36

Minerals and Gems

CHAPTER PREVIEW

We begin this chapter by explaining why we're including gems in a text on ceramics. Gems have been intimately linked with many developments in the use of ceramics or have been the motivation for what has become a leap forward in ceramic processing or application. We saw earlier how the efforts by August Verneuil in the early 1900s to produce synthetic ruby lead to an industry that produces 2×10^5 kg of single-crystal Verneuil sapphire each year. Similarly, flux-growth techniques and hydrothermal quartz owe much to the desire to create gems. Gemstones use some special properties of ceramics: they can be transparent but with a range of colors; they scatter light (the sparkle); the valuable ones are generally very stable (the less valuable have often been treated—actually, most gemstones have been processed in some way). We discuss the well-known gems and a few of the lesser known (for their special features). The most important gems are diamond, ruby, sapphire and emerald. However, many other gems that are less well known may often be more valuable. Incidentally, the weight of a gemstone is usually given in carats (5 ct = 1 g). We also use this chapter to summarize the links between some preceding topics, including history. If a friend hands you a blue (or red, yellow, green, colorless) faceted sparkling stone and asks you to identify it (because you studied ceramics), what do you do or say? So when you read this chapter, keep asking yourself—what ceramic science is involved here?

36.1 MINERALS

Mining and mineral engineering are not always popular topics today. Many gemstones and mineral specimens are found during mining operations. The bulk of the minerals are then processed by physical or chemical means. Ceramists should have some knowledge of mineral processing because it can be the clue to understanding why certain impurities are present in powders used to produce high-tech ceramics (hence our discussion of raw materials in Chapter 19), but minerals and gemstones have many commercial, in addition to decorative (ornamental), uses.

Grinding is a particularly simple example of physical processing. It has been used to make pigments, early cosmetics, and the ingredients for the potter's slip. It is a key step in modern ore processing (see Chapter 19), but it has been used for centuries to make powders.

Grind hematite to produce the red pigment *ochre*.
Grind cinnabar to produce the major component of *vermillion*.
Crush lapis lazuli like the Persians did to make *ultramarine*.
Grind azurite like the ancient Egyptians did to produce the blue pigment *azure*.
Grind tin oxide like the Romans did to make a white cosmetic paste.
Be cautious about using ground *talc* on your body.

Of course, grinding is also the principle of the abrasives industry. Powders may be made by grinding or used for grinding/polishing, as we discussed in Section 18.12.

A crystal of galena was used in the cat's whisker radio (in the "point-contact" diode); Cu wire was slowly moved across the galena crystal to tune the device. Thin slices of tourmaline crystals were used in making the pressure gauges that measured the power dissipated by the first atom bomb explosions (tourmaline is piezoelectric).

Chalcedony is "noncrystalline" quartz. Examples of chalcedony are agate, jaspar, and carnelian; they form by hydrothermal growth—hence the banding you see on stones in museum shops. The color depends on the impurities, and not much impurity is needed (it can easily be changed/dyed). We discuss flint and opal separately, although they are closely related. Flint tools, like obsidian tools, were used thousands of years ago. Flint consists of fine-grain silica (the black color is caused by trapped carbon) and fractures like obsidian, producing sharp edges that are ideal for cutting.

C.B. Carter and M.G. Norton, *Ceramic Materials: Science and Engineering*,
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Alabaster, gypsum ($CaSO_4.2H_2O$) and plaster of Paris ($2CaSO_4.H_2O$) are all calcium sulfate (the last of these has been treated to produce the hemihydrate). Fine-grain gypsum is easily carved: fractures do not propagate far. Alabaster ornaments were made in Assyria (Iraq) before 2,000 BCE and plaster of Paris was used by the Egyptians in ~3,000 BCE in making mortar.

NATURAL GLASS THREAD

Pele's hair (the Hawaiian goddess of volcanoes, not the footballer) consists of natural threads of basalt glass often containing crystals of olivine. Like obsidian and pumice it forms in volcanic eruptions.

36.2 WHAT IS A GEM?

Gems are often characterized as expensive sparkling stones. The value is not necessarily as obvious as we might hope. Even so, you can spend significant money on gems.

A gem can be real (natural), synthetic (grown in the laboratory or factory), or a simulant (one material made to look like another).

Gems can provide a link between ceramics, geology, crystallography, mechanical testing, solid-state, physical, and inorganic chemistry, and electrical engineering. They provide the ceramist with many challenges, such as, identify this ceramic (gem) without removing it from the gold band it's set in. Table 36.1 lists some of the best-known gemstones with some of their special features.

TABLE 36.1 Gemstones

Hard and resistant to chemicals	*Chrysoberyl*, $BeAl_2O_4$
	Corundum, Al_2O_3
	Quartz and *chalcedony*, SiO_2
	Spinel, $MgO.Al_2O_3$
Gem carbonates (not so hard)	*Calcite*, $CaCO_3$
	Malachite, $Cu_2(OH)_2CO_3$
	Rhodochrosite, $MnCO_3$
Gem phosphates (not so hard)	*Apatite*, $Ca_5(F_2Cl)(PO_4)_3$
	Turquoise, a complex hydrated phosphate of copper and aluminum
Gem silicates (hard and durable)	*Beryl*, $Be_3Al_2(SiO_3)_6$
	Feldspar group gems—aluminum silicates in combination with calcium, potassium or sodium
	Garnet group gems—silicates of various combinations of magnesium, manganese, iron, calcium, aluminum and chromium
	Jadeite, $NaAl(SiO_3)_2$
	Nephrite, complex calcium, magnesium or iron silicate
	Peridot, $(Mg,Fe)_2SiO_4$
	Rhodonsite, $MnSiO_3$
	Topaz, $Al_2(F_2OH)_2SiO_4$
	Tourmaline, a complex borosilicate of aluminum and iron
	Zircon, $ZrSiO_4$

One challenge is to identify a particular gemstone.

The scientist's way: use X-ray diffraction (XRD), X-ray energy dispersive spectroscopy (XEDS), wavelength dispersive spectrometry (WDS), or a comparable technique for chemical analysis.

The gemologist's way: use the refractive index or the thermal and/or electrical conductivity.

The difference, of course, is that the gemologist must often identify the gemstone in the field (in the home, in the mine, or really in the field) without taking the sample to the laboratory. With experience, you can, for example "feel" if a stone is a good thermal conductor.

Some questions you might be asked:

- Is this stone really diamond not cubic zirconia (CZ), white sapphire, or even moissonite?
- Why is the Black Prince's ruby so dark? (It's in the English Crown Jewels, and it's not a ruby.)
- Is this stone peridot or green glass? (If you can't tell, need you care?)
- Is this natural turquoise? (Probably, but the better question is: has it been treated?)
- Are there defects in my emerald? (Yes.)
- Is natural emerald better than synthetic emerald? (Synthetic is usually more perfect.)
- Should I wash my opal with water or with alcohol? (No.)

The questions emphasize the need for techniques to aid the eye in examining these materials or the need to understand the structure and chemistry of gemstones when handling them.

36.3 IN THE ROUGH

The traditional mining of gemstones is illustrated in Figure 36.1. Because many mines are in less developed countries and very small stones can be very valuable, the mining tends to rely on manual labor. Open mines such as the one shown here are inexpensive to establish and in many cases have not changed in centuries. Miners then and now often have to endure brutal conditions. The following quotation, which is believed to be dated about 1830 BCE describes the conditions suffered by Egyptian turquoise miners in the Sinai.

> [The Pharaoh] dispatched the Seal-Bearer of the God, the Overseer of the Cabinet, and Director of *Lances*, Hor-ur-Re, to this mining area. This land was reached in the 3rd month of the second season [June, an almost unbearably hot season in Sinai], although

> it was not at all the season for coming to the mining area. The Seal-Bearer of the God says to the officials who may come to this mining area at this season:
>
> Let not your faces flag because of it. Behold ye, Hat-Hor [Egyptian goddess of the Sinai mines] turns it to good. I have seen (it so) with regard to myself. I came from Egypt with my face flagging. It was difficult, in my experience, to find the (proper) skin for it, when the land was burning hot, the highland was in summer, and the mountains branded an (already) blistered skin. When the day broke for my leading to the camp, I kept on addressing the craftsmen about it: "How fortunate is he who is in this mining area!" But they said: "Turquoise is always in the mountain, but it is the (proper) skin which has to be sought at this season. We used to hear the like, that ore is forthcoming at this season, but, really, it is the skin that is lacking for it in this difficult season of summer!"

Examples of gemstones *in the rough* are shown in Figure 36.2; many of these natural stoned show have shapes that are determined by their crystallography. Sources of sapphire, ruby, emerald, and diamond are given in Table 36.2. Sapphire tends to grow with a hexagonal shape, as seen in these images; the best-quality natural sapphire is shaped like a double hexagonal pyramid. Many of the harder gemstones (especially diamonds, sapphires, and garnets), are found in rivers, where they have been deposited after removal from their native (natural) softer matrix.

Some specimens of natural gemstones are much larger than you might think. Just to remind you: amethyst *cathedrals* and *wheels* are the results of natural hydrothermal growth. The cathedrals can be >2 m tall.

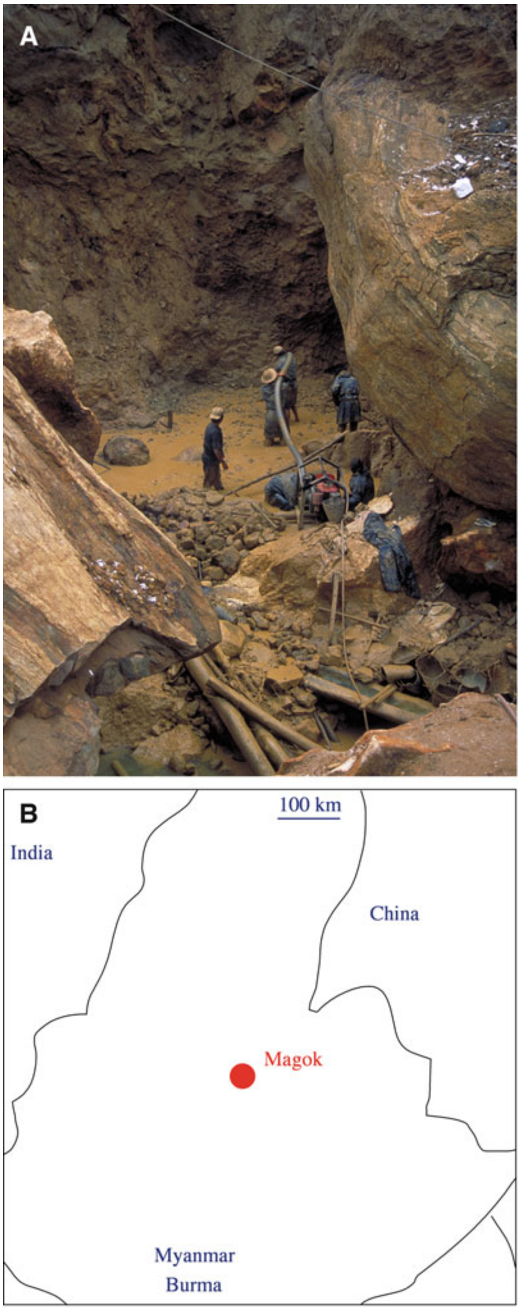

FIGURE 36.1. Open cast mining in the Magok region of Myanmar (Burma).

TABLE 36.2 Gemstone Locations

Ruby	Myanmar (formerly Burma)
Sapphire	India
Emerald	Colombia
	Madagascar
Diamonds	Russia
	South Africa (the Kimberley pipe)
Tanzanite	Tanzania
Amethyst	Brazil (Minas Gerais)

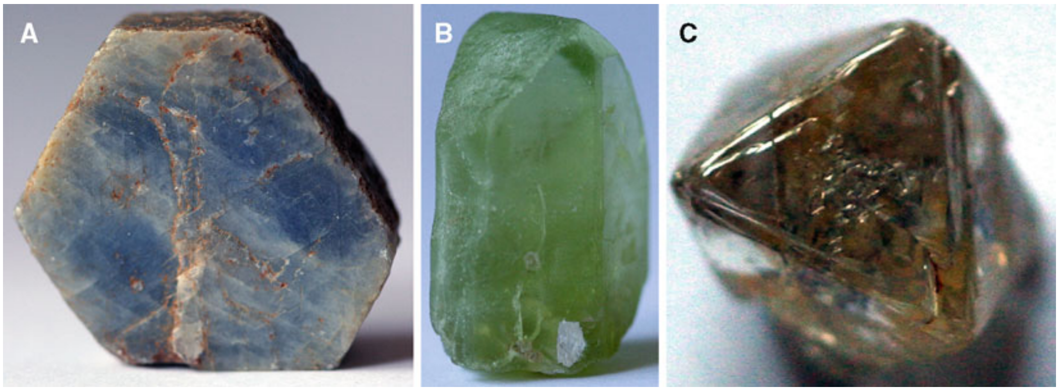

FIGURE 36.2. As-collected samples of rough: (A) Sapphire. (B) Peridot. (C) Diamond.

36.4 CUTTING AND POLISHING

Idar-Oberstein started polishing agates in the 1800s and is now a center for polishing gemstones. Antwerp and Amsterdam have been the centers for diamond cutting for many years, although much of this trade is now carried out in Asia. The basic processes are the saw and the polishing wheel. The saw is tipped with SiC, alumina, or diamond for precision work. Originally, the polishing pads used jeweler's rouge, but they now uses various compounds including Syton™, alumina, zirconia, and ceria. For most polishing, the process used actually has both a chemical and mechanical component and is thus known as chemical/mechanical polishing (CMP). The professional polisher uses a dop stick and wheel. In the diamond trade, this has been partly automated using a tripod device (not unlike the tripod used for polishing transmission electron microscopy, or TEM, samples) to replace, or to help steady the hand of, the polisher; these are illustrated in Figure 36.3.

There are numerous books describing the shapes produced by polishers of gemstones. Figure 36.4 shows the main parts of a faceted stone to illustrate the terminology. For faceted stones, the upper part is called the crown and consists of the table and the bezel. The girdle separates the crown from the pavilion, which is also called the base or the back. If a face is polished on the pavilion parallel to the table, it's called the culet. If you can see straight through the stone from the table through the culet, then the stone has a window. The shape of a brilliant-cut diamond is designed so that the light is all reflected back to the source placed directly in front of it—the pavilion facets act as mirrors. The term *en cabochon* refers to the shape (a cabochon—e.g., a skull) shown in the lower part of Figure 36.4, which is essentially a nonfaceted stone.

The {111} plane of diamond is the hardest plane to polish, which is why diamonds were initially left with {111} surfaces

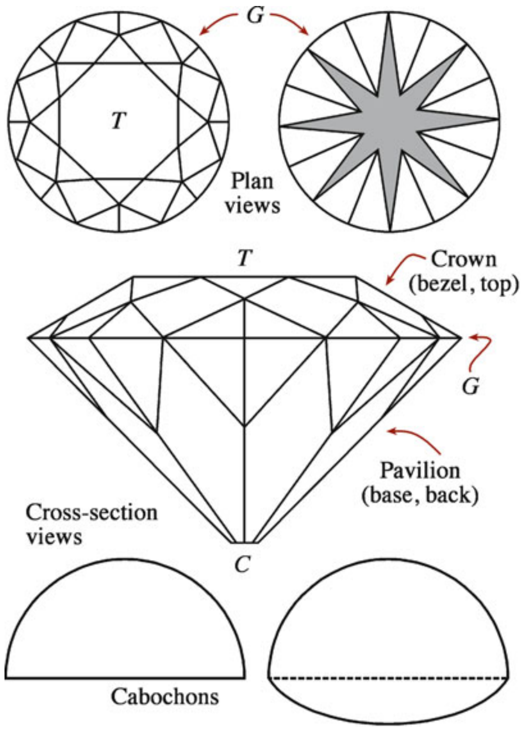

FIGURE 36.4. Different regions of polished (cut, faceted) stones and two cross sections of cabochons. T table, C culet, G girdle.

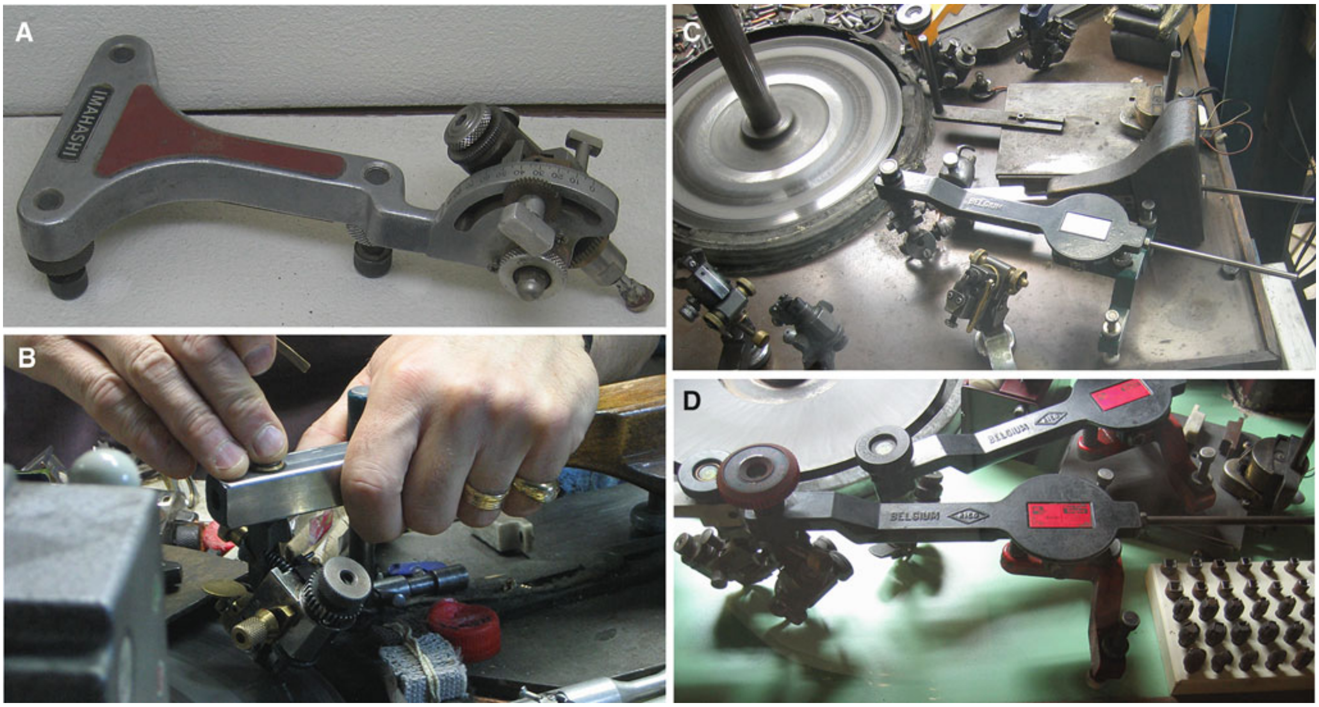

FIGURE 36.3. Equipment used for polishing gemstones.

and just the tip was polished off. Small, naturally occurring octahedral crystals of diamond are quite common.

Carving minerals and gemstones is an old art. An example of a rock crystal goblet is shown in Figure 36.5. Old jade statues, fluorite bowls, and alabaster figures are museum pieces, but new ones are still being produced. The challenge in carving the harder minerals and gemstones is simply that they are hard and you reduce the weight of the stone as you carve it.

36.5 LIGHT AND OPTICS IN GEMOLOGY

The gemologist judges diamonds by the four C's: color, clarity, cut, and carat (weight). Here, cut may actually mean cleave followed by polish. You would rather avoid cutting a stone because that wastes material. Remember, 1 carat is 0.2 g (about the weight of a carat—a small seed used in ancient Egypt as a unit of weight). As diamonds can be expensive, you may also encounter points (100 points in 1 ct).

FIGURE 36.5. Examples of natural mineral specimens that have been shaped: (A) Buddha in garnet; 45 mm tall. (B) Rock-crystal bowl (~150 mm diameter).

The important optical properties that contribute to the attractiveness associated with precious gems are:

Color. Color is one of the main features we consider when choosing a gemstone. There are many different reasons for these colors (e.g., Cr makes emerald green and rubies red).

Refractive index. The higher the value of the refractive index (n or RI) of a properly cut gem, within limits, the more light returns to the eye of the viewer, resulting in brilliance, sometimes also termed life or liveliness. Diamond has a particularly high value of $n = 2.417$.

Dispersion. The dispersion is usually given as the difference in n for the b and g Fraunhofer solar spectrum lines. The Fraunhofer lines serve as reference markers across the spectrum. The b line is in the green part of the spectrum, and the g line is in the violet. The dispersion is 0.044 for diamond, one of the highest values for a natural gemstone. Dispersion causes rays of light to be split into their colored components, which then emerge in slightly different directions to produce what the trade calls *fire*.

We discuss the causes of color in gemstones separately, but the point to remember here is that color is determined by the wavelength of the light, λ, and the n of a crystal depends on λ (dispersion). Table 36.3 gives examples of

TABLE 36.3 Refractive Index of Gemstones and Related Crystals

Al_2O_3, α -alumina	1.761, 1.769	KCl (sylvite)	1.49
AlSb	3.2, 3.2	$MgAl_2O_4$	1.723
CaF_2 (fluorite)	1.434	MgF_2, (sellaite)	1.378, 1.39, 1.378
CaS (oldhamite)	2.137	MgO (periclase)	1.735
CdS, cubic	2.506, 2.529	Mn_3O_4 (hausmannite)	2.15, 2.46
CdS, Hexag. (greenockide)	2.32	Mullite, $3Al_2O_3$–$2SiO_2$	1.64
CdTe, cubic	2.5	PbO (litharge)	2.535, 2.665
Cordierite	1.54	PbS (galena)	3.91
Diamond, natural	2.419	Sb_2O_3 (senarmontite)	2.087
Fe_2O_3 (hematite)	2.91, 3.19	Sb_2O_3 (valentinite)	2.18, 2.35, 2.35
Fe_2O_3 (maghemite)	2.63	SiC (moissanite)	2.648, 2.691
Fe_3O_4 (magnetite)	2.42	SiC, (wurtzite structure)	2.654
GaAs	3.309	Silica aerogel 1 -	1.05
GaP	3.2	SiO_2 (alpha quartz)	1.544, 1.553
GaSb	3.8	SiO_2 (cristobalite)	1.484, 1.487
Ge mullite, $3Al_2O_3$–$2GeO_2$	1.664	SiO_2 (tridymite)	1.475, 1.476, 1.479
Glass (fused quartz)	1.46	SnO_2 (cassiterite)	2.006, 2.097
Glass 96% silica	1.458	ThO_2 (thorianite)	2.2

(continued)

TABLE 36.3 (continued)

Glass borosilicate	1.474	TiO_2, anatase	2.488, 2.561
Glass Corning Pyrex® 7740	1.474	TiO_2, brookite	2.583, 2.584, 2.7
Glass Corning Vycor® 7907	1.458	TiO_2, rutile	2.9, 2.609
Glass GE 214 fused-quartz	1.4585	ZnO, (zincite)	2.013, 2.029
HgO (montroydite)	2.37, 2.5, 2.65	ZnS, sphalerite	2.356
Ice	1.31	ZnS, wurtzite	2.356, 2.378
InAs	3.5	ZnSe	2.89
InP	3.1	ZnTe, cubic	3.56
InSb	3.96	ZrO_2 (baddeleyite)	2.13, 2.19, 2.2

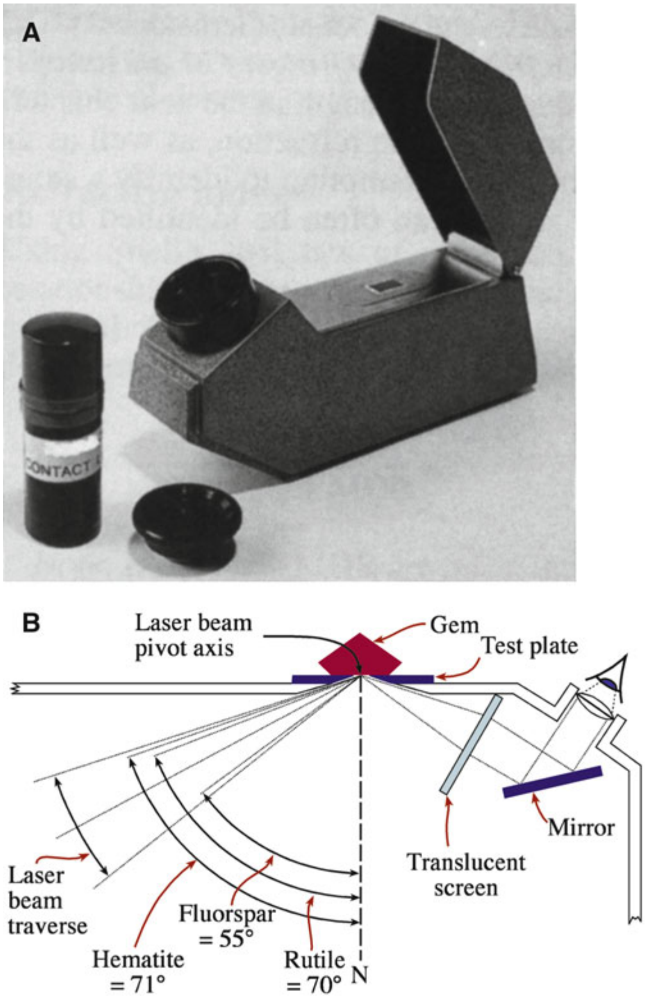

FIGURE 36.6. (A) Portable jeweler's refractometer for measuring the critical angle. (B) Optics of determining the critical angle using the refractometer.

FIGURE 36.7. Goniometer-style refractometer.

the *n* values of minerals and related materials, which are determined by measuring the critical angle on a hand-held refractometer (Figure 36.6) or a bench-top goniometer-style refractometer (Figure 36.7). Not all materials are transparent to visible light when they are too thick (i.e., we think of them as being opaque). Sphalerite, for example, is a grey crystal, but it is an orange gemstone with an *n* of 2.36.

Absorption. The other factor that is particular to different materials is the optical absorption. The absorption spectrum can easily distinguish different gems. Although laboratory instruments are best, gemologists can use a hand-held spectrometer. Hematite is gray unless the light passes through it, in which case it appears red (hence its name). A streak of hematite appears red for the same reason; hematite with powder on the surface appears red. The reason for the red color is that hematite absorbs blue light. Two types of absorption spectrometer are used: one based on prisms and the other using a diffraction grating (both are shown in Figure 36.8). The wavelengths that are absorbed are well defined and are characteristic of both the doping (if it colors the stone) and the matrix itself, as illustrated in Figure 36.9, where you can see stones with the same color clearly differentiated.

Facets. The faceted gemstone is ideally shaped to optimize its sparkle, which is simply saying we want to maximize the amount of light that is reflected back to the observer, as shown in Figure 36.10. The objective of faceting, then, is to make the most of internal reflection. Note that the facets that you see on most gemstones are not crystallographic planes; the gemologist essentially never uses XRD to orient the sample!

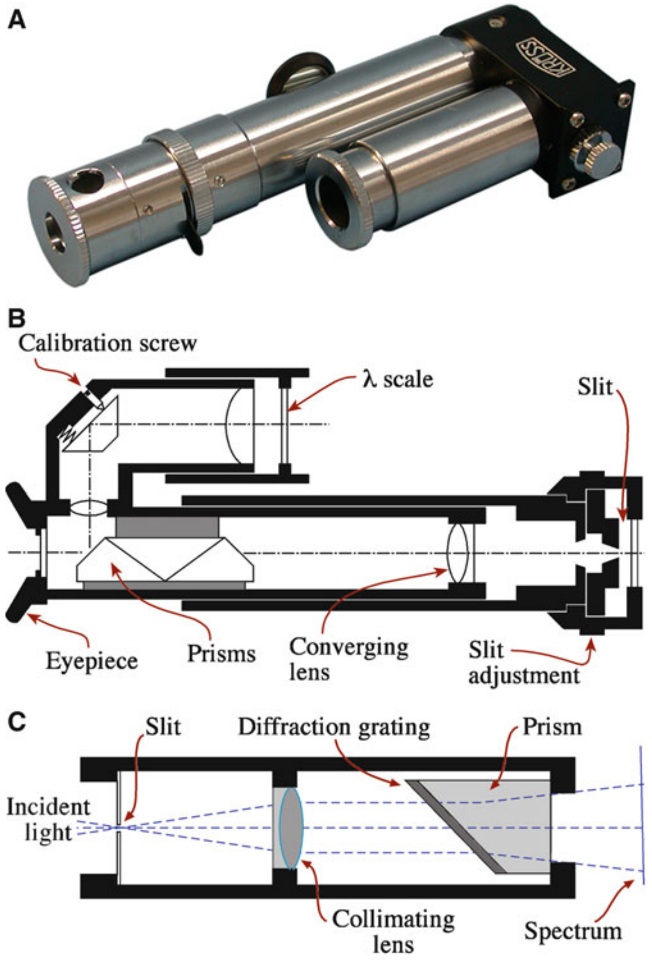

FIGURE 36.8. (A) Photograph of a spectrometer. (B) The prism spectrometer. (C) The absorption spectrometer.

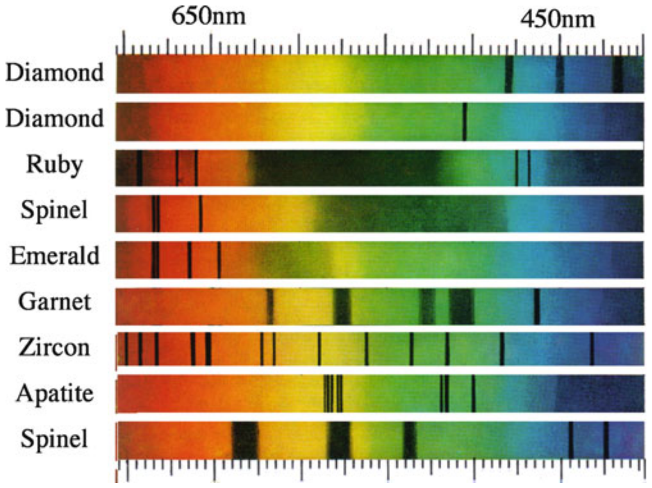

FIGURE 36.9. Spectra from different minerals.

Immersion. A simple method for estimating the refractive index is to use liquid immersion. The stone is immersed in a series of liquids of known refractive index (values of the n values for different liquids are given in Table 36.4). The idea is that the gemstone "disappears" when placed in a liquid that has the same n (Figure 36.11). The principle is that there is no longer a change in refractive index at the surface of the stone, so that even if it is faceted it does not reflect light internally. Of course, the technique is not good if the solvent can penetrate the stone or dissolve any filler.

Reflection. A more accurate method for determining the n of a gemstone is to measure the critical angle (the Brewster angle, θ_B) for reflection using a reflectometer. The principle is that the refractive index of a material is given by

$$n = (\sin \theta_I)/(\sin \theta_E) \tag{36.1}$$

Here the angle is defined as the angle to the normal (θ_I = incident angle; θ_E = exit angle). In the reflectometer, we place the gemstone in contact with a prism, the n of which is chosen to be large. We then adjust the incident angle until it is θ_B and deduce the n of the stone from equation 36.2.

$$n_{\text{gemstone}} = n_{\text{prism}} \times \sin \theta_B \tag{36.2}$$

Figure 36.6B illustrates the optics of the reflectometer.

Pleochroism. When the n of a crystal varies with the direction in which light travels through it, the absorption can be different in different directions. The crystal then shows a different color when viewed in different directions, which gives another method for identifying the crystal. If there are two distinct directions, the crystal is said to be dichroic (tetragonal, trigonal, and hexagonal crystals). Iolite (cordierite, $Mg_2Al_4Si_5O_{18}$) and tanzanite [the purple form of zoisite, $Ca_2Al_3(SiO_4)_3(OH)$] are two of the best-known examples. Crystals can show three colors: orthorhombic, monoclinic, and triclinic crystals are trichroic. Pleochroic means either dichroic or trichroic. The dichroscope (Figure 36.12) is a simple handheld device that is used to estimate the dichroism of a gemstone. It uses a crystal of calcite to separate the polarized rays and then compares them side-by-side to see how the color differs. Calcite has strong double refraction. You have to rotate the stone because dichroism is not present when viewed along the optic axis. In the laboratory, you might use the polarizing visible light microscopy (VLM) instead of the handheld device.

36.6 COLOR IN GEMS AND MINERALS

We treat color separately for the different minerals and just add a few notes here. The importance of dopants is clear from Table 36.5. There are several different causes of color in gemstones. Most are associated with local trapped charges.

- Metal ions can give up an electron, which may remain trapped locally. Tsavorite is green because of the V^{3+}, but the same ion causes tanzanite to be purple.

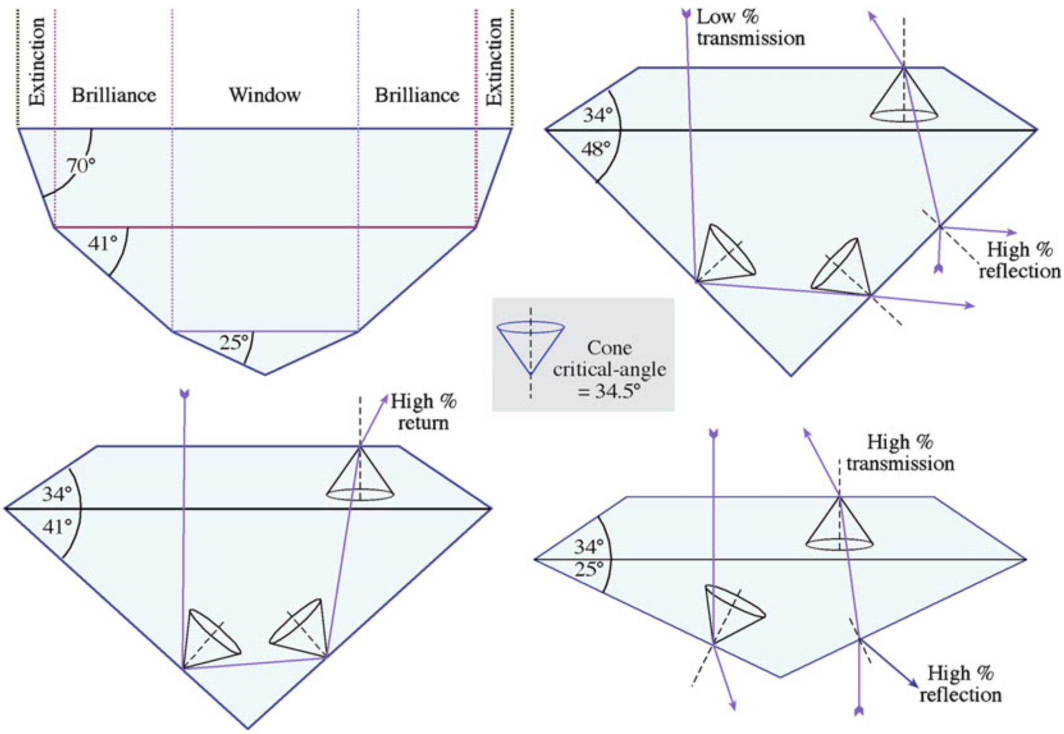

FIGURE 36.10. Origin of the sparkle in gemstones: total internal reflection.

TABLE 36.4 Refractive Index of Liquids

Liquid	*n*
Water	1.33
Ethyl alcohol	1.36
Acetone	1.36
Amyl alcohol	1.41
Glycerine	1.46
Olive oil	1.48
Toluene	1.49
Xylene	1.49
Benzol	1.50
Clove oil	1.53
Ethyl dibromide	1.54
Monobromobenzene	1.56
Bromoform	1.60
Monoiodobenzene	1.62
α-Monobromaphthalene	1.66
Methylene iodide	1.74

- When we have two metal ions in different oxidation states, we can have intervalence charge transfer. The interplay between Fe^{2+} and Ti^{4+} causes the blue in blue sapphire and blue kyanite, but it also makes dravite brown. Mn^{2+} and Ti^{4+} combine to cause elbaite to be yellow.
- Instead of using a reactor or other source of radiation, natural ionizing radiation can excite electrons in a crystal. Fluorite can be red, green, or purple due to natural irradiation. The same irradiation can cause topaz to be brown (see below).
- The arrangement of defects (as in labradorite feldspar) or of grains (as in opal) can cause diffraction of the light.

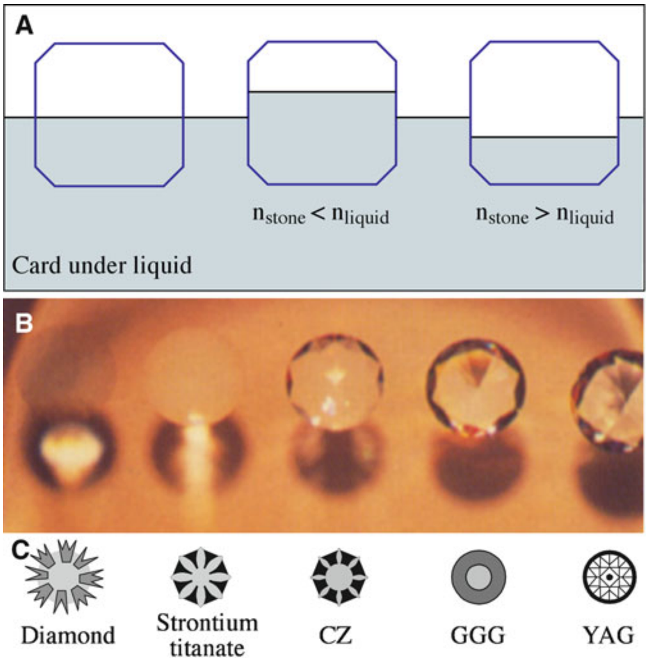

FIGURE 36.11. Determining the shadow patterns when stones are immersed in methyl iodide or liquid of another *n*. Different liquids are given in Table 36.4.

- The mineral may be a semiconductor, as in the case of sphalerite.

Blue. The common blue stones are sapphire, lapis, and irradiated topaz. Less common gemstones include blue

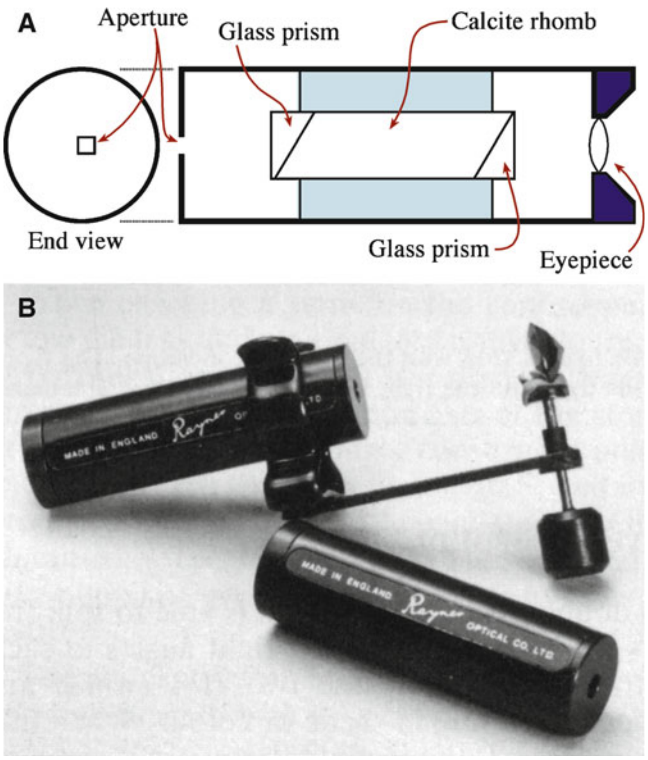

FIGURE 36.12. Dichroscope for estimating the dichrosism of a stone and the optics on which it is based.

TABLE 36.5 Transition Element Dopants and Color

Titanium	Blue sapphire (with iron), blue zoisite (tanzanite)
Vanadium	Grossular garnet (tsavorite), green vanadium beryl, synthetic corundum (alexandrite simulant), some synthetic emeralds, blue/violet sapphire
Chromium	Ruby, emerald[a], red spinel, pyrope garnet, chrome grossular garnet, demantoid garnet, uvarovite garnet[b], chrome diopside, green jadeite, pink topaz, alexandrite, hiddenite
Manganese	Rhodochrosite[b], rhodonite[b], spessartite garnet[b], rose quartz, morganite variety of beryl, andalusite
Iron	Sapphire, sinhalite[b], peridot[b], aquamarine, blue and green tourmaline, enstatite, amethyst, almandine garnet[b]
Cobalt	Synthetic blue and green spinel, synthetic blue quartz (except for a rare blue spinel, cobalt is not found in any natural transparent gemstone); cobalt glass
Nickel	Chrysoprase, synthetic green and yellow sapphires
Copper	Diopside, malachite[b], turquoise[b], synthetic green sapphire

[a] In UK and Europe only beryl colored by chromium may be described as emerald.
[b] Idiochromatic gemstones.

diamond, although such stones could be common if irradiated more often.

Green. The green stones include emerald, malachite, and both uvarovite and tsavorite garnets.

Red. The red stones include ruby and both pyrope and almandite garnet (almandine).

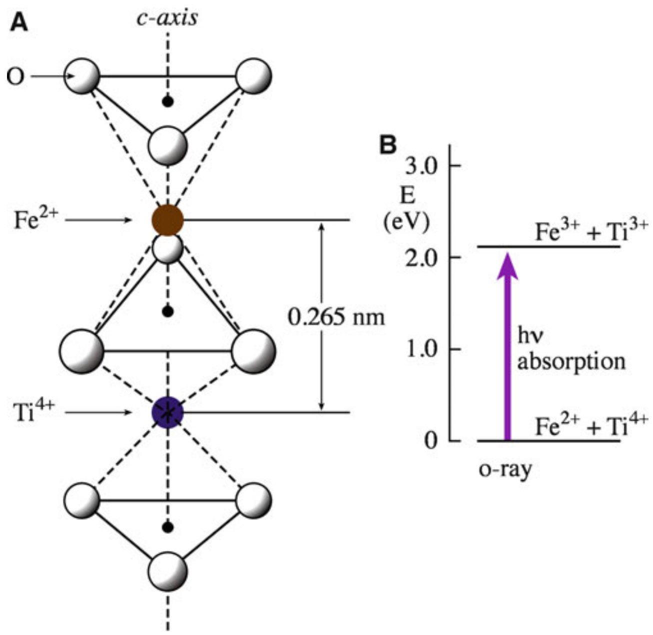

FIGURE 36.13. (A) Combined effect of incorporation of Ti and Fe in sapphire. The distance between the dopant cations is 0.265 nm. (B) Corresponding energy band diagram for the excitation shows how a gemstone with blue coloration is obtained by absorption.

Yellow. Yellow stones are less common but include citrine, yellow sapphire, and yellow diamond.

The color of *ruby red* and *emerald green* is the result of a transition metal in a ligand field (see Section 32.5). In both cases, the coloring ion is Cr^{3+} substituting for an Al^{3+} ion. Ruby is red corundum (Al_2O_3) containing about 1% Cr_2O_3. The Cr^{3+} ion, which is only a little larger than Al^{3+}, is easily accommodated into the corundum structure. The five 3d orbitals in the Cr^{3+} ion split in the distorted octahedral ligand field. This is a slightly more complicated case than for the simple octahedral ligand field we described in Section 32.5 and involves further splitting of the 3d levels, as shown in Figure 32.9. Nevertheless, absorption of selected values of λ in the visible spectrum is due to electron transitions. Absorption is strongest in the green and violet and least in the red and blue; this gives ruby its red color with a slight purple overtone. In emerald, the color is again due to the Cr^{3+} ion replacing Al^{3+} in a distorted octahedral arrangement very similar to that in corundum. Emerald without the chromium impurity is beryl, which has the chemical formula $3BeO.Al_2O_3.6SiO_2$ or $Be_3Al_2Si_6O_{18}$. Because of the presence of the other constituents (it's a ring silicate), the overall bonding is a little weaker and the ligand field is less strong. As a result, the splitting of the energy levels is different, with strong absorption occurring in the yellow-red and violet regions and strong transmission in the blue-green.

For *sapphire blue*, the color results from a charge transfer mechanism. Sapphire shares the corundum structure with ruby, but the impurities are now small amounts of both iron and titanium oxides. Both Fe^{2+} and Ti^{4+} take the place of Al^{3+} in the corundum structure. If they are present on adjacent sites, as shown in Figure 36.13, an interaction between them becomes possible. In this configuration, there is enough overlap of the $d_z{}^2$ orbitals of the two ions that it is possible for an electron to transfer from the Fe^{2+} ion to the Ti^{4+} ion as follows.

$$Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+} \qquad (36.3)$$

The energy of the combination on the right side of equation 36.3 is 2.11 eV higher than that on the left side, as shown in Figure 36.13. If light of this energy falls on blue sapphire, it is absorbed while producing the charge transfer shown in equation 36.3. You can produce the blue color by doping with Ni or Co, but the mechanism is different.

36.7 OPTICAL EFFECTS

Chatoyancy. The scattering of light by aligned fibers or channels within a matrix gives the optical effect seen in the minerals cat's eye and tiger-eye; the effect is termed chatoyancy. The crystals are cut *en cabochon*, with the long axis parallel to the fibers because you don't need the internal reflection from the surfaces. Tiger-eye (or tiger's eye) is quartz that contains oriented fibers of crocidolite. The mineral started as crocidolite (a form of asbestos) and was partly replaced by silica, which then becomes the matrix to the crocidolite fibers. This effect is shown together with others caused by interference in Figure 36.14.

Precious, or oriental, cat's eye is the rarest and most highly prized form of chrysoberyl; it is a green mineral called cymophane. The chatoyant effect is due to parallel arrays of pores.

Asterism. This term refers to the star effect that can occur in sapphires, rubies, and garnets. The effect is illustrated for sapphire, where it is often the strongest (Figure 36.15). In this case, aligned precipitates in the single crystal cause the optical effect. Because sapphire has a threefold axis, the precipitates reproduce this symmetry by aligning along particular directions giving the sixfold star. In black sapphire, the needles are hematite; in essentially all other sapphires, they are rutile. Some star sapphires from Thailand contain both hematite and rutile (sometimes called silk because they are so fine) and show 12-fold stars. In star garnets and diposide, the star shows fourfold symmetry. In garnet, the crystals lie at 90° along [001] directions; in diopside, they lie at 73° to one another.

Iridescence. The best known form of iridescence is opalescence. The reason opals show different colors when viewed in different directions is that the silica spheres are just the right dimensions to diffract light, as illustrated in Figure 36.16.

Labradorescence and adularescence (shiller). These are two forms of iridescence caused by planar interference in a transparent mineral. Labradorite is a plagioclase feldspar named after the Labrador Peninsula in Canada; spectrolite is a special feldspar found in Finland. Labradorescence results from the presence of lamellar intergrowths inside the crystal; two phases of slightly different composition separate out as the mineral cools. The interference occurs when light is reflected from the different interfaces. The color we see (illustrated in Figure 36.17) depends on the effective thickness of the layers and thus on the viewing angle. Moonstone is transparent feldspar that shows this effect. The planar defects in these feldspars are actually lamellar twin boundaries arising from chemical twinning.

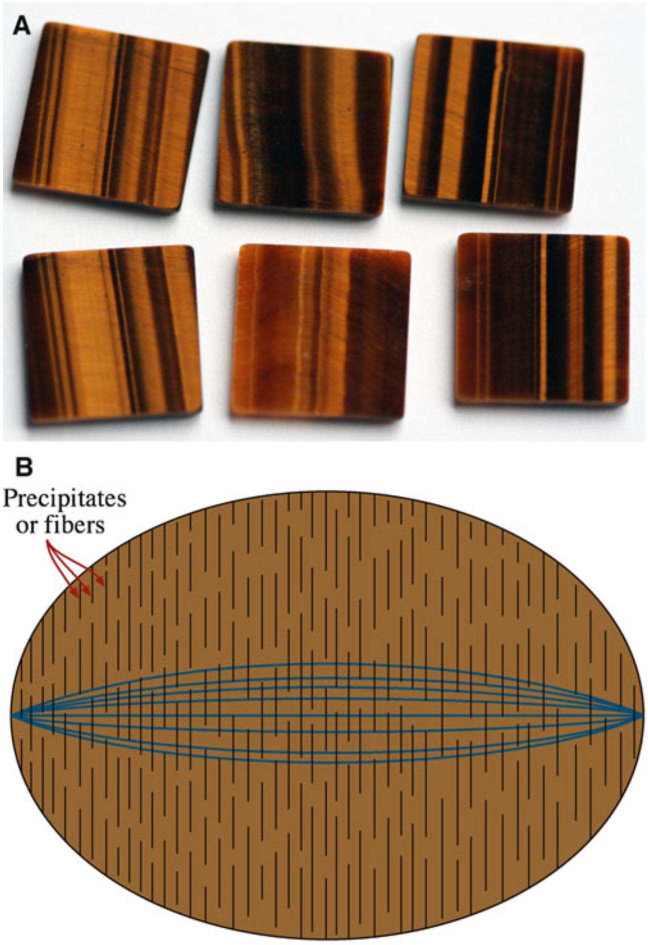

FIGURE 36.14. Chatoyancy: scattering of light by aligned fibers or precipitates.

36.8 IDENTIFYING MINERALS AND GEMS

Because many gemstones appear quite similar, which is why they can be simulated, it is important to be able to distinguish the real from the synthetic or from the simulant. If you have scanning electron microscopy (SEM) available, the latter task is not a problem; but usually this is not the case in the field (or the shop). The basic tests are for thermal conductivity, optical properties, and mechanical

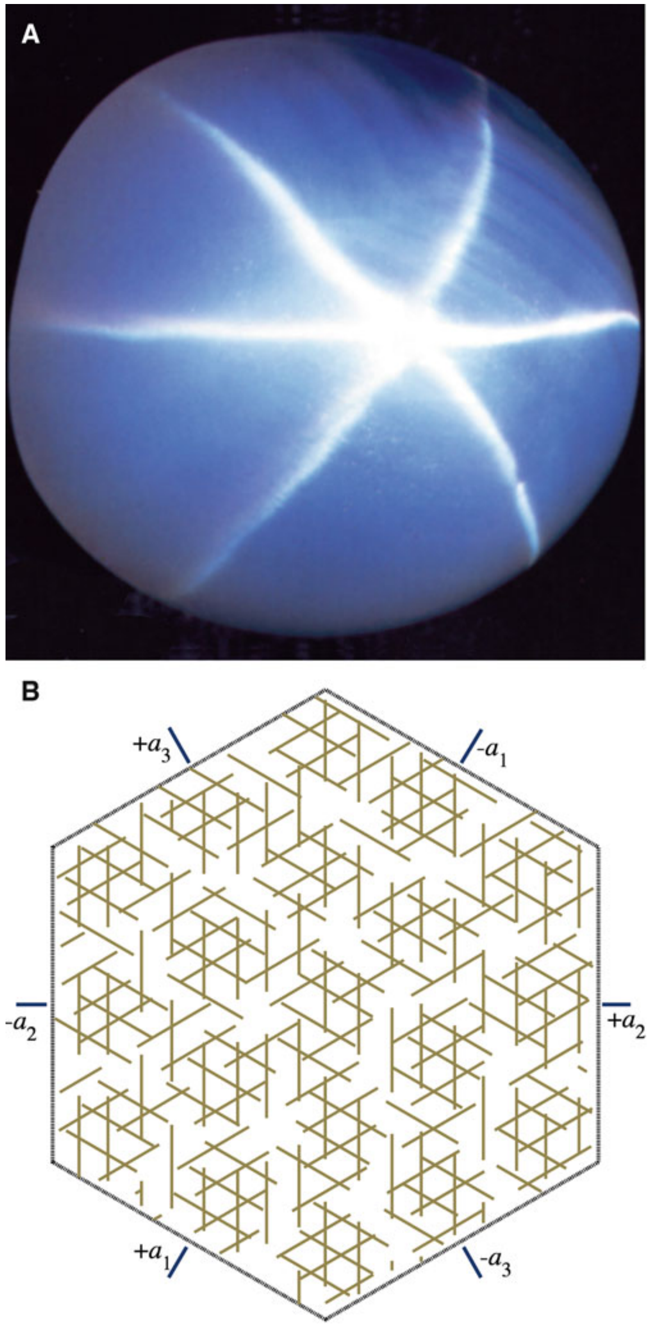

FIGURE 36.15. Asterism: effect of precipitates oriented along several different directions, giving rise to the star in star sapphire.

properties. Using a mechanical test to characterize a material that you don't want to damage is clearly tricky, so the use of hardness measurements is directed more toward minerals than gemstones.

36.8.1 Hardness (Toughness)

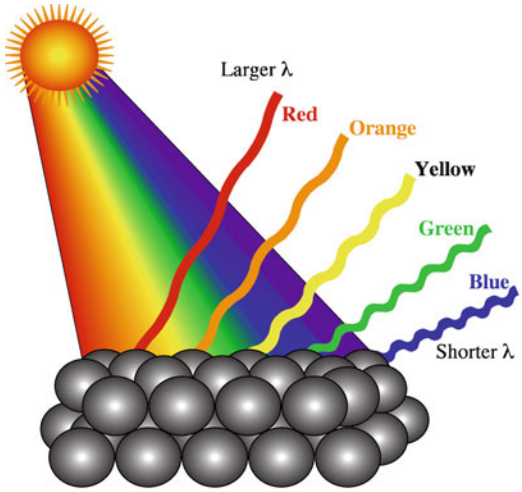

FIGURE 36.16. Origin of opalescence: Bragg scattering of light from a surface of ordered spheres. Best known in opals.

FIGURE 36.17. Laboradite causes an iridescence due to scattering by twin planes in the feldspar crystal.

Indentation has been discussed in Section 16.3. Although these tests could be used for gemstones, they are not, except as a calibration. The Mohs scratch hardness scale is much more popular because the principle is to test what the stone does scratch, not what scratches the stone.

The Mohs hardness test (the word scratch is assumed) is almost a nondestructive test. The hardness of a gemstone is usually referred to as its Mohs hardness. As this *hardness* value is determined by a scratch test, it is not actually a *hardness*. The scale has many drawbacks, including the fact that it is not linear, it does not necessarily relate to wear resistance, and it damages the specimen—so it's not ideal for polished stones.

Table 36.6 gives Mohs hardness values for the *Gem Scale* and for some other materials as a comparison. (Note that in Chapter 16 we consider the extended version as defined by Ridgeway but it is not nearly so widely used in the gem industry). The table also includes a "relative" hardness scale. Remember that minerals are anisotropic, so the Mohs hardness of kyanite is ~4.5 when scratched parallel to the long axis and ~6.5 when scratched perpendicular to the long axis. Incidentally, this material is not

TABLE 36.6 Classical Mohs Hardness Scale for Gems

Mohs #	*Abs #*	*Classic mineral*	*Other materials*
1	1	Talc	Pencil lead (graphite)
2	3	Gypsum	Your fingernail (2.2)
3	9	Calcite	Chalk (3), gold (2.5–3.0), dolomite (3.5–4.0), ZnS (3)
4	21	Fluorite	Copper penny (3.2)
5	48	Apatite	Knife blade (5.0), window glass (5.5), strontium titanate (5.5), sodalite (5.5–6.0), hematite (5.5–6.5)
6	72	Orthoclase	Steel file, other feldspars, pumice (6), pyrite (6.5), magnetite (6), porcelin (6–7), Anatase (5.5–6.0)
7	100	Quartz	Streak Plate (7.0), zircon (6.5–7.5), olivine (6.5), garnet (6.5–7.5), rutile (6.5)
8	200	Topaz	Spinel (8), YAG (8), ZrO_2 (8), chrysoberyl (8.5)
9	400	Sapphire	WC (9)
10	1,600	Diamond	Scratches everything! B_4C_3 (9–10), SiC (9–10)

TABLE 36.7 Thermal Conductivity

Mineral	*Thermal conductivity* $(Wm^{-1}{}^{\circ}C^{-1})$
Diamond	1,000–2,600
Synthetic moissanite	200–500
Silver	430
Copper	390
Gold	320
Platinum	70
Corundum	40[a]
Zircon (high)	30[a]
YAG	15
GGG	8
Rutile	8[a]
Quartz	8[a]
CZ	5
Glass	1

[a] Mean value between *c* axis and *z* axis directions

confused with kaolinite using this test because the latter has a Mohs hardness of 2.0–2.5.

An additional problem in using mechanical tests for minerals is that many tend to cleave. Wear (or abrasion) might be a better test, but it's more difficult for the gemologist.

36.8.2 Thermal Conductivity

The thermal conductivity of gemstones provides a useful way of identifying a mineral in the field. Table 36.7 lists values used for gemstones. The common assumption is that gemstones are poor conductors of heat. Diamond is actual a much better thermal conductor than Cu. The measurement of thermal conduction of gemstones is particularly attractive as a test because it can be applied to stones that are already mounted (e.g., in a ring). The instrument supplies the heat, and the sink is either the ring or another part of the device. The device shown in Figure 36.18 measures the change in temperature of its tip when the tip is placed in contact with the gemstone. When testing the poorer thermal conductors, the temperature of the tip is allowed to fall until it reaches a first set value, when the subsequent decrease to the next set value is timed—much like taking a blood pressure reading.

FIGURE 36.18. Pocket-size instrument for measuring thermal conductivity.

36.9 CHEMICAL STABILITY (DURABILITY)

Gemstones are usually thought of as being chemically stable. Some are; some are certainly not. Opal contains a significant amount of water; if this water is removed, the opal fractures and degrades. Emeralds are slightly different in that they usually already contain many fractures that have been filled with oil or polymer. If this filler is removed—for example, by cleaning with a solvent—the fracture may extend. Even though the diamond in an engagement ring is durable, the 18 k gold setting holding it in place may not be, especially if it is exposed to chlorine-containing liquids, such as in a swimming pool or hot tub.

36.10 DIAMONDS, SAPPHIRES, RUBIES, AND EMERALDS

Why diamond? Yes, it's hard, but it is its optical qualities (and great advertising) that have made it so popular. The refractive index of diamond is 2.42, whereas rutile (once proposed as a diamond simulant) and moissanite (now being used as such) have refractive indices of 2.6/2.9 and 2.65/2/69, respectively, so they do not have the best optical properties (for internal reflection).

Diamonds can now be synthesized to weigh more than 0.6 g (3 ct). This is an art in regard to the color and clarity. The production of gem-quality synthetic diamonds (see Section 29.14) gives a deep yellow color. Colored diamonds tend to be more valuable than colorless ones simply because they are more rare. The Dresden green diamond weighs 40.70 ct and is the largest known green diamond in the world. Natural red, pink, and yellow diamonds can also command prices of near $1 million per carat. The danger is that diamonds can also be artificially colored by irradiating them; diamond was perhaps the first irradiated gem. Blue B-doped diamond is a semiconductor, whereas blue irradiated diamond is still an insulator. A concentration of 10^{-6} B in diamond gives it a deep blue color as seen in the Hope diamond. A B-doped diamond fluoresces under ultraviolet (UV) light and continues to glow for minutes afterward.

Diamonds are actually mined in large quantities in South Africa and Russia, with newer sources in Sierra Leone and northeast of Yellowknife in Canada's Northwest Territories. Natural diamonds are created 150 km beneath the earth's surface and are transported to the surface by volcanic activity. The Kimberley Pipe is the remains of such volcanic activity. A pipe is a carrot-shaped volcanic neck; there is a cluster of 11 pipes at Kimberley—they are about 1.2 billion years old. The largest kimberlite pipe is now the Premier Mine at Cullinan, which produces 1.6 million ct annually. The original location of kimberlite is now known as Kimberley's "Big Hole."

Nitrogen causes both synthetic and natural (e.g., the Tiffany Yellow) diamonds to be yellow. A Florida company has up to 200 diamond-making growth chambers, each weighing about 4,000 lbs (cost ~$50,000 each). Each chamber can produce eight 3-ct rough stones per month. A little history: a team of five Russian scientists in Novosibirsk, Siberia, managed to create gem-quality diamonds at the relatively low pressure of 60,000 atm. in 1989, which avoids the high pressure of the so-called GE process used to make industrial diamond. Carter Clarke, an American entrepreneur, paid $57,000 in 1996 for a "diamond-growth chamber" during a business trip to Russia; the chamber was the size of a washing machine. He then founded Gemesis.

DIAVIK DIAMOND MINE

Production began in 2003 in Lac de Gras 300 km north east of Yellowknife; it may be the richest diamond lode in the world. It has estimated reserves of 30 million tons and yields over 3 ct per ton of ore (more than three times the world average). In 2009, 5.6 million ct were extracted valued at over US$ 1.3 billion.

For some time, mixtures of H_2 and natural gas have been used for chemical vapor deposition (CVD) growth of diamond-like carbon (DLC) films. It is now possible to use this technique to grow diamond seed crystals to produce clear, perfect, colorless diamonds. Diamonds grown by the high-pressure methods are invariably doped and thus colored. One company, Apollo, has used the technique to grow 1-ct diamonds.

Examples of famous diamonds are listed in Table 36.8. One feature that is obvious when you think about it: these gemstones were all cut from much larger rough stones. When first extracted from the Premier Mine near Pretoria, the *Cullinan* diamond weighed 0.621 kg. It was later cut into 9 major gemstones (the largest 2 being in the list and shown in Figure 36.19) and 96 other stones. The *Hope* diamond, thought to be from the Kollur Mine in Golconda, India, was first cut into a triangular $112\frac{3}{16}$-carat stone. In 1673, it was recut to give a $67\frac{1}{8}$-carat stone and then presumably cut again to give the current 45.52 ct. We say "presumably" because the diamond disappeared for 20 years following looting after the French Revolution in 1792 (the current Hope could indeed fit inside the old Hope). The *Presidente Vargas* was found in the Rio Santo Antonio in Minas Gerais and weighed 726.6 metric carats (56.2 × 51.0 × 24.4 mm) but was cut into 29 separate stones.

TABLE 36.8 Famous Diamonds

Name	*Weight*	*Notes*
Hope	45.52 ct	Blue due to B doping L = 25.60 mm, W = 21.78 mm, D = 12.00 mm In the Smithsonian
Koh-I-Noor (Mountain of Light)	105.60 ct	Originally 186 carats Tower of London
Cullinan I (Great Star of Africa)	530.20 ct	Original rough Cullinan Diamonds 3,106 ct Tower of London (10 × 6 × 5 cm)
Cullinan II (Lesser Star of Africa)	317.40 ct	In the British Imperial Crown Tower of London
The Regent	140.50 ct	In the Louvre
The Centenary	273.85 ct	Found in 1986 (de Beers Centenary). Rough wt. 599 ct. In the Tower of London
The Tiffany Yellow	128.51 ct	Found in De Beers mine, Kimberly 1887. Rough weight 287.42 ct Still at Tiffany's in New York

Figure 36.20 shows the different facets found on natural diamonds; all these shapes just involve {001} and {111} surfaces. Modern diamond faceting does not need to take into account the crystallography because, as a face-centered cubic (fcc) crystal, diamond is structurally quite isotropic.

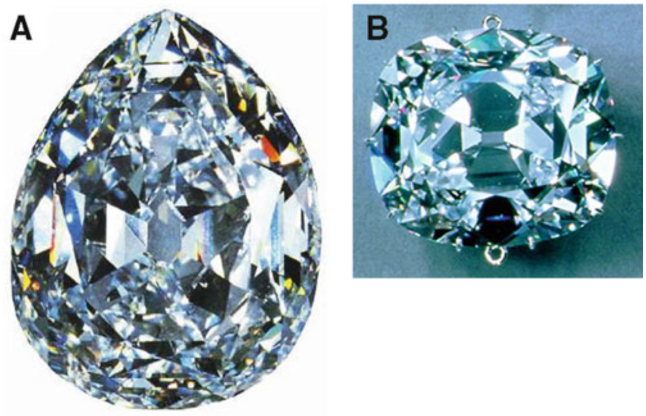

FIGURE 36.19. Two examples of blue diamonds. Both were cut from the same Cullinan rough diamond.

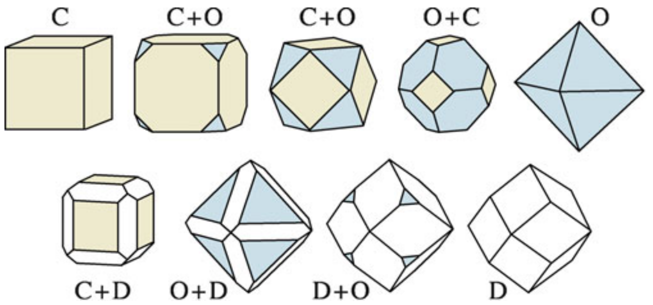

FIGURE 36.20. Different diamond shapes produced by diamonds faceting on three different crystallographic planes while keeping the same symmetry.

TABLE 36.9 Beryl ($Be_3Al_2Si_6O_{18}$)

Name	*Color*	*Dopant*	
Beryl	Blue	Cr	
Emerald	Green	Cr or V	
Aquamarine	Blue/light green	Fe	
Morganite (rose beryl)	Pink	Mn	Also in red beryl
Heliodor	Gold-yellow	Fe	
Goshenite	None		

36.10.1 Sapphire and Ruby

Sapphire and ruby are both mainly Al_2O_3. If the stone is red, it is called ruby; if it's any other color, it is called sapphire or fancy sapphire. There are many ways to produce the color, as summarized in Section 36.6. Ruby is Cr-doped, whereas the blue gemstones contain the Fe-Ti complex (see Section 36.7).

Sapphires can be colored by diffusing in dopants. Co gives blue, and Be gives yellow. Doping with Be is quite new; the Be diffuses much more quickly that Co and can penetrate the whole crystal, so there are no telltale effects at the facets. The process involves surrounding the sapphire with chrysoberyl ($BeAl_2O_3$) powder and heating to ~1,300°C.

36.10.2 Emerald and Beryls

The mineral is generally referred to as beryl and is found is several forms, as summarized in Table 36.9. Commercially, the mineral beryl is the principal source of Be. Beryl occurs in three forms: emerald, aquamarine, and precious beryl (everything else); this is somewhat analogous to the naming of sapphires. Some precious beryls do have their own names in the gem trade. In the field, gemologists use the Chelsea filter specifically to identify emeralds. The Chelsea filter is a dyed gelatin film designed to transmit the red but absorb the green; through it, emeralds appear red. The filter became less useful when synthetic emeralds became common.

The formula is $Be_3Al_2Si_6O_{18}$ (with up to 1 H_2O); it has $n = 1.595$. The crystal structure is hexagonal and is composed of sixfold rings of SiO_4 tetrahedra, which make up the Si_6O_{18} unit. It cleaves along both $\{10\bar{1}0\}$ and (0001) faces; fractures on these planes do not need to break Si-O bonds. Actually, cleavage is so easy that essentially all natural emeralds contain fractures. The so-called emerald cut, shown in Figure 36.21, has the corners removed; it was developed to minimize the likelihood of fracture (while maximizing the size of the stone).

FIGURE 36.21. Emerald cut in the classical style that minimizes the likelihood of fracture.

Synthetic emerald can be grown by the flux method or hydrothermally (like synthetic quartz and natural emeralds), as shown in Figure 29.15, and is much more perfect. The largest natural single crystal of gem-quality aquamarine was found in Minas Gerais and weighed 110.5 kg. In one form of aquamarine known as *Maxixe*, the blue is enhanced by irradiation, but the color is not permanent. The coloring of morganite can often be improved by heating the gem to >400°C. The same treatment can change green beryl into blue aquamarine. The likely effect is that the process reduces Fe^{3+} to Fe^{2+}. Not included in Table 36.9 are Co and Ni doping, which produces pink/violet and pale green, respectively.

36.11 OPAL

Natural opal was deposited in fissures in rocks or fossilized (silicified) wood from water-based solutions at relatively low temperatures, as illustrated in Figure 36.22. *Precious opal* consists of perfect arrays of identical spheres of SiO_2, as shown in the SEM image in Figure 36.23. The spheres

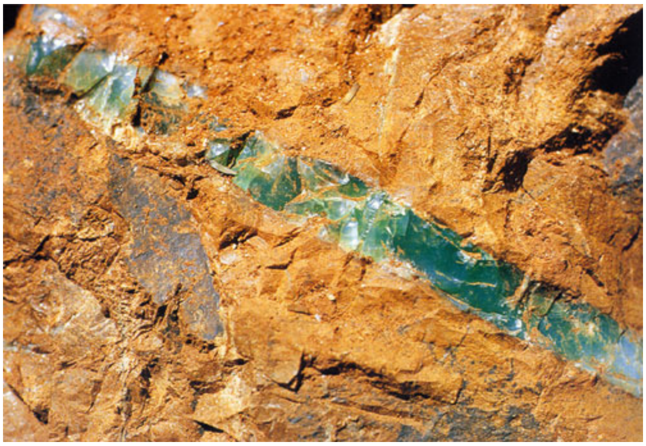

FIGURE 36.22. Natural opal in a vein.

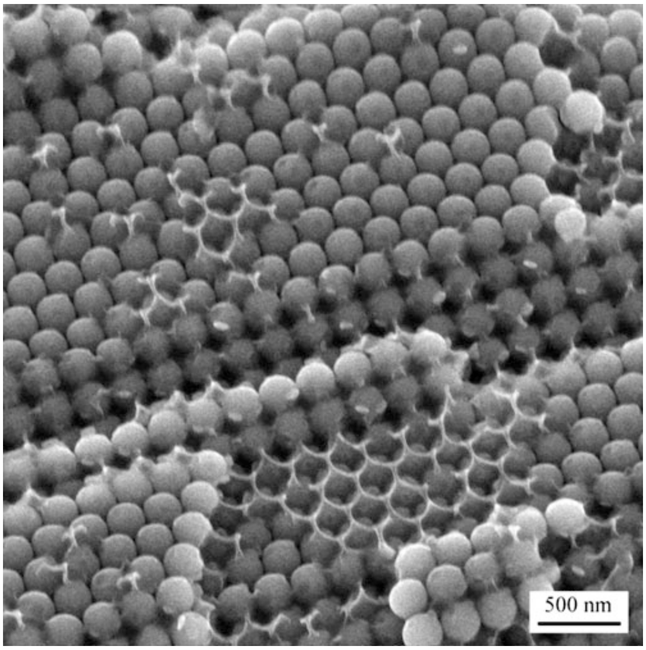

FIGURE 36.23. Scanning electron microscopy image of a Gilson opal.

have a radius of ~300 nm, so arrays of the spheres look like crystals (three-dimensional diffraction gratings) to incident visible light. Thus, the light is diffracted (in the actual "reflection" Bragg geometry), which is why we see different colors when viewing the opal from different directions. The spheres can be amorphous or partially crystalline. Not all opal shows these colors because the term opal refers to any material made up of such SiO_2 spheres; other examples are common opal or fire opal. A key component of opal is the included water, which is typically present at 3–9 wt.% but may be as much as 20 wt.%. It is a little tricky to polish opal (a fine example is shown in Figure 36.24), partly because you mustn't remove the water and partly because it is quite soft. Opal thus has much in common with chalcedony, another form of fine-grain quartz.

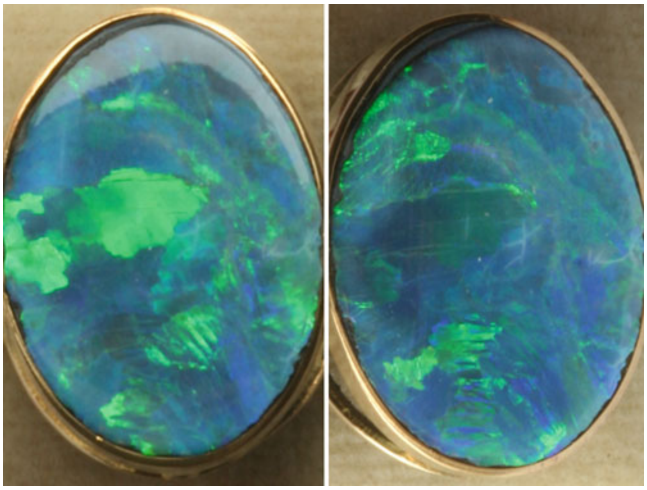

FIGURE 36.24. Polished precious opal.

FIGURE 36.25. Amethyst crystals from a section of a cathedral. The crystals were initially inside the geode.

Opals are synthesized commercially, as we saw in Chapter 28. Because the structure is quite open, it is easy to diffuse a dye into the matrix to change the overall color. We can produce inverse opals in a similar way using latex spheres instead of SiO_2 and then various sols such as TiO_2 instead of the dye. When the impregnated polymer is burned out, the inverse opal has potential as a photonic band gap material. The last point reminds us that opal was the first photonic material; we are now exploring how we can exploit this natural phenomenon using synthetic materials.

36.12 OTHER GEMS

Quartz crystals are known by several different names. The colorless form is known as rock crystal. Amethyst is single-crystal quartz. The crystals grow naturally by a hydrothermal process and are found as cathedrals and wheels, as shown in Figure 36.25. The purple color can be caused by Fe that is in the excited 4+ state due to natural (or artificial) irradiation or Mn. The Fe concentration is probably in the range 20–40 ppm. Smoky quartz is gray also due to irradiation, but the dopant is probably Al^{3+}. When heat-treated, the stones become yellow-orange-brown and are known as citrine. Rhinestones were originally quartz pebbles collected from the River Rhine. The lesson is that each of these forms of quartz grew by natural hydrothermal processes and were then "treated" by nature (or humans).

Topaz is a silicate with the general formula $Al_2SiO_4(F_2OH)_3$. It is the hardest silicate, testing at 8 on the Mohs scale. The crystal structure is unusual. It is orthorhombic, consisting of chains of AO_6 octahedra linked together with SiO_4 tetrahedra. Cleavage is parallel to the basal plane as there are no Si-O bonds crossing this plane. It is found in a variety of shades of blue and the Imperial Yellow. Figure 36.26 shows a natural single crystal. Color is produced either by high-energy neutron irradiation in a nuclear reactor or in a gamma cell (in Brazil they use ^{60}Co to produce γ-rays) or with a *lin*ear *ac*celerator (linac), producing a high-energy electron beam. The stones may be radioactive for some time after processing (a few weeks for the sky blue produced by the linac; several months for the London blue produced with neutrons). One story concerns a gem dealer who was surprised to find that the gems in his pocket were still hot. Gamma radiation can produce both yellow and blue centers, giving a brown color; the yellow can be annealed out at ~450°C, leaving the blue, which lasts a lifetime (but may not be an heirloom).

Tourmaline is another mineral that can show many colors because it can contain different cations, some of which are listed in Table 36.10. This table is quite new and still being developed. For example, the Y ion in dravite can be replaced by Mn(II) or V(II); Mn doping can be as high as 9 wt.% and makes tourmaline pink. Some cations tend to share the Y site, compensating charge. Color variation is especially known for the variant watermelon tourmaline, which is naturally pink in the interior and green on the outside, as illustrated in Figure 36.27. As always, we have to be careful because electron irradiation can change

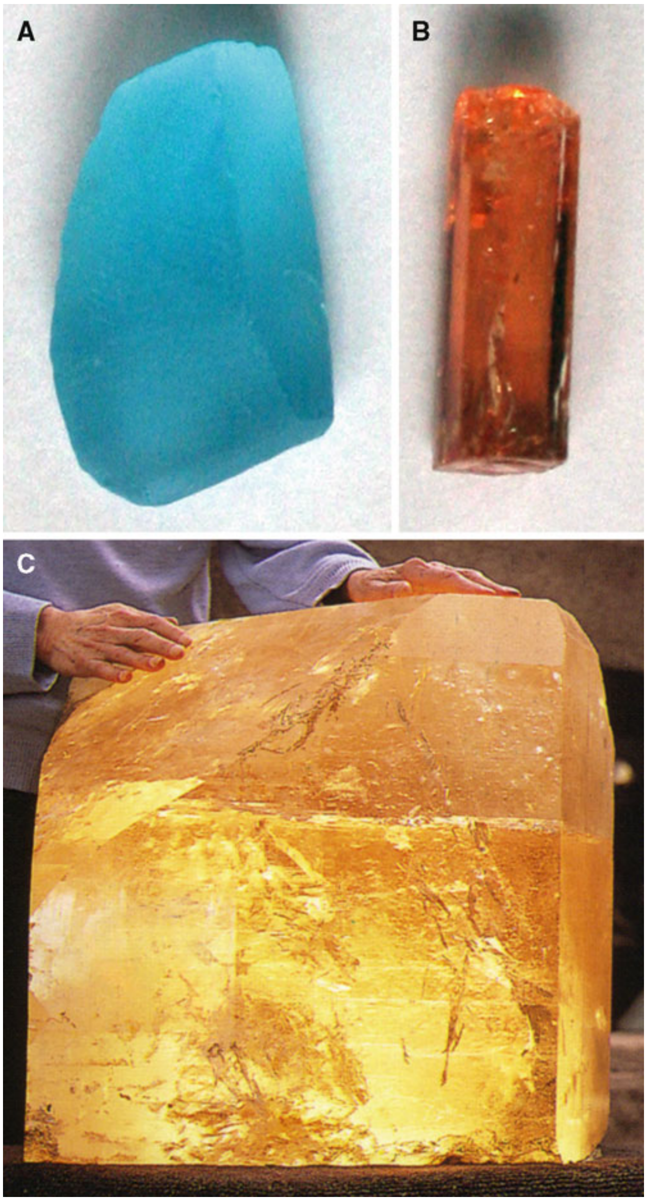

FIGURE 36.26. Topaz. Examples of irradiated rough, natural imperial topaz and a huge natural single crystal.

TABLE 36.10 Tourmalines

Species	*X*	*Y_3*	*Z_6*	*T_6O_{18}*	*V_3*	*W*	*Color*
Elbaite	Na	$Li_{1.5}Al_{1.5}$	Al_6	Si_6O_{18}	$(OH)_3$	(OH)	
Dravite	Na	Mg_3	Al_6	Si_6O_{18}	$(OH)_3$	(OH)	
Chromdravite	Na	Mg_3	Al_6	Si_6O_{18}	$(OH)_3$	(OH)	
Schorl	Na	$Fe(II)_3$	Al_6	Si_6O_{18}	$(OH)_3$	(OH)	Black
Olenite	Na	Al_3	Al_6	Si_6O_{18}	O_3	F	
Buergerite	Na	$Fe(III)_3$	Al_6	Si_6O_{18}	O_3	F	
Uvite	Ca	Mg_3	$MgAl_5$	Si_6O_{18}	O_3	F	
Rossmanite	Ca	$LiAl_2$	Al_6	Si_6O_{18}	$(OH)_3$	(OH)	
Foitite	vac	$Fe(II)_2Al$	Al_6	Si_6O_{18}	$(OH)_3$	(OH)	

FIGURE 36.27. Watermelon tourmaline.

yellow-brown tourmaline into pink tourmaline. The terms red tourmaline and blue tourmaline have now replaced the names rubellite and indocolite because they are not distinct minerals. Natural crystals of schorl can be >15 cm inches long. Tourmaline is an unusual crystal in that it has true threefold symmetry; the space group is R3m with $a = 1.594$ nm and $c = 0.7138$ nm, but the actual values of a and c depend on which cations are present. Commercially, this mineral is a principal source of boron. We mentioned the piezoelectric property earlier; it is strongest along the c-axis but quartz is now used more often except in special pressure sensor applications.

Spinels are less common gemstones but sometimes quite famous even if known by another name. The Black Prince's Ruby (5 cm long) and the Timur Ruby (polished but not faceted, 361 ct) in the English imperial state crown are both spinels. The largest known natural spinel crystal weighed 104 g (520 ct). Although the spinel structure can accommodate wide variations in chemistry, most spinel gemstones are actually naturally doped $MgAl_2O_4$. One variation is gahnite, the zinc aluminate spinel, $ZnAl_2O_4$. The best known spinel, magnetite ($FeFe_2O_4$), is not very attractive as a gemstone. Synthetic spinels can be doped in many colors and have the advantage over synthetic sapphire that they are more nearly isotropic.

Garnet crystals are some of the older popular gemstones and a special class of mineral (much like spinel). The crystal structure is able to accommodate many different cations, which then produce different colors. All those shown in the box are natural silicates, although several synthetic garnets are now available; synthetic garnets produced for gemstones are usually doped yttrium aluminum garnet (YAG).

All natural garnets have the general formula $R_3M_2(SiO_4)_3$, where R is Ca, Mg, Fe(II), or Mn; M is Al, Fe(III), or Cr. They form two groups.

- Pyralspites
- Ugrandites

Natural garnets are rarely pure. Natural almandines usually contain Ca, Mg, and Fe^{3+} so they denote the end-member garnets. We then use whichever name most closely matches the composition we have. There is then a whole extra array of names. Rhodolite lies between pyrope and almandite; tsavorite is a green variation of grossular; demantoid (the most valuable garnet) and the black melanite are andradite garnets. Pyrope is also known as Bohemian garnet and was the favorite red stone in the 1700s and 1800s but can look very similar to almandite. Almandite is Dana's name for almandine, which is also known as precious garnet and was probably called alabandine (after the ancient Turkish city of Alabanda) by Pliny, so the two names are used interchangeably.

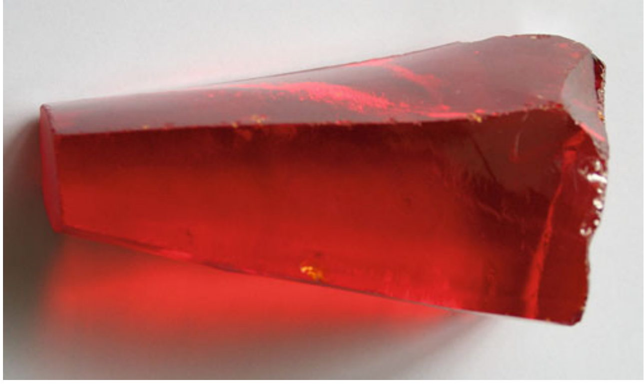

FIGURE 36.28. As grown crystal of rare-earth-doped cubic zirconia.

FIGURE 36.29. Single-crystal of rare earth (RE)-doped synthetic cubic zirconia that has been cut and polished.

SILICATE GARNETS

Pyralspites: named according to the dominant R cation present:
Mg^{2+}: *Pyrope* [$Mg_3Al_2(SiO_4)_3$]
Fe^{2+}: *Almandine* [$Fe_3Al_2(SiO_4)_3$]
Mn^{2+}: *Spessartine* [$Mn_3Al_2(SiO_4)_3$]
The dominant M cation in these garnets is Al; usually with Fe^{3+}
Ugrandites (calcic garnets with R = Ca): named after the dominant M cation.
Cr^{3+}: *Uvarovite* [$Ca_3Cr_2(SiO_4)_3$]
Al^{3+}: *Grossular* [$Ca_3Al_2(SiO_4)_3$]
Fe^{3+}: *Andradite* [$Ca_3Fe_2(SiO_4)_3$]

Cubic zirconia is a special case in that it is ubiquitous as a synthetic gemstone; an example of an as-grown stone is shown in Figure 36.28 and a polished and faceted stone in Figure 36.29. Naturally occurring zirconia is rare and then only as the monoclinic baddeleyite.

Peridot is better known as the mineral olivine. The gemstones usually have a composition close to $(Mg_{0.9},Fe_{0.1})_2SiO_4$ and have a unique green color. Peridot was mined for 3,500 years on the island of Zabargad (St. John's Island) in the Red Sea near Aswan, Egypt. The largest cut peridot (319 ct) was found on this island.

Alexandrite is a variety of chrysoberyl. It is special because absorption is so different in two directions. When viewed along the different crystallographic axes, its color changes from red to orange-yellow to emerald-green. In daylight the color is green; in artificial light it is red.

Tanzanite is a purple variety of zoisite. Most stones are green when mined and become purple when heat-treated. The stone is particularly interesting (valuable) because it is only found in one place. It is quite hard (Mohs 6.5–7.0), can be essentially perfect, and is pleochroic.

36.13 MINERALS WITH INCLUSIONS

Inclusions in gemstones are quite common and are often used as an indication that the stone is *natural*. The best-known gems with inclusions are the star stones, where the stone can be sapphire, garnet, etc. Perfect star sapphires can now be synthesized.

Quartz crystals containing a hematite *seed* and the rutile needles are particularly interesting. You can also see hematite needles in quartz. When considering the origin of such structures, you should know that the same arrangement of seed and needles occurs without the quartz matrix, as shown in Figure 36.30. The name *cat's eye* originally referred to chrysoberyl, which contains inclusions, but the effect is seen in many other gemstones as well.

FIGURE 36.30. Rutile growing in hematite. This combination often causes patterns in quartz crystals.

36.14 TREATMENT OF GEMS

Two methods that are widely used to enhance the color of gemstones are irradiation and heating, usually in that sequence. Table 36.11 summarizes some of the heat and irradiation treatments that have been used. The reason for treating (processing) gemstones is invariably to enhance their appearance and thus increase their value. We review the general features of the different treatments and the science behind them here but refer you to the sections on particular materials for discussions of the details. All irradiated samples are heated.

Heating. Sapphires. Over-heating can cause good stones to become so dark that they are not transparent. Most citrine is produced by heating amethyst. This process can also occur naturally.

Irradiation. Topaz is sold as Swiss blue, London blue, etc. In all cases, the material has been irradiated and heated.

Composite stones can be constructed by joining different stones, as illustrated in Figure 36.31. One of these methods is essentially equivalent to making a bicrystal with an amorphous (polymer) intergranular layer.

Filling cracks with oil, polymer, or glass is commonplace. The different procedures produce a similar result, the difference being mainly how long it takes until the result degrades. The extreme example of this is the transformation of turquoise chalk to something that looks like the *real thing*, as shown in Figure 36.32. In 2004, some highly priced rubies were found to have had internal fractures filled with Pb-containing glass (chosen to match the n).

TABLE 36.11 "Treatment" of Gems: Its Effectiveness and "Publicity"

Treatment	*Stable?*	*Detectable?*	*Disclosure?*
Aquamarine turned from green to blue by heat	Yes	No	No
Zircon heated to turn colorless or blue	Virtually all	No, but these colors are very rare in nature	No
Sapphire or ruby heated to remove silk	Yes	Usually	Yes
Sapphire heated to modify or develop a blue color	Yes	Usually	Yes
Topaz turned blue by irradiation	Yes	No	Explained
Topaz or sapphire irradiated to a yellow or brown color	No	No, only fact of fading	Explained
Beryl irradiated: Maxixe-type blue color	No	Yes	Yes
Turquoise or opal impregnated with a colorless stabilizer	Usually	Usually	Yes
Emerald or ruby impregnated with a colorless substance	Variable	Yes	Yes
Beryl or emerald impregnated or coated with color	No	Yes	Yes
Sapphire impurity diffused to produce a surface color or surface asterism	Yes/No	Yes	Yes
Fracture-filled diamond	Yes/No	Yes	Yes

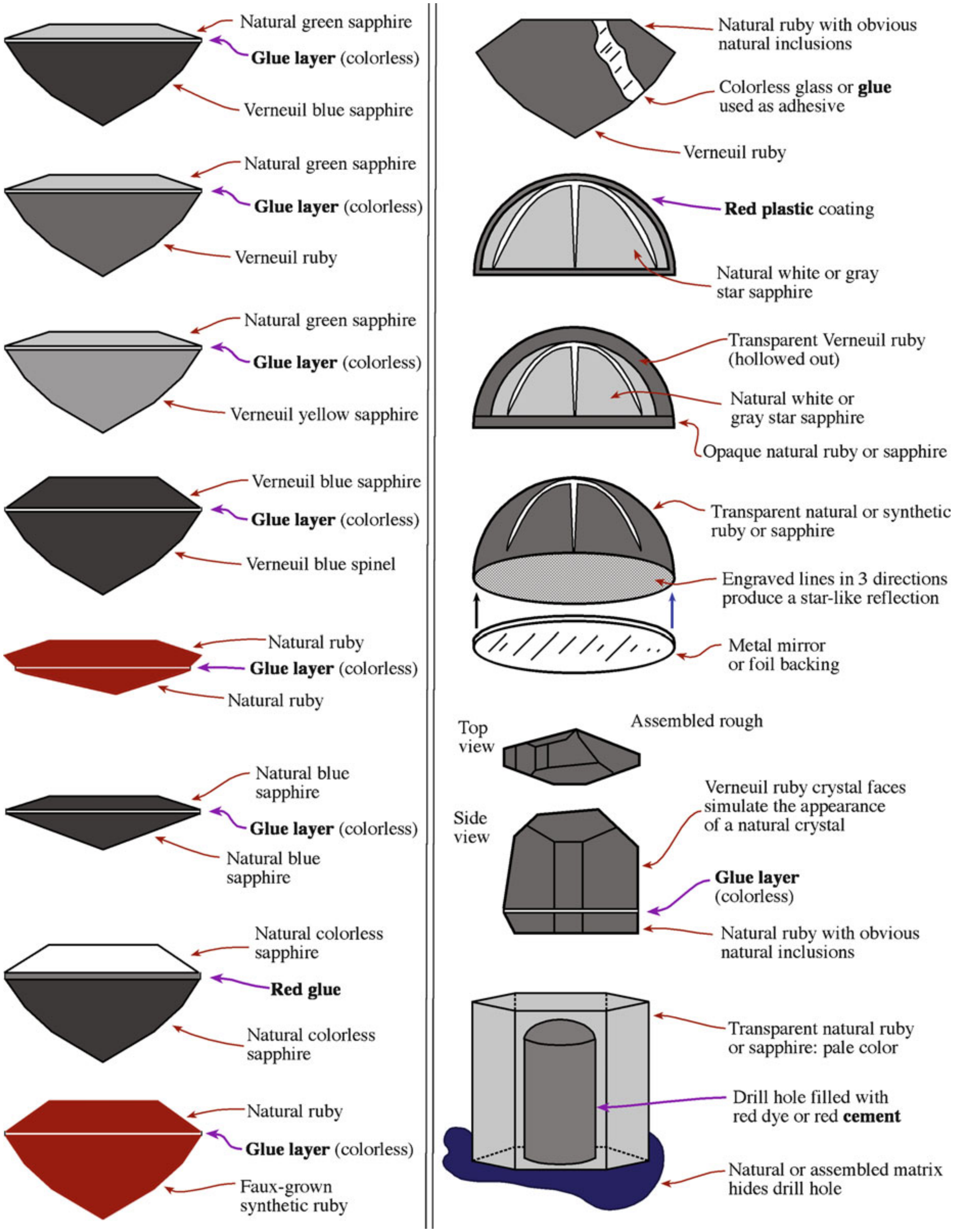

FIGURE 36.31. Different methods of simulating (faking) gemstones by forming composites (e.g., bicrystals).

Lasers are used to drill channels into diamonds to remove internal blemishes, afterward filling the hole with glass having a similar *n*. This is a variation on the technique is used to created three-dimensional images inside glass blocks for use as decorations. In either process, a pulsed laser is focused on a small area at the required location in the crystal and then pulsed to create an internal fracture (in the glass model) or ablating material (in the gemstone). This process is illustrated in Figure 36.33.

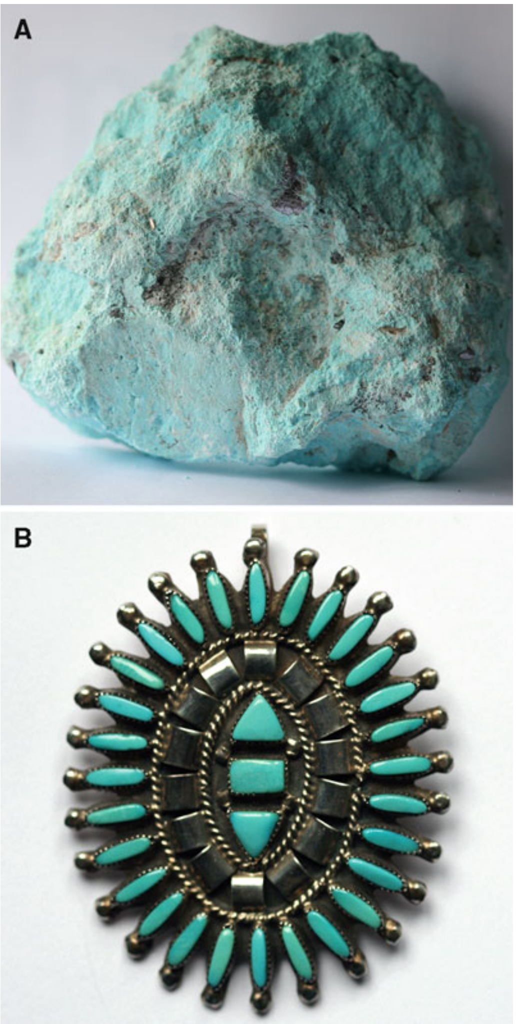

FIGURE 36.32. Examples of turquoise (A) before and (B) after processing. Both samples are real turquoise. An old method of infiltration to modify the properties of a material is common for turquoise.

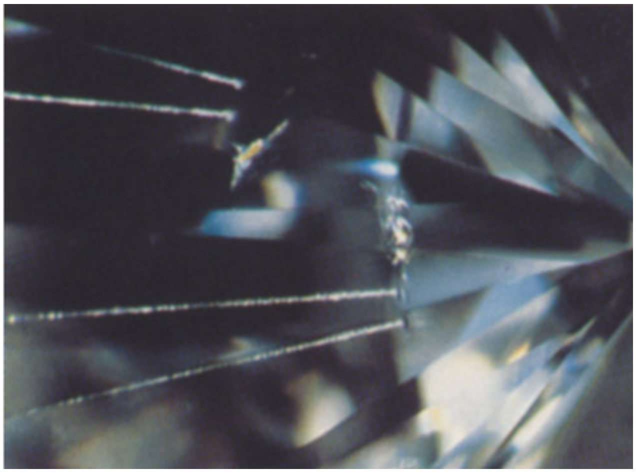

FIGURE 36.33. Laser etching to remove inclusions in a gemstone.

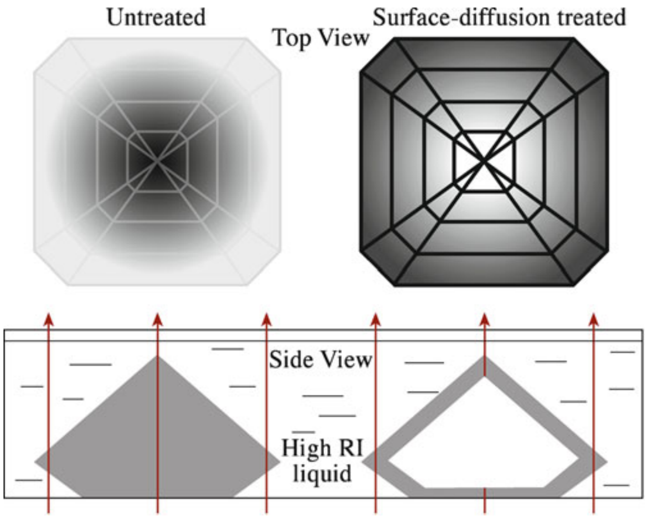

FIGURE 36.34. Diffusion to modify the color of a gemstone.

How effective *diffusion* is depends on the rate of diffusion. If the intention is to improve the color of a gemstone, then you want the color to be uniform throughout the stone. Hence, after diffusion, the stone should be equilibrated for a long period to remove the concentration gradient. This equilibration would take too long for the gem trade, so the dopant has a concentration profile peaking at the surface. You diffuse dopant into the cut stone because otherwise the surface region has a different color when you facet it. In the case of Co, which produces a blue color in sapphire, diffusion is slow so that the facets have a color different from that of the bulk. The color difference is particularly obvious at the facet junctions, as shown in Figure 36.34.

36.15 THE MINERAL AND GEM TRADE

There are many interesting international aspects to the history of gems. Economies of countries have been based on gem production. Though not usually as bad as precious-metal mines, the effect of gem mines on the environment can be very negative. The Kimberley Mine is always associated with "Big Hole," which by 1914 when work on it stopped was the largest man-created excavation in the world, having a depth of 215 m, a surface area of ~17 ha, and a perimeter of ~1.6 km; 22.5 million tons of earth were excavated to produce 2,722 kg of diamonds. In the 1990s and later, the diamond trade in Sierra Leone became associated with raising funds to fund ongoing wars. The stones were referred to as "blood diamonds," and international organizations tried to minimize the trade in these stones. Now these diamonds account for 0.2% of diamonds sold, down from a peak of 4%.

It is often very difficult to reach the mines in Myanmar (Burma), but historically Magok is the center of the ruby-producing region. Many gemstones are exported through Thailand, which is a worldwide center for processing (cutting and polishing) gemstones.

In Brazil, the most important production area for gems and minerals in Minas Gerais. It is a more remote region of Brazil but with a growing industrial presence.

BLOOD DIAMONDS IN POP CULTURE

Diamonds from Sierra Leone by Kanye West won a 2006 Grammy for Best Rap Song.

Blood Diamond starring Leonardo DiCaprio and Jennifer Connelly was released by Warner Brothers in 2006.

FarCry2 a 2008 video game set in a Central African country in the midst of civil war uses diamonds as currency.

The book *Diamonds in the Shadow* by Caroline B. Cooney (Delacorte Books for Young Readers, 2007) involves a refugee family smuggling blood diamonds into the United States from Africa.

In 2010 war-crimes trial of Liberian leader Charles Taylor, supermodel Naomi Campbell admits he gave her "dirty rocks."

In India, the major source of talc is located in the Dagota District. The talc is prepared by crushing boulders that have been produced in the soapstone mines. Mining is threatening the existence of the Indian tiger (see Section 37.6).

The history of De Beers and the diamond trade has been covered in several books, so we do not examine it here except to say that it makes for a fascinating story. It surprises some to hear that diamonds are not rare. One aspect of the diamond business is that the stones are very portable and easily can be made unrecognizable. The company De Beers is now based in Amsterdam and Antwerp. A new development is to use a laser to inscribe each diamond with a code number after it has been faceted (another "modification" using lasers). The diamonds from Canada's Northwest Territories have a laser-inscribed polar bear and are known as "Polar Bear Diamonds".

There are, of course, many other uses of gemstones, including jewel bearings for watches and other precision machinery; but here we have concentrated on their use in decoration and the science behind the preparation of the gemstone from the rough. There is also a worldwide trade in mineral specimens such as you may see in museums that can be priced in excess of $100,000.

CHAPTER SUMMARY

The topic of this chapter is unusual in a ceramics textbook. It is an example of real-world ceramics, where mineralogy, chemistry, physics, materials science, art, and commerce meet.

PEOPLE AND HISTORY

Cullinan, Sir Thomas owned the mine where, in 1905, the world's largest diamond was found.

De Beer, Johannes Nicholas and *Diederik Arnoldus* are brothers who owned the farm that became the Kimberley "Big Hole."

Mohs, Fredrich (1773–1839) introduced the term "scratch hardness" in 1826. He was born in Gernrode/Harz Germany, studied at the University of Halle and at Freiberg. He later worked in Austria.

Moisson, Ferdinand Frederic Henri (1852–1907) discovered naturally occurring SiC in 1905 in a meteorite from the Diablo Canyon in Arizona (USA). He developed the electric furnace, which he used to make carbides and prepare pure metals. He received the Nobel Prize in 1906 for successfully isolating fluorine (1886).

Winston, Harry (1896–1978) A key figure in the diamond trade, he opened his business in New York City in 1932. In 1958, he donated the Hope Diamond to the Smithsonian.

EXERCISES

36.1 What are the lines in Figure 36.9?

36.2 In Figure 36.11 the stones are immersed in a liquid. Why is this liquid chosen? Show that the observations are what you would expect.

36.3 What can you deduce regarding the size, shape, and alignment of the particles causing the stars in Figure 36.15?

36.4 Explain the phenomenon of labradorescence seen in Figure 36.17.

36.5 What is the common flaw found in natural emeralds? Explain your answer from a crystallographic point of view.

36.6 If you had a good means for measuring thermal conductivity, would you prefer such a test to Mohs' scratch test? How sensitive would your apparatus need to be? We can use a handheld tester to distinguish diamond and moissanite. How is this fact connected to the electronics industry?

36.7 Why must you be particularly careful when polishing opal? How is opal related to today's electronics industry?

36.8 What do the stabilization of turquoise, the treatment of emerald, and ZnO varistors have in common?

36.9 Diamond has a high n and is also a very hard material. (a) Are these two features linked? (b) If so, explain why $SrTiO_3$ has a higher n but is not as hard.

36.10 Explain, using your knowledge of ceramic processing, how you might take turquoise powder and turn it into a gemstone.

36.11 We answered the question: is this turquoise natural? Clarify the answer.

36.12 When asked how to wash an opal, we answered: "No." Why?

36.13 Diamonds have now been found in Zambia. Where else are they found worldwide?

36.14 Diamond is known for its sparkle. Which gemstones sparkle more? Why are they less valuable than diamond?

36.15 Watermelon tourmaline ranges in color from green to pink. Did the color affect its use as a piezoelectric? Explore and discuss.

36.16 You can make green tanzanite purple, white turquoise "blue," and colorless topaz blue. What are you doing in each case, and how does each one relate to more technologically relevant ceramics?

36.17 Beryllium can be diffused into sapphire to produce a yellow color that is quite rare in nature. How would you, as a ceramist, show that it had been doped?

36.18 Talc has been used for many years. Discuss how its crystal structure influences its use.

36.19 Natural garnet occurs in many different colors. So does synthetic cubic zirconia. Discuss what features these two materials have in common to facilitate this coloration.

36.20 Why can we say that opal was the first photonic material?

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WHERE TO SEE GEMSTONES

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