

# Learn About ...

## THE COLORS OF GEMSTONES

The most common cause of color in gemstones is the presence of a small amount of a transition metal ion. These transition metal ions have an incomplete set of  $3d$  electrons. Changes in the energy of these electrons correspond to the energy of visible light. When white light passes through a colored gemstone or is reflected by it, some of the energy of the visible light is absorbed, causing  $3d$  electrons in the transition metal ion to undergo an energy change. The light that is transmitted or reflected appears colored, because those colors corresponding to  $3d$ -electron energy transitions have been absorbed. The table lists several common gemstones, their chemical compositions, colors, and the origins of these colors.

A ruby is a crystal of alumina, aluminum oxide, containing a trace of chromium(III) ions replacing some of the aluminum ions. In ruby, each  $\text{Al}^{3+}$  ion and  $\text{Cr}^{3+}$  ion is surrounded by six oxide ions in an octahedral arrangement.

Gem	Formula	Color	Origin of color
Ruby	$\text{Al}_2\text{O}_3$	Red	$\text{Cr}^{3+}$ replacing $\text{Al}^{3+}$ in octahedral sites
Emerald	$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$	Green	$\text{Cr}^{3+}$ replacing $\text{Al}^{3+}$ in octahedral site
Alexandrite	$\text{Al}_2\text{BeO}_4$	Red/Green	$\text{Cr}^{3+}$ replacing $\text{Al}^{3+}$ in octahedral site
Garnet	$\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$	Red	$\text{Fe}^{2+}$ replacing $\text{Mg}^{2+}$ in 8-coordinate site
Peridot	$\text{Mg}_2\text{SiO}_4$	Yellow-green	$\text{Fe}^{2+}$ replacing $\text{Mg}^{2+}$ in 6-coordinate site
Tourmaline	$\text{Na}_3\text{Li}_3\text{Al}_6(\text{BO}_3)_3(\text{SiO}_3)_6\text{F}_4$	Pink	$\text{Mn}^{2+}$ replacing $\text{Li}^+$ and $\text{Al}^{3+}$ in octahedral site
Turquoise	$\text{Al}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$	Blue-green	$\text{Cu}^{2+}$ coordinated to 4 $\text{OH}^-$ and 2 $\text{H}_2\text{O}$
Sapphire	$\text{Al}_2\text{O}_3$	Blue	Intervalence transition between $\text{Fe}^{2+}$ and $\text{Ti}^{4+}$ replacing $\text{Al}^{3+}$ in adjacent octahedral sites

This arrangement splits the five  $3d$  orbitals of  $\text{Cr}^{3+}$  into two sets, the  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  orbitals and the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. These two sets have different energies. The energy difference between these sets corresponds to the energy of visible light. When white light strikes a ruby, the gem absorbs the light of energy corresponding to the transition of an electron from the lower-energy set of  $3d$  orbitals to the higher-energy set. The ruby reflects or transmits the remainder of the light. Because this light is deficient in some energies (those that were absorbed), the light appears colored.

The origin of the color of emeralds is similar to that of the color of rubies. However, the bulk of an emerald crystal is composed of beryl, beryllium aluminum silicate, instead of the alumina which forms rubies. The color is produced by chromium(III) ions, which replace some of the aluminum ions in the crystal. In emeralds, the  $\text{Cr}^{3+}$  is surrounded by six silicate ions, rather than the six oxide ions in ruby. These silicate ions also split the  $3d$  orbitals of  $\text{Cr}^{3+}$  into two sets. However, the magnitude of the energy difference between the sets is different from that produced by the oxide ions in ruby. Therefore, the color of emeralds is different from that of ruby.

Chromium(III) also produces color in alexandrite. The color of this gem is very unusual, because in bright sunlight it appears green, but in incandescent light it appears red. This unusual behavior is a result of the way human vision works. Our eyes are most sensitive to green light. Alexandrite reflects both green and red light. In bright sunlight, the proportion of green light is greater than it is in the light from an incandescent lamp. The light reflected by alexandrite in bright sunlight is rich in green light, to which our eyes are most sensitive, and we perceive the gem as green. The light reflected by alexandrite in incandescent light is much richer in red, and we see the stone as red under these conditions.

Energy transition of the  $3d$  orbitals of other transition metal ions are responsible for the colors of other gemstones. Iron(II) produces the red of garnets and the yellow-green of peridots. Manganese(II) is responsible for the pink coloration of tourmaline, and copper(II) colors turquoise.

In some gemstones, the color is caused not by energy changes in a single transition metal ion, but by the exchange of electrons between two adjacent transition metal ions of differing oxidation states. The energy needed to transfer an electron from one ion to another corresponds to the energy of visible light. An example is sapphire. The bulk of sapphire is alumina, as in rubies, but some adjacent pairs of  $\text{Al}^{3+}$  ions are replaced by an  $\text{Fe}^{2+}$  ion and a  $\text{Ti}^{4+}$ . When light of the appropriate energy strikes the crystal, energy is absorbed, and an electron moves from the  $\text{Fe}^{2+}$  to the  $\text{Ti}^{4+}$ . Such a movement is called an intervalence transition. An intervalence transition is also responsible for the blue color of aquamarine. In aquamarine, adjacent  $\text{Al}^{3+}$  ions in beryl are replaced by an  $\text{Fe}^{2+}$  ion and an  $\text{Fe}^{3+}$  ion.

Not all gem colors are produced by transition metal ions. In some gemstones, the colors are produced by the presence of foreign atoms with a different number of valence electrons than the ones they replace. These foreign atoms are called color centers. Because the replacement atoms have the wrong number of valence electrons, they can supply or receive an electron from another atom by an intervalence transition. These color centers are often produced by nuclear transformation. An example of such a transformation is the change of a radioactive carbon-14 atom in diamond into a nitrogen atom through beta particle emission. This leaves an atom of nitrogen in place of the original carbon atom. The nitrogen atom has one more valence electron than the carbon atom. These nitrogen atoms are the cause of the coloration of blue and yellow diamonds. Color centers can be caused

artificially as well, by irradiating the gem in a nuclear reactor. Many bright blue and bright yellow diamonds are produced artificially in this manner.

## **REFERENCES**

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*Scientific American*, October 1980, page 124.