the chemistry of color

by Linda Bloomfield

Understanding how to use color can happen in many different ways, including learning what happens at the atomic scale to make the colors we see.

Defining the Terms

Additive Color: Color created by mixing a number of different colors of light, with red, green, and blue being the primary colors making up white light.

Coordination Complex: A central atom or ion surrounded by an array of bound ions or molecules.

Crystal Field Theory: The theory of the color of complex compounds, where there is a central transition metal atom surrounded by electron rich atoms or molecules. These are called coordination complexes and commonly have six-fold or four-fold coordination. In a glaze, the surrounding molecules are silica, as well as sodium and calcium ions. The molecules are linked but disordered and are free to move around in the molten glaze. This movement and behavior of ions affects the color of the glaze.

Ion: An atom or molecule that has lost or gained an electron.

Octahedral: A six-fold coordination central atom surrounded by six equally-spaced ions forming an octahedron.

Orbitals: Regions in which electrons of a particular energy spin around the nucleus. The orbitals are named s,p d, and f.

Subtractive Color: When starting with white light, colorants between the viewers and the light source subtract wavelengths from the light, giving it color.

Tetrahedral: A four-fold coordination central atom surrounded by four equally-spaced ions forming a tetrahedron.

Transition Metal: An element or ion with an incomplete inner electron shell.

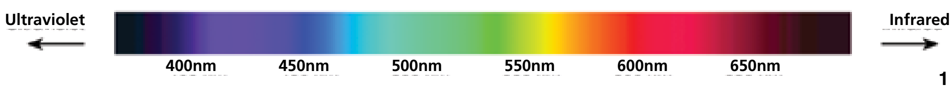
Science of Light

Why are some materials transparent and others opaque? Light can be thought of as a beam of light particles called photons, each one a packet of light energy. When a photon of light hits an atom, it can be absorbed by electrons, which can jump to higher energy levels. This only happens if the light has the right amount of energy required for the electron to jump to a higher level. Light in the form of photons will have a frequency that our eyes interpret as color. The amount of energy of a photon depends on the particular frequency of the light, or its color. In glass, visible light does not have sufficient energy to move the electrons up to the next level, so instead it passes straight through and the glass looks transparent. Light with higher frequency such as ultraviolet (UV) light, does have enough energy, which is why UV light does not pass through glass. In this case, the glass absorbs the energy from the UV light and becomes warmer. The atoms in the glass become excited and vibrate, which can be felt as heat.

Why are Things Different Colors?

The origin of color can be understood by investigating what happens at the atomic scale. Atoms are not colored in themselves. Carbon in graphite (pencil lead) is metallic gray and in its other well-known form, diamond, it is transparent and colorless. The colors we see all around us are the effects of light hitting objects and being partially absorbed. The remaining light that is not absorbed is reflected into our eyes. When the same objects are viewed in different colored light, they appear to be different colors. Transparent, colorless materials absorb no light, while black objects absorb all the light. Because color only exists in the reflected light from an object or in the light that passes through a transparent object, it is accurate to say that when it is dark and an object has no light hitting it, then it has no color. Light is a form of energy, the visible part of the electromagnetic spectrum between ultraviolet and infrared (1). Invisible parts of the spectrum are X-rays, microwaves, and radio waves.

The structure, composition, and impurities in a crystal affect the material's interaction with light and hence its color. Colors in gemstones such as sapphire and ruby are caused by trace amounts of transition metal elements. Both these minerals are crystalline alumina, also known as corundum. In ruby, trace amounts of chromium produce a red color, while in sapphire, iron and titanium cause a blue color. The red color in ruby comes from the way the electron cloud around the chromium atom is affected by the surrounding oxygen atoms in the alumina crystal, which is explained by crystal field theory. However, in the case of sapphire, the blue color comes from the transfer of electrons between the iron and titanium ions when light shines on the crystal.



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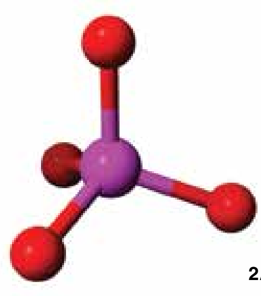
Coloring Glazes

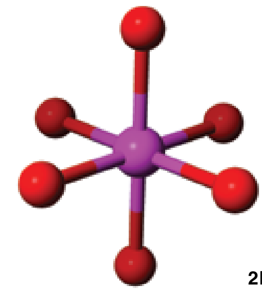
Glazes can also be colored by adding transition metal oxides. The transition metal elements have an inner orbital that is only partially filled, allowing electrons to move between the different energy levels in the same way that a solitaire board has an empty hole to allow the player to move the marbles around. When these elements form oxides or silicates in a glass, the energy levels of their electrons split into two groups. The energy gap corresponds exactly to the wavelength of a certain color of light, particularly (in glazes) yellow, orange, or red light. When light passes through a colored glaze, electrons are able to move from the lower energy level to the higher one by absorbing a specific wavelength of light. The remaining light is the color we see. For example, cobalt silicate in glazes absorbs yellow light, so the reflected light we see is the complementary color, blue. Why don't we see other colors that are not absorbed? When a particular color of light is absorbed, the remaining colors of light blend together and as a result we see the complementary color. Our eyes interpret the combination of blue and red light as purplish cobalt blue.

Transition metals are able to bond with oxygen in either six-fold (octahedral) (2b), or four-fold (tetrahedral) (2a) coordination. Blue cobalt silicate has four-fold coordination while pink cobalt silicate occurs in pyroxene crystals, which have a higher ratio of oxygen to silicon, with six-fold coordination. The color of light absorbed is affected by the shape of the electron cloud around the metal atom and hence the splitting of the energy levels.

In glazes, the fluxes present will also influence the shape of the electron cloud. For example, copper oxide in a glaze fired in oxidation absorbs red light, so the color we see is green. If the glaze is high in sodium and low in alumina, the electron cloud becomes distorted, the energy gap becomes wider, orange light (with higher energy than red light) is absorbed, and the color we see is turquoise. The transition metal oxides tend to give blues, greens, and brown colors in glazes. The glaze color depends on the transition metal, the predominant fluxes in the glaze, and whether it is fired in oxidation or reduction. Red, orange, and yellow are more difficult to produce (in either oxidation or reduction), often requiring industrially produced stains made from cadmium and selenium.



2A



2B

Stains

Stains are made by calcining (heating) together coloring oxides, silica, and some alumina in a kiln. They are ground into a powder that can be mixed into a glaze or used as an underglaze color. The colored stains do not dissolve in the glaze like coloring oxides, but remain suspended as small particles. As they have already been fired, the color usually does not change when fired in a glaze. Blue and green stains can be made by heating vanadium oxide with zirconium silicate. The vanadium is substituted for some of the zirconium and gives a range of blue-green colors. Yellow and red stains are made using cadmium and selenium. The stain particles can be stabilized by including them in a matrix of zirconium silicate. These are known as inclusion pigments or encapsulated stains. Other types of stains, such as chrome-tin pink, are stabilized using tin oxide.

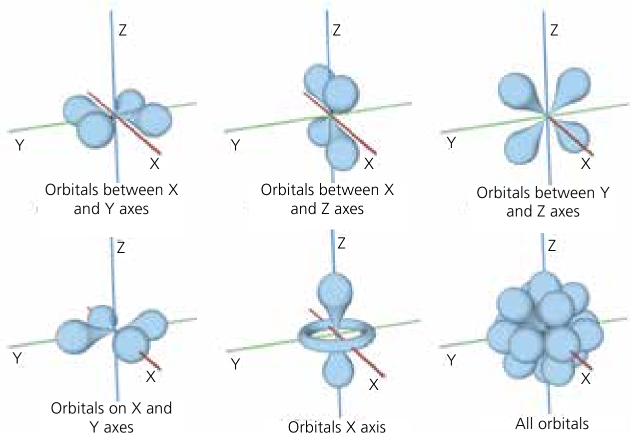
As a result, stains often cause glazes to become more opaque, while coloring oxides will dissolve to give transparent colored glazes. The solubility of coloring oxides increases with firing temperature and the presence of fluxes such as sodium, lithium, barium, and boron.

The Effect Orbitals Have On Color

We have touched on the importance of the shape of the electron cloud around transition metal atoms. Here is a more detailed explanation of why transition metal ions are colored. This is quite complex chemistry but also very interesting and begins to reveal how colors emerge from the ingredients that make up a glaze.

In my "Chemistry for Potters" article (CM February 2016, p. 60) the structure of the atom was described as having electrons arranged in orbitals like planets in the solar system. The orbitals are actually much more complicated. Each shell of electrons contains sub-orbitals, each of which can hold two electrons that, rather than following a path like a planet, can be anywhere within the orbital. Unlike planets, the electrons can act like both particles and waves and can vibrate. The first orbitals to fill with electrons are spherical and are named s orbitals. The alkali metals and alkaline earth metals only have s orbitals in their outermost shell and are called s-block elements. The second set of orbitals to fill are shaped like a figure eight and are called p orbitals. Electrons can be anywhere within in the two lobes of the p orbital. There are three p orbitals, each orientated in a different direction around the nucleus. The third set of orbitals are called d orbitals. These each have four lobes and there are five of them, each arranged in a different orientation, including a strange ring-shaped one (3). The transition metals have d orbitals in their third shell and are known as d-block elements. In transition metals, the s orbitals in the fourth shell start to fill before the d orbitals in the third shell, leaving some of the inner orbitals empty. This is what allows the electron transitions that give rise to color. The electrons need more energy to move into some of the d orbitals than others, absorbing certain colors of light to get there. The rare earth elements at the bottom of the periodic table also have seven f orbitals, which have even more complicated shapes. When all the orbitals are superimposed, the atom looks like a blackberry, with multiple lobes where the electrons are located. Only elements or ions with incomplete d or f orbitals can form colored compounds. The shapes of the d orbitals are important in explaining how some minerals, gemstones, and glazes appear colored.

When coloring oxides are fired in a glaze, they react with the silica to become silicates and the electron cloud around each coloring metal atom changes from the arrangement in an oxide to a different arrangement in a silicate. This is why coloring oxides usually change color upon firing. Once the glaze has cooled and solidified with a particular arrangement of atoms, the color is locked into the glaze.



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the author *Linda Bloomfield studied engineering at Warwick University, with a year at MIT during her PhD studies. She started her pottery career while living in California, and became familiar with US potters' materials. She now lives in London, where she makes porcelain tableware and writes pottery books.*

1 The color spectrum of visible light showing the wavelength in nanometers). A shorter wavelength means higher energy. **2A** Tetrahedral arrangement, with metal atom e.g. cobalt in the center. The red atoms are oxygen. This arrangement with cobalt gives a blue color in glazes. **2B** Octahedral arrangement, with metal atom e.g. cobalt in the center. The red atoms are oxygen. This arrangement with cobalt gives a pink color in glazes. **2A, 2B** *Diagrams by Elin Barrett.* **3** Transition metals have unfilled inner orbitals, called d orbitals. Up to two electrons are located in each orbital. There are 5 d orbitals, each orientated in a different direction. When they are superimposed, the electron cloud looks like a blackberry. **1, 3** *Diagrams by Henry Bloomfield.*