

## 23.1: The Colors of Rubies and Emeralds

Why is a ruby red? The mineral **corundum** is a crystalline form of alumina:  $\text{Al}_2\text{O}_3$ . A pure crystal of corundum is colorless. However, if just 1% of the  $\text{Al}^{3+}$  ions are replaced with  $\text{Cr}^{3+}$  ions, the mineral becomes deep red in color and is known as **ruby** ( $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ ). Why does replacing  $\text{Al}^{3+}$  with  $\text{Cr}^{3+}$  in the corundum structure produce a red color?

Ruby is an *allochromatic* mineral, which means its color arises from trace impurities. The color of an *idiochromatic* mineral arises from the essential components of the mineral. In some minerals the color arises from defects in the crystal structure. Such defects are called *color centers*.

The mineral **beryl** is a crystalline beryllium aluminosilicate with the chemical formula  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ . A pure crystal of beryl is colorless. However, if just 1% of the  $\text{Al}^{3+}$  ions are replaced with  $\text{Cr}^{3+}$  ions, the mineral becomes green in color and is known as **emerald** ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}:\text{Cr}^{3+}$ ).

Why does replacing  $\text{Al}^{3+}$  with  $\text{Cr}^{3+}$  in corundum produce a red mineral (ruby) while replacing  $\text{Al}^{3+}$  with  $\text{Cr}^{3+}$  in beryl produces a green mineral (emerald)?

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of  $\Delta_o$ , which depends on the structure of the complex. For example, the complex  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  has strong-field ligands and a relatively large  $\Delta_o$ . Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain  $\text{Cr}^{3+}$  in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different ( $\text{Al}_2\text{O}_3$  in rubies and  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$  in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes  $\Delta_o$  relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large  $[\text{Si}_6\text{O}_{18}]^{12-}$  silicate rings; this results in decreased d orbital–ligand interactions and a smaller  $\Delta_o$ . Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



A piece of ruby and emerald is shown with a glassy crystalline exterior. Ruby is deep red in color and emerald is deep green.

Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of  $\text{Cr}^{3+}$  impurities in octahedral sites in an otherwise colorless metal oxide lattice.

### Contributors and Attributions

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