# **Glass Processing Course**

# Lecture 4. COLOR IN COMMERCIAL GLASSES



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Contributions to Observed Color

- Absorption/Reflection Spectrum of Material (transparent, opaque, diffuse scattering)
- Spectrum of Light Source (various light bulbs, sun, etc.)
- Spectral Detection Sensitivity of Eye (most sensitive to green/yellow, least at violent and red ends)

Contributions to Light Beam

S + T + A + R = 100%

S = Scattering (surface and bulk)

T = Transmission

A = Absorption (bulk)

R = Reflection (surface, e.g. coatings)

#### **Beer-Lambert Law**

A = CEL

A = Absorption (log 1/T)

- C = Concentration
- E = Extinction Coefficient
- L = Sample Thickness

Color Sources

- Ionic (charge transfer, ligand field)
- Metal Colloids (Au, Ag, Cu, As, Sb, Pb, others)
- Semiconductor Particles (primarily Cd based)
- Insulator Particles (opal glasses)
- Defects (radiation, solarization)

# Iron in Glasses

- Most common colorant in commercial glasses
- Produces varying shades of green in flat glass
- Produces green and amber in container glass
- Produces color via both charge transfer and ionic absorption processes
- Most common impurity in naturally sands used in commercial glass production
- Iron is used not only to produce colors but also to control ultraviolet and infrared transmission of commercial glasses
- Concentration and redox control used to vary color and transmission window of glass

#### Spectrum of Ferric/Ferrous Ions in Silicate Glass



Visible coloration due to iron

Ionic absorption by ferric and ferrous ions due to ligand field effects results in 3 bands due to ferric ions (385, 420, 435 nm) and one band due to ferrous ions (1050 nm). The extinction coefficients for these bands are much smaller than for the charge transfer bands, lying in the range of 1 to 10, with that of the 1050 nm ferrous ion band being about an order of magnitude greater than that of the strongest ferric ion band at 385.

These bands control the color of the most common commercial flat glasses.

#### Edge View of Float Glass Colored with Iron Oxide



#### Effect of Iron Oxide Content on Color of Float Glass Flat View



#### Effect of Iron Oxide Content on Color of Float Glass Edge View



# Absorption in UV

Both ferric (225 nm) and ferrous (200 nm) ions cause charge transfer bands in the ultraviolet region. These bands have extinction coefficients in the range of1000 to 2000, resulting in very strong absorptions for very low concentrations.

These absorptions provide considerable protection from uv rays. Since iron is such a common impurity in sands, the apparent uv edge of commercial glasses occurs at about 310 nm and is due to the tail of these bands and not due to the inherent uv edge of the base composition.

"Water white" glass production requires elimination of most of the iron oxide impurities.

# Effect of ferric ions on color

The most intense band due to ferric ions lies just outside the visible at about 385 nm. The tail of this band into the visible, combined with lesser absorption due to the other two ferric bands removes the blue-violet light from the transmitted beam, resulting in a yellow-green color, as shown by the sample on the left in the earlier figure.

The production of highly oxidized flat glass is limited to applications requiring a maximization of absorption of uv and visible light at the high energy end of the spectrum. The color is not particularly pleasing to the eye and is not very useful for most common applications.

# Effect of ferrous ions on color

The most intense band due to ferrous ions lies well outside the visible at about 1050 nm. This band is very broad, with a tail that extends well into the visible, removing or reducing the red, orange, and yellow contributions to the transmitted beam, resulting in a blue-green color, as shown by the sample on the right in the earlier figure.

The production of highly reduced flat glass is limited to applications requiring a maximization of absorption of infrared and visible light at the red end of the spectrum. This color is more pleasing to the eye than that of highly oxidized glass. Balance of ferric/ferrous absorption

Most applications of coloration by iron in flat glass involves balancing the contributions from the two ionic states. The ferric/ferrous ratio can be controlled by changes in raw materials, addition of carbon, or changes in furnace atmosphere.

Replacement of some sodium carbonate by sodium nitrate will increase the relative concentration of ferric ions.

Choice of iron oxide will affect this ratio, I.e.  $Fe_2O_3$  versus FeO.  $Fe_3O_4$  will produce more equal concentrations of the ions.

Balance of ferric/ferrous absorption (cont).

A shift toward ferrous ions can be obtained by adding carbon to the melt, e.g. powdered coal, sugar, sawdust, etc.

The iron can be added as a carbon containing salt such as an oxalate.

The atmosphere can be adjusted by changing the oxygen/fuel ratio. While this can be done in a melting furnace, it may be difficult to bring the melt to equilibrium with the atmosphere. On the other hand, glassblowers routinely change the atmosphere when using a torch.

#### Why change the color?

Production of glass for table tops, shower doors, and many other objects requires as little color as possible ("water white"). These glasses are made by using the lowest iron oxide content sand available.

Window glass typically contains a small increase in concentration of iron above that from the other raw materials. By adding iron oxides, variations in raw material lots can be compensated. These glasses are light green, with only slight color showing in typical 6 mm thicknesses. When viewed on edge, these glass are very green (as a function of optical path length).

Automotive glasses contained more iron. Protection from uv damage to plastics is obtained from ferric ions, while a high content of ferrous ions will aid in controlling the temperature inside the vehicle from exposure to sunlight.

Greenhouse glass requires high uv transmission, while infrared transmission is minimized to prevent overheating.

## Bottle glass (clear, green, amber)

Clear glass is produced using low iron raw materials. The faint green from low iron sand is often not noticeable due to the thin wall of the bottle.

Green glass is produced in different shades as described above by controlling iron concentration and ion ratio. In many cases, chromium is added to make other green shades. Copper can also be added in some cases for special colors.

Amber (brown) glass for beverages and pharmaceuticals is designed to prevent uv damage to contents. The amber color results from a iron-sulfur chromophore, with multiple proposed models to explain the absorption. All models do involve charge transfer. Replacing S by Se will result in a black glass.

#### Amber glass spectrum



#### Other ionic colors

Cobalt - blue, largest extinction coefficient of ionic colorants, use low concentration or glass will be so dark that it is effectively opaque in common thicknesses.

Chromium - green in soda lime glasses due to balance between yellow green of hexavalent ions and emerald green of trivalent ions. Highly oxidized glass are an unpleasant yellow green. Reduction of hexavalent content is obtained by reduction by atmosphere or use of a reducing agent to produce more attractive color.

Manganese - purple due to trivalent ions. Equilibrium exists with divalent ions, but extinction coefficient for trivalent ion is roughly 100 times that of the covalent ion.

Cobalt oxide spectrum



### Cobalt blue glass

- The sample shown is about 1/2 inch thick and 2 inches wide. It contains less than 100 ppmwt of CoO.
- Upper photo shows color when viewed from top surface.
- Lower photo shows effect of viewing through the edge, i.e. longer path length.





#### Nickel oxide spectrum



Nickel -- brown in soda lime glasses. Yellow in lithia lime glass, purple in potash lime glass. Blue in crystallized aluminosilicate glass.



#### Previous samples in transmitted light.



#### Copper oxide spectrum



Copper glasses are blue or green, depending on base glass composition. Replacement of sodium by potassium will shift the absorption band toward the infrared and the resulting color toward green. Color is due to divalent ions. Monovalent ions are colorless, but will fluoresce white light.



# Effect of CuO concentration on color of glass.



#### Chromium oxide spectrum



# Rare Earth Colors

Many of the rare earths (lanthanides) are used as coloring agents. The cost of these oxides, however, generally prevents their use in mass quantities. They are primarily used in small quantities of glasses produced for glassblowers and other glass artists and in the production of glass lasers.

Nd is an exception to this rule. A low concentration of Nd is found in light bulbs designed for home lighting. These bulbs have a faint bluish color. Nd is also used to produce a very wide range of glass lasers, including the massive system used for at LLNL for laser fusion studies.

# Rare Earth Colors

The color produced by the rare earth ions is due to ligand field effects within the 4f shell. Since there are 7 f levels, the spectra produced by these ions are much more complex than those produced by the 3d transition ions. Two examples are shown on the next slide.

The large number of sharp bands makes prediction of the color induced by these ions quite difficult. Since the 4f levels are not the outermost levels in these ions, colors produced by the rare earth ions are relatively independent of the overall glass composition. Most of these ions only exist in the trivalent state in glasses, so redox conditions have no effect on their colors. Many of these glasses are dichroic, exhibiting different colors under different lighting conditions. In some cases, their color is dependent on concentration and glass thickness.

# Spectra of Er and Sm ions in glasses



#### Colors of some rare earth glasses



# Nd laser glass



# **Colloidal Colors**

Metallic colloids (Au, Cu) dispersed in glasses are the primary source of red glasses. Silver colloids produce a variety of yellow to brown colors. Colloidally colored glasses have been produced for around 2000 years for art objects and are still routinely used by glassblowers and other glass artists.

The color is produced by a process known as plasma resonance, which results in extremely large extinction coeffs. In the range of 10,000 to 100,000. Very small quantities of colloids are needed to produce strong colors.

Other metallic colloids produce either grey to black (Pb, Co, Ni, In, Bi) or brown to black (As, Sb) glasses. The Pb glasses are used in a number of special optical applications.

# Striking the color

The color can be produced from melts containing the ions of the colorant or by diffusion on those ions into the surface of the glass. Silver, gold, and monovalent copper ions do not produce color. The ion must be reduced to the atomic state, followed by diffusion to grow colloids before color appears. The process of producing the color is known as striking.

The glasses used to produce bulk colloidal colors also contain an easily oxidized ion. The most common ions used are those of tin. At melting temperatures, the redox couple between Au and Sn, e.g., results in ionic Au and stannous ions. If the glass is held at a temperature in the upper transformation range, the couple reverses to form atomic Au and stannic tin. The atomic Au rapidly diffuses to grow into colloids. Similar processes are used for producing Cu rubies and Ag yellows.

# From left to right - Au, Cu, Au colloidally colored glasses



# Transmission spectra for glasses containing Ag or Cu colloids



# Lead Colloids in an optical fiber preform. Color produced by heating in hydrogen gas.



#### Surface colloids

Production of colloids in the surface of a glass provides a more controlled method for coloring glass. The silver colloid yellow glasses shown earlier were produced by applying a silver film to one half of a glass sample.

The light yellow glass is a microscope slide. After applying the silver, the sample was heated in air to 500° C to allow interdiffusion of Ag and Na ions. The sample was the reheated in hydrogen to reduce the Ag and strike the color.

The dark yellow and red glasses were produced by sputtering silver or copper films on the tin-rich side of float glass and then heating in air to introduce the Ag and Cu ions into the glass. Reaction of these ions with the Sn in the glass strikes the color.

#### Semi-conductor colors

Semi-conductor crystals in glasses produce color if the band gap lies in the visible region. Photons with energy greater than the band gap are absorbed with high efficiency (large extinction coeff.) while those with less energy are not absorbed at all. This resuls in sharp cutoff in the transmission curve, as shown on the next slide. Since CdS forms a continuous solid solution with both CdSe and CdTe, semiconductors of any desired band gap can be produced. Colors can be very fine tuned within the yellow, orange, red portion of the spectrum, as shown by the rods in the figure. These samples are produced for use by glassblowers, but commercial optical cutoff filters of very precise wavelengths are also produced by this method.

## Striking of semi-conductor colors

Semicondutor colored glasses are produced using a method similar to that of the metallic colloids. The glass is melted at temperatures above the melting point of the semiconductor crystal. After cooling, the glass is reheated to a temperature where crystallization will occur, striking the color.

It should be noted that Cd, Se, and Te have varying degrees of toxicity. These elements are well contained in the solid glass, but the vapor released during glass working, or the use of fine powders, can release these chemicals. Handling should be done with care.

# Spectra of Cd(S,Se,Te) filters



# Cd(S,Se,Te) Colored Glasses



Defects in glasses can absorb photons by electron transfer processes. The defects are usually formed by exposure to radiation at uv or higher energies. Defect formed by exposure to sun light are said to result from solarization, with use of higher energies is usually termed radiation damage.

High energy radiation removes electrons from ions, forming hole centers. Most of these centers absorb in the uv and thus do not contribute to color. Aluminum impurities in silica form AIOHC, which absorb in the center of the visible, producing purple glasses. Other center can form in other glasses, usually resulting in brown glasses.

# Solarization

The classic solarization defect is found in old soda-lime-silica glasses exposed to many years of sun light. At one time, glass was "decolorized" by adding  $MnO_2$  to the melt. The purple color from trivalent Mn "filled in" the iron spectrum. In addition, redox between ferrous ions and tetravalent manganese ions resulted in oxidation of ferrous ions to less strongly coloring ferric ions, while the Mn ions were reduced to the colorless divalent state.

Exposure to uv light slowly photo-oxidizes the divalent Mn ions to trivalent ions, increasing absorption in the visible and yielding a purple glass. Modern glass no longer show this effect since Mn is no longer used as a decolorant.

#### Coloration of Vitreous Silica due to AIOHC



Silica irradiated to different doses (upper 2 samples) and an irradiated borosilicate glass (brown sample).



# Opal glasses

Opal glasses are produced by light scattering from interfaces within the glass. If the particles are comparable in size to the wavelength of light or larger, they scatter light by reflection and refraction processes, which are roughly independent of wavelength, resulting in a white, opaque glass.

Phase separation results in two intermixed glasses of different refractive indices. Since the indices are different, scattering occurs at the interfaces. If the scale of the separation is very fine, the scattering will be wavelength dependent and the glass will have a bluish tone in reflection and orange in transmission. If the scale is larger, wavelength independent scattering results in opal glass.

#### Phase Separated Lithium Borosilicate Opal Glass

