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products of chemistry

Glass and Glassmaking

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Glasses have been formed by the rapid cooling of magmas and lavas throughout the history of the earth. Obsidian, which is a black glass commonly used for primitive cutting tools and arrowheads, is probably the best known example. Glasses of different chemical composition have also been recovered from both the moon and from meteorites. They have yielded important insights into the genesis of the solar system.

Although the history is unclear, synthetic glass was probably first produced in Egypt at least 3500 years ago, primarily for decoration. By the Roman period, techniques for blowing glass had been developed, and glass items became relatively common. Since then glass has continued to evolve from a unique, decorative material to a common material with a wide variety of uses. This evolution is due partly to scientific investigations by a diverse group of researchers from a variety of disciplines.

Despite the prevalence of glass, researchers cannot agree on a satisfactory description. It is most commonly identified as "an inorganic product of melting that has cooled to a rigid state without crystallizing" (*1*). This description is not entirely satisfactory because organic glasses are well-known. Also, glasses can be formed from a variety of alternative methods, including evaporation from solution and vapor deposition. Still the definition is adequate for the vast majority of cases.

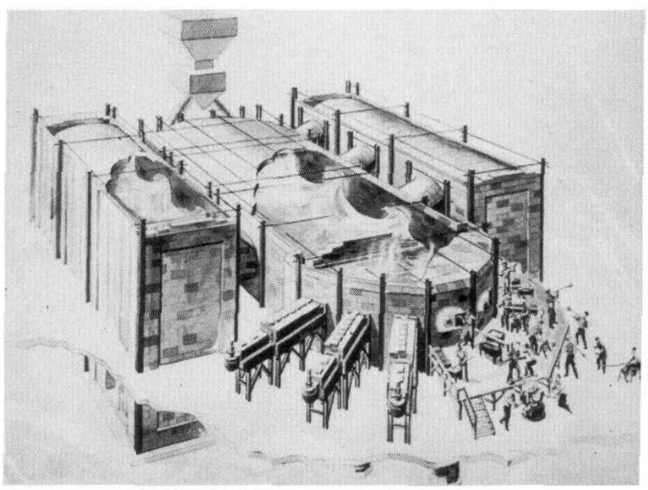

Figure 1. Illustration of a gas-fired, continuous melting glass furnace. Batch is added and melted at the rear and cooled to forming temperatures at the front. Then it is removed and formed. Obviously, most modern glass-melting facilities are far more complex and mechanized than this early illustration.

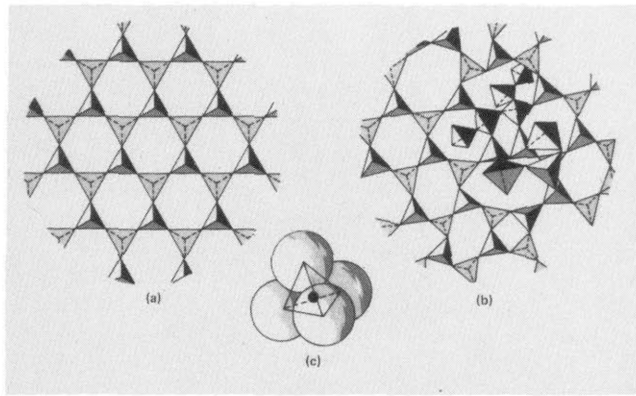

Figure 2. (a) Structure of crystalline SiO_2 (b) Schematic structure of SiO_2 glass (c) The tetrahedra shown in (a) and (b) represent a silicon atom (filled circle) coordinated by four oxygen atoms (large open spheres).

Natural glasses are generally rich in Si. They contain large amounts of other metals such as Fe, Na, K, Ca, Mg, and Al, which are all coordinated with oxygen. Commercial glasses are similar and are usually formed by melting mixtures, or batches, of SiO_2 and other inorganic oxides at high temperature. Such glasses are typically melted in large, refractory-lined, gas-, oil-, or electrically heated tanks, using both minerals and chemicals as batch sources (Fig. 1). Melting units are often continuous; raw materials are continually loaded into the furnace at one end, while molten glass is continually removed from the other end and formed into the desired shape.

Forming can take a variety of forms: blowing, pressing, or casting into molds, drawing from specially designed orifices, and others. In the Pilkington float process, a ribbon of molten glass floats on the surface of a bath of molten tin for enough time to smooth out all surface irregularities. Most of the sheet glass in the world is made by floating.

Glass Structure

The structure of a simple glass is relatively easy to envision. Schematic diagrams of pure SiO_2 glass and crystalline SiO_2 (quartz) are shown in Figure 2. Both materials consist of silicon atoms bonded to four oxygen atoms in a tetrahedral configuration. The crystalline material is distinguished by the presence of long-range order. In theory, knowing the position of one unit cell in the crystal can be used to predict the location of all other atoms. Although

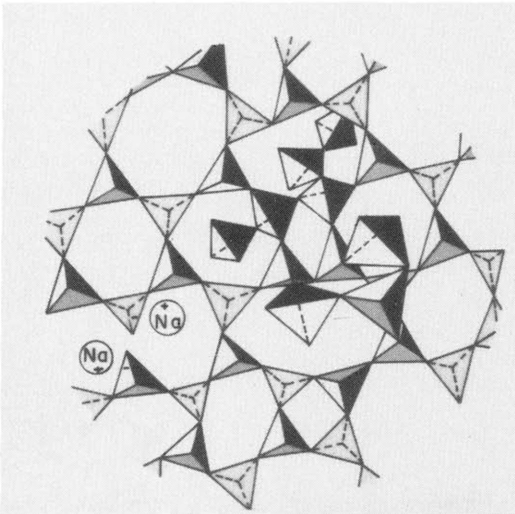

Figure 3. The addition of Na_2O to the glass disrupts the glass network, reducing the viscosity of the analogous melt at constant high temperature.

glass sometimes has an orderly structure over distances of several atomic diameters, it lacks such long-range order.

SiO_2 glass has many desirable properties, including excellent chemical durability, the ability to withstand large and sudden temperature changes, and transparency to a wide range of wavelengths of light. Unfortunately, the melting temperature of SiO_2 is extremely high (1723 °C), and its viscosity makes it difficult to form into usable shapes. As a result, SiO_2 glass can only be formed from a melt with difficulty. One method for lowering both the melting temperature and the viscosity of SiO_2 glass is the introduction of network modifiers (atoms which break the –Si–O–Si– network). In Figure 3, the effect of the addition of Na_2O, a typical modifier, is shown. As the network is broken, glass viscosity and melting temperature decrease, and usable shapes can be formed at practical temperatures.

Most elements of the periodic table can also be incorporated into synthetic glass as either a network former or modifier. This characteristic means that a wide range of physical and chemical properties can be "engineered" into glassy materials simply by varying their chemical composition. As a result, current applications for glass range from the simple (bottles and windows) to the highly complex (telecommunications, liquid–crystal displays, lasers, medical prostheses, and optical computing).

Chemistry of Common Glasses

Although it is tempting to concentrate on the newest applications of glass, the chemistry of simple, everyday items based on glass can be deceptively intricate and interesting. The most common glass composition used throughout the world is a mixture of Na_2O, CaO, and SiO_2, with minor amounts of other oxides. It is appropriately referred to as soda-lime glass. Soda-lime offers a number of advantages over other glass compositions.

Its components are common and inexpensive.
It is resistant to crystallization during cooling.
It melts at relatively low temperatures (about 1300 °C).
It is fairly resistant to atmospheric corrosion.

As a consequence, bottles, jars, window glass, light bulbs, and fluorescent tubing are commonly made using soda lime glass.

Soda-lime glass can also be easily colored. The addition of small concentrations of transition metal ions, for example, causes absorption of light in the visible region of the spectrum due to transitions of 3d electrons. An example is the familiar green color observed looking down the edge of window glass, which is cause by small quantities of Fe^{3+}. Other common colorants are Co^{2+} for blue, Mn^{3+} for purples, and Cr^{3+} for greens. Since transitions in these ions occur in 3d electrons, the resultant colors depend on the environment surrounding the ion. As a result, the colors often change with variations in glass composition. However, the rare earth elements can also be used to color glass, and their electronic transitions occur in inner orbitals. Thus, transitions are not affected by the environment surrounding the ion, and the resultant color is not a function of glass composition.

Soda-lime glass also has some deficiencies. It is not particularly durable. While glass is commonly thought of as an inert material, many glasses are chemically reactive. Possible reactions take many forms, but two are important. In acidic solutions, exchange of H^+ ions exposed to the surface of the glass with alkali ions in the glass can readily occur. This ion exchange often causes formation of an iridescent, soluble layer on the glass surface. Conversely, exposure to basic solutions can disrupt the glass structure by introducing OH^- ions that can eventually cause complete dissolution of the glass. The formation of a white film on glassware after prolonged exposure to dishwasher detergent is a well-known example of the latter process.

Soda-lime glass is also not particularly resistant to high temperatures or thermal shock. Since thermal expansion (change in dimensions with temperature) of soda lime glass is high, sudden changes in temperature can cause undesirable stresses at the glass surface and cracking or breaking.

One solution to these problems was the development of borosilicate glasses. An example of durable, heat-resistant borosilicate glass is Corning Code 7740 glass (Pyrex). Borosilicates have a wide variety of uses, including labware and consumer housewares. Adding B_2O_3 to the glass com-

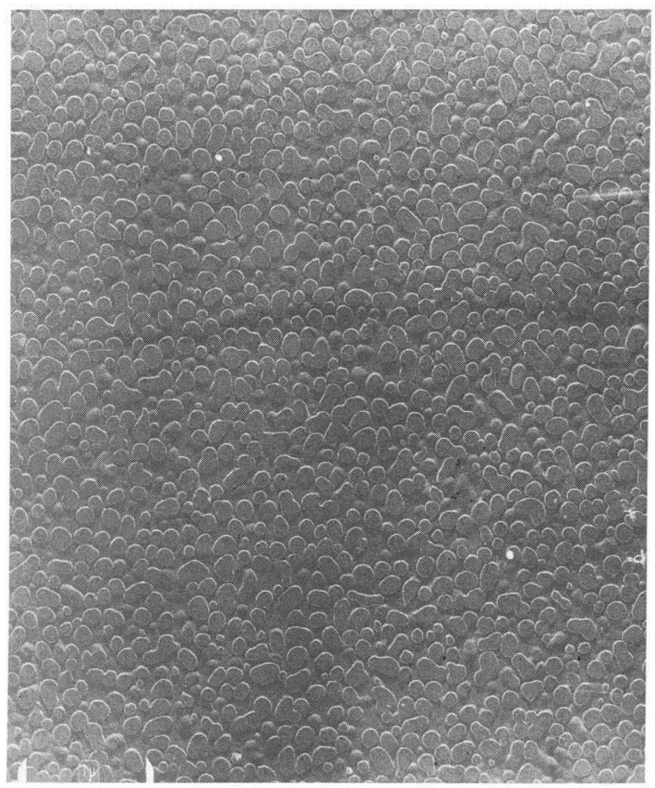

Figure 4. Transmission electron micrograph of a phase-separated (opal) glass. Two discrete glassy phases are evident. One is continuous. The other forms small immiscible droplets. A 1-μ scale is given in the lower left corner.

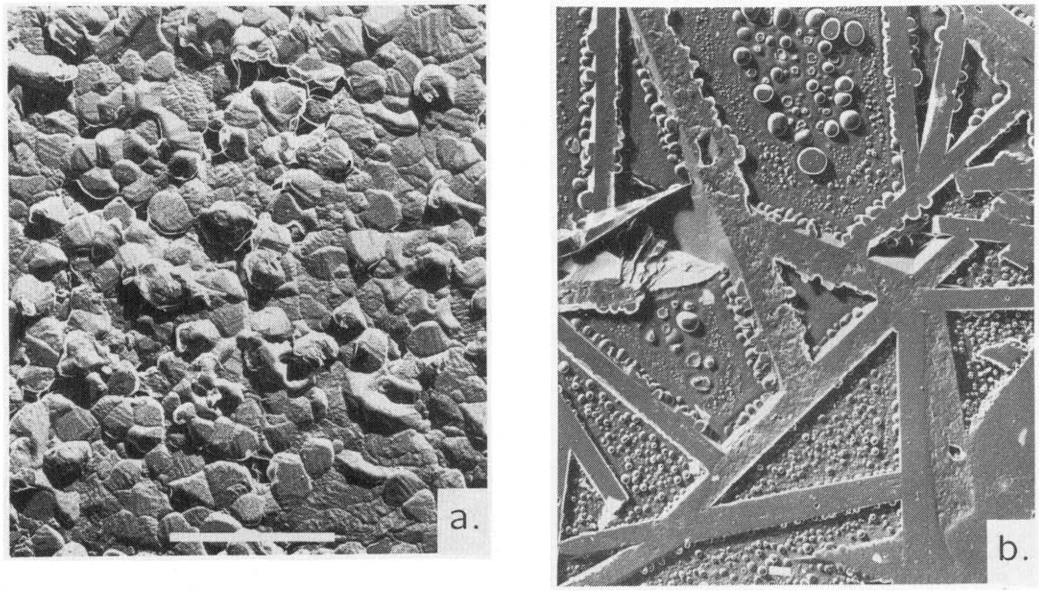

Figure 5. a) Transmission electron micrograph of a stuffed β-quartz glass–ceramic showing the high degree of crystallinity characteristic of these materials. The white bar is one micron long. The combination of small crystal size and low thermal expansion makes the glass–ceramics suitable for many uses such as transparent cookware. (b) Transmission electron micrograph of a fluormica glass–ceramic. The "house of cards" structure of the interlocking elongate flakes of fluormica deflects and blunts cracks, giving a machinable material. The white bar is one micron long.

positions yields two advantages. B_2O_3 lowers the thermal expansion up to 50%, thus increasing the resistance of any article to thermal shock. Also, the durability of the glass is dramatically enhanced.

The causes for enhanced chemical durability in borosilicates are unclear. A prevalent theory is that as the glass cools, it separates into two immiscible phases: a discontinuous phase rich in Na_2O and B_2O_3 and a continuous phase rich in SiO_2 (*2*). Since the SiO_2-rich phase is dominant, the durability of the glass is enhanced without losing the ability to form the glass at reasonable temperatures. Since the diameter of the discontinuous phase is well below the wavelength of visible light, the transparency of the material is maintained.

The phenomena can also be used to create another well-known item: opal glasses. Many glasses are designed to separate into two phases with morphologies such that internal refraction and scattering of light will yield either a translucent or opaque material. Both phases can be glass (Fig. 4), or in some instances, one phase can be crystalline. Examples of opal glasses include some translucent bakeware and thick, white dinner plates.

There are other standard glass compositions. Aluminosilicate glasses have properties similar to borosilicates, but they can withstand higher operating temperatures. Lead glasses have a wide range of applications due to three important properties: high refractive index, easy melting and forming, and shielding of high-energy radiation. The first two properties lend themselves to a variety of applications, including art glass, optical glass, and "lead crystal" (a misnomer for a glass). The latter property is important for applications ranging from radiation windows to television bulbs. Borate, phosphate, germanate, and chalcogenide glasses also have some commercial applications.

Glass–Ceramics

Glass–ceramics constitute a bridge between glasses and crystalline ceramics. Glass–ceramics are best defined as "microcrystalline solids produced by the controlled devitrification of glass" (*3*). Glasses are melted and formed using standard techniques and then heat-treated to produce uniformly grained crystalline materials. Glass–ceramics are distinguished from opal glasses by the degree of crystallinity; glass–ceramics generally contain 50% crystals by volume.

The specific properties of glass–ceramics are controlled by the physical properties of the individual crystals and by the textural relationship between the crystals and the residual glass. As a result, glass–ceramics can offer a wide variety of properties not available in conventional glasses, including strength, machinability, and exceptional thermal-shock resistance (Fig. 5).

An example of this phenomenon is the Corning product Visions made by the heat treatment of Li_2O–Al_2O_3–SiO_2 glass containing small amounts of both TiO_2 and ZrO_2. Upon heat treatment, small crystals of zirconium titanate

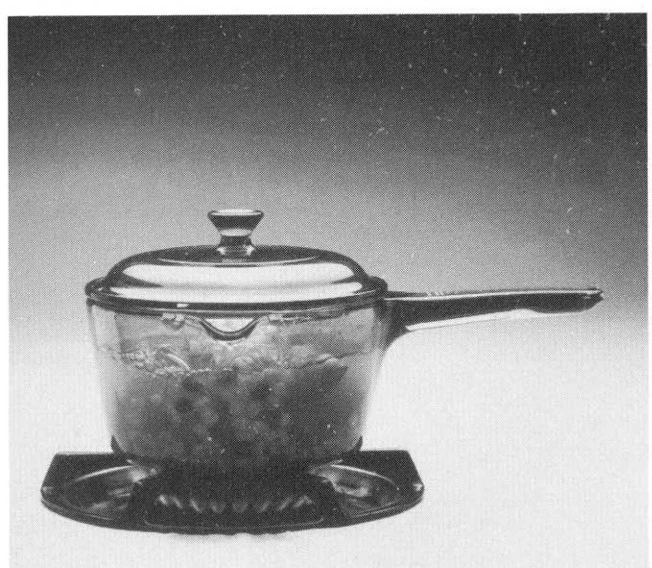

Figure 6. The Corning product Visions is an example of a transparent glass–ceramic formed from glasses in the Li_2O–Al_2O_3–SiO_2 system.

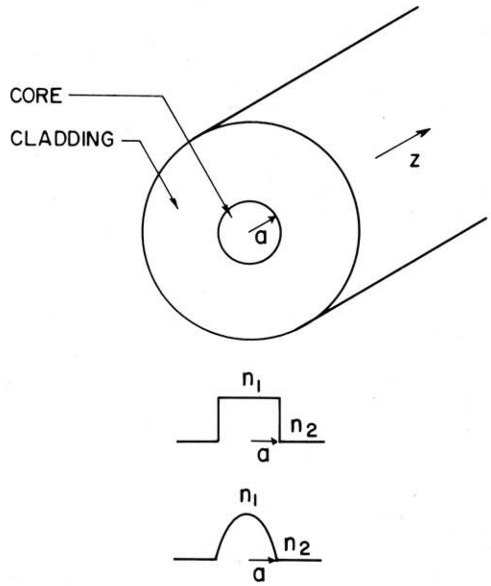

Figure 7. Schematic diagram of glass optical waveguide. The refractive index of the core of the fiber (n_1) is slightly higher than that of the cladding (n_2), with either an abrupt or gradual boundary. Light introduced to the core of the fiber is reflected at the core-cladding interface and is transmitted down the core when light-absorbing impurities are absent. Typically, the fiber is pure SiO_2, with suitable dopants added to lower the refractive index of the cladding glass (e.g., F_2) or to raise the refractive index of the core (e.g., GeO_2). The radius of the core is in tens of microns.

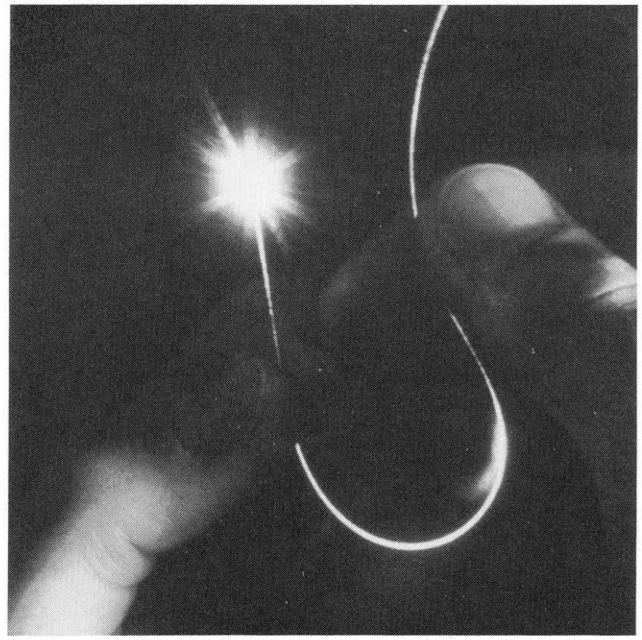

Figure 8. An optical waveguide.

precipitate from the glass and provide nucleation sites for the growth of lithium aluminosilicate crystals from the glass. Since the lithium aluminosilicate crystals (known as stuffed β-quartz) have exceptionally low thermal expansion, these glass–ceramics can withstand the sudden temperature changes associated with stovetop cooking. Furthermore, since the size of each crystal is significantly below the wavelength of light and since the refractive index of the crystals matches that of the residual glass, light scattering does not occur and the materials are transparent (Figs. 5a and 6) (*4*).

Optical Fibers

Finally, one of the simplest glasses (pure SiO_2) is used in one of the most important new glass products: optical waveguides for telecommunications. Such fibers, whose principles of operation are outlined in Figures 7 and 8, require extremely high purity to transmit light over tens of kilometers. Impurities such as transition metals or dissolved H_2O must be avoided at even the part per billion level because they absorb significant quantities of light over long distances. Production of a pure SiO_2 fiber is even further complicated by the difficulties encountered when melting the pure SiO_2 mentioned above.

As a result, SiO_2-based optical fibers are generally formed using an unconventional glass-forming technique: chemical-vapor deposition. In one variant of this technique, outside-vapor deposition, a mixture of $SiCl_4$ and O_2 is burned in a CH_4–O_2 flame. One of the reaction products is amorphous SiO_2 soot, which deposits on the outside of a glass rod. The rod is removed, and the soot is consolidated into a glass by heating at high temperature. The resultant glass is then drawn into a thin, ultrapure fiber (*5*). By controlled addition of other halides (e.g., $GeCl_4$) to the flame, the refractive index profile of the resultant fiber can be controlled with high precision, giving the refractive index profile illustrated in Figure 8.

A variety of other commercial glass and glass–ceramic compositions are sold throughout the world. Both the development of techniques, such as chemical-vapor deposition, and research into the fundamental chemistry and structure of glass continue at a variety of industrial and academic laboratories. There is every reason to expect that this research will continue to manifest itself in many ways that affect everyday life.

Literature Cited

1. Boyd, D. C.; Thompson, D. A. in *KirkOthmer: Encyclopedia of Chemical Technology*; Wiley: New York, 1980; pp 807–880.
2. Doremus, R. H. *Glass Science;* Wiley: New York, 1973.
3. Beall, G. H. in *Commercial Glasses*; Boyd, D. C.; MacDowell, J. F., Eds.; American Ceramic Society: Columbus, 1986; pp 157–173.
4. Beall, G. H.; Karstetter, B. R.; Rittler, H. L. *J. Amer. Cer. Soc.* **1967,** *50*(4), 99.
5. Scherer, G. W.; Schultz, P. C. in *Glass: Science and Technology, Volume 1, Glass Forming Systems;* Uhlmann, D. R.; Kreidl, N. F., Eds.; Academic Press: New York, 1983; pp 49–106.