cubic	3.64	1.73	0.020	8.00
Emerald	Be ₃ Al ₂ Si ₆ O ₁₈	Hexagonal	2.7	1.58	0.014	8.00
Topaz	Al ₂ SiO ₄ (F, OH) ₂	Orthorhombic	3.5	1.62	0.014	8.00
Tourmaline	Complex borosilicate	Hexagonal	3.0	1.63	0.017	7.20
Quartz	SiO ₂	Trigonal	2.65	1.55	0.013	7.00
Tanzanite	Ca ₂ Al ₃ (SiO ₄) ₃ (OH)	Orthorhombic	3.25	1.70		6–6.5
Strontium	SrTiO ₃	Cubic	5.13	2.41	0.190	5.50
Opal	SiO ₂ n.(H ₂ O)	Amorphous	1.98–2.25	1.43–1.47		5.5–6.5

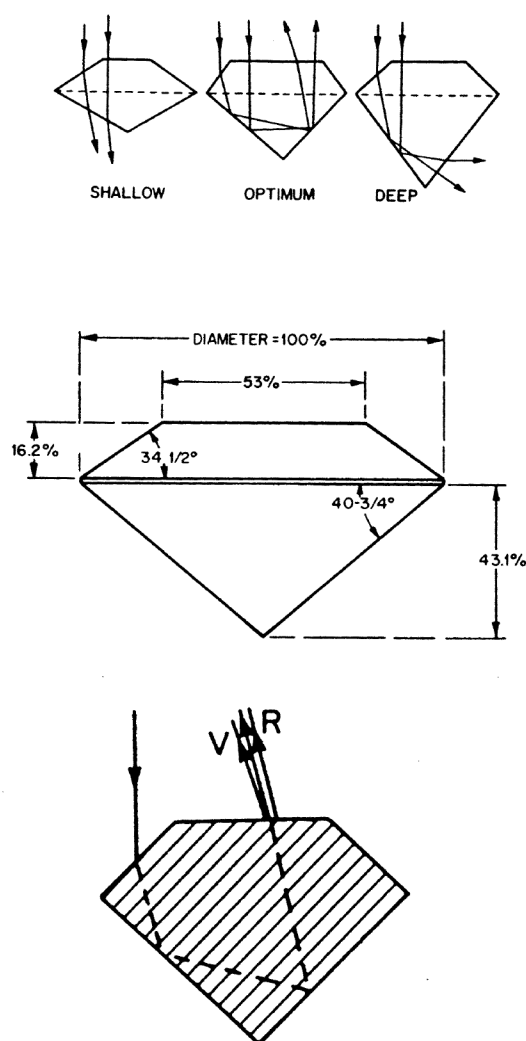


Figure 2. A correctly proportioned gemstone returns almost all the light entering, by total internal reflections. This will result in maximum brilliance, as shown at the top centre. A shallow cut or deep cut leads to leakage of light and loss of brilliance. (Middle) Optimum proportions and angles of cut for diamond, whose refractive index (RI) is 2.417. RI determines the angle for total internal reflection. (Bottom) Dispersion of white light in passing through a gemstone, the cause of 'fire' in a gem. The greater the dispersion, the greater the 'fire'. (Copyright, Nassau, K., used with permission¹.)

fashioned as cabochons to bring out the star pattern and these are very attractive. Perfect spheres of star ruby and star sapphire make a very appealing gem. Emeralds are commonly shaped in a tabular form (Figure 1) with facets on its side and terminating into a rectangular pyramidal shape on the pavillion side. This particular shape goes by the name 'emerald cut'.

Other gemstones such as tourmaline varieties, tanzanite, topaz, aquamarines, amethyst, etc. come in large sizes and are fashioned as emerald-cut and in round or oval shapes. Cubic zirconia which is a very good diamond imitation, is usually brilliant-cut as in the case of diamond and is quite attractive, at a fraction of the cost of diamonds. Further, cubic zirconia can be doped with transition metal ions during growth to produce coloured varieties. Moissanite is the recently introduced synthetic material which is a challenge to diamond, for its properties are so similar.

In this article we intend to give a broad survey of gem materials, both natural and synthetic^{1–10}. Some general aspects of the preparation techniques will be briefly covered. Much information on synthetic gems is covered by patents and only scanty details are available in the open literature. This is a serious problem in presenting the subject.

Crystal growth techniques for synthetic gems

There are several techniques^{1,3,8–10} available for growing gem materials, namely flame fusion, growth from the melt, flux method and hydrothermal technique. These have variants within them. For instance, there are many ways to grow single crystals from the melt, namely solidification in a crucible, Czochralski pulling technique and flame fusion itself. The choice of a particular method depends on the properties of the melt, the melting temperature, the size requirements and the cost of the vessel, especially when platinum or iridium containers are involved. For synthetic gemstones, the three commonly used

techniques are flame fusion (Verneuil's process or modifications of it), Czochralski pulling from the melt and flux method. The so-called 'skull' melting technique¹ has been used only in the case of cubic zirconia, because of the very high melting temperature of the ZrO_2 . Hydrothermal growth¹ uses high pressure vessels that operate at 1000 to 1500 atmospheres and at a few hundred degrees centigrade in temperature. To this must be added the very high pressure and high temperature technique which is employed in the making of synthetic diamonds. These are illustrated in Figures 3–9.

Colour of gemstones

With the exception of diamond and diamond simulants, colour is the main appeal for the majority of gemstones; ruby, emerald, blue sapphire, alexandrite, blue topaz, tanzanite, citrine, amethyst, tourmalines, spinels, etc. With diamonds, perfect white stones (colourless) are regarded as the top of the grade. Yellow, blue and green diamonds are gaining some popularity. These are found in nature occasionally and are extremely high-priced. It is now

possible to produce coloured diamond varieties by irradiation and heat treatment of natural stones. In the recent Minerals and Gems show at Tucson, Arizona, the present writer saw quite a few traders offering coloured diamonds, ranging from red, orange, yellow, green and blue. Enquiry revealed that they were made by special treatment and their cost was comparable to the colourless medium quality counterparts.

Many gem materials are colourless when pure. The colours are caused by the presence of small amount of impurities or defects in the lattice^{11–17}. Such a colour goes under the name 'allochromatic' in the gemmological literature. With yellow and green diamonds, nitrogen is the most common impurity. Blue diamonds contain boron¹³. Other transition metal and rare earth ions are known to be present in diamonds.

The red colour of the ruby, the captivating green of the emerald and the shifting greenish-blue to raspberry-red colour of alexandrite are all due to optical absorption bands in the visible, caused by the presence of chromium as an impurity in the lattice¹¹. Why the same impurity gives rise to different colours becomes clear by looking at the energy levels of Cr^{3+} ion in these crystals. This is

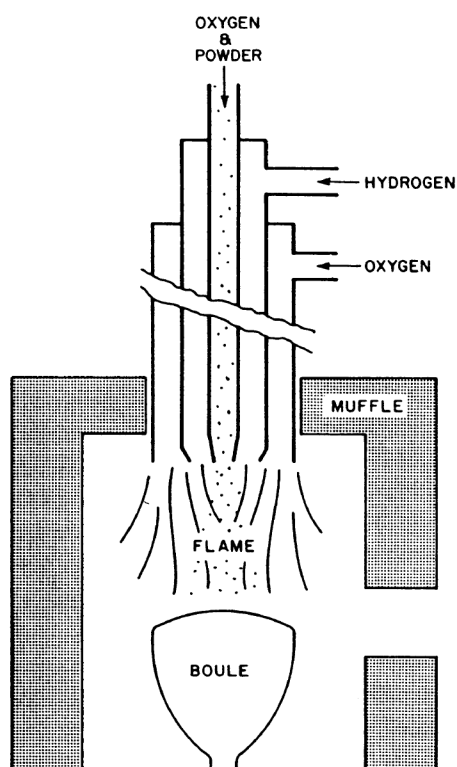


Figure 3. Diagrammatic sketch of the flame fusion (Verneuil's technique) method, originally developed for growing large ruby boules. Finely-powdered Al_2O_3 with a small percentage of Cr_2O_3 is fed through the oxy-hydrogen torch at a controlled rate. Melting occurs in the hottest part of the flame and the melt solidifies on the boule, which is slowly withdrawn downwards as it grows. A rotational motion of the boule during growth is necessary. The method is used for growing sapphire of different colours, ruby, star sapphire and star ruby and other gem materials. (Copyright, Nassau, K., used with permission¹.)

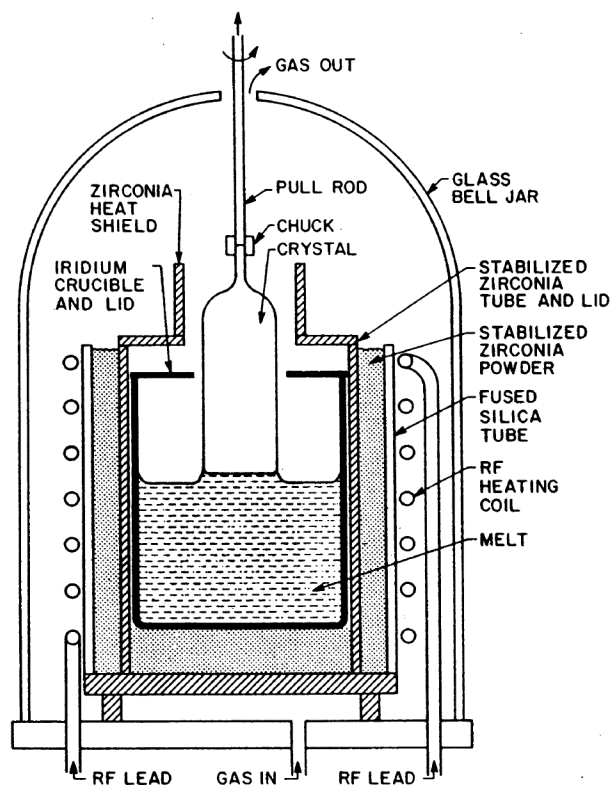


Figure 4. Schematics for the Czochralski-pulling technique for growth of single crystal rods of high-melting oxides and other materials, directly from the melt. Once the growth conditions are optimized, high quality single crystal rods can be grown. Used for growing synthetic ruby, garnets, etc. Crucible as large as 15 cm in diameter has been used. Precision pulling and rotating mechanical devices necessary are not shown in the figure (Copyright, Nassau, K., used with permission¹.)

illustrated in Figure 10 for ruby and emerald. On the left are shown the energy levels of Cr^{3+} and on the extreme right are shown the resulting absorption bands due to excitations of electrons within the crystal field-split 3-d levels of the Cr^{3+} ion. This splitting occurs¹⁴ because of the electric field exerted by the surrounding negatively charged oxygen ions on the 3-d electronic states of Cr^{3+} . The relevant energy levels and the corresponding absorption bands are shown in Figure 10. The broad absorption bands are due to interaction of the 5-d levels with the vibrational states of the crystal. The levels have different energies in ruby and emerald, because of different Cr–O ligand distances^{1,11}. In ruby the green–yellow and violet regions are strongly absorbed, which results in its red colour (by transmission). On the other hand, the absorption bands in emerald lie in the yellow–red–violet regions, with the absorption minimum in the blue–green region. This results in the free transmission of light in this region of the spectrum. Thus, it is the location of the absorption minima which determines the observed colour. However, in both ruby and emerald the red fluorescence is at about the same wavelength, as can be seen from the position of the levels involved in the emission of light. In alexandrite, the ligand field is intermediate between that of ruby and emerald^{1,11,15}. This fact, combined with the maximum sensitivity of the human eye for green is responsible for the observed shifting colour of alexandrite with the nature

of illumination, the so-called ‘alexandrite effect’. Alexandrite appears greenish-blue when viewed in fluorescent light and reddish in incandescent light.

This effect is also observed in corundum (Al_2O_3) containing V^{3+} impurity, which has an absorption spectrum similar to that of alexandrite. Consequently V^{3+} -doped corundum passes as an imitation alexandrite. The blue tanzanite (zoisite) and the green tsavorite (grossular garnet) owe their colour to V^{3+} . The pink colour of tourmaline (rubellite) and morganite (beryl) is caused by Mn^{3+} and Mn^{2+} impurity, respectively. The presence of Co^{2+} in spinel accords it a blue colour.

Another related property of gem materials is pleochroism, which is due to different absorption for differently polarized light with respect to the principal optical directions in the crystal. For instance, ruby is dichroic, the colours being violet–red for the ordinary ray and orange–red for the extraordinary ray. Alexandrite is trichroic, with yellow, purple–red, and blue–green, respectively for the three principal optical directions in the crystal. These colours can be seen by viewing the specimens in polarized light and rotating the specimens appropriately to coincide

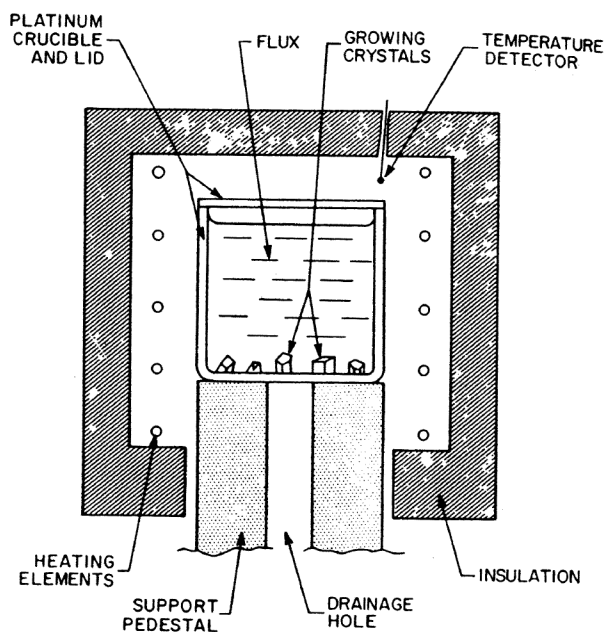


Figure 5. Schematic diagram for single crystal growth using a flux, in which the constituents dissolve and recrystallize, usually at a much lower temperature compared to the melting point of the gem material. This arrangement was used at Bell Labs by J. P. Remeika for growing very high quality crystals of ruby and spinels. Once the crystals have grown to the size targeted, the flux is poured out while still molten by ingenious methods, including puncturing the Pt crucible to drain the flux. Subsequent boiling in nitric acid will release the crystals. (Copyright, Nassau, K., used with permission¹.)

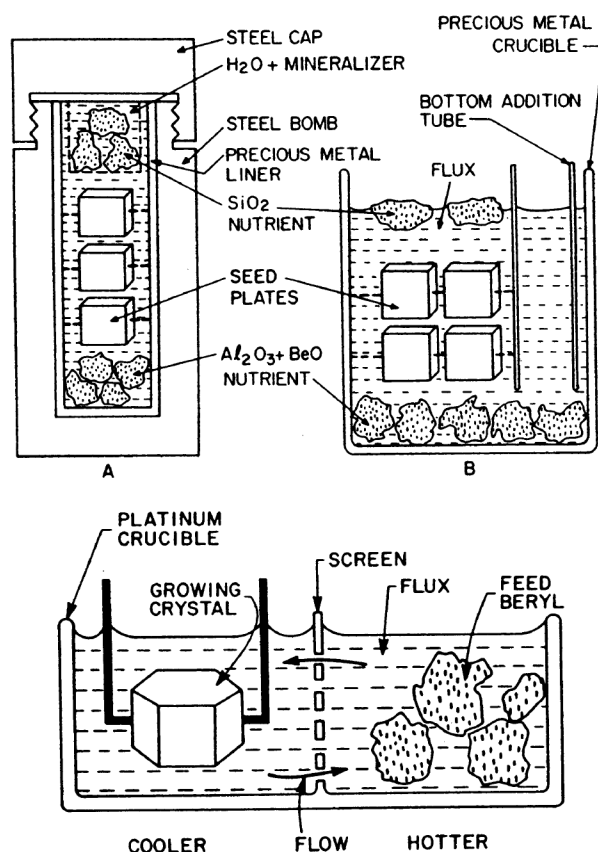
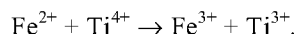


Figure 6. Diagrammatic sketch of the hydrothermal and flux methods for the growth of emerald crystals on seeds. (Top) Placement of the constituents (under hydrothermal conditions), which react to form emerald and deposit on the seed plates. (Bottom) Flux growth of beryl. The latter dissolves in the flux and regrows as a single crystal on the seed. (Copyright, Nassau, K., used with permission¹.)

with the principal directions. It must be noted that the 'alexandrite effect' is not due to pleochroism.

The colour of blue-sapphire owes its origin to a totally different mechanism^{11,12,16}. Pure sapphire is colourless. However, if it contains a small amount of titanium and iron, the combination results in a deep blue colour. With either Ti or Fe alone this blue colour is not obtained. The mechanism that is responsible for the blue colour has been shown to be the result of intervalence charge transfer effect^{11,15,16}, namely the transfer of electrons from the Fe to the Ti in adjacent sites.



This process involves absorption of yellow light, resulting in the transmission of the complementary blue colour. In aquamarine, it is the charge transfer between $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ which causes the blue colour. The charge transfer absorptions produce intense colours, even when the concentration of impurities is a few hundredths of one per cent, unlike the forbidden transitions between the crystal field-split intra 5-d transitions encountered in ruby. Ruby needs several per cent Cr^{3+} to get a strong tint.

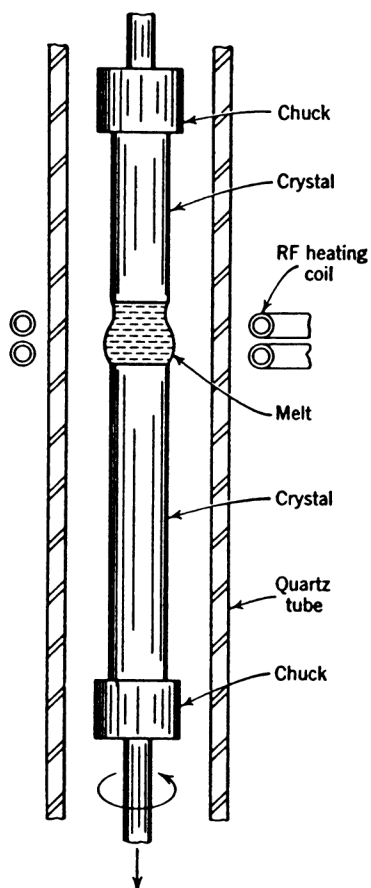


Figure 7. Zone melting technique to purify and grow long, single crystal bars. The RF coil heats a small segment to melting. The molten zone is swept from one end of the bar to the other, by moving the RF coil across the length. (Copyright, Nassau, K., used with permission¹.)

The colours of gemstones, both natural and synthetic, can be modified by irradiation and heat treatment^{12,13,17-19} and the subject is a substantial part of gemmology. The article by Shigley in this issue covers this briefly.

Identification

This is the most important aspect of gemmological science, which offers the main guidance to identifying a gemstone. Visual inspection, assisted by a 5 or 10 power hand lens is the easiest option available to examine a gemstone on the spot, and to the experienced this reveals a lot. In the usual gem trading this is the only method that would be readily available. However, there are powerful scientific methods to identify gems. In these, various physical properties of crystalline materials are used, viz. crystal structure determination by X-ray diffraction, spectroscopic methods including light scattering, density, refractive index and birefringence. Shigley's article in this

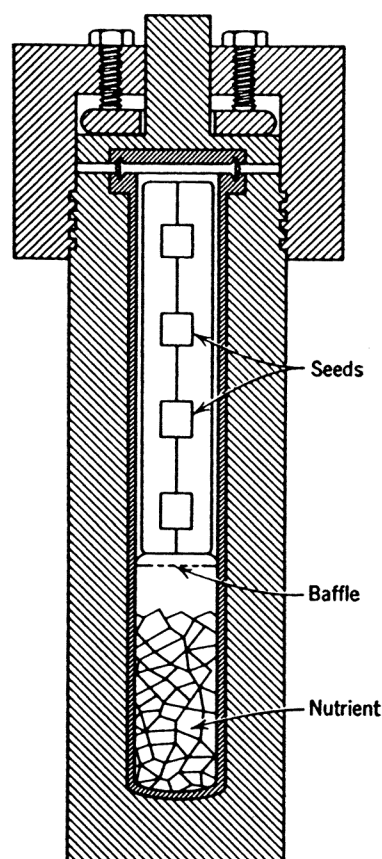


Figure 8. Diagrammatic sketch of the high pressure-high temperature autoclave used for hydrothermal synthesis of quartz crystals. The nutrient is pure quartz aggregate. The seed plates on which growth occurs are shown. Quartz which is insoluble in water assumes significant solubility in high pressure-high temperature water. A thermal gradient helps to transport the dissolved SiO_2 to the seed plates. Pioneering work on hydrothermal quartz synthesis was carried out in Bell Laboratories by R. A. Laudise, A. A. Ballman and others, which resulted in the large-scale manufacture of synthetic quartz. (Copyright, Nassau, K., used with permission¹.)

issue very briefly covers these aspects and the instrumentation specifically developed for gemmology. While these techniques can be definitive to differentiate the real from the imitations, they cannot distinguish the natural from the synthetic. For this, gemmologists rely on criteria that they have been able to set from observations based on experience.

Specific gem materials

We now focus on several gem materials, both natural and synthetic, either for their value as gemstones, or for the purpose of serving some technological application.

Diamond

There is no gemstone equivalent to diamond for its beauty, brilliance and sparkle. In India, diamond as a gem has occupied a special place from time immemorial and some of the famous diamonds, viz. 'Kohinoor', and 'Hope diamond' originated from there. The earliest diamond findings are believed to be from alluvial sources near the Golconda area, Godavari basin, and Madhya Pradesh. However, the Indian sources dried up in the 18th century, following which the Brazilian sources opened up. With the discovery of diamonds in South Africa and deeper mining efforts, large-scale production of diamonds started. The largest diamond, known as 'Cullinan', is of South African origin. The African sources still dominate the diamond market, for the size, variety and quantity.

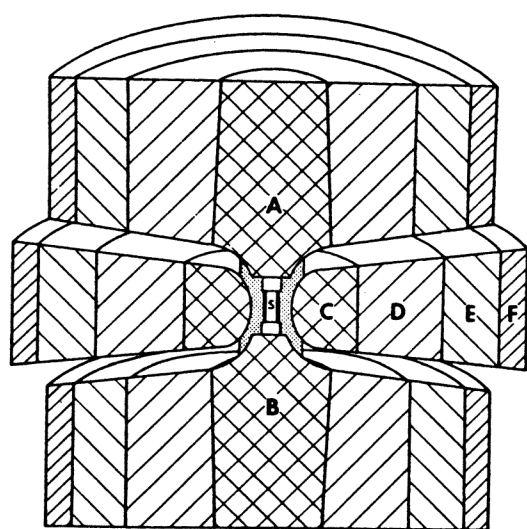


Figure 9. The so-called Belt apparatus in which diamond was first synthesized in the G. E. Lab, Schenectady, by H. T. Hall and coworkers. (Copyright, Nassau, K., used with permission¹.)

Both Australia and Russia are recent entrants, as major producers of the diamond.

Scientific studies have revealed that diamond is a dense polymorph of carbon, with a hardness unequalled by any material known to science. Its occurrence in nature in beautiful geometric shapes, its luster and ability to scratch and wear even the hardest rocks were perhaps the reasons that attracted the early attention of man, who bestowed magical powers to the stone. Over millennia, its status as the most sought-after gem has grown to unprecedented levels. Advances in cutting, shaping and polishing techniques have enhanced the beauty and appeal of diamond.

A milestone in history of the diamond is its successful synthesis in 1955 at the General Electric Research Laboratory in Schenectady, New York. To geologists and geophysicists it was known that natural diamonds were formed in the deep interior of the earth, at depths of 200 km and below, under high pressure-temperature conditions. They were transported to the surface through fissures along with the molten rock-forming silicate material during volcanism and remained embedded in them. The silicate material with which diamonds are usually associ-

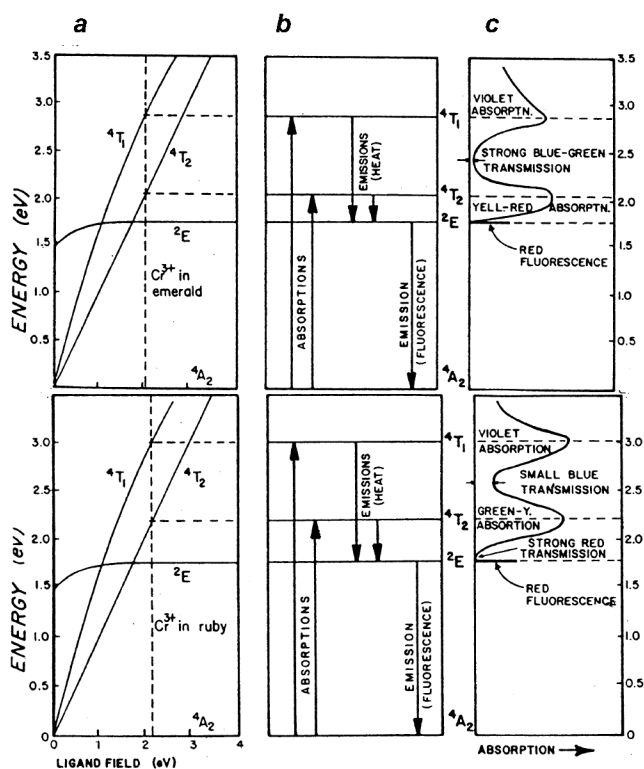


Figure 10. *a*, Cr^{3+} crystal field-split energy levels as a function of ligand field. The ligand fields appropriate for ruby and emerald are indicated by the dotted vertical lines. *b*, Absorption and emission of light associated with the levels, and *c*, resultant absorption bands. Emerald has a green colour as opposed to the red of ruby, due to a slight shift in the position of the absorption bands, caused by the shift in the ligand field. In ruby red is freely transmitted without any absorption, while for emerald a deep minimum in the absorption is located in the blue-green. T, E and A are spectroscopic designations for the energy levels. (Copyright, Nassau, K., used with permission¹.)

ated is known as 'kimberlite', and the fissures 'kimberlite pipes'. Through erosion over eons the diamonds were exposed and were waiting to be discovered. Thus it was known that the diamond is a high pressure-high temperature product of carbon and can be made under appropriate high pressure-high temperature conditions. Once forced into the diamond form it will remain metastably forever under ambient conditions. Only when heated to red-hot temperatures will the diamond transform to carbon and burn away.

After many attempts on diamond synthesis by celebrated scientists like Moissan, Bridgman and others, the laboratory synthesis was achieved in 1955. It was through a combination of understanding the thermodynamic stability field of diamond-graphite (Figure 11) and fabrication of apparatus (Figure 9) that reach pressures and temperatures in the neighbourhood of 7–8 GPa (one GPa is about 10,000 atmospheres) and 1500–1700°C to rapidly convert graphite to diamond, the successful synthesis became possible. The story behind the history of diamond synthesis is told by Robert Hazen in his fascinating book *The Diamond Makers*⁸. Millions of carats of industrial quality diamonds are produced for abrasive industry and for cutting tool manufacture, using the synthetic route.

Gem quality diamonds of 1–2 carats in size have been successfully produced at the G.E. facility²⁰, but these are too expensive to compete with natural diamonds, cost-wise. High quality stones and even isotopically pure ones (with C¹⁴ or C¹² only) can be made, and these diamonds are valuable for scientific purposes. These can also be doped with impurities to produce blue diamonds and semiconducting diamonds.

Ruby and sapphire

Natural ruby and sapphire are relatively more abundant than diamond. Their appealing colour, high density and

hardness have earned them a reputation as highly precious gemstones. They are derivatives of the mineral known as corundum, chemically Al₂O₃. The crystal structure is trigonal and the material has no cleavage unlike diamond which cleaves along certain crystal planes. The beautiful red colour of ruby owes its origin to the presence of small amounts of Cr³⁺ (0.5 to a few per cent) in place of Al in the lattice^{1,11}, the depth of colour depending upon the Cr³⁺ concentration. Presence of other transition metal ions in sapphire results in different colours. For instance, the colour of blue sapphire is due to the simultaneous presence of Fe and Ti impurities¹¹.

Ruby is one of the very first synthetically produced gemstones by Verneuil's flame fusion process. The history behind the evolution of this process and its present-day forms for producing synthetic ruby are covered in an excellent book by Nassau¹. The majority of synthetic ruby and sapphire for gemstone use and for certain industrial applications is produced by the Verneuil process, because of the low cost of production by this technique.

Large high quality single crystal boules have been grown by Czochralski technique and nearly perfect single crystals, smaller in dimension, by the flux method¹⁰. The Czochralski method of pulling from the melt provides high quality crystals needed for laser rods of ruby for the ruby lasers. Pure Al₂O₃ with the desired addition is melted in an iridium crucible. Although Pt as a crucible material is acceptable, iridium is preferred because of its higher melting temperature of 2420°C. The melting point of Al₂O₃ is 2050°C. A small seed crystal is used to initiate growth and the process is started by contacting the melt surface with the seed and gradually withdrawing the latter from above. If the temperature of the melt is right, crystal growth from the melt will start and high quality long crystal bars can be obtained by combining rotational motion and vertical pulling at the optimum rate. Heating is effected by using an RF generator of high power and stabilized output.

Almost perfect ruby and sapphire crystals can be made by the flux method. The flux used and patented in 1963 (ref. 1) by J. P. Remeika of Bell Laboratories consisted of PbO with a small amount of B₂O₃. The ingredients, namely Al₂O₃ and Cr₂O₃ were dissolved in the flux which was held at 1300°C. A small Pt crucible served as the container. Slow cooling at 2°C per hour over an eight-day period produced ruby crystals at 915°C. At that point the flux was poured away and the ruby crystals were freed by dissolving the remaining flux in dilute nitric acid. Since then the most popular fluxes have been PbF₂, or a combination of this with PbO and PbO–B₂O₃. Although good-sized crystals can be produced for the gem market by the method, it is too costly and time consuming. Also, flux inclusion can adversely affect the quality.

Synthetic star ruby and sapphire have been produced by the addition of TiO₂ powder during growth in Verneuil torch, followed by appropriate heat treatment to precipi-

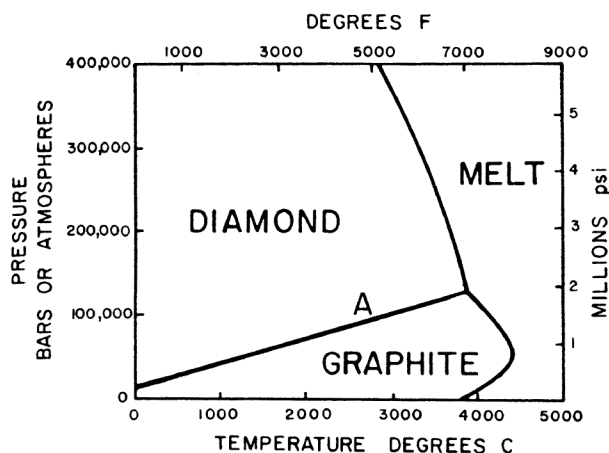


Figure 11. P–T phase diagram of carbon showing the diamond-graphite equilibrium line. Rapid conversion from graphite takes place under 70,000 atmospheres and 1600–1700°C region. (Copyright, Nassau, K., used with permission¹.)

tate TiO_2 . The latter is in the form of fine needles which align themselves along the crystallographic directions of ruby. Reflection of light by these fine needles produces the star effect. Another way to make stars involves diffusion of TiO_2 into Al_2O_3 at high temperature (1800°C), to improve the star in natural stones or in synthetics. However, this would be a treatment process rather than synthetic.

Emerald

There is a large group of gems derived from 'beryl', which is beryllium aluminium silicate of basic composition $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, consisting of $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. Natural beryls usually contain water trapped in the structural channel. In the mineralogical literature^{1,5} the colourless variety is known as 'goshenite', the blue as 'aquamarine' and the pink as 'morganite'. The colour of aquamarine is due to the presence of Fe. Manganese is the cause of the pink colour of morganite and it can also produce the rare red beryl. Surprisingly, the green colour of emerald owes its origin to the Cr^{3+} , in substitution for Al in Al_2O_3 . It may be noted here that Cr^{3+} in Al_2O_3 is the cause of the red colour of the ruby. Vanadium oxide produces a similar green colour in beryl. Water is always present in natural emerald, having entered the structure during formation. Most natural emeralds are flawed and in fact this is one way to distinguish them from imitations. Also, water band is another way to differentiate natural from flux grown synthetic emerald¹².

Flux growth of synthetic emerald¹⁰ was achieved quite some time ago by C. C. Chatham in USA and Pierre Gilson in France. Their process involved the use of lithium molybdate as flux. Growth took place spontaneously, or on seeds of beryl kept in the middle compartment (see Figure 6). SiO_2 and other components were kept separately in the adjacent compartments (see Figure 6). The grown emerald was sawn off from the seed and cut and fashioned as gems. They were in the market but not in any great quantity. Linde Division of Union Carbide produced emerald for some time by the hydrothermal process similar to that used for quartz. They used autoclaves with gold lining inside to prevent Fe contamination. Typical growth conditions, according to Nassau, were 700–1400 to bars pressure at temperatures in the range $500\text{--}600^\circ\text{C}$. A temperature gradient of 10 to 25°C between the bottom and top portions of the vessel was maintained during growth. The nutrients were $\text{Al}(\text{OH})_3$, $\text{Be}(\text{OH})_2$, SiO_2 and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. Growth rates as high as 1/3 mm per day were typical according to Nassau¹. In the autoclave, quartz was kept on the top and other ingredients at the bottom. As the water-filled autoclave is heated to the right temperature, quartz dissolves and the SiO_2 descends downwards, while other ingredients dissolve in the bottom portion and raise upwards. The solutes meet in the middle and react to form emerald, which deposits on the seed crystals kept in the

middle part of the vessel. The growth parameters have to be optimal for this and these are patented information. Some of the growth parameters are listed by Nassau in his book¹. According to him, none of the emerald growth techniques is easy and they are all slow processes. Apparently the synthetics have not affected either the demand or the value of natural emerald. Colombian emeralds by far dominate the market and plentiful supply of them, from poor to top quality can be bought. The present writer was amazed to see at the Gems and Mineral Show in Tucson, the quantity and variety of Colombian emeralds that were available for trade. Emeralds are highly valued when the stones have the deep green colour and high clarity. Emerald crystallizes in the hexagonal system and has a hardness of 7.5–8 in the Moho's scale. However it is somewhat brittle and shock and heat-sensitive.

Alexandrite, spinel, garnets and diamond substitutes

Alexandrite is chrysoberyl BeAl_2O_4 with Cr^{3+} as an impurity. As mentioned earlier its colour depends on the type of illumination; in fluorescent light blue dominates, while red is predominant when viewed in light from a tungsten lamp. This is the so called 'alexandrite effect'. The most desirable colour change is rich blue–green to a deep raspberry red, and the shade of the colour can vary. The gem was named after Czar Alexander II of Russia, the best natural source being the Ural mountains in Russia. The impurity that produces the colour in alexandrite is Cr^{3+} , but the ion sits in a different crystal environment and hence experiences a different ligand field. Synthetic alexandrite gemstones have been produced since 1973 and patented by Creative Crystals Inc of San Ramon, California, according to Nassau¹. Both melt techniques and flux methods have been used. It is a very attractive gem material. Recently it has found application as a laser material, the so called alexandrite lasers.

Spinel occurs in nature in different colours and has been synthetically produced as well¹. The colour of synthetic spinel depends on the type of impurity and stoichiometry. Spinel is chemically MgAl_2O_4 . With the appropriate impurity in the lattice, spinels can be produced to imitate almost any precious naturally occurring gemstone material. As for synthesis, the Verneuil growth technique, melt and fusion methods can be used, similar to those for sapphire.

Garnet is a well-known silicate mineral with the general formula $\text{A}_3\text{B}_2\text{Si}_3\text{O}_{12}$, where (A) is a divalent, (B) a trivalent and Si a quadrivalent ions. The naturally occurring blood-red variety of garnet is known as pyrope whose chemical make up is $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. The red colour is due to the presence of Fe as an impurity. (A), (B) and Si occupy dodecahedral, octahedral and tetrahedral sites, respectively in the oxygen skeletal network. However, Si

can be totally replaced with ions whose sizes can be tolerated in the above sites, even though their valence states may be different. But it is essential that the charge balance is maintained. Based on this crystal chemistry several garnets of the type $A_3B_5O_{12}$ where (A) is a rare earth element and (B) is Fe, Al, Ga and SC were synthesized²¹ at Bell Laboratories in Murray Hill, New Jersey in the early sixties. The first crystals of $Y_3Fe_5O_{12}$ (YIG) and $Y_3Al_5O_{12}$ (YAG) were grown from fluxes consisting of PbO or from a mixture PbO and PbF₂. Yttrium iron garnet (YIG) was of great interest to technology because of its magnetic properties. Nielsen, who first made these materials at Bell Laboratories, indicated the possibility of using the new garnets as a gem material. Since then large Czochralski-pulled high quality YAG crystals became available. Coloured varieties of YAG were also made, simulating many precious gem stones. Another material in this line is the so called GGG ($Gd_3Ga_5O_{12}$). The crystals have been produced almost flawless. Both the garnets were good diamond imitations for some time with GGG having an edge over YAG, because of its higher refractive index. However, these have high density, which was a drawback.

Cubic zirconia

In its monoclinic form, zirconium oxide (ZrO_2) is known as baddeleyite, but it is the cubic modification which has attained notoriety as simulated diamond. It is thermodynamically unstable and can exist at ambient pressure and temperature, only when certain additives are present, viz. a few per cent CaO, MgO or Y_2O_3 . This is known as stabilized cubic zirconia. Since the melting point of ZrO_2 is very high (2750°C), laboratory growth of single crystals of cubic zirconia is carried out by a growth technique called skull melting^{1,22}. The technique was originally developed in Russia and has been adopted for producing the material. Details are patented information. Briefly, the method employs a water-cooled ZrO_2 shell as the container, which is filled with ZrO_2 powder plus the stabilizer. A small amount of Zr metal chips is mixed in with the charge to couple the RF energy. Through the gaps in the surrounding water-cooled copper tubes the RF energy penetrates and initially helps in heating the charge. As heating proceeds, ZrO_2 becomes conducting and couples directly with the RF. Then the whole charge melts except for a relatively thin layer next to the water-cooled copper tubes. Additional ZrO_2 powder with the stabilizer could be added at this stage to fill the skull to the desired level. The contents are kept molten for several hours to ensure homogeneity and to get rid of the impurities through boiling. Then the electrical power is reduced and the skull is lowered very slowly out of the heating coil. The crust solidifies, but growth of parallel columns of crystals takes place, nucleated from the bottom of the crucible. The

power is shut off when the melt has solidified. The crystals are then annealed at about 1400°C in air for 12 h to release residual strains. According to Nassau, with a 1 kg charge a maximum of about half a kilogram of facettable material has been obtained. With large skulls single crystals larger than 10 cm in dimension could be made readily by the technique¹. Cubic zirconia have a sparkle and lustre quite close to that of diamond. The only drawback is their rather low hardness. Coloured varieties of cubic zirconia can be produced by transition metal oxide additions to the initial charge.

Quartz and opal

Quartz (SiO_2) which is one of the most commonly occurring minerals, also occurs as crystallized clusters and as large single crystals. In its cryptocrystalline form it is the basic part of agates, chalcedony, and other silica materials found in nature. Amethyst, citrine, rose-quartz and smoky-quartz are other coloured varieties, all of which comprise quartz family gemstones. Most of the natural materials of the quartz family are of hydrothermal origin. Flawless quartz crystals in their purest form have technological applications and for this reason much effort was put into synthetically making them in large quantities by the hydrothermal process, almost half a century ago.

The most successful hydrothermal growth technique was developed in Bell Laboratories^{1,23} in the early sixties. The method used high pressure autoclaves operating at about 1.5 kilobar pressure and temperatures in the range of 300°C. Under these conditions, the water insoluble quartz has a significant solubility in water. Sodium hydroxide was added to increase the solubility. Pure Brazilian crushed quartz crystals serve as the nutrient and are placed in the bottom of the vessel (Figure 8). A series of seed plates of quartz are suspended by wires from the top for growth into large crystals. Under a temperature gradient between the bottom and top portions of the vessel, typically around 40–50°C, crystal growth takes place. In the large-scale operation, one hundred quartz crystal bars of about 7" long and 2" in thickness can be grown over a period of 30 days, with 90 kg of feed quartz.

Coloured varieties can also be produced with Fe additions, resulting in yellow citrine-like material. By irradiation, the iron impregnated quartz can be turned into amethystine colour, a popular precious gem material widely used in jewellery. Another variety is 'smoky quartz' which is an irradiation-induced colour associated with aluminum impurities. Blue and green quartz can also be produced by radiation and heat treatment. Quartz has a hardness of 7 in the Moh's scale and does not have any cleavage direction. In its purest form it is known as 'spatik' in Sanskrit, symbolizing purity, and has long been known in India.

Opal

Opal ($\text{SiO}_2\cdot n\text{-H}_2\text{O}$) has been one of the favoured precious gemstones for many centuries. Though beautiful, it is very fragile and is damaged quite easily. Opals of Australian origin are the best known in the gem market (see Figure 12). Most of these have a milky-white body and exhibit brilliant play of colours emanating from inside. The colours are due to optical diffraction effect from the regularly-spaced structure inside. To bring out the optical effect opals are generally shaped as 'cabochon'. The Mexican variety of opals are generally colourless and clear. However, the best known Mexican 'fire opal' is of orange or reddish colour. Another variety is black opal which is rare and very beautiful, because the black background enhances the diffraction colours. It is very expensive also. Generally opals do not show any crystalline X-ray diffraction pattern, signifying that they are structurally amorphous. Some Mexican opals, however, do show powder X-ray diffraction pattern characteristic of alpha or beta-cristobalite, polymorphs of SiO_2 .

The origin of colours in opals has attracted the attention of some of the greatest physicists, like C. V. Raman²⁴. He hypothesized that there should be multiple layered struc-

tures in the matrix opal, of silica material having a slightly different refractive index. While this explanation is almost close to the truth, a definitive and detailed answer was given in 1964 by J. V. Sanders and coworkers²⁵ in Australia, based on an electron microscopic study of opals. They established that there is a close-packed arrangement of silica spheres of uniform size inside the $\text{SiO}_2\cdot n\text{-H}_2\text{O}$ matrix and that these regions produce the colour. The size and spacing of the spheres and their orientations differ, which produce the 'opal effect' and the coloured reflections are similar to Bragg reflections of visible light. The successful synthesis of opal in the laboratory confirms this explanation. The synthesis of opal has been a tough task and is a recent achievement.

Three steps necessary to produce synthetic opal, according to Nassau¹ are (i) to form silica spheres of exactly the same size, (ii) allowing them to settle into a close-packed arrangement, and (iii) to fill the interspace with the material of appropriate refractive index, with $\text{SiO}_2\cdot n\text{-H}_2\text{O}$ combination. While the first two steps are relatively easy to carry out, the third and final step involves the use of right pressure and temperature combination to make the final product. The details are trade secrets. Synthetic opals are sold in the market as 'Gilson

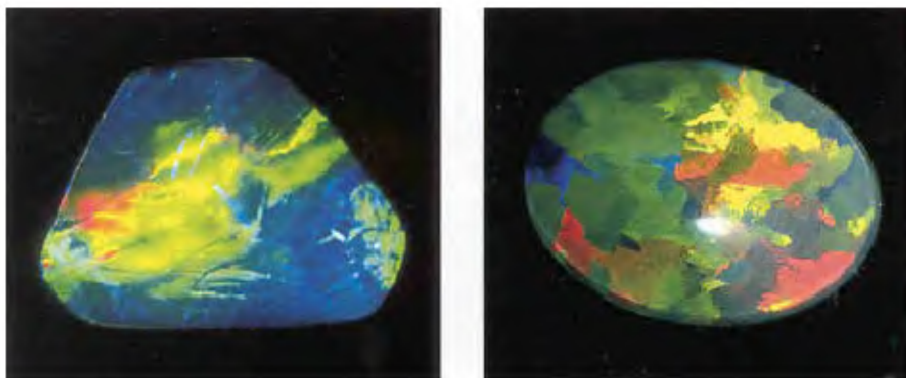


Figure 12. Precious opal (left) and Gilson synthetic opal (right). Photo reproduced with permission of Office of Minerals and Energy, PIRSA, Australia.

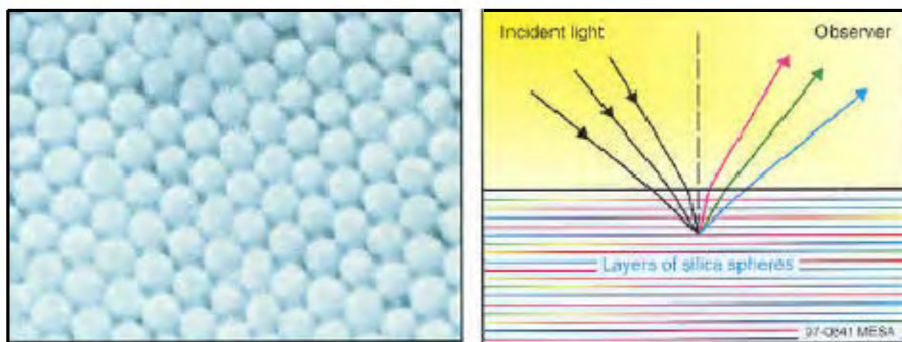


Figure 13. Scanning electron micrograph of opal ($\times 40000$) showing the regular arrangement of silica spheres approximately 200–350 nm in size (Photo reproduced with permission of Office of Minerals and Energy, PIRSA, Australia) on the left reflection spectrum from the layers of regularly spaced silica spheres embedded in gold is shown.

created opal'. They are not, however, quite like the natural opal.

In the context of the presently active area of optical physics of photonic crystals, it seems that opal is a kind of frozen photonic crystal, with nanospheres of silica arranged in an orderly fashion on the optical scale, to form diffraction gratings inside the matrix (see Figure 13).

Among the other gem materials, turquoise, lapis lazuli and coral have been produced synthetically, as well as many glass, ceramic and composite imitations. There are the very attractive unmixed feldspar minerals, viz. moonstones, sunstones, labradorite and peristerite compositions which are used as gem stones. Synthesis of these is for the future. The latest challenge to diamond has come from moissanite which has been synthesized in the colourless variety. This is dealt with in the article by K. Nassau in this issue.

Concluding remarks

India is richly endowed with gem minerals, and the precious gemstones have been in use for centuries, in royal jewellery and in temples. These were collectively called 'navaratnas'. Of these, diamond, ruby and emerald were regarded highly and were set in jewellery as pendants, in ear and nose rings and as adornment in head dresses. Among the three, ruby was the most popular and affordable gem. When set in yellow-gold, small round cabochon-shaped ruby jewellery is attractive. Further, they had a special appeal, for they were natural and hand-crafted one hundred per cent. People were able to identify them, guided by experience and advice from trusted goldsmiths and traders. In the modern age, with imitations and synthetics flooding the market, one needs the help of a gemmologist to distinguish fake from the real, synthetic from natural and genuine from imitation.

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