21

Glass and Glass-Ceramics

CHAPTER PREVIEW

The structure of glass, particularly silica glass, was introduced at the end of Chapter 7. In this chapter, we discuss the different types of glass and some of their various applications. Then, in Chapter 26, we concentrate on processing glass and the wide variations in compositions. We have only two chapters devoted to glass due to space limitations; don't take this as a reflection on its importance. Glass is arguably our most important material. It is used for windows, containers, lenses, optical fibers, insulators, glazing and enameling, surgical knives, spectacular art, and road signs! Glass is usually recyclable and environmentally friendly. The Egyptians were great glassworkers, but they were not the first. Glass was actually used much earlier; and obsidian, a natural black volcanic glass, was important during Paleolithic times. We can say that glass has played a major role in shaping our civilization.

However, there is some difficulty in defining a glass. We discuss why the words glassy, vitreous, and amorphous are all used to describe glass and try to answer the question: what is glass? Two thoughts to keep in mind while studying this chapter:

- The assertion by Sturkey: "glass at high temperatures is a chemical solution."
- If glass is a supercooled liquid, it's not a solid so it's not a ceramic (but it is).

The mechanical, optical, and electrical properties of glasses are discussed in detail, along with other ceramics, in these topical chapters.

21.1 DEFINITIONS

The classic definition of glass is based on the historical method of formation: this is a very unusual way of defining any material. The result is that glass is now defined in several different ways.

The classic definition: *glass is a super-cooled liquid.*
The problem with this definition is that, in some cases, a particular glass can be prepared such that it never has been in the liquid state.

The American Society for Testing and Materials (ASTM) definition: *an inorganic product of fusion that has cooled to a rigid condition without crystallizing.*
This essentially says the same thing as the classic definition but excludes polymer glass. It is clearly not ideal to rely on the method of production to define a class of materials. We wouldn't consider doing this for crystalline materials.

Alternative definition 1: *glass is a solid material that does not show long-range order.*
"No long-range order" means not longer than, say, one, two, or three times the basic building block of the glass. This definition is consistent with experimental observations—e.g., using X-ray diffraction (XRD), transmission electron microscopy (TEM)—but is clearly a little arbitrary because it depends on the size of the building block.

Alternative definition 2: *glass is a liquid that has lost its ability to flow.*
This definition is consistent, but broader, than the one given by ASTM and uses a mechanical property to describe glass. It is actually close to the more modern physicist's view of glass.

The main glasses we discuss are the network oxide glasses, specifically the silicates. Then, our definition of such a glass is:

Alternative definition 3: *a solid assembly of vertex-sharing tetrahedra lacking long-range order.*
We are concerned only with ceramic glass, but you should know that there are metallic glasses and polymer glasses. How metallic glasses are formed gives a clue as to why they exist: they have complicated compositions to "frustrate" crystallization when they are quenched quickly from the melt (a process known as splat quenching). For the same

C.B. Carter and M.G. Norton, *Ceramic Materials: Science and Engineering*,
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reason, glycerin can be a glass below −90°C. With this *understanding* in mind, we can discuss the basic features of glasses.

21.1.1 Structure

Glasses are essentially noncrystalline (or amorphous) solids often obtained by freezing supercooled liquids. Long-range order (LRO) in the atomic arrangement does not exist over distances greater than, say, 1 nm. The regular arrangement resulting from the distribution over long distances of a repeating atomic arrangement (unit cell), which is characteristic of a crystal, is missing. There is often evidence of a short-range order (SRO) in glasses, which corresponds to the atomic arrangement in the immediate vicinity of any selected atom. Numerous attempts have been made to explain the formation or the nonformation of glasses. We have two basic approaches.

- Consider the structure
- Consider the kinetics of crystallization

In the first case, we examine the geometry of the constituent entities that make up the glass, the nature of the interatomic bonds, or the strength of the bonds. In the second, we consider how the liquid transitions to a solid as the temperature drops below the melting point.

21.1.2 Glass Transition Temperature

We consider a plot of specific volume as a function of temperature, as shown in Figure 21.1. This is a form of time–temperature–transformation (TTT) diagram for a glass. On cooling the liquid from a high temperature, two phenomena may occur at the point of solidification, T_m.

- If the liquid crystallizes, there is a discontinuous change in V and a discontinuity in the rate of cooling (associated with the heat of crystallization).
- If no crystallization occurs, the liquid passes into a supercooled state and V decreases at about the same rate as above T_m.

TERMINOLOGY

The words “vitreous”, “amorphous” and “glassy” are not actually synonymous but tend to be used interchangeably anyway.

Vitreous: from the Latin word for glass (*vitrum*)

Amorphous: means having no definite form (Strictly speaking, shapeless from the Greek *amorphos*). Now the lack of “form” implies “not crystalline.” Liquids are generally without form, so a “solid liquid” is amorphous.

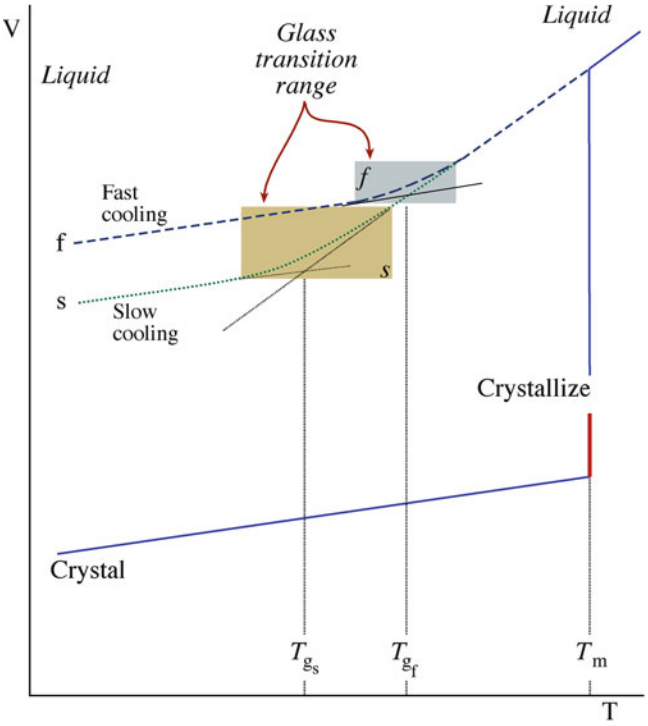

FIGURE 21.1. Plot of volume versus temperature for a liquid that forms a glass on cooling and one that forms a crystalline solid. The glass transition temperature, T_g, depends on the cooling rate and is not fixed like T_M.

At the glass transition temperature, T_g, the slope of the curve decreases to become close to that of the crystalline solid. This break in the cooling curve marks the passage from a supercooled liquid to a glass. Below T_g, the glass structure does not relax very fast because it is now a solid. In the region of T_g, the viscosity is about 10^{13} dPa·s. The expansion coefficient for the glassy state is usually about the same as that for the crystalline solid. If slower cooling rates are used so that the time for the structure to relax is increased, the supercooled liquid persists to a lower temperature, and the resulting glass may have a higher density, as shown in Figure 21.1.

The physics of glass examines the concept of fragility; this is actually a property of glass-forming liquids above T_g and is a measure of the strength of the interatomic bonding. We talk about water dissolving glass or glass containers for water; what is less well know is that you can freeze water into the glassy state by quenching it in liquid ethane. It is a fragile glass, but it is thought that most of the water in the universe exists in this state!

21.2 HISTORY

In Chapter 2, we gave a brief history of glass. We expand on that discussion here. Glass, like flint, is intimately connected with human history because of the use of obsidian, which is a natural glass. Nobody knows for sure when the first glass objects were made. The oldest finds date back to ~7,000 BCE or possibly even earlier. Methods of

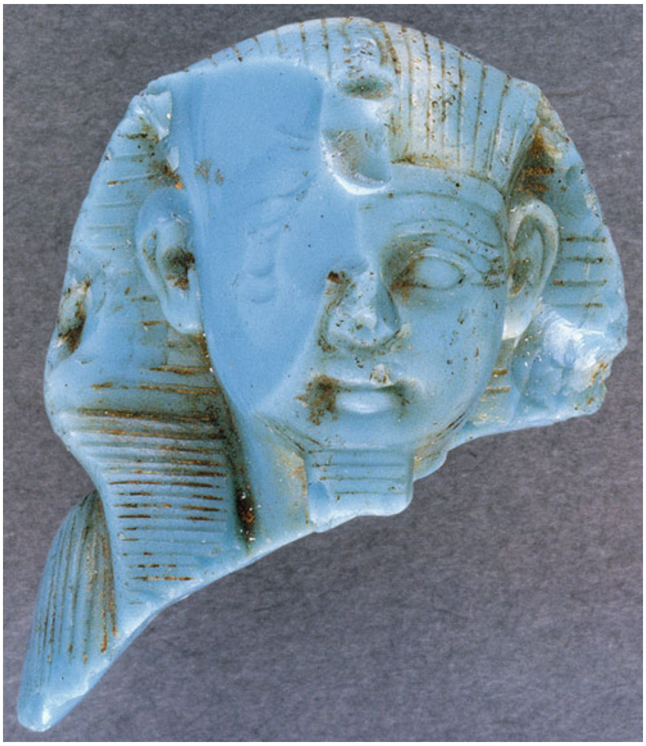

FIGURE 21.2. Glass head of a pharaoh (believed to be Amenophis II) as a Sphinx (1,400–1,390 BCE). It was made by lost-wax casting and is ~3.2 cm high.

FIGURE 21.3. Core-formed bottle shaped like a bulti–fish (1,390–1,336 BCE). This example is unusual because it is in polychrome glass. The length is ~14.5 cm.

manufacturing glass for its own sake, not just as a glaze for pots, had already been discovered in Mesopotamia by approximately 4,500 BCE. The use of glass as the glaze in pottery dates back even earlier.

Around 3,000 BCE, Egyptian glassmakers systematically began making pieces of jewelry and small vessels from glass. Glass had both a functional and a decorative role. Pieces of glass jewelry have been found on excavated Egyptian mummies; an example is the turquoise blue glass figure shown in Figure 21.2. By about 1,500 BCE, Egyptian glassmakers during the reign of Tuthmosis III had developed a technique to make usable hollowware. A most striking example is the core-formed bottle in the shape of a *bulti*-fish, shown in Figure 21.3. This vessel was made between 1,352 and 1,336 BCE and was believed to be used for holding scented oil (based on the narrowness of the neck). The wave pattern is very typical of core-formed objects and was made by drawing a sharp object along the softened glass.

The Roman author Pliny the Elder (23–79 CE) explained the invention of glass in his encyclopedia *Naturalis Historia*

> There is a story that once a ship belonging to some traders in nitrum put in here [the coast of modern Lebanon] and that they scattered along the shore to prepare a meal. Since, however, no stones for supporting their cauldrons were forthcoming, they rested them on lumps on nitrum from their cargo. When these became heated and were completely mingled with the sand on the beach a strange liquid flowed in streams; and this, it is said, was the origin of glass.

Nitrum is a naturally occurring soda, an important ingredient in both ancient and modern glasses. The ashes of plants also provided the glassmaker with a rich source of sodium. The plants saltwort and glasswort (known as halophytes) were both used to supply sodium.

Aside: Gerard's Herbal (1633) says that "saltwort was called Kali by the Arabians": hence the word *alkali* and the ashes are called *soda*.

One of the most common methods used to form glass is glassblowing. Although this technique was developed over 2,000 years ago, the glassblowing pipe has not changed much over that time. The main development that has been made in glassblowing is the automated blowing processes that are used to produce glass containers and light bulbs and the technique of blowing the glass inside a mold. Most of the important milestones in the history of glass, particularly in the twentieth century, are associated with developments in manufacturing technology. These developments have led to the low-cost production of commercial glasses (e.g., window glass) and the use of glass in new applications, such as optical fibers.

Many of the topics summarized here have been rediscovered many times. Now we have the tools, but we can see that nature often preempted humans.

21.2.1 Ancient History

50,000–1,000 BCE—Glass used in potter's colored glazes.
7,000–1,500 BCE—Ancient glass artifacts (possibly as early as 10,000 BCE).
2,600 BCE—Earliest actual dated glass.
1,500 BCE—Egyptians manufacturing glass articles.
1,200 BCE—Earliest glass molding.
100 BCE—Blown glass invented with the glassblowing pipe (Romans in Syria).
c100 BCE—In Alexandria, the introduction of manganese oxide into the glass composition together with improvements in the glass-melting furnaces enabled the first successful production of colorless glass.
450 CE—Stained glass used.

21.2.2 Beginning to Engineer Glass

1200s—In Germany, a new process was developed to make mirrors. The back of a piece of flat glass was coated with a lead-antimony layer to produce a quality ("silvered") mirrors. The mirror format remains essentially unchanged today.

1268—Eyeglasses described by Bacon. They had convex lenses for the correction of near sightedness.

1291—Murano, a small island near Venice, became a glass center. Glass workers on Murano were generally not allowed to leave the island.

c1590—The first telescope lenses were made in Italy and later, in 1604, in The Netherlands.

1609—Glass was made in Jamestown (Virginia, USA).

1612—Publication of the textbook *L'Arte Vetraria* by Antonio Neri in Pisa. The first systematic account of the preparation of the raw materials for glassmaking.

1676—George Ravenscroft, an English glassmaker, developed lead-crystal glass (also known as flint glass). The addition of lead oxide to the glass formula yielded a glass of high brilliance and a pure ring. It's not crystal, but it does contain a lot of lead and it's heavy.

1688—Bernard Perrot, a glassmaker in France under Louis XIV, invented the plate-pouring process. This process allowed mirrors with a large surface area to be produced. Examples are the magnificent wall of mirrors in the Galerie des Glaces at Versailles.

Late 1700s—Joseph von Fraunhofer (1787–1826), a German mirror maker and student of glassmaking technology, produced optical quality glasses for telescopes and microscopes. (Fraunhofer diffraction and the Fraunhofer Institutes are named in his honor).

21.2.3 Modern "Times"

1857—William Clark of Pittsburgh patented a sheet-drawing process: a plate glass.

1861—A British patent was granted to C.W. and F. Siemens. Their patent included a discussion of the application of the principle of regeneration to glass melting. Regenerative heating is still used in glass-melting furnaces today.

1865—A U.S. patent was issued for a press-and-blow process.

1875—Corning Glass Works was incorporated. The company was founded by Amory Houghton Sr. (1812–1882) and was named after the town in upstate New York where it is still located. Houghton already owned the Brooklyn Flint Glass Works but moved to Corning because real estate was cheaper.

1881—Thomas Edison brought out his first incandescent electric lamps using glass bulbs made by the Corning Glass Works.

1884—Otto Schott (1851–1935), Ernst Abbe (1840–1905), Carl Zeiss, and Roderick Zeiss establish the Glastechnisches Laboratorium Schott und Genossen, which later became the Jenaer Glaswerk Schott und Gen and in 1952 the Schott Glaswerke. In 2006, this company was the leading European glass company.

1893—The Enterprise Glass Company in the United States develops a press-and-blow mold that led to the widespread production of wide-mouth containers.

1903—The automatic bottle-blowing machine invented by the American Michael Owens (1859–1923) began production. A machine for drawing large cylinders of glass that were then flattened into window glass was developed by another American, John Lubbers.

1913—Emile Fourcault, a Belgian, developed a flat-glass machine for commercial operation.

1917—Edward Danner at the Libbey Glass Company introduced an automatic method for tube making. The company remains in operation today and is the largest manufacturer of glass dinnerware in the United States.

1926—The Corning ribbon machine for high-speed automatic production of glass light bulbs was developed.

21.2.4 Present Technology

1957—Corning introduced the Pyroceram® brand of glass-ceramics.

1959—Sir Alastair Pilkington's float process for producing flat glass worked.

1960—Glass-ceramics was patented by S. Donald Stookey of Corning Glass Works.

1966—Optical fibers were developed.

1975—Glass recycling became accepted/required.

1980—Acid-leaching process was introduced for producing 99.6–99.9% silica fibers that resist devitrification up to 1,370°C. These fibers were used as insulation for the space shuttle.

1991—Schott produced an 8.2-m diameter telescope blank from their glass ceramic ZERODUR®, which had been introduced in 1968.

1997—Corning produces glass for the Subaru Telescope mirror. Weighing 27 t and measuring more than 26 ft across, it is one of the largest pieces of glass ever made.

2001—Pilkington introduces the first "self-cleaning" window glass—Activ™. It has a photocatalytic TiO_2 coating applied.

2009—Corning produces Gorilla® glass that is used in most smartphones. The glass has a high compressive strength.

New and improved methods for processing glass are being developed. One of the main thrust areas for these activities is our concern for the environment. Reducing energy costs and reducing polluting emissions are important in the modern glass industry.

21.3 VISCOSITY, η

Viscosity is a key property of glass. We need to know its viscosity at different temperatures so it can be formed, shaped, and annealed. The concept of viscous flow was

TABLE 21.1 Viscosity Values for Glass Processing

Viscosity (dPa·s)	*Example*
$10^{1.5}$–$10^{-2.5}$	ASTM melting
$10^{3.7}$–$10^{3.8}$	Casting plate glass
$10^{3.8}$	Seal glass to metal
$10^{5.3}$	Begin updrawing or downdrawing
10^{6}	Sinter glass powder to produce a porous body
10^{8}	Sinter glass powder to produce a solid body
$10^{11.3}$–$10^{11.7}$	Glass deforms under gravity
$10^{12.7}$–$10^{12.8}$	Practical annealing range (stress relief in seconds)

described (and illustrated) in Chapter 17 because this is the process by which permanent deformation occurs in glasses. Viscosity is a mechanical property. Consider the tangential force, F, required to slide two parallel plates a distance d apart past one another when they are separated by a layer of viscosity, η.

$$\eta = (Fd)/(Av) \qquad (21.1)$$

where A is the common area, and v is the velocity of the planes relative to one another. Essentially, then, viscosity is a measure of the liquid's response to shearing. Liquids have viscosities measured in centipoises (cP), and gases have viscosities measured in micropoises (µP). In the SI system, we would say that liquids have viscosities in millipascal-seconds (mPa·s), and gas viscosities are tenths of micropascal-seconds (µPa·s) (so we stick with the poise).

VISCOSITY & POISE

If a force of 1 dyn is required to move an area of 1 cm^2 of liquid or gas relative to a second layer 1 cm away at a speed of 1 cm/s, then the viscosity is one P (poise).

$$1\text{P} = 1\text{dPa·s}$$

Table 21.1 lists some of the viscosity values that are important for glass processing. The values given in Table 21.2 are used to define certain characteristics of a glass (again with an emphasis on processing). Many of the values listed in this table of viscosities are "standards." For example, ASTM C338-93(2003) is the "Standard Test Method" for determining the softening point of glass.

> Determine the softening point of a glass by determining the temperature at which a round fiber of the glass, nominally 0.65 mm in diameter and 235 mm long with specified tolerances, elongates under its own weight at a rate of 1 mm/min when the upper 100 mm of its length is heated in a specified furnace at the rate of 5°C/min.

The viscosities of some common liquids are given in Table 21.2 for comparison. Notice that at the working point the glass has a viscosity similar to that of honey at room temperature. For a typical soda-lime–silicate flat-glass composition, this viscosity is achieved in the temperature range 1,015–1,045°C. The other key reference value to remember is that a solid has a viscosity of $>10^{15}$ dPa·s.

TABLE 21.2 Viscosity "Milestones"

Viscosity (dPa·s)	*Example*
10^{-2}	Water at 20°C
10^{0}	Light machine oil
10^{1}	Heavy machine oil
10^{2}	Olive oil at 20°C
10^{4}	Runny honey at 20°C. Some measure it to be 10^{2} dPa·s
10^{4}	Glass at its *working point*. Begin working at 10^{3}
$10^{7.6}$	*Shortening point* (deforms under its own weight; softening at $10^{7.7}$)
10^{8}	Upper limit for low viscosity
10^{13}	*Annealing point* (ASTM)
$10^{13.4}$	Glass at T_g
$10^{14.6}$	The *strain point* of glass (ASTM)
$>10^{15}$	Solid
10^{16}	Upper limit for measuring viscosity

The shortening point is also called the softening point.

The viscosity of glass varies dramatically with temperature, as shown in Figure 21.4A for various silicates. The fictive temperature, T_f, is the temperature at which the liquid structure is frozen into the glassy state and is defined by the crossing of the extrapolated curves from high and low temperatures on the η against T plot. The fictive temperature such as T_g is related to structural transformations in glass; T_g is slightly lower.

Figure 21.4B shows the temperature dependence of viscosity for the main glass-forming oxides as a function of temperature. You can notice that from the slope of these lines we can obtain the activation energy for viscous flow, E_v (see Section 17.13). Table 21.3 some gives some values for η and some measured crystallization velocities, v. The latter term refers to the rate of movement of the solid/liquid interface. The very low v for SiO_2 is indicative of its excellent glass-forming ability: it is very difficult to crystallize a solidifying melt of SiO_2.

There are several methods for measuring viscosity—which one is used depends on the expected value of the viscosity.

Mergules viscometer	$\leq 10^{7}$ dPa·s
Fiber elongation	$\leq 10^{7}$–10^{9} dPa·s
Beam bending	$\leq 10^{9}$ –10^{14} dPa·s

Figure 21.5 illustrates the first two approaches to measuring η. The viscometer is used for low viscosities, and the method is similar to the concentric cylinder viscometer used to determine the sol–gel transition that we describe in Chapter 22. The spindle is rotated at an angular velocity, ω, and the resistance to its motion is measured.

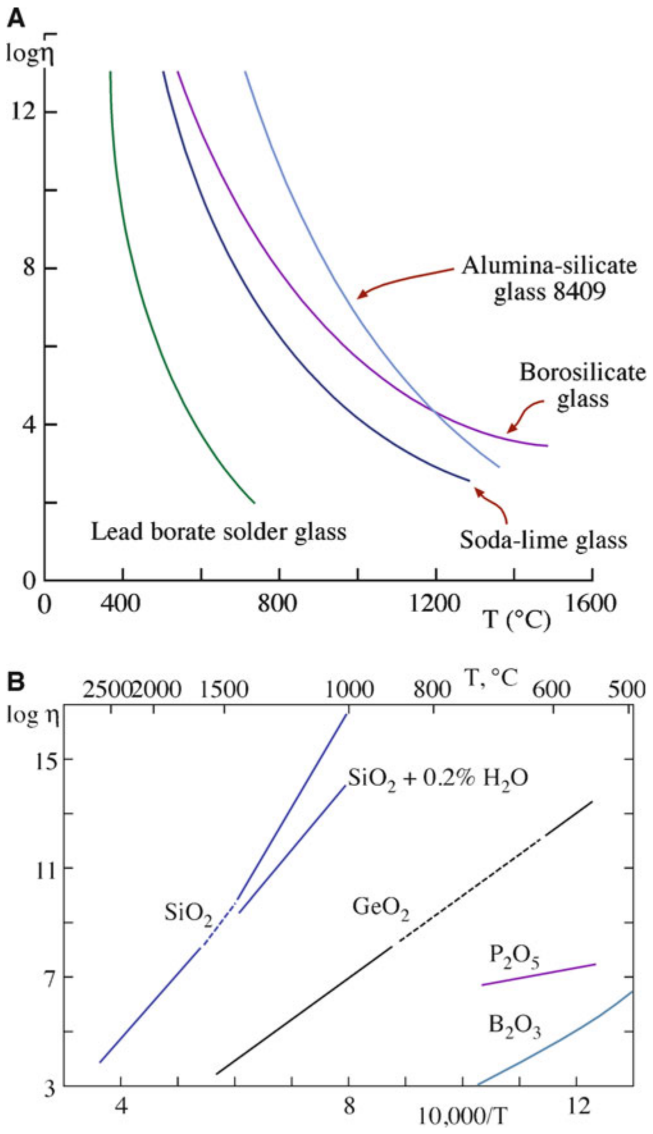

FIGURE 21.4. (A) Viscosity as a function of temperature (T) for several silicate glasses: units of η are dPa·s. (B) Viscosity as a function of temperature ($1/T$) for the main glass-forming oxides. Notice the effect that a small amount of water has on the viscosity of silica glass.

TABLE 21.3 Crystallization Velocities and Viscosities of Glass-Forming Liquids

Glass	T_M *(°C)*	v_{max} (cm/s)	*Temp. for* v_{max} *(°C)*	*Log* η *at* T_M *(dPa·s)*
Vitreous SiO_2	1,734	2.2×10^{-7}	1,674	7.36
Vitreous GeO_2	1,116	4.2×10^{-6}	1,020	5.5
P_2O_5	580	1.5×10^{-7}	561	6.7
$Na_2O{\cdot}2SiO_2$	878	1.5×10^{-4}	762	3.8
$K_2O{\cdot}2SiO_2$	1,040	3.6×10^{-4}	930	
$BaO{\cdot}2B_2O_3$	910	4.3×10^{-3}	849	1.7
$PbO{\cdot}2B_2O_5$	774	1.9×10^{-4}	705	1.0

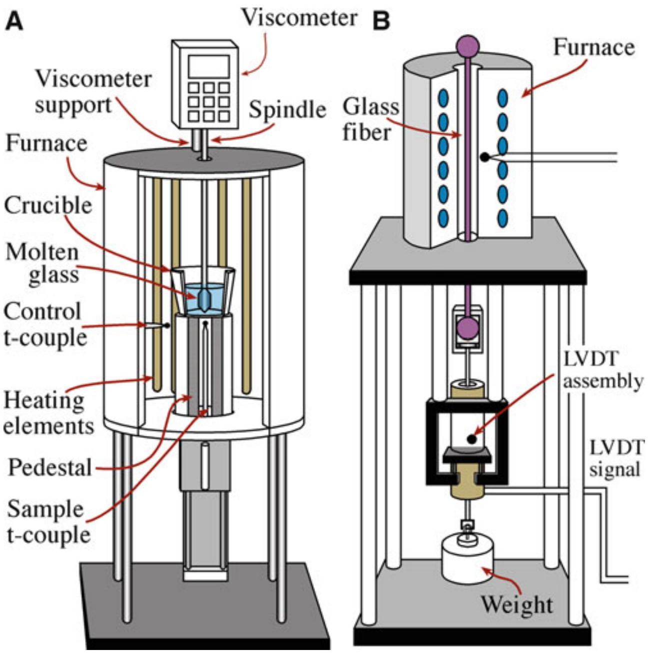

FIGURE 21.5. (A) Instruments used to measure viscosity. (A) Viscometer. (B) Fiber elongation method (Source: From Orton website The molten-glass viscometer).

For higher viscosities the fiber elongation method is used. A load is attached to a glass fiber, which can be heated to a range of temperatures. The strain rate of the fiber as it elongates is then measured.

21.4 GLASS: A SUMMARY OF ITS PROPERTIES, OR NOT

We can summarize what we *know* about glass—and probably be wrong.

Glass is inert. This depends on the environment. It's nearly true if the glass is a silicate and essential if it is going to contain radioactive waste; but not all glasses are inert. Bioglass® is designed not to be inert.

Glass is homogeneous. This depends on how the glass was formed and its composition. We can process glass to make it inhomogeneous.

Glass can be reshaped. This is generally true and is the reason why glass is so recyclable. Some glasses are designed so that they can be modified by light, by diffusion, by irradiation, etc.

Glass has a small expansion coefficient. This is usually true, but not all glass is Pyrex™.

Glass is transparent. This is essential for optical fibers, but we can make it translucent or opaque (see Figure 21.2). Most early glasses were not very transparent because they contained impurities and inclusions.

Glass is cheap. This has been true for window glass since the invention of the float-glass process. Thin films may be expensive. Some glass is colored red by doping it with Au. Some vases can cost >\$50,000.

Glass is a bulk material. This is true unless we grow it as a thin film, or it is present as an intergranular film (IGF) or is a pocket in, or on, a crystalline ceramic.

Hence, the lesson is: beware of your preconceived ideas when thinking about glass.

The mechanical, optical, thermal, and electrical properties of glasses are discussed in detail, along with other ceramics, in these topical chapters. Here, we just give you some things to think about in relation to glass.

21.4.1 Some Mechanical Properties of Glass

The theoretical strength of silicate glass is around 10 GPa (using the criterion given in Section 18.2), but this is usually much reduced by the presence of surface flaws (cracks and seeds). Glasses are elastic but break in tension. They can be strengthened by creating a compressive surface layer (by ion exchange or tempering) or by removing the surface flaws (acid-polishing or applying a protective coating). Prince Rupert's drops are an interesting and entertaining illustration of the effect of residual stress on the mechanical properties of glass. Small gobs of molten glass are dropped into cold water to form tadpole-shaped drops. The surface cools much more rapidly than the surface creating internal residual stresses and a very high surface tension. The solidified drops can be hit with a hammer without breaking. But if the tail is broken off the entire drop shatters into powder.

21.4.2 Some Electrical Properties of Glass

Glass usually has a high electrical resistivity because of the large band gap energy (see Chapter 30). In cases where they are conductive, the charge is carried by ions, with alkali ions (e.g., Na^+) being the fastest. Thus, conductivity increases significantly as T is increased; and it is different for silicate glasses, borate glasses, and phosphate glasses because the glass network is different in each. The mixed alkali effect is an interesting phenomenon that occurs in glasses that contain more than one different alkali ion. The resulting conductivity has been found experimentally to be significantly lower than what you would expect from simply adding their individual conductivities. This has application in, for example, high-wattage lamps.

The dielectric constant of glass is quite high but not high enough for some advanced memory applications such as dynamic random access memories (DRAMS) (see Chapter 31). The capacitance is a measure of the amount of charge stored and is related to the thickness of the dielectric. As the layer gets thinner the capacitance increases, but electrical breakdown can occur. SiO_2 glass has a high dielectric strength, but it's not as high as some polymer dielectrics, (e.g., phenolic resin).

21.4.3 Some Optical Properties of Glass

Transmission in the ultraviolet (UV), visible, and infrared (IR) depends on several factors including Rayleigh scattering, which is determined by impurities. The IR edge and the UV edge are the values where transmission of these frequencies cut off. A UV edge blocker removes the UV, and a UV edge transmitter allows it through.

Refraction depends on the refractive index and on dispersion. Reflection, which occurs at the surface, can be internal. Because the optical properties of glass are so important, a lot of Chapter 32 is devoted to this topic.

21.4.4 Some Thermal Properties of Glass

Expansion coefficients of glass are generally smaller than for metals, but often we want to make the connections to metals. For example:

Glass-to-metal seals: an obvious important technological process.

SiO_2: metal–insulator junctions for the electronics industry.

Graded seals: for example, a graded seal structure can be constructed by joining a series of glass pieces, each of which has a slightly higher thermal coefficient of expansion (α).

Thermal conductivity is ~1% of that of a metal. The implications and applications of this fact are obvious.

21.5 DEFECTS IN GLASS

The idea is that although glass does not have a crystalline matrix, it can still contain point defects and precipitates, undergo segregation, and contain internal interfaces. Glass can be used to trap radioactive elements as point defects or as a "second phase." The future value of this capability depends in part on how fast components can diffuse through glass. This applies to whether the radioactive material is diffusing out or other components are diffusing in (perhaps to leach out the trapped material).

21.6 HETEROGENEOUS GLASS

Just because glass is a "supercooled" liquid doesn't mean it must be homogeneous. Certain glasses can separate into two phases, which need not be a crystallization process. When these two phases are both glassy, there may be no barrier to the separation (a spinodal decomposition), or as in the case of liquid/liquid phase separation there may be a nucleation step. In either case, diffusion is important.

The principle of immiscibility in glass is very important to today's technology. For example, immiscibility plays a role in forming glass-ceramics, making Vycor® and opal glass, and precipitation in glass. Many of the binary and ternary oxides with silica as a component show miscibility gaps. A miscibility gap is a region in the phase diagram where a liquid separates into two liquids of different composition (see Section 8.11). The following are examples of systems exhibiting this effect.

SiO_2–Al_2O_3 SiO_2–BaO SiO_2–MgO
Na_2O–B_2O_3–SiO_2 Na_2O–CaO–SiO_2

Figure 21.6 shows the silica-rich side of the phase diagram for several SiO_2-R_2O systems. In the low-T corner of the diagram, one liquid phase separates into two chemically distinct, different liquid phases below the immiscibility dome. For the SiO_2-K_2O system, the dashed line represents the estimated region of immiscibility. The difficulty in making these measurements is that phase separation occurs at lower T, where the kinetics are slower. There is an interesting comparison with crystallization. Phase segregation may be energetically less favorable than crystallization, but it is easier to accomplish because it requires only the segregation, not the correct rearrangement of the atoms.

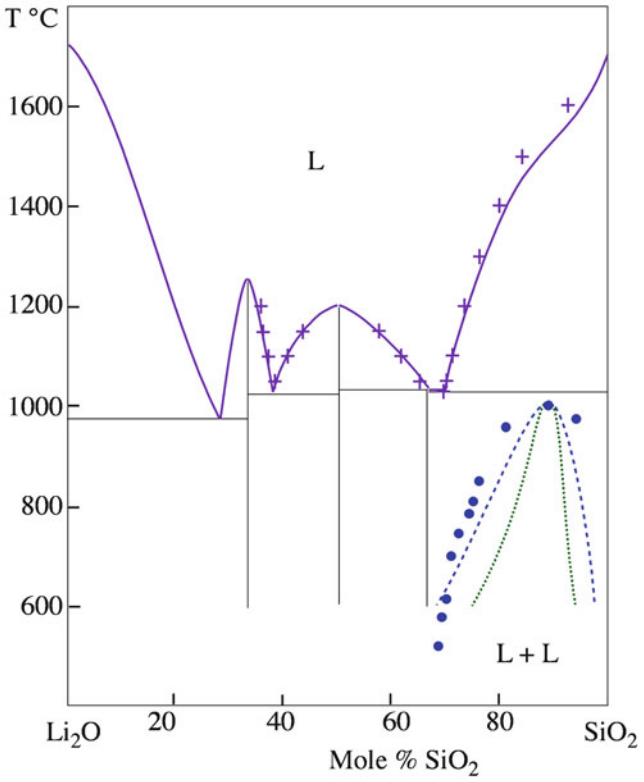

FIGURE 21.6. Regions of liquid–liquid immiscibility for various silicates of the form SiO_2-R_2O. Notice that we are only showing the silica-rich end of the phase diagrams.

As a general rule for silica, immiscibility is increased by the addition of TiO_2, but decreased by the addition of Al_2O_3.

The Vycor process described in Chapter 8 uses the principle of phase separation. The resulting glass is 96% SiO_2 and 4% pores, which is used as a filter and a bioceramic where porosity is important. It can be densified (after shaping) to allow processing of a pure SiO_2 shape at a lower T than for pure quartz glass.

21.7 YA GLASS

Yttrium–aluminum (YA) glasses can be formed in the composition range ~59.8–75.6 mol% Al_2O_3. With 59.8–69.0 mol% Al_2O_3, a two-phase glass forms with droplets of one phase in the other. The glass can spontaneously crystallize to form YAG or a mixture of Al_2O_3 and $YAlO_3$ (YAP, where P represents perovskite). These YA glasses show a phenomenon known as polyamorphism, meaning that they exist with different amorphous structures.

21.8 COLORING GLASS

Although many applications for glass require a colorless product, others require colored glass. Windows in a church do not look as impressive when all the glass is colorless. Glass is often colored by adding transition-metal oxides or oxides of the rare-earth elements to the glass batch. Table 21.4 lists the colors produced by some of the common glass colorants. We look at how these additives result in the formation of color in Chapter 32, but at this stage you should already know why glass bottles are often green. Bright yellow, orange, and red colors are produced by the precipitation of colloids of the precious metals. Au produces a ruby red coloration, but it is not cheap. CdS produces a yellow coloration, but when it is used in conjunction with Se it produces an intense ruby red color.

The questions are:

- How does coloring "work"?
- What causes the colors?
- Is it the same as for crystals?

Glass is intentionally colored by adding dopants (we are creating point defects in the glass). The color of the glass depends on the dopant and its state of oxidation. The explanation is the same as for coloring crystals; but because the glass structure does not have LRO, the absorption spectra can be broader.

Combinations of dopants can decolorize, mask, or modify the effect. For example, we can compensate the coloring effect of Fe by adding Co; if too much Cr^{3+} is added, Cr_2O_3 can precipitate out. When the glass is blown, these platelets of Cr_2O_3 can align to give "chromium aventurine." Cu was used to produce Egyptian blue glass. Co is present in some twelfth century stained glass and, of course, was used in the glazes on Chinese porcelains in the Tang and Ming dynasties. The color it produces is known as cobalt blue.

In a CdS-doped glass, adding more Se can result in "Selenium Ruby." The details of all these colorings depend on just what glass batch is used and the firing conditions.

Corning makes microbarcodes (i.e., very small barcodes) by doping glass with rare earths (REs); the REs have particularly narrow emission bands. Of 13 RE ions tested, four (Dy, Tm, Ce and Tb) can be excited with UV radiation used in fluorescence microscopy but don't interfere with other fluorescent labels. These microbarcodes can be used for biological applications since they are not toxic; tags using quantum-dots may be less benign. These bar codes can even label genes. The REs can be used together to give more color combinations.

Some special colored glasses:

Ruby and cranberry glass. Ruby glass is produced by adding Au to a lead glass with Sn present. Cranberry glass is paler (usually a delicate pink) because it contains less gold. It was first reported in 1685. The secret of making red glass was lost for many centuries and rediscovered during the seventeenth century.

Vaseline glass or uranium glass. Uranium produces a deep red when used in high-Pb glass. There are other uranium-containing glasses: the so-called "uranium depression ware" glass (also called Vaseline glass), which has a green color. True "depression ware" is actually greener than Vaseline glass because it contains both iron and uranium oxides. What is special is that the glass actually fluoresces when illuminated with UV radiation (Vaseline ware more strongly because of the higher uranium concentration). Since 1940 or so, only depleted uranium has been used as a dopant, and it is quite plentiful; but for the previous 100 years, natural uranium was used. Figure 21.7 shows an example of Vaseline ware.

FIGURE 21.7. Example of Vaseline ware produced by coloring with uranium.

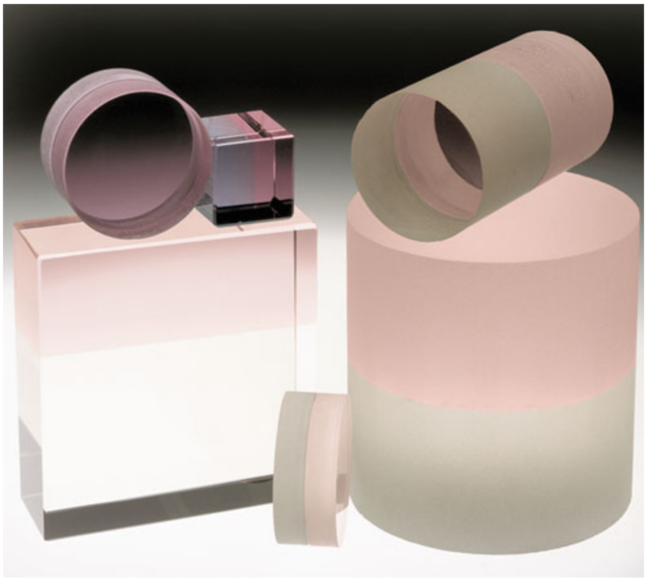

FIGURE 21.8. Examples of phosphate laser glass. Individual laser rods vary from 0.6 to 1.2 mm in diameter.

21.9 GLASS LASER

Rare-earth elements (e.g., Nd) are used to dope glass to create lasers and other optical devices (Figure 21.8). The Nd-doped glass laser works like the ruby laser but has some differences, which relate to the glass. The laser rod is about ¼–½ in. diameter and usually pumped by a helical lamp to give a longer discharge length than from a linear lamp. The energy is stored in a capacitor (e.g., 500 mF) with a charge voltage of ~4 kV, giving a pulse duration of ~0.8 ms. The Nd:glass laser gives efficiencies up to 2%, which is four times that of the ruby laser, and the Nd:glass rod can be made even bigger. The thermal conductivity of the glass is lower, so it requires more time to cool between firings.

21.10 PRECIPITATES IN GLASS

Precipitation in glass is generally inevitable given time. The question is only how long it requires to occur, especially if nucleation is homogeneous (i.e., no seeds are present). We may introduce seeds to produce particular effects. Nucleation of crystals in glass follows the classic theory. We examine the topic more in Chapter 26 and see there that precipitates can also cause the coloring of glass.

21.11 CRYSTALLIZING GLASS

We address processing these materials in Chapter 26. Here we explain what a glass-ceramic is and relate it to other two-phase ceramics. We can crystallize a droplet of glass, as shown in Figure 21.9, or a complete film, as shown in Figure 21.10. We can also crystallize a bulk object almost completely to produce a glass-ceramic. The basic idea is that there is sometimes a great advantage in processing a ceramic as a glass but producing the finished object as a polycrystalline body.

Opal glass has a milky (opalescent) appearance caused by the formation of small crystallines. Even window glass crystallites; given time it devitrifies to form devitrite.

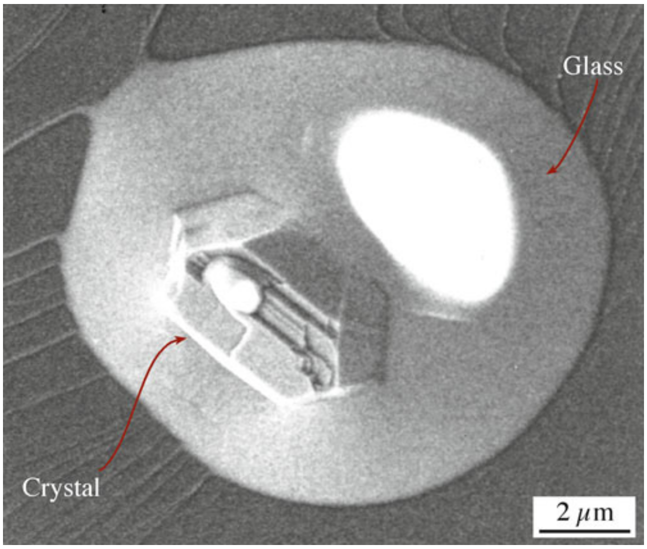

FIGURE 21.9. Example of crystallization in a glass droplet.

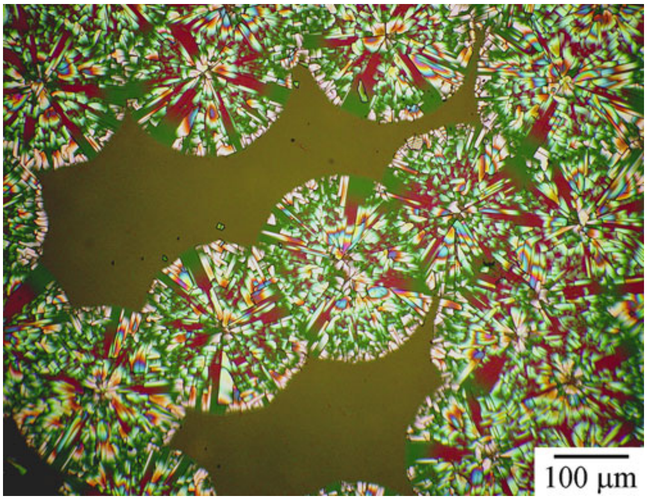

FIGURE 21.10. Spherulitic crystallization of an amorphous SiO_2 film on SiC. Spherulites are crystobalite.

The visible light microscopy (VLM) image shown in Figure 21.11 illustrates the growth of perfectly symmetric individual crystals inside a glass matrix. The crystals and the matrix are all transparent, so the full shape can be appreciated. The scanning electron microscopy (SEM) images in Figures 21.12 and 21.13 show that the glass and crystal appear very different even on a fractured surface. Breaking a sample can quickly reveal a "grain" size down to ~0.1 μm. To probe the structure on a near-atomic level with high spatial resolution, TEM can be used, as shown in Figure 21.14; but its use has been limited, in part because of the difficulties of preparing the TEM sample: the thickness of the sample tends to be greater than the dimensions of the crystalline phase.

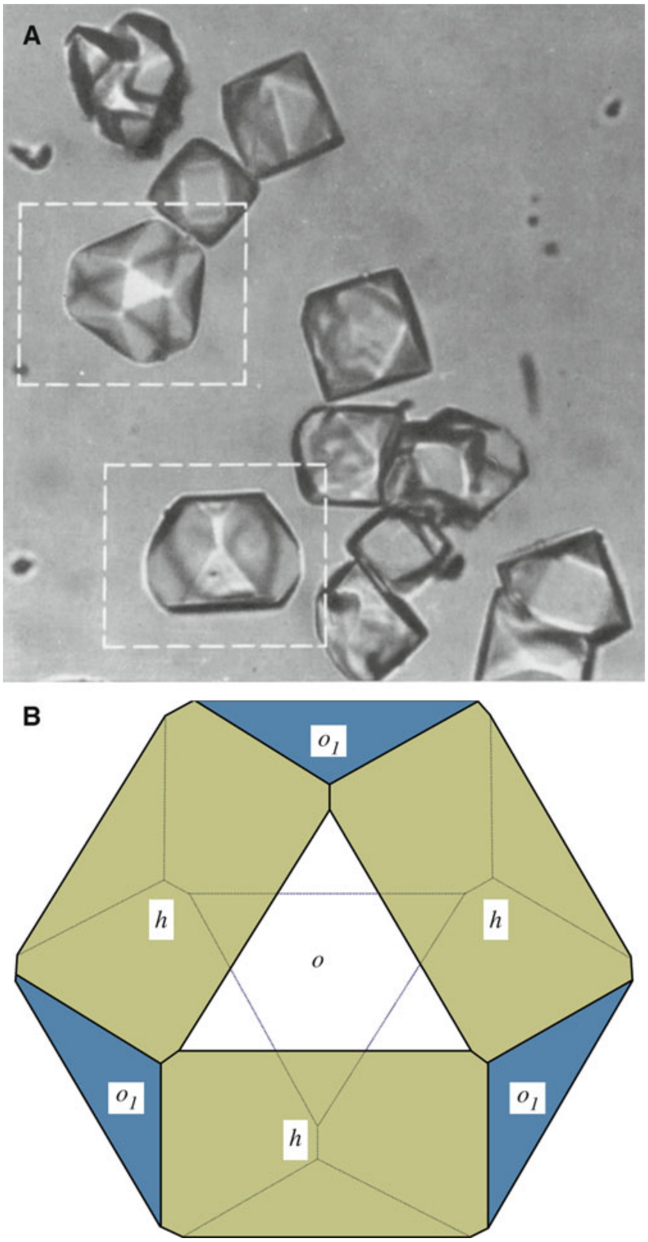

FIGURE 21.11. Visible light microscopy image showing crystallization in a glass.

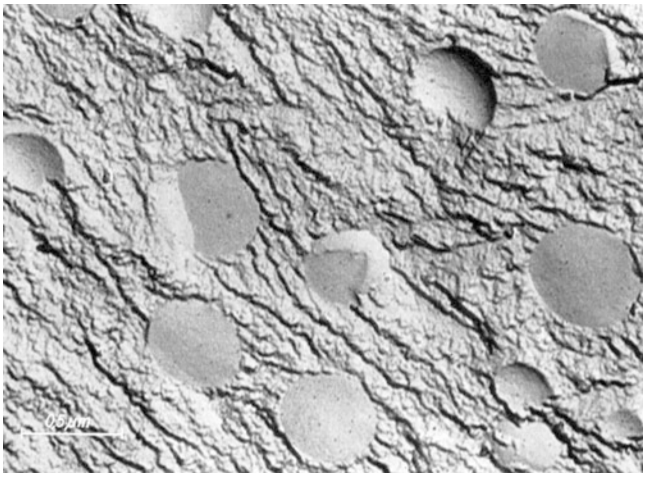

FIGURE 21.12. Scanning electron microscopy (SEM) of crystallized glass. The glass is a binary Li-Be fluoride opal glass 40 mol% LiF, 60 mol% BeF_2 containing small amounts of Ag and Ce (0.001 and 0.01 mol%, respectively). The glassy droplets (BeF_2-rich) are surrounded by crystallized matrix.

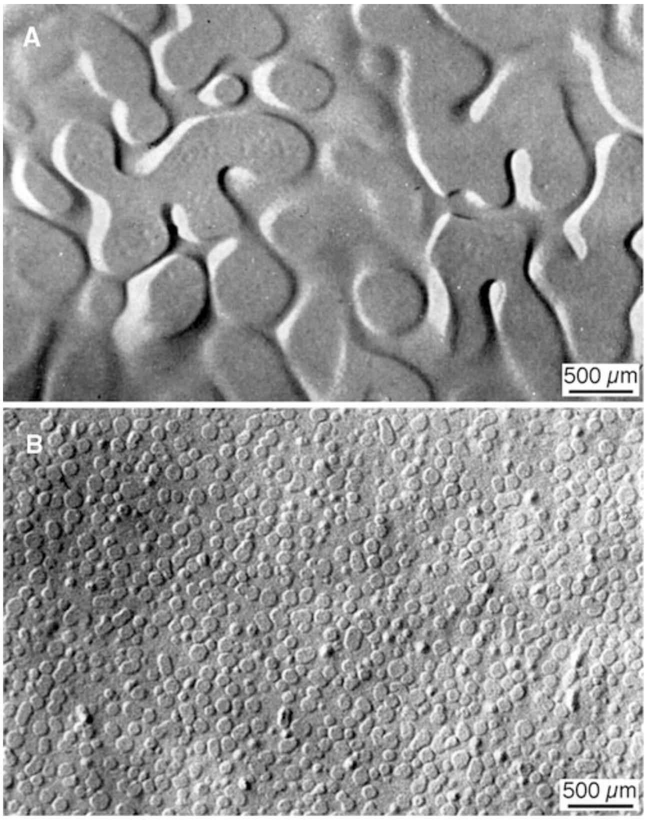

FIGURE 21.13. SEM images of (A) Na-Be and (B) K-Be fluoride glass 15 mol% KF (or NaF), 85 mol% BeF_2. This glass is cloudy; if the droplets were smaller, the glass would be clear. Replacing K by Rb actually reduced the droplet size to 10–20 nm.

21.12 GLASS AS GLAZE AND ENAMEL

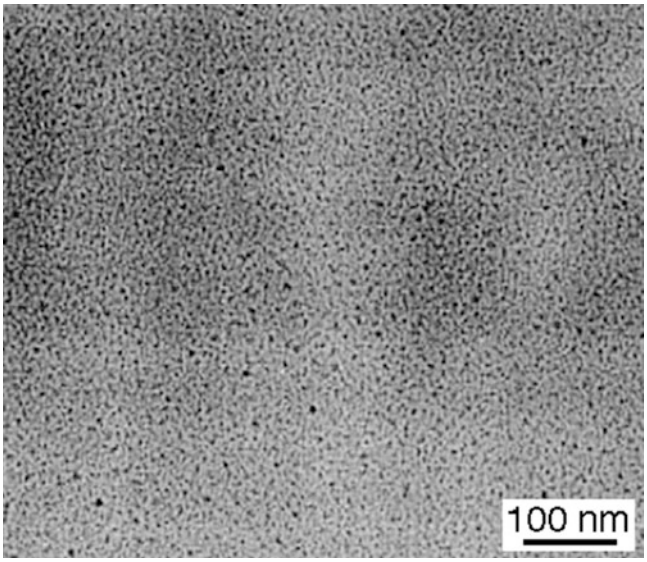

FIGURE 21.14. Transmission electron microscopy shows crystallization on a nanometer scale in a lithium aluminum silicate (LAS) glass-ceramic.

Glazes are everywhere, just as glass is. In this section, we summarize the topic of complete books, namely the glazes on pottery and enamels. Glazing uses the viscous properties of glass to form a (usually) smooth continuous layer on a ceramic substrate (a pot); enameling does the same thing for a metal substrate. One thing that you may notice is that generally when it comes to ceramics potters did it first. The science of ceramics is often still unraveling just what they did. (In materials science, ceramists usually did it first).

FLUX AND MODIFIERS

The flux in a glaze is a modifier in glass. The clear glaze is glass: i.e., silica and alumina with added modifiers. The clear glaze may contain lead but Pb should not be used for modern food containers. Strong colored glazes also often contain heavy metals.

First, we summarize some terms in pottery. (The processing of pottery was summarized in Chapter 2).

Underglaze. When a pot—white bisqueware (also called biscuit) is ideal—is decorated, the first coating is the underglaze. This is essentially a paint layer made by mixing oxide, carbonate, sulfate, etc., an opacifying agent to make it opaque, and a flux to make it adhere better to the pot. The mixture is calcined, ground, and then usually combined with a liquid to allow smooth application. The decorated pot is then typically coated with a clear glaze before it's fired. In the majolica technique, the pot is coated with an opaque white glaze first, then decorated, and fired so that the colors bond to the white coating, forming an in-glaze (rather than under-glaze) decoration.

Glaze crawling. The glaze separates from the underlying pot—it dewets the pot surfaces during firing.

Crackle glazes. If the α of the glaze is greater than that of the underlying ceramic, the glaze may fracture as it cools; this crackling can easily be achieved using higher concentrations of Na or K in the glaze. In most technological applications, this is not desirable. Some glazes, however, are designed to have a pattern of hair-like cracks for the artistic effect; they are known as crackle glazes. Fast cooling produces a finer pattern of glazes.

Celadon, tenmoku, raku, and copper glazes are particular glazes that you find in the ceramics art world.

Celadon glazes (first produced 3,500 years ago) vary from light blue to yellow-green and can be quite dark. The color is produced by iron (0.5–3.0 wt% Fe_2O_3 added to the glaze). The glazed pot is then fired a second time at about 1,300°C. An example of Korean celadon pottery is the small water container, 23 cm tall, given to former U.S. President Harry Truman in 1946 by the government of Korea. It is now valued at $3M.

Tenmoku glaze (from the Sung Dynasty) is dark brown or even black; 5–8 wt% Fe_2O_3 is included in the glaze to produce the effect. An interesting variation of the tenmoku glaze is the oil-spot tenmoku, where bubbles begin to form in the glaze as it starts to melt; if the potter catches them just in time, they leave spots all over the surface. If a tenmoku glaze is fired in reducing conditions, the Fe_2O_3 is partially reduced to FeO, which acts as a modifier instead of an intermediate, in glass terms. Hence, this glaze behaves differently under oxidizing and reducing conditions, and the color changes. Copper glazes may use 0.5 wt% $CuCO_3$ as the Cu source, but it breaks down to give CuO during firing, and this reacts with CO in the furnace to give particles of Cu in the glaze. These particles of Cu give the red color.

Raku glazes often appear metallic as if produced by coating with Ti metal. One modern method of raku glazing involves firing the pots in the usual way and then plunging them into a reducing environment (e.g., sawdust) and then quenching them before they can oxidize. These glazes are often the exception to the rule in that they can change with time. This is simply because they oxidize when treated as other pots. The glaze is thus not as inert as others and is used only for decoration. (However, see the historical note on Chojiro Rakuyaki).

Crystalline glazes. These are decorative glazes but are directly related to the formation of technologically important glass-ceramics. The crystals form by slowly cooling the glaze to allow a few large crystals to grow. The growth is interesting because the glaze is typically only ~0.5 mm thick and the crystals must therefore form as platelets. A seed of TiO_2 is usually used to nucleate the crystal in a low-viscosity glaze, giving what is termed "rutile breakup," which is actually the formation of $PbTiO_3$. The chemistry of the glaze is thus important, with SiO_2 and Al_2O_3 being low and PbO at 8–10 wt%. The growing crystal tends to incorporate Fe from the glaze but can also preferentially exclude other dopants.

FIGURE 21.15. Spherulitic crystallization in a glass.

SPHERULITES

Dana described spherulites in obsidian in 1863; these are the snowflakes in snowflake obsidian. In 1879 Rutley noted that artificial glass may develop a spherulitic structure.

Modern potters tend to use Zn as the modifier and produce willemite crystals. [Willemite is a somewhat rare zinc mineral (except as kidney stones) but is abundant at Franklin, New Jersey]. The technique is tricky because the addition of large amounts of Zn (a network modifier) to the glaze causes its viscosity to remain low even at low temperatures, so that it tends to run off the pot! The crystals appear to grow out from a seed as in the spherulitic growth seen by VLM in Figure 21.15. Each spherulite is actually a mass of radiating crystals that are similarly aligned with respect to the center of the spherulite.

Opaque glazes. If crystals are added to the molten glaze, it can be made opaque. SnO_2 was long the standard, but zircon is much cheaper. ZnO_2 is used to make zircon glazes white. TiO_2 is less used because larger rutile crystals are a golden color and thus make the glaze yellow. We can also make the glaze opaque by forming crystals (e.g., wollastonite; $CaSiO_3$) using a suitable thermal treatment, by trapping gas (F_2 or air), or by causing a liquid/liquid phase separation.

Matt glazes are produced by forming very small crystals—e.g., wollastonite for a "lime matt" or willemite (Zn_2SiO_4) for a "zinc matt"—across the surface of the glaze. The wollastonite can be formed by adding calcite (also known as whiting) to an SiO_2-based glaze. An alternative is to add so much crystalline material to the glaze that it remains unchanged by the firing. A satin or vellum glaze, with smaller crystal sizes, might contain 18% SnO_2 or ZnO and 4% TiO_2 in a high-lead glaze fired at 1,000°C.

FIGURE 21.16. Example of glaze color produced by nanoparticles.

TABLE 21.4 Colors Produced by the Inclusion of Different Ions in a Glass

Copper	Cu^{2+}	Light blue (red ruby glass for Cu nanoparticles)
	Cu^{+}	Green and blue (includes turquoise blue)
Chromium	Cr^{3+}	Green
	Cr^{6+}	Yellow
	$Cr^{3+} + Sn^{4+}$	Emerald green
Manganese	Mn^{3+}	Violet (present in some Egyptian glasses)
	Mn^{2+}	Weak yellow/brown (orange/green fluorescence)
Iron	Fe^{3+}	Yellowish-brown or yellow-green
	Fe^{2+}	Bluish-green
	FeS	Dark amber (add C to reduce it)
Cobalt	Co^{2+}	Intense blue (especially if K^{+} is present); in borates and borosilicates, pink
	Co^{3+}	Green
Nickel	Ni^{2+}	Grayish-brown, yellow, green, blue to violet, depending on glass
Vanadium	V^{3+}	Green in silicates; brown in borates
Titanium	Ti^{3+}	Violet (melting under reducing conditions)
Neodymium	Nd^{3+}	Reddish-violet
Praseodymium	Pr^{3+}	Light green
Cerium	Ce^{3+}	Green
	Ce^{4+}	Yellow
Uranium	U	Yellow (known as Vaseline glass)
Gold	Au	Ruby (ruby gold, Au nanoparticles)

Color in glass and glaze is the subject of much active research, with the realization that some colors are produced by nanoparticles in the glass/glaze as for the luster-glazed plate in Figure 21.16. In general, Ag and Au nanoparticles produce the gold color, and Cu nanoparticles produce the red; in the case of Cu especially, the ions may be reduced to the metal during processing. Explanations for the color of glazes is actually more complicated than for glass because the glaze is supported by a substrate and does not have to be transparent; so it can be a thin film or a multilayer and fired in a reducing or oxidizing environment. This is a very big topic being condensed into a paragraph! Cipriano Piccolpasso described luster preparation in 1557. Who says the use of nanomaterials is new!

Colored glazes must use stable ceramic pigments if the color is to be consistent over repeated batches (e.g., for industrial production of sanitaryware, tiles). You can use cheaper metal oxide colorants when variability is acceptable or desirable, as in the pottery crafts. Of course, many glaze colorants are the same as we use for coloring glass (see Table 21.4). Co_3O_4 is a black powder but $<1\%$ gives a glaze a deep blue color, although it is usually added as the carbonate. Because Co^{2+} is present when it dissolves, it changes the viscosity of the glaze. Cr_2O_3 (2–3% can be added but only 1.5% dissolves in the glaze) is intriguing because you expect green but can produce red, yellow, pink, or brown. The red can occur if Pb is present in the original glaze; if Zn is present, the glaze becomes brown unless Pb is also present, when the glaze becomes yellow. MnO_2 (added as the carbonate) gives a brown glaze but can produce red, purple, or even black; the color depends in part on how much Na is present in the initial glaze. CuO is equally interesting: 1–2% added to an Na-rich glaze gives turquoise, whereas an up to 3% addition produces a clear green-blue. If even more CuO is added, the glaze can give a metallic appearance like pewter. If the glaze (0.3–2.0% CuO) is fired in a reducing atmosphere, the classic copper red is formed. This color is caused by the presence of colloidal Cu. If you see the bright yellow glaze, this might be the CdS/CdSe yellow (which also produces orange and red) glaze. If Pb is present, then PbS can form, which makes the glaze black. Zircon is used in industry to help stabilize these Cd-based colors. In fact, $(V,Zr)SiO_4$ (vanadium zircon blue) and $(Pr,Zr)SiO_4$ (praseodymium zircon yellow) are most important in the whitewares industry. Uranium is added to glazes but tends to produce a dark brown rather than the pale yellow found in Vaseline glass; it can be yellow or bright red-orange, but this depends on the glaze composition.

Salt glaze. The pot is reacted with salt in the furnace while at temperature. In practice, the potter actually throws salt over the pot when it is in the kiln. The technique was used by early potters in Iran and by the English in the 1700s. You can see many examples in Germany where a blue coloring is often produced using metal oxides. The salt reacts with the clay, forming a glass layer on the surface; essentially, the process is high-temperature soda corrosion of the fired clay.

The term *enamel* usually implies a glaze applied to a metal, but it can be a glaze applied on top of a glaze.

The market is large, varying from toilet fixtures (whitewares) to jewelry. Enamel is the ever-lasting paint with the organic component replaced by glass.

21.13 CORROSION OF GLASS AND GLAZE

We think of glass as being inert. Citric acid and acetic acid (present in lemon and vinegar, respectively) can chelate with metal ions present in a glass and form water-soluble complexes. (A chelate is a complex compound with a central metal atom attached to a large molecule, a ligand, in a ring or cyclic structure like the claw of a crab). The effect can actually be greater than for what we think of as stronger acids (sulfuric, nitric, and hydrochloric acids readily attack metals and skin). The Ca, Mg, and Al ions usually increase the chemical durability of a glass but react with these "food" acids. The tannic acid present in red wine and tea can have a similar effect. Thus, Pb can be released from glass when the glass is in contact with acid (even fruit juice). This means that we shouldn't use Pb in glazes; however, it has often been done because such glazes can be so brightly colored.

Silicate glass is strongly corroded by hydrogen fluoride (HF). The process of "frosting" glass light bulbs was carried out for many years by blowing HF vapor into the glass envelope and then evacuating it after a short period.

FIGURE 21.17. Example of iridescence in Roman glassware.

Glass dissolves in water, particularly at elevated temperature and pressure: we use this fact for growing all the quartz crystals used by industry. Dishwashers make glass dull. Roman glass (Figure 21.17) is iridescent because the glass has reacted with acid in the soil. (The iridescence was not present in Roman times.) The corrosion products form several distinct layers and hence generate the interference known as iridescence. It can easily be duplicated, as shown by Tiffany and others.

Not all glass is attacked equally readily. As we described in Chapter 8, we leach one component of a phase-separated glass during the preparation of Vycor but leave the other intact.

It is possible to minimize these reactions to some extent by adding inhibitors, such as Zr or Be, to the glass. This question of reactivity is closely related to the phenomenon of ion exchange.

H^+ can replace alkali ions when glass is weathered.
K^+ can replace Na^+ and Na^+ can replace Li^+ when we want to strengthen the surface of glass.
Ag^+ and Cu^+ can replace Na^+ to "stain" glass.

A special feature here is that we have point defects (and large defects) in glass just as we do in crystals. Our challenge is to understand what determines the properties (e.g., diffusion) of such defects when we don't have a reference lattice.

21.14 TYPES OF CERAMIC GLASSES

Not all glass is based on the silica tetrahedron. The structural units are summarized in Table 21.5, and some representative glass compositions given in Table 21.6.

21.14.1 Silicate Glass (Soda-Lime Glass)

Silicate glass is based on SiO_2–Na_2O–CaO (usually containing MgO and Al_2O_3). It is relatively inexpensive and durable and is widely used in the building and packaging industries. It is not negligible, and it's not a good insulator. The main uses are in sheet glass, bottles, tableware, and in the light industry for envelopes (bulbs). The alkaline aluminosilicate glasses (SiO_2–Al_2O_3–RO, where R is the alkali) have low α values, are durable, and are better electrical

TABLE 21.5 Structural Elements in Glasses

Silicates	SiO_4
Borates	BO_3
Phosphates	PO_4
Fluorides	F
Chalogenides	S

TABLE 21.6 Approximate Composition (wt%) of Some Commercial Glasses

Glass	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*CaO*	*MgO*	*BaO*	*Na_2O*	*K_2O*	*SO_3*	*F_2*	*ZnO*	*PbO*	*B_2O_3*	*Se*	*CdO*	*CuO*
Container flint	72.7	2.0	0.06	10.4		0.5	13.6	0.4	0.3	0.2						
Container amber	72.5	2.0	0.1	10.2		0.6	14.4	0.2	S-0.02	0.2						
Container flint	71.2	2.1	0.05	6.3	3.9	0.5	15.1	0.4	0.3	0.1						
Container flint	70.4	1.4	0.06	10.8	2.7	0.7	13.1	0.6	0.2	0.1						
Window green	71.7	0.2	0.1	9.6	4.4		13.1		0.4							
Window	72.0	1.3		8.2	3.5		14.3	0.3	0.3							
Plate	71.6	1.0		9.8	4.3		13.3		0.2							
Opal jar	71.2	7.3		4.8			12.2	2.0		4.2						
Opal illumination	59.0	8.9		4.6	2.0		7.5			5.0	12.0	3.0				
Ruby selenium	67.2	1.8	0.03	1.9	0.4		14.6	1.2	S-0.1	0.4	11.2		0.7	0.3	0.4	
Ruby	72.0	2.0	0.04	9.0			16.6	0.2		Trace						0.05
Borosilicate	76.2	3.7		0.8			5.4	0.4					13.5			
Borosilicate	74.3	5.6		0.9		2.2	6.6	0.4					10.0			
Borosilicate	81.0	2.5					4.5						12.0			
Fiber glass	54.5	14.5	0.4	15.9	4.4		0.5			0.3			10.0			
Lead tableware	66.0	0.9		0.7		0.5	6.0	9.5				15.5	0.6			
Lead technical	56.3	1.3					4.7	7.2				29.5	0.6			
Lamp bulb	72.9	2.2		4.7	3.6		16.3	0.2	0.2				0.2			
Heat absorbing	70.7	4.3	0.8	9.4	3.7	0.9	9.8	0.7		Trace			0.5			

insulators. They also have a high strain point. Uses include combustion tubing, envelopes for halogen lamps, and substrates in the electronics industry.

21.14.2 Lead Glass

Generally, the composition of lead glass is a lead-alkali silicate glass SiO_2–PbO–R_2O, so the PbO replaces the CaO in soda-lime glass. These glasses have high resistivity, a large α, a low softening temperature, and a long working range. The reason that Pb glass has been used to make so-called lead crystal glass is that it has a high refractive index. Besides being used in art objects, it is used for lamp tubing, TVs (the "bulbs"), and thermometer tubing. In a traditional English lead crystal, the concentration of PbO is at least 30%: a European Union (EU) directive required that glass must contain $\geq$24% to be lead crystal. The EU then had to exempt crystal glass from recycling laws! Lead glass used for radiation shielding may contain as much as 65% PbO. Applications include TV tubes, although Ba glass may be used in the face or panel of the TV. The electrons hitting the TV screen can create X-rays that the glass must then absorb. Lead-borate glasses can be used as glass solder—they contain little SiO_2 or Al_2O_3 and are quite inert.

Flint glass is a high-dispersion, lead-alkali silicate glass and was originally made by melting flint rock, which is a particularly pure form of silica. Note that this rock is now calcined and is still used extensively in the pottery industry.

Crown glass has quite a low dispersion and is based on soda-lime glass. It is still made by initially blowing the glass, flattening it, and transferring it to the pontil (a solid iron rod rather than the blow pipe), where it is spun until it is in the form of a disc that can be 1.5 m in diameter (Figure 21.18). The disk shows concentric ripples from the spinning and has a bull's-eye at the center of the crown. The disk can be very smooth, having been flame-annealed without mechanical polishing. Historically, windowpanes could be cut around the bull's-eye or could contain it.

FIGURE 21.18. Crown glass with bull's-eye.

21.14.3 Borate Glass (Borosilicate Glass)

The alkali borosilicates, SiO_2–B_2O_3–R_2O (where R is the alkali), are special for their low α. They are durable and have useful electrical properties. The cookware material, Pyrex™ is a borosilicate. Borosilicate glass is widely used in the chemical processing industry. Some borate glasses melt at very low temperatures (~500 ± 50°C), so they can be used to join together other glasses. Zinc-borosilicate glass, known as passivation glass, contains no alkalis, so it can be used for Si electronics components.

21.14.4 Fused Silica

Being essentially pure SiO_2, fused silica is the glass used for high-temperature applications. It has a near-zero α. It is known as ultra-low expansion (ULE) silica and is used for telescope mirrors and substrates. ULE® glass containing 7% TiO_2 is being used for photolithography masks—for extreme UV lithography (EUVL)—at a wavelength of 13.4 nm. Another silica glass that can be used for 157-nm lithography was made by removing the water and adding fluorine ions to change the composition of the silica; this process allows transmission of wavelengths down to 157 nm. We've already discussed Vycor, which can be pure (porous) silica after we remove the second phase.

21.14.5 Phosphate Glass

Phosphate glasses are important because they are semiconducting. One application is in the manufacture of electron multipliers (hence amplifiers) using Er-doping (with Er_2O_3). The cations here are usually V and P but Oak Ridge National Laboratory (ORNL) developed a lead indium phosphate glass that has a high index of refraction and a low melting temperature and is transparent over a wide range of wavelengths. As it can also dissolve significant concentrations of rare-earth elements (it was designed to be a container for radioactive waste), it is being explored for new optically active devices (e.g., fiberoptic amplifiers and lasers). Nd-doped (using Nd_2O_3) phosphate glasses are being used in solid-state lasers (1.054 μm wavelength). The typical composition is 60 P_2O_5–10 Al_2O_3–30 M_2O (or MO); the Nd concentrations is ~0.2–2.0 mol%. We see more on calcium phosphate glass when we discuss bioceramics in Chapter 35.

21.14.6 Chalcogenide Glass

Based on As, Se, and Te, these glasses are IR transparent. They are nonoxide semiconductors and are used in special electronic devices and lenses. The devices use the abrupt change in electrical conductivity that occurs when a critical voltage is exceeded. The applications have to be special because these glasses are not durable and have low softening temperatures.

21.14.7 Fluoride Glass

In general, halide glasses are based on BeF_2 and $ZnCl_2$ and are used in optical waveguides (OWGs), where the cost can be justified.

21.15 NATURAL GLASS

It surprises some people that not only does glass occur in nature it is relatively common.

Tektites are formed within the impact craters of meteors. Moldavite is a green glass from Moldavia in the Czech Republic. Libyan desert glass is formed the same way but is yellow.

Fulgarites are fragile tubes of glass that can be formed when lightning strikes a sandy soil.

Obsidian is the glass formed in volcano flows. The usual black color is due to impurities; green and red obsidian also occur. Obsidian was used to make tools during the Paleolithic period. The advantages of using glass for scalpels have only recently been rediscovered: the cut made by a glass knife is particularly even, so it heals fast. It has been proposed that the Aztec Civilization may not have developed metallurgy because it was so adept at using obsidian. There are many sources of obsidian in the volcanic mountain ranges of Peru and Ecuador in particular.

Pumice is another glass formed in volcanic eruptions. It can be very porous if it contains a high concentration of gas. Pumice is thus the porous form of obsidian.

Trinitite is not really a natural glass but one that we might say forms unintentionally. This glass has been found at the Trinity site where the nuclear bomb was exploded in New Mexico.

Diatoms. Why are we including this topic here? Because it is both interesting and surprising. Not all living things on Earth are based on carbon. Diatoms are small aquatic microorganisms, or one-celled plants that live by ingesting silica that is dissolved in water—we usually think of seawater, but it can be a freshwater lake. The diatoms then use the silica to form and grow a pair of shells, illustrated in Figure 21.19. The two shells resemble a pillbox. The shells come in many varieties—there are thousands of species of diatoms. When the microorganisms die, their siliceous skeletons have formed layers up to 3,000 ft thick: they are not rare! The result is that there are regions where deposits of silica have built up to form what is known as diatomite or diatomaceous earth. The comparable process for carbon-based creatures would be the formation of limestone and chalk. Diatoms do contain chlorophyll, so they are plant-colored while alive.

The *Venus flower basket* (genus *Euplectella*) is a sponge that lives in the deepest parts of the oceans in the tropics. It has a skeleton that looks like a mesh of glassy silica fibers (Figure 21.20). Each fiber actually consists of coaxial cylindrical layers with different optical properties. It is reminiscent of the cladding used today on commercial optical fibers, but nature did it eons earlier. The optical properties of the natural fibers are not as good as those of human-made fibers, but they are more resistant to breaking. Note that these layers are deposited at ambient water temperatures!

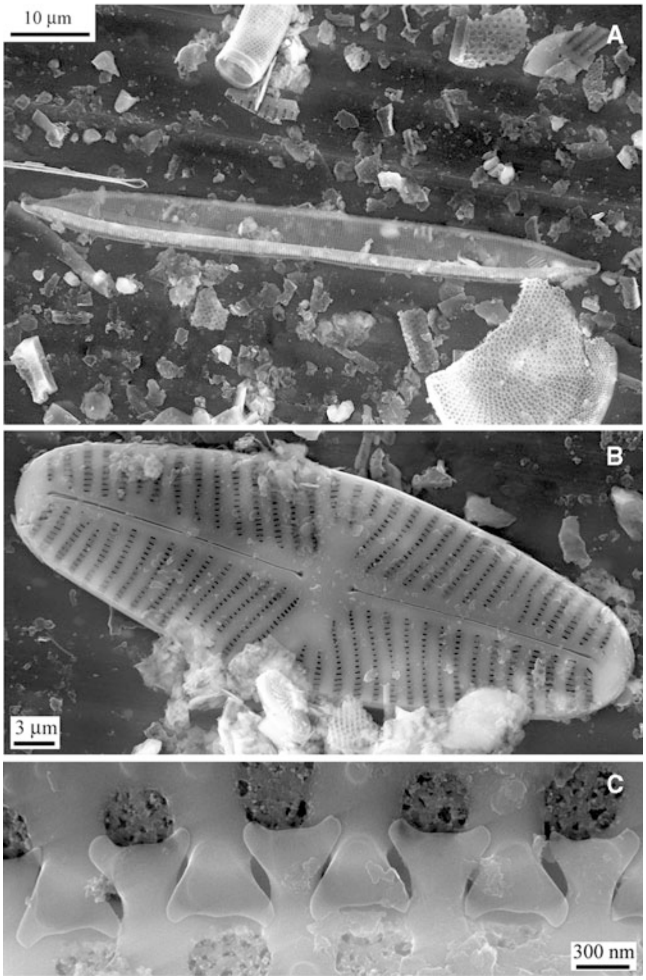

FIGURE 21.19. SEM image of diatoms.

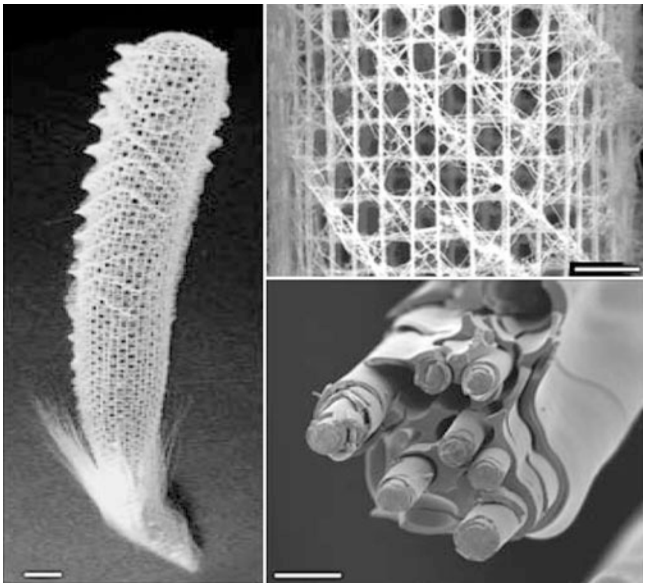

FIGURE 21.20. Sea sponge.

21.16 PHYSICS OF GLASS

We now discuss glass from the physicist's point of view. We've left this topic until last so as either to confirm your excitement or not completely put you off the subject.

The idea is that glass is a condensed phase—just as liquids and crystals are. The atomic interactions can be described by a potential energy function, ϕ.

If we describe the energy of a glass plotted against the coordinates of the glass, we would find a multidimensional energy hypersurface, which is multiply dented with structured valleys. The glass structure corresponds to one of those valleys, but there may be another valley or a minimum not far away on the surface. Then, we have the concept of polyamorphism where the glass can have several distinct amorphous structures. (The comparison to crystalline materials is instructive!)

The experimental observation is that the viscosity of some glasses decreases suddenly above T_g in a non-Arrhenius way. It's as if the structure of the glass collapsed because it was fragile (the term fragile strictly refers to the liquid, not the glass). Hence, fragility is a property of some glass-forming liquids above T_g, but we talk about fragile and strong glasses. If we plot log η versus T_g/T (the reduced T_g, as shown in Figure 21.21A), the curve would be straight if it was Arrhenius-like behavior. For SiO_2 and other highly polymerized network glasses (strong glass-formers), it is nearly straight. If the bonds are not directional, the plot deviates significantly from Arrhenius behavior; this is a fragile glass-former. Two approaches have been used to explain this behavior.

- Free volume
- Configurational entropy

Each connects η to the macroscopic quantities of either volume or entropy. A newer approach considers factors

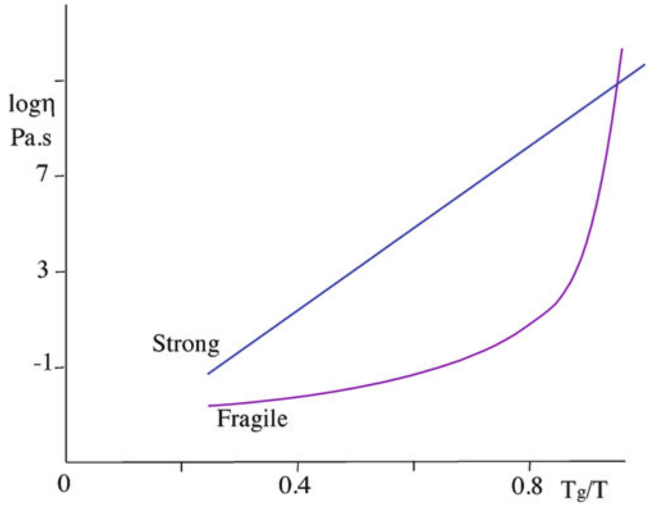

FIGURE 21.21. Viscosity versus temperature for strong and fragile liquids.

affecting the kinetics of the transformation. There are fast relaxation processes (known as β processes) and low-frequency processes that contribute to the dynamic structure factor. In the glass's vibrational spectra detected by Raman or neutrons, these features are known as the boson peak. The boson peak is large for strong glass-formers; low-frequency excitations in a glass suggest intermediate-range order: thus, more order indicates a stronger glass.

The molar heat capacity, c_p, is a well-defined quantity. At very low temperatures ($T < 1$ K: a temperature familiar to physicists but less so to ceramists), glasses show a linear term in c_p due to an anharmonic contribution. At $T \sim 5–10$ K, an excess vibrational (harmonic) contribution causes a bump in c_p. The excess vibrational contribution to c_p at this bump (i.e., $c_p - c_D$) can be plotted against the fragility of the glass. The resulting correlation suggests that the excess vibration and the fragility have a related origin. Therefore, SiO_2, a particularly strong glass, has a large c_p/c_D, whereas a fragile glass, such as CKN, $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$, has a small c_p/c_D.

CHAPTER SUMMARY

The location of the chapter is after "powders" but before "processing" because we are still emphasizing the material. Glass is an extremely important material—society might not be civilization without glass, so the history of this topic is particularly rich. Remember that glazes on pots and enamels on metals are essentially two variations on a single theme—protecting other materials by coating them with glass. The variety of glasses is large, and we have only touched on the range here. Remember that, historically, silica-based glass was for a long time synonymous with the word glass. It has dominated our thinking about glass. New glasses are being developed that may contain no Si, and the properties may be very different: there is not just one material called glass any more than there is one material called crystal. Glass crystallizes given time; although glass-ceramics were the new materials of the 1960s, they were already old friends to the potter. The basic science of glass is more difficult than for crystals because we have no "frame of reference." However, there are point defects in glass (remember the origins of color). Glass has both internal and external interfaces. Glass does have special structural features. Of the many important properties, transparency and viscosity must be the most important; but for many applications, the small, or controllable, expansion coefficient is the key to the value of glass.

As we explained from the beginning, glass appears throughout our discussion of ceramics. The processing of glass is treated in Chapter 26, mechanical properties are in discussed in Chapter 18, and Bioglass is in Chapter 35. The reason we treat glass separately is partly historical and partly because its behavior is often so different from that of crystalline ceramics, which underlines the point we made in Chapters 5–7 that bonding and structure determine the properties and thus the applications.

PEOPLE AND HISTORY

Bacon, Roger a Franciscan Friar who described reading glasses made using two lenses in 1268. Salvino D'Armate of Pisa is sometimes credited with the invention in 1284.

Cassius, Andreas (1685) in the book *De Auro*, described how to produce this ruby red color, which thus became known as "Purple of Cassius."

La Farge, John created a "Colored-Glass Window" (patent no. 224,831; February 24 1880), which was the original patent on opal glass, followed shortly by Louis Comfort Tiffany's patent (no. 237,417; February 8 1881) with the same title "Colored-Glass Window."

Lipperhey, Hans was a lens grinder in The Netherlands; applied to patent the telescope in 1608.

Pascal, Blaise (1623–1662) was born in Clermont-Ferrand, France and died in Paris. The SI unit of pressure (stress) is named after him. Argued against Descartes in favor of the existence of vacuum.

Perrot, Bernard (1619–1709) was a well-known early French glassmaker.

Poiseuille, Jean Louis Marie was the French physician (1799–1869) after whom we named the Poise.

Prince Rupert of Bavaria (1619–1682) was grandson of James I of England and nephew of Charles II. He introduced his drops to England in the 1640s, where they became party pieces in the court of Charles II. The famous diarist Samuel Pepys wrote about them in his diary on January 13, 1662.

Rakuyaki, Chojiro, (died 1859) was the first member of the family that began the tradition of raku. Their home is now an exquisite museum illustrating tea bowls made by 15 generations.

van Leeuwenhoek, Anton (1632–1723) was born in Delft, Holland and worked as a cloth merchant. He devised a simple microscope that succeeded so well because he was a skilled lens grinder. The microscope itself was invented in the 1500s and was used by Robert Hooke.

Warren, Bertram Eugene (1902–1991) was at M.I.T. 1930–1976. He is known for his textbook on X-ray diffraction and his studies of the structure of glass and carbon black. His work began small-angle scattering research into nonperiodic and nearly periodic structures.

EXERCISES

21.1 What causes refraction in glass?

21.2 Why is smoky quartz smoky?

21.3 If you increase the wavelength, how does the refractive index change?

21.4 What is dispersion, and why does glass cause it?

21.5 If Pb were added to a typical lead crystal glass, what weight percent would be added? What atomic percent of Pb would the glass then contain? What is actually added in industrial practice, and will this practice continue in the future?

21.6 If you are given crystalline SiO_2, quartz glass, silica gel, and a sample of liquid SiO_2, how would you analyze the bonding of the Si in each case? Would you detect a difference?

21.7 How would you expect the properties of GeO_2 glass to differ from those of SiO_2 glass? Be as quantitative as possible.

21.8 We can make glass based on B and on P. What are the bonding characteristics of these two glasses? Suggest three modifiers for each glass. Compare the densities you expect for these glasses.

21.9 Libyan desert glass was produced naturally. Is pressure or temperature the more important factor? Explain your reasoning as quantitatively as possible.

21.10 Na is a network modifier for SiO_2 glass. How would Li and K compare to Na in this role? Similarly, Ca is present in soda-lime glass. If the Ca were replaced by an equal atomic percent of Mg or Ba, how would the properties of the glass change?

21.11 We define the glass transition temperature using Figure 21.1. Why does it depend on the cooling rate, and how does this affect the definition?

21.12 Which is the better word to describe glass: amorphous or vitreous? Explain.

21.13 How was the bulti fish made?

21.14 If Amenophis's head was made by the lost-wax technique, is this the oldest use of the technique? What other materials is this used for?

21.15 Diatoms have interesting structures and abundant. Are there any applications for diatoms? Describe these applications and remember to cite your sources.

21.16 Explain why Mergules viscometer and fiber elongation are both used to measure viscosity but not necessarily on the same glass. Could they be used on the same glass?

21.17 Why would you use $10^{3.8}$ dPa·s to make a glass-to-metal seal but 10^{8} dPa·s to sinter glass?

21.18 Discuss the following statement: "glass is simpler than crystals because we don't have to worry about lattices or dislocations."

21.19 What is the difference between glass, enamel, and glazes? Discuss carefully!

21.20 When you have read the chapter, discuss Sturkey's assertion.

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