COLOR IN GEMS:
THE NEW TECHNOLOGIES

By George R. Rossman

Advances in technology have brought great advances in our ability to impart color to natural gemstones as well as to create synthetics. Simultaneously, technologies are also being developed to distinguish natural from artificial colors as well as natural from synthetic materials. This article discusses some of the work being done to enhance color in gemstones today and some of the techniques used by the laboratories at the California Institute of Technology to determine whether a color originates naturally or in the laboratory. Dyed jade, synthetic turquoise, heat-treated beryl and zircon, irradiated spodumene, and topaz that has been irradiated and heated to produce a pleasing blue color are some of the specific examples included.

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One of the most important attributes of a gem material is its color. For centuries, man has used a variety of technologies to enhance the color of natural gems and to produce materials that imitate natural stones. Today, these technologies have grown in sophistication to the point that the gemologist faces formidable problems in identifying some of the products of these technologies. Concurrently, much scientific activity has been directed toward understanding the origin of color in minerals. Sophisticated instruments are being used in a number of laboratories to investigate color and other physical and chemical properties of minerals almost to the level of atomic resolution.

This article will consider a number of case studies, drawn largely from the experience of the laboratories at the California Institute of Technology, which illustrate methods used to study color in gem minerals. The examples presented have been chosen to show how the scientific study of the basic properties of minerals can provide useful gemological information for determining whether the color in a particular gem originates naturally or in the laboratory. Included in the discussion are jade, turquoise, beryl, zircon, spodumene, and topaz, as well as a variety of other materials that have also been the subjects of color experimentation.

JADEITE

The dominant constituent in this variety of jade is the mineral jadeite, a sodium aluminum silicate [NaAlSi_{2}O_{6}]. Yet the properties of the sodium, aluminum, and silicate ions are such that they are incapable of imparting color to a mineral. If jadeite were chemically pure, it would be colorless. It is the impurities, the minor substituents, in the jade that bring about the color. The color of the light green jadeite in figure 1 results from the presence of a small amount of iron, which occurs in the 3+ oxidation state.
state in substitution for aluminum. If chromium is the substituent, a dark, emerald green results (again, see figure 1). The chromium occurs in the 3+ oxidation state in substitution for aluminum. There are other ways to make jade green, however, as evidenced by the synthetically dyed stone in figure 2. Chemicals similar to those used for food coloration have been carefully tailored to reproduce desirable color in jade.

The fact that any one of several sources may be responsible for the color in a stone raises the question of how to determine the origin—natural or synthetic—of that color. In the case of jade, we turn to the spectrophotometer to study the optical absorption spectrum of the stone. In our studies, we not only examine the visible spectrum from 400 to 700 nm, but we also routinely measure the spectrum from about 250 nm in the ultraviolet range to 2500 nm in the infrared range. The types of spectra measured by the researcher contain broad absorption features that are often weak in intensity. These particular features are difficult to detect with the hand-held spectrosopes that are often used in gemological testing, but they are readily observed in instruments that scan broad wavelength ranges and display the results on chart paper.

The absorption patterns produced by chromium, iron, and dye in jade are highly distinctive. Iron 3+ produces the pattern shown at the top of figure 3. It consists of two broad absorption bands of low intensity, near 850 nm and 620 nm, a sharp spike near 440 nm, and a narrow band near 380 nm. Theoretically, this type of pattern will appear whenever iron 3+ occurs in a mineral in a site in the lattice that has six oxygens surrounding the iron in the geometry of an octahedron. Chromium 3+ produces the pattern shown at the bottom of figure 3. There is a departure from the smooth curve—known as structure—in the 600–700 nm region of this spectrum that is diagnostic of chromium. This is in contrast to the dyed sample (the center pattern in figure 3), which has a broad absorption band in the same region as the chromium but lacks the detailed structure seen when Cr3+ is present and which is diagnostic. All the samples are approximately the same color because they all transmit light at about 520 nm. The intensity of the color, however, depends on
the extent of absorption on either side of the transmission band at 520 nm.

TURQUOISE

Turquoise \( \text{[CuAl}_2\text{(PO}_4\text{)}_2\text{(OH)}_6\cdot5\text{H}_2\text{O]} \) is blue because it contains copper as an essential constituent. Although other natural materials may be made to look like turquoise by the addition of an appropriate dye, it is easy to distinguish such materials from turquoise by their absorption spectra or X-ray diffraction patterns, or by chemical analysis. A more interesting challenge is the identification of synthetic turquoise.

The manufacturer of the synthetic stone shown in figure 4 had so much confidence in his product that he advertised that there was no test known to science that could distinguish his synthetic material from natural turquoise. To meet this challenge, we passed a beam of infrared radiation through a minute amount of the synthetic material (scraped from a sample) and then recorded the amount of infrared radiation absorbed over a broad range of wavelengths. We found that the absorption patterns obtained from natural turquoise differ significantly from those obtained from the synthetic turquoise (figure 5). The natural turquoise is well crystallized; the atoms are...
Figure 6. Examples of various colors of beryl. Iron in the beryl produces the yellow, green, and blue. Manganese produces various shades of red.

arranged with a high degree of regularity within each crystallite. On the infrared absorption spectrophotometer, a pattern of sharp absorption lines with abundant structure is produced as light entering the crystal causes the phosphate groups to vibrate within only a few well-defined frequencies. This means that only particular wavelengths of light will be absorbed. The absorption pattern of the synthetic turquoise tested has similar features, but in this case the lines are broad, ill-defined, and poorly separated. This happens because synthetic turquoise contains a significant amount of a component with atoms that are poorly ordered. This component is referred to as X-ray amorphous because it does not show up in the X-ray patterns commonly used for mineral identification. Because the synthetic material contains crystalline turquoise in addition to the X-ray amorphous component, an X-ray of the synthetic produces a turquoise pattern. However, while X-rays cannot detect this difference conveniently, the infrared absorption technique can make the distinction readily.

BERYL

Another material that we have studied in detail is beryl (Goldman et al., 1978). Chemically, beryl is a beryllium aluminum silicate \( \text{Be}_2\text{AlSi}_3\text{O}_8 \). Yet beryllium, aluminum, and silicate are all incapable of causing color. Like jade, if beryl were chemically pure, it would be colorless. Also like jade, impurities are responsible for the various colors of beryl. Unlike jade, though, with golden, yellow to yellow green, green, and blue beryls (figure 6), only one element is responsible for the color. This element is iron. To understand how minor amounts of this one element cause such a range of colors, we must first determine: (1) where, in terms of the atomic structure of beryl, the iron is located, and (2) what the oxidation state of the iron is. Furthermore, we know that beryl is often treated in the field or in laboratories with a heat-treatment process that removes the yellow and the green components and leaves the crystal blue. We must also determine, then, how the heat treatment influences the iron in the beryl to bring about this type of color transformation.
To address these issues, we take a submicroscopic look at the structure of beryl. Beryl is composed of three fundamental building blocks. First, there are atoms of beryllium surrounded by four oxygens which form units in the shape of a tetrahedron. Next, atoms of silicon surrounded by four oxygens form units that are also in the shape of a tetrahedron. Finally, atoms of aluminum are surrounded by six oxygens arranged in the form of an octahedron. These three building blocks fit together in three-dimensional space to form beryl with the structure shown in figure 7. Iron could potentially reside in any one of these sites, or even inside the channels that are formed by the rings of silicon. Furthermore, the iron could be iron $^{2+}$ or it could be iron $^{3+}$.

Through a variety of experiments we have found that iron in beryl exists primarily in the aluminum site. Whether the iron is present in the $^{2+}$ or the $^{3+}$ oxidation state, however, it has almost no effect on the color of the stone, at least not in the thicknesses that are common for faceted gems. One would have to have a very thick crystal to see the color brought about by iron in the aluminum site. Similarly, iron may reside to a small extent in the beryllium site in the $^{3+}$ oxidation state, but this too will have no effect on the color of the material.

The color seen in beryl (in the thicknesses usually encountered in faceted gems) is derived from relatively small amounts of iron situated in the channels formed by the silicate ions, which run parallel to the c-axis of the crystal. If the iron present in these channels is in the $^{2+}$ oxidation state, the color is blue; if the iron is in the $^{3+}$ oxidation state, the color is golden yellow. Mixtures of golden-yellow iron $^{3+}$ and blue iron $^{2+}$ give rise to the intermediate shades of yellow, green, blue, green, etc. Heat treatment of aquamarine reduces the iron in the channel from the $^{3+}$ to the $^{2+}$ oxidation state to bring out the blue.

Support for these conclusions was obtained via detailed study of the optical absorption spectra. The absorption pattern of a yellow beryl in figure 8 shows two traces, one a solid line and one a broken line, which represent the two orientations of polarized light. The spectrum in the solid line was obtained with light polarized along the c-axis of the crystal; the spectrum illustrated by the broken line was measured with the light polarized perpendicular to the c-axis. We can see features that arise from iron $^{2+}$ in the channel at about 1000 nm, and features from iron $^{2+}$ in the aluminum site in the 800 to 1100 nm region. The iron in the aluminum site absorbs light only in the infrared portion of the spectrum and does not cause color. By studying the splitting among components in the spectrum, we learn about the size and distortions of the site in which the iron resides. From the intensity of absorption observed with the different polarizations of light, we learn about the orientation of the iron in the structure. From the wavelengths of absorption, we determine the oxidation state of the iron. We can even see several sharp absorption lines caused by water in the channels.

ZIRCON

Zircon provides another example of color changes that can be brought about by heat treatment. Zircon is a zirconium silicate ($\text{ZrSiO}_4$). Zirconium is present in the $^{4+}$ oxidation state and, like silicate, is intrinsically incapable of causing color. When zircon is recovered from its host rock, the crystals are often brownish red (figure 9). With
heat treatment, however, the stones can be turned colorless, rusty yellow, or sometimes blue (figure 10). The brownish red of untreated zircon results from the presence of small amounts of uranium and thorium in the crystal, natural substituents incorporated during growth. Because these elements are radioactive, they undergo radioactive decay and emit gamma rays, alpha particles, and electrons which pass through the zircon. The gamma rays shooting through have enough energy to dislodge electrons from ions inside the crystal (figure 11) and send them cascading through the stone, bouncing from atom to atom, until they gradually lose energy, slow down, and are finally trapped as defects inside the crystal, perhaps in sites where atoms are missing. Such a site is called an electron trap. Although much about electron traps remains a mystery, we do know that the electron is trapped at an energy level higher than normal, but cannot readily escape because it is in an energy well. From the study of advanced physics and quantum mechanics, we learn that a charged particle, like an electron, trapped in a field of electrostatic charge—as when it is surrounded by oxygen atoms inside a crystal—may have the ability to absorb light and cause color. Electrons caught in these electron traps are responsible for the color in zircon and in many other minerals. Heat treatment of the stone provides the energy required for the electron to overcome the barrier, leave the trap, and return to its normal position. If the stone contains only a single trap level, it will become colorless when heated. However, zircon may have several trap levels; some of

Figure 8. Absorption spectra of a yellow beryl (solid line = spectrum taken with light polarized along the c-axis; broken line = light polarized perpendicular to the c-axis) which indicate the presence of iron in both the channel and the aluminum (octahedral) site. Water molecules in the crystal can also be identified with these spectra, from the numerous sharp absorption bands.
these may impart the reddish color, others may contribute brown, while still others will produce blue. Each trap has its own characteristic energy barrier. When zircon is heat treated, the level of heat is controlled so that just enough energy is furnished to liberate the electrons from the red and brown traps, but not enough to liberate the electrons from the blue traps.

SPODUMENE

Radiation plays an important role in the coloration of many minerals. Natural processes are constantly at work providing low levels of radiation for long periods of time. It is now easy to subject minerals to high levels of radiation artificially for comparatively short periods of time, so bringing about color changes. Gem spodumene illustrates what can be accomplished. Spodumene is a lithium aluminum silicate (LiAlSi2O6). Lithium, aluminum, and silicate are all intrinsically incapable of causing color. Spodumene occurs in several colored varieties, including kunzite (lavendar to pink) and hiddenite (brilliant green). The color in kunzite results from the presence of manganese in substitution for aluminum, while hiddenite derives its color from chromium in the same substitution. Because of the far greater value of hiddenite (see figure 12), attempts have been made to transform the lavender of kunzite into the green of hiddenite by artificial means. If kunzite is placed in a chamber containing the radioactive isotope cobalt-60 and exposed to a large dose of gamma rays, a radiation damage effect ostensibly turns the lavender into green.

The resulting product is remarkably attractive (see figure 13), the color is also remarkably unstable. The samples I tested bleached out after about three hours of exposure to sunlight, although other samples of the same material retained their color for many months when stored in darkness. There has been a moderate amount of investigation to understand the chemical nature of these transformations. In summary, the transformations apparently involve the oxidation state of the manganese. The manganese in kunzite is present naturally as manganese 3+. When the stone is subjected to extreme doses of radiation, however, manganese 4+ is formed. Manganese 4+ is intrinsically unstable in spodumene, although it may have a lifetime of several months.
if kept in darkness. Once the irradiated material is heated or exposed to sunlight, the manganese 4+ is completely lost and may revert to manganese 2+, which produces so little color that the stone usually appears colorless. The whole process can be cycled repeatedly. To my knowledge, no one has yet found a way to stabilize the radiation-induced green color in spodumene, although natural hiddenite is intrinsically color stable. Even though nature is constantly bombarding kunzite with low doses of radiation, the radiation damage does not accumulate fast enough to build up a large amount of manganese 4+. Manganese 4+ does occur in some Afghanistan kunzites, but its intrinsic instability is so great that it usually bleaches out spontaneously in the earth, before it has a chance to accumulate, or else is quickly bleached by sunlight. Although it is likely that much of the kunzite initially crystallized in nature with manganese 2+, over eons of geologic time the manganese 2+ appears to have been slowly converted into relatively stable manganese 3+ by natural irradiation.

**TOPAZ**

Topaz represents one of the great commercial success stories involving radiation technology applied to gem minerals. Topaz is an aluminum silicate \([\text{Al}_2\text{SiO}_4[\text{F,OH}]]\) which should be colorless if free of impurities. In nature, however, topaz generally occurs as yellow or yellow brown, pale blue, or colorless. Upon exposure to natural radiation, most topaz will turn cinnamon brown. This color, which has some value for gemstones, can be readily generated in the laboratory by artificial irradiation as well. Figure 14 illustrates natural brown topaz and its irradiated counterpart. The artificially induced brown color is usually unstable and will fade when the stone is exposed to sunlight, which is just as capable of supplying energy to electron traps as is heat.

A more interesting case is provided by the blue topaz that results when irradiated brown topaz from some mines is carefully heated (figure 15). The blue material has gained much popularity as
a gemstone because of its pleasing color and the stability of the color. Even though blue topaz has received a great amount of study, we do not yet know the ultimate cause of its color. The fact that most properties of irradiated blue topaz are essentially the same as those of natural blue topaz has suggested the possibility that the natural color is itself a product of natural irradiation.

Because the properties—chemistry, color, indices of refraction, etc.—of natural and irradiated blue topaz are almost identical, the gemologist is faced with the formidable task of distinguishing the natural from the irradiated material. After considerable investigation, we have developed one method that has been effective in the laboratory for making this distinction. It involves thermoluminescence, that is, light caused by heat.

When an irradiated topaz is heated, a small amount of light will be emitted at temperatures below those that cause incandescence. The emitted light represents the energy released by the trapped electrons as they return to their most stable configuration. An accurate recording of the intensity of the emitted light as a function of the sample temperature constitutes the thermoluminescence experiment, as illustrated in figure 16. The details of the thermoluminescence curve vary from sample to sample depending on such variables as the trace chemical elements in the sample and the details of its radiation exposure (McDougall, 1968).

The thermoluminescence behavior of a natural blue topaz is compared to that of its irradiated counterpart in figure 17. The most obvious difference, the broad emission region centered at about 250°C, is of no value in identifying artificially irradiated topaz because its absence or presence does not correlate with the blue color or the irradiation history of the stone. What we have found to be useful for making this distinction is the temperature at which the steep rise in emission intensity occurs. With natural blue samples, the rise begins around 350°C, whereas for irradiated blue topaz, it begins at lower temperatures, typically at or below 300°C.

This difference exists because in nature topaz is exposed to low levels of radiation over long periods of time, whereas the artificially irradiated material is given massive doses of radiation in a short time. Electron traps that have low to moderate stability will decay spontaneously in nature because of the long time over which the natural irradiation occurs. These same traps will be occupied in large numbers in the irradiated material. If, however, their lifetime is tens to hundreds of years they will not fade over the course of a single human lifetime. These moderately stable traps may not necessarily contribute to the color of the topaz, but they will contribute to the stone’s
thermoluminescence behavior at high temperatures.

At this time, the thermoluminescence method is not suitable for routine testing in the jeweler's or gemologist's lab because the extreme heat required for the measurement bleaches the blue color. It is possible to scrape a small quantity of material from the edge of the stone to make the measurement, about 500 micrograms is ideal. Although a small amount of repolishing where the stone was sampled would remove the scrape marks, even this method is not suitable for routine testing because of the time involved in sample preparation.

ADDITIONAL EXAMPLES OF RADIATION-INDUCED COLOR IN MINERALS

Radiation plays a role in the coloration of many other minerals as well. For example, common salt, the mineral halite [NaCl], is one of the substances most often used in studies of radiation damage. An amber color develops when salt is exposed to gamma rays, and with a high enough dose the salt can be turned black. It is important to remember that salt, like all minerals, does not become radioactive when irradiated by X-rays or by the more energetic gamma rays.

Fluorite is frequently colored by natural radiation. Rare earth elements such as cerium, samarium, and europium are often present in fluorite and respond to irradiation by producing specific colors. For example, radiation will reduce samarium from the $\text{3}^+$ to the $\text{2}^+$ oxidation state and impart green to the stone (Bill and Calas, 1978).

Smoky quartz (figure 19) results from the application of radiation to quartz, which contains aluminum as a minor impurity. Detailed studies have indicated that additional mechanisms also contribute to a smoky color in natural and synthetic samples (Nassau and Prescott, 1977). Colorless quartz crystals that have been irradiated to produce the smoky color have found commercial acceptance as mineral specimens and, in some markets, as gemstones.

Amethyst (figure 20) results when quartz with minor amounts of iron is irradiated either in nature or artificially (Cox, 1977; Hassan, 1972). The mechanism is believed to involve oxidation of the iron by radiation from the $\text{3}^+$ to the $\text{4}^+$ oxidation state. When amethyst is heat treated to form citrine, the iron is reduced back to the $\text{3}^+$ oxidation state (Nassau, 1981).

A deep-blue variety of beryl known as Maxixe beryl (figure 21) also derives its color from irradiation (Nassau et al., 1976). This unstable color is thought to form as the result of radiation-induced chemical changes involving carbonate ions in the channels (Edgar and Vance, 1977). If this color could be stabilized and produced in sufficient quantity, the stone would have great potential as a gem material.

What about rubies, emeralds, and sapphires? Radiation treatment does not play a role in their coloration, although heat treatment is being used to modify the color of the corundum gems. A
Amethyst color is the result of the irradiation (natural or artificial) of quartz that contains low concentrations of iron. This is a natural amethyst specimen from Vera Cruz, Mexico.

The deep blue of Maxixe beryl is the result of natural irradiation. The color is unstable.

Golden-yellow corundum can be produced with the use of radiation, but the color is too unstable to be anything other than a laboratory curiosity. Considerable scientific effort has been directed toward the study of color in diamond and its response to radiation (Davies, 1977). Laboratory irradiation of diamond can be used to bring about dramatic changes in color. For example, irradiation of a light- to medium-yellow diamond with gamma rays can produce a green stone (figure 22), which is the result of trapped electrons. If a high-energy electron beam were used to irradiate the same diamond, it might turn blue instead (figure 23). It has been hypothesized that the color difference between gamma-ray and electron irradiation may be the result of local heating of the stone which occurs with electron irradiation. Heat treatment itself can bring about further changes in the color of irradiated diamonds, usually producing various shades of orange through yellow (figure 24). The best yellows that result from heat treatment can rival the best naturally occurring canary diamonds. However, the origin of the artificially induced color is completely different from that of the natural. The latter results from high concentrations of nitrogen in the stone, while the former is a product of a variety of radiation damage centers. Both natural and irradiated yellow diamonds have a high degree of color stability.

CONCLUDING THOUGHTS

Several things should be evident from the discussion above: first, that the color of a gemstone may have one of several origins; second, that many sources of color that occur naturally can be either duplicated or enhanced in the laboratory; third, that our ability to determine the origin of color has increased rapidly as the technologies available to the research gemologist grow in sophistication; and fourth, that the technologies used in gem treatment are also rapidly increasing in sophistication. As interest in colored gems continues to expand, it is likely that identification of sources of color will gain even greater impor-
tance. Particular attention will continue to be
given to the distinction between artificially pro-
duced and natural colors. Whether this distinc-
tion should be a matter of concern is open to dis-
cussion, particularly in the cases where natural
colors are enhanced by artificial means. Ulti-
mately, personal value judgments must be the
deciding factor. Many forms of technological ma-
nipulation of gem materials are totally accepted
today, for example, heat treatment of aquama-
rine, tanzanite, and zircon. Certainly, even grind-
ing and polishing represent substantial, but ac-
ceptable, technological manipulation of the rough
gem stone.

In any event, the study of color in minerals
and gemstones provides us with a wealth of un-
derstanding about the physical and chemical
properties of these materials. Such studies also
establish the scientific basis for technologies that
will be used in the future for the characterization
gem materials, and for their manipulation. As

Figure 22. Diamond turned green by gamma-
ray irradiation.

Figure 24. Heat treatment of irradiated diamonds
produces orange and yellow colors.

the tools of the researcher grow in sophistication,
the gemologist must continue to upgrade his or
her technical sophistication to keep abreast of the
technologies currently being used in both the
manipulation and characterization of gem ma-

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