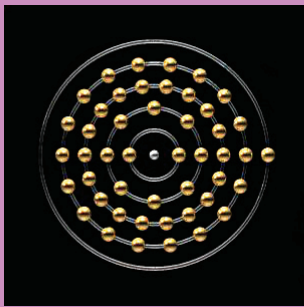


Amber/Purple Glass— A Molecular Approach

by Jesse Kohl

Having been schooled in the art of lampworking by two colorists, my passion for glass has spanned the horizons of both the artistic and scientific skies. I first began blowing glass at the age of fourteen under the tutelage of Paul Trautman Jr., the founder of Northstar Glassworks. My training in lampworking continued under the watchful eye of Suellen Fowler, who schooled me in the art of hand mixing color. In conjunction with my pursuit of lampworking, I devoted much of my time throughout my high school and early college years to the development and study of colored borosilicate glass. While acting as the technical director of Northstar Glassworks, I had the privilege to further study these glasses in an industrial setting.

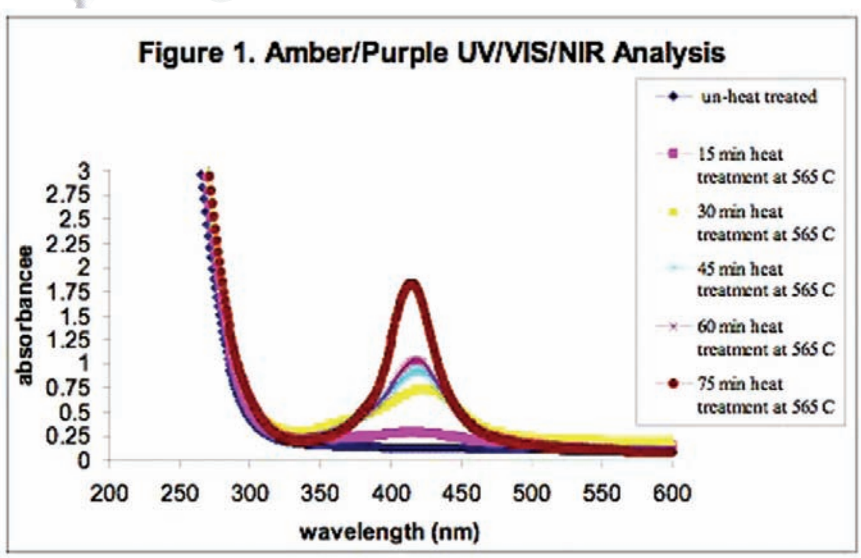
These invaluable experiences imbued in me a drive to gain the education necessary to develop an understanding of these glasses on a molecular level. While at Bard College, I majored in chemistry and devoted my senior thesis to the study of silver- and germanium-containing sodium borosilicate glasses. In the lampworking community, these glasses are known as the "Amber/Purples." This study was conducted in cooperation with Corning Incorporated and was undertaken at their Sullivan Park Research Facility in Painted Post, New York. The project was advised by one of Corning's distinguished glass scientists, Dr. Matthew J. Dejneka, and supervised by Dr. Kim Touchette of Bard College. This unprecedented study refutes the currently proposed theoretical understanding of these glasses and offers a chemical explanation that is founded in scientific research. This thesis not only establishes a comprehensive understanding of the color-generating mechanism displayed by these glasses but also the chemical role of germanium dioxide in this reaction.

The intent of this article is to summarize the findings of this study and offer the lampworking community a more complete scientific understanding of these alluring colors. Though this information is not central to working glass, I believe it is imperative to share this knowledge so as to broaden our collective understanding of this timeless medium.

Color Generation

In virtually all silver-containing glasses, color is generated by the formation of randomly distributed spheres of silver metal that range in size from five to thirty nanometers (nm) in diameter. The resultant color is a deep honey/amber brown that gives rise to an absorption peak centered at 410 to 420 nanometers. This color arises when a beam of light passes through the glass and collides with the nanosized particles of metallic silver. This collision causes the light to scatter, which gives rise to the color. This type of scattering is called Mie scattering. It is similar to Rayleigh scattering, the phenomenon that makes the sky appear blue. The quantity of metallic silver nanospheres determines the percent of absorbance (intensity) and the size of the particles determines the frequency of the absorbance (resultant color). Only silver-halide glasses give rise to color-generating crystals.

In the amber/purple glasses, it was found that two color-generating phenomena simultaneously take place. In the core of the glass, it was determined that color was generated solely by metallic silver nanospheres. This was first determined by conducting a UV/VIS/NIR spectrophotometer analysis of these glasses. It was found that when the glass was colorless and transparent, it absorbed no light in the visible spectrum. The longer the glass was heat-treated in an electric annealing oven, the greater the absorbance at 420 nm became and, in turn, the darker the color became (see fig. 1). This experiment confirms that the striking process gives rise to the formation of metallic silver nanospheres. The longer the glass is struck, the larger and more numerous the metallic spheres become.



Amber/Purple samples prepared for UV/VIS/NIR analysis. From left to right: 1.) Not heat-treated. 2.) Heat-treated for 15 minutes at 565°C. 3.) Heat-treated for 30 minutes at 565°C. 4.) Heat-treated for 45 minutes at 565°C. 5.) Heat-treated for 60 minutes at 565°C. 6.) Heat-treated for 75 minutes at 565°C.

The presence of metallic silver nanospheres was also confirmed by looking at these samples under magnification on the order of 100,000 times with a transmission electron microscope (TEM). When the glass was completely unstruck and colorless, there were no metallic silver nanospheres detected (see fig. 2). In the heat-treated samples, however, large quantities of metallic silver nanospheres were detected (see fig. 3).

Figure 2

Figure 2 is a TEM image of unstruck amber/purple glass. Note that there are no dark splotches. This indicates that there is no metallic silver present.

Figure 3

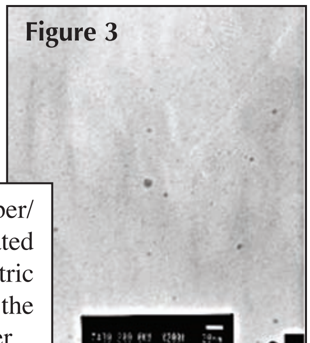


Figure 3 is a TEM image of amber/purple glass that has been heat-treated for 120 minutes at 565°C in an electric oven. The small dark splotches in the image are spheres of metallic silver.

The second color-generating phenomenon that was found to take place in amber/purple glass is the surface precipitate that forms under reducing conditions. In the lampworking community, this layer has been referred to as a "film" or as a "haze." By an electron microprobe analysis (EMPA), this layer was determined to be composed solely of large deposits of metallic silver spheres on the surface of the glass.

Figure 4

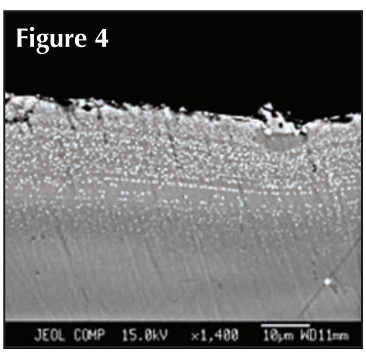


Figure 4 shows an EMPA cross-sectional view of a heat-treated amber/purple sample. The small white dots that are aligned on the surface edge of the sample and fan into the sample core are composed solely of metallic silver.

This surface cladding is what gives the amber/purple glasses their signature range of colors. The resultant color is determined by the thickness of the surface cladding. When the cladding is very thin, the color is a brilliant purple hue. As the cladding becomes thicker, the color shifts to a smoky blue and then turns to a more metallic sheen. In this case, the color is generated by light hitting the surface and being partially reflected. This is referred to as interference. The thicker the layer, the more the light is reflected. If the layer of metallic silver were thick enough, these amber/purple glasses would resemble a mirror. By heat-treating amber/purple glasses in a tube furnace under reducing conditions for specific durations of time at specific temperature, the thickness of the metallic silver layer and thus the resultant color could be empirically controlled (see figure 5).

Figure 5 is an image of an Amber/Purple glass that has been heat-treated under reducing conditions. From left to right: 1.) Heat-treated for 50 minutes at 635°C. 2.) Heat-treated for 90 minutes at 700°C. 3.) Heat-treated for 60 minutes at 800°C. 4.) Heat-treated for 120 minutes at 800°C. 5.) Heat-treated for 40 minutes at 875°C. 6.) Heat-treated for 60 minutes at 900°C.

As determined, in both of the color-generating phenomenon that take place in the amber/purple glasses, it is solely metallic silver that gives rise to color. No color-generating crystals were detected in any samples.

The Role of Germanium

Based on previous research and observations made by Suellen Fowler, it was found that when there is insufficient germanium, the color generating reaction could not be easily controlled. The glass cannot be returned to the unstruck, colorless state upon remelting. Instead, the result is a muddy amber/brown color. When there is no germanium, silver forms poorly distributed metallic clumps, and only a pale yellow color results. This suggests that there is a chemical reaction that takes place between the silver and the germanium. It is known that when a silver-containing glass is colorless, the silver is in the (+1) oxidation state. Therefore to generate color, the colorless silver (+1) must be reduced to the color generating metallic silver (0). Because the color can be generated and also depleted numerous times, that indicates that the oxidation state of silver shifts back and forth from the colorless (+1) state to the colored (0) state. This type of reaction that involves the transfer of electrons is referred to as a redox reaction.

Because this reversible color-generating reaction could occur in an inert environment (under nitrogen), it indicates that within the glass itself there is a constituent present that can donate and also accept electrons from the silver. It was determined that germanium is the constituent that facilitates the flow of electrons to and from the silver. When amber/purple glass is melted, electrons from the metallic silver flow to the germanium. This, in turn, causes the silver to reside in the colorless (+1) state. When a molten sample of amber/purple glass is rapidly cooled (in water), this colorless state can be observed. When the molten amber/purple glass is slowly cooled or heat-treated at or above the annealing temperature, electrons from the germanium flow to the silver. This facilitates the formation of color-generating metallic silver spheres. In summary, germanium is the redox couple for the silver in the amber/purple glasses. In addition, germanium does not play any role in the actual observed color, nor does it act as a nucleating agent. In other words, germanium is the silent partner that facilitates the reversibility of this color-generating reaction.

This chemical reaction between silver and germanium was proven with a complex series of experiments that employed numerous analytical techniques. Fully reviewing these experiments would go beyond the scope of this article. This relationship between silver and germanium, however, can be clearly demonstrated by a composition overlay map generated by an electron microprobe analysis (EMPA) of the amber/purple glass (see fig. 6). This map illustrates that the metallic spheres of silver form only at the face of or near the germanium-rich regions. There were no pockets of metallic silver found at any great distance from the germanium.

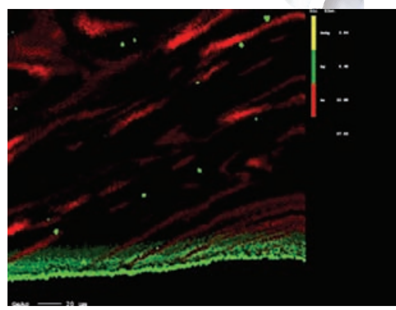


Figure 6 is an EMPA-generated overlay map that is composed of the silver and germanium composition maps. Note that metallic silver (green) always appears in close proximity to the germanium-rich regions (red).

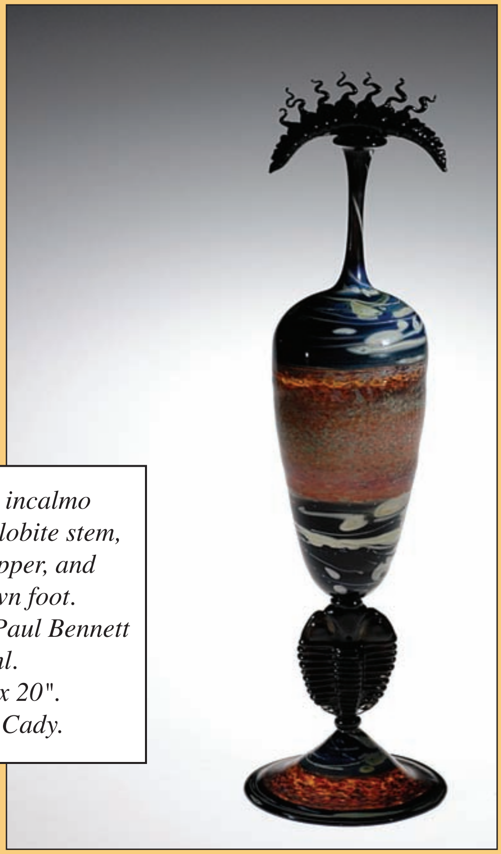
Conclusion

In offering this glimpse into the molecular workings of these glasses, it is humbling to think of the chemical mysteries yet to be unlocked. It is with that thought that I urge all to continue to question the boundaries that are set forth, break them when necessary, and be forever inquisitive. Since I first put a rod of amber/purple in the flame, I was tantalized by what unfolded before me. Being driven by that fascination and having the opportunity to tackle the mystery has been a powerful and rewarding experience. I extend my deepest gratitude to my mentors, Paul Trautman Jr. and Suellen Fowler, for the generous sharing of their knowledge and passion for glass. I thank Dr. Matthew J. Dejneka and the people of Corning Incorporated for their generous efforts in facilitating and funding this project. I would also like to extend my gratitude to the late Charles Byles for his encouragement and support of this project.

FLOW

Jesse Kohl began working glass at the age of fourteen under the tutelage of Paul Trautman Jr. at Northstar Glassworks in Tigard, Oregon. He then studied under Suellen Fowler and has acted as her teaching assistant at numerous classes. In conjunction with developing colored glass while employed as the technical director of Northstar Glassworks, Jesse has offered classes in the John Burton method of flameworking and has played an active role in the creation of the Northstar Boro News Newsletter.

Mr. Kohl has taught at Corning Glass and The Hadamar Glass School in Germany, and has served as a demonstrator at the New Orleans Glass Art Society (GAS) conference, the 2005 International Society of Glass Beadmakers (ISGB) conference, and the Glasstec convention in Germany. Jesse is a recent graduate of the chemistry program at Bard College and plans to earn his PhD in a field relating to glass technology.



Collaborative incalmo vessel with trilobite stem, sculptural stopper, and matching blown foot. By Jonathan Paul Bennett and Jesse Kohl. Height:Approx 20". Photo by Ann Cady.