glass

an inorganic solid material that is usually transparent or translucent as well as hard, brittle, and impervious to the natural elements. Glass has been made into practical and decorative objects since ancient times, and it is still very important in applications as disparate as building construction, housewares, and telecommunications. It is made by cooling molten ingredients such as silica sand with sufficient rapidity to prevent the formation of visible crystals.

The varieties of glass differ widely in chemical composition and in physical qualities. Most varieties, however, have certain qualities in common. They pass through a viscous stage in cooling from a state of fluidity; they develop effects of colour when the glass mixtures are fused with certain metallic oxides; they are, when cold, poor conductors both of electricity and of heat; most types are easily fractured by a blow or shock and show a conchoidal fracture; they are but slightly affected by ordinary solvents but are readily attacked by hydrofluoric acid.

Commercial glasses may be divided into soda–lime–silica glasses and special glasses, most of the tonnage produced being of the former class. Such glasses are made from three main materials—sand (silicon dioxide, or SiO_2), limestone (calcium carbonate, or $CaCO_3$), and sodium carbonate (Na_2CO_3). Fused silica itself is an excellent glass, but, as the melting point of sand (crystalline silica) is above 1,700° C (3,092° F) and as it is very expensive to attain such high temperatures, its uses are restricted to those in which its superior properties—chemical inertness and the ability to withstand sudden changes of temperature—are so important that the cost is justified. Nevertheless the production of fused silica glass is quite a large industry; it is manufactured in various qualities, and when intended for optical purposes the raw material used is rock crystal rather than quartz sand.

To reduce the melting point of silica, it is necessary to add a flux; this is the purpose of the sodium carbonate (soda ash), which makes available the fluxing agent sodium oxide. By adding about 25 percent of the sodium oxide to silica, the melting point is reduced from 1,723° to 850° C (3,133° to 1,562° F). But such glasses are easily soluble in water (their solutions are called water glass; *q.v.*). The addition of lime (calcium oxide, or CaO), supplied by the limestone, renders the glass insoluble again, but too much makes a glass prone to devitrification—*i.e.*, the precipitation of crystalline phases in certain ranges of temperature. The optimum composition is about 75 percent silica, 10 percent lime, and 15 percent soda, but even this is too liable to devitrification during certain mechanical forming operations to be satisfactory.

In making sheet glass it is customary to use 6 percent of lime and 4 percent of magnesia (magnesium oxide, or MgO), and in bottle glass about 2 percent alumina (aluminum oxide, or Al_2O_3) is often present. Other materials are also added, some being put in to assist in refining the glass (*i.e.*, to remove the bubbles left behind in the melting process), while others are added to improve its colour. For example, sand always contains iron as an impurity, and, although the material used for making bottles is specially selected for its low iron content, the small traces of impurity still impart an undesirable green colour to the container; by the use of selenium and cobalt oxide together with traces of arsenic trioxide and sodium nitrate, it is possible to neutralize the green colour and produce a so-called white (decolourized) glass.

Glasses of very different, and often much more expensive, compositions are made when special physical and chemical properties are necessary. For example, in optical glasses, a wide range of compositions is required to obtain the variety of refractive index and dispersion needed if the lens designer is to produce multicomponent lenses that are free from the various faults associated with a single lens, such as chromatic aberration. High-purity, ultratransparent oxide glasses have been developed for use in fibre-optic telecommunications systems, in which messages are transmitted as light pulses over glass fibres.

When ordinary glass is subjected to a sudden change of temperature, stresses are produced in it that render it liable to fracture; by reducing its coefficient of thermal expansion, however, it is possible to make it much less susceptible to thermal shock. The glass with the lowest expansion coefficient is fused silica. Another well-known example is the borosilicate glass used for making domestic cookware, which has an expansion coefficient only one-third that of the typical soda–lime–silica glass. In order to effect this reduction, much of the sodium oxide added as a flux is replaced by boric oxide (B_2O_3) and some of the lime by alumina. Another familiar special glass is the lead crystal glass used in the manufacture of superior tableware; by using lead monoxide (PbO) as a flux, it is possible to obtain a glass with a high refractive index and, consequently, the desired sparkle and brilliance.

The agents used to colour glass are generally metallic oxides. The same oxide may produce different colours with different glass mixtures, and different oxides of the same metal may produce different colours. The purple-blue of cobalt, the chrome green or yellow of chromium, the dichroic canary colour of uranium, and the violet of manganese are constant. Ferrous oxide produces an olive green or a pale blue according to the glass with which it is mixed. Ferric oxide gives a yellow colour but requires an oxidizing agent to prevent reduction to the ferrous state. Lead gives a pale yellow colour. Silver oxide gives a permanent yellow stain. Finely divided vegetable charcoal added to a soda-lime glass gives a yellow colour. Selenites and selenates give a pale pink or pinkish yellow. Tellurium appears to give a pale pink tint. Nickel with a potash–lead glass gives a violet colour, and a brown colour with a soda–lime glass. Copper gives a peacock blue, which becomes green if the proportion of the copper oxide is increased.

An important class of materials is the chalcogenide glasses, which are selenides, containing thallium, arsenic, tellurium, and antimony in various proportions. They behave as amorphous semiconductors. Their photoconductive properties are also valuable.

Certain metallic glasses have magnetic properties; their characteristics of ease of manufacture, magnetic softness, and high electrical resistivity make them useful in the magnetic cores of electrical power transformers. Many different useful and decorative articles have been made from glass over the centuries. The history of glass as a creative art has been determined partly by technical advances in its manufacture and decoration and partly by the history of taste and fashion.

Glass was first made in the ancient world, but its earliest origins are obscure. Egyptian glass beads are the earliest glass objects known, dating from about 2500 BC. Later in Egyptian civilization, a type of glass characterized by feathery or zigzag patterns of coloured threads on the surface of the glass vessel was made.

The real origins of modern glass were in Alexandria during the Ptolemaic period and, later, in ancient Rome. Alexandrian craftsmen perfected a technique known as mosaic glass in which slices of glass canes of different colours were cut crossways to make different decorative patterns. Millefiori glass, for which the canes are cut in such a way as to produce designs reminiscent of flower shapes, is a type of mosaic glass.

Molded glass was also developed early, glass being pressed into a mold to form a particular shape. Various types of decoration involving engraving and colour were also possible.

Glassblowing was probably developed during the 1st century BC by glassmakers in Syria. With this technique the possibilities of shaping glass into desired forms were endless. Glass could be blown into a mold or shaped completely free-form. The Romans perfected cameo glass, in which the design has been produced by cutting away a layer of glass to leave the design in relief.

The next major developments in the history of glass came during the 15th century in Venice. As early as the 13th century the Venetian island of Murano had become the centre for glassmaking. At first, Venetian glassmakers made use of many of the ancient and medieval decorative techniques to produce richly coloured and ornamental pieces having motifs characteristic of the Italian Renaissance.

Later they developed a clear glass similar to crystal, called *cristallo*, which was to form the basis for a thriving export trade and spread throughout Europe. Simple blown glasses of this type were much in demand in the 16th century. Such glass lent itself to decoration by the engraving of delicate designs; used from the early 16th century, the technique remained popular well into the 18th century throughout Europe. Diamond-point engraving was practiced in particular in The Netherlands and in Germany.

Late in the 17th century Bohemia became an important glass-producing area and remained important until early in the 20th century. By the 17th century England was making glass in the Venetian tradition that was notable for its simplicity. The glassmaker George Ravenscroft discovered about 1675 that the addition of lead oxide to Venetian-type glass produced a solid, heavier glass. Lead crystal, as it was known, thereafter became a favourite type of glass for fine tableware.

Enameling came into fashion in the middle of the 18th century in England, leading to the development of the type of glass sometimes called Bristol glass. In the 18th century glass cutting came into fashion. As this technique was perfected, great richness of effect became possible. Eventually, by the end of the 18th century, when the technique was further developed in Ireland, the whole surface of glass was being deeply cut to reflect light. This English and Irish cut lead crystal was imitated in Europe and in the United States and has remained popular to the present day. Waterford crystal is an important example of this type.

The Art Nouveau period saw some important changes. The Favrile glass invented by Louis Comfort Tiffany, with its flowing shapes derived from naturalistic forms and its lustrous surface, was much admired and particularly influenced glassmakers in central Europe. The French glassmaker Émile Gallé and the firm of Daum Frères were also important designers in the Art Nouveau epoch.

René Lalique, one of the leaders of French glass art, made glass characterized by relief decoration. The Steuben Glass Company of New York produced clear glass objects, really crystal sculptures, often with engraved or incised designs. Their products have become classics of 20th-century glassmaking. In the 20th century Scandinavian glass gained fame for its elegance and simplicity of design.

Industrial glass   Properties of glass

At ordinary temperatures, glass is a nearly perfect elastic solid, an excellent thermal and electrical insulator, and very resistant to many corrosive media. (Its optical properties, however, vary greatly, depending on the light wavelengths employed.) The more or less random order of atoms is ultimately responsible for many of the properties that distinguish glass from other solids. One unique attribute of special importance may be called the isotropicity of properties, meaning that such properties as tensile strength, electrical resistance, and thermal expansion are of equal magnitude in any direction through the material.

As a glass-forming melt is cooled through the transition range, its structure relaxes, or changes continuously, from that of a liquid to that of a solid. The properties of solid glass reflect the extent of this structural relaxation. Indeed, glass can be said to retain a memory of the temperature-time schedule through the transition. Evidence of this “thermal history” is wiped out only after the glass has been reheated to the liquid state.

Most properties of glass—except for elastic and strength behaviour in the solid state—are sensitive to its chemical composition and, hence, its atomic structure. (The role of composition and structure in the formation of the glassy state is described in Glass formation: Atomic structure.) In oxide glasses, the specific composition-structure-property relationships are based upon the following factors: (1) the coordination number of the network-forming (NWF) ion, (2) the connectivity of the structure, as determined by the concentration of nonbridging oxygens, which, in turn, is determined by the concentration and nature of network-modifying (NWM) ions, (3) the openness of the structure, determined, again, by the concentration of NWM ions, and (4) the mobility of the NWM ions. Thus, tetrahedrally connected networks, such as those formed by silicates and illustrated in Figure 2, are more viscous than triangularly connected networks, such as those formed by borates. In silicates, the addition of network-modifying alkali ions would raise the concentration of nonbridging oxygens, and the resulting lowered connectivity would lead to a lowering of viscosity. Networks in which the interstitial spaces are less filled with NWM ions possess lower density and allow greater permeation of gases through them. Since alkali ions are the most mobile species through interstices of oxide glasses, the higher the alkali concentration, the lower the chemical durability and electrical resistivity of the material.

Because glass generally acts as if it were a solution, many of its properties can be estimated by applying what are known as additivity relationships over a narrow range of compositions. In additivity relationships, it is assumed that each ingredient in a glass contributes to the properties of the glass by an amount equal to the concentration of that ingredient multiplied by a specific additivity factor. Many properties of soda-lime-silica glasses follow such relationships closely.

Physical properties Density

In the random atomic order of a glassy solid, the atoms are packed less densely than in a corresponding crystal, leaving larger interstitial spaces, or holes between atoms. These interstitial spaces collectively make up what is known as free volume, and they are responsible for the lower density of a glass as opposed to a crystal. For example, the density of silica glass is about 2 percent lower than that of its closest crystalline counterpart, the silica mineral low-cristobalite. The addition of alkali and lime, however, would cause the density of the glass to increase steadily as the network-modifying sodium and calcium ions filled the interstitial spaces. Thus, commercial soda-lime-silica glasses have a density greater than that of low-cristobalite. Density follows additivity behaviour closely. (The densities of representative oxide glasses are shown in Table 2.)

Properties of glass Optical properties Transparency, opacity, and colour

Because electrons in glass molecules are confined to particular energy levels, they cannot absorb and reemit photons (the basic units of light energy) by skipping from one energy band to another and back again. As a consequence, light energy travels through glass instead of being absorbed and reflected, so that glass is transparent. Furthermore, the molecular units in glass are so small in comparison to light waves of ordinary wavelengths that their absorption effect is negligible. Radiation of some wavelengths, however, can cause glass molecules to vibrate, making the glass opaque to those wavelengths. For instance, most oxide glasses are good absorbers of, and are therefore opaque to, ultraviolet radiation of wavelengths smaller than 350 nanometres, or 3,500 angstroms. These glasses can be made more transparent to ultraviolet radiation by increasing the silica content. At the same time, silicate glasses absorb wavelengths greater than 4 micrometres, making them virtually opaque to infrared radiation. Heavy-metal fluoride glasses, on the other hand, transmit wavelengths up to about 7 micrometres, while some chalcogenide glasses transmit as far as 18 micrometres—properties that make them transparent into the middle infrared region.

Glass to which certain metallic oxides have been added will absorb wavelengths corresponding to certain colours and let others pass, thus appearing tinted to the eye. For instance, cobalt gives an intense blue tint to glass, chromium generally gives green, and manganese imparts purple.

Properties of glass Optical properties Photosensitivity

In some glasses containing small amounts of cerium oxide and ions of copper, silver, or gold, exposure to ultraviolet radiation causes the oxidation of cerium and the reduction of the latter elements to the metallic state. Upon subsequent heating, the metal nuclei grow, or “strike,” developing strong colours (red for copper and gold, yellow for silver) in the ultraviolet-exposed regions of the glass. This technique has been used to produce “three-dimensional photographs,” but a more recent use is in microphotolithography for the production of complex electronic circuits.

Traditional photochromic eyeglasses are generally alkali boroaluminosilicates with 0.01 to 0.1 percent silver halide and a small amount of copper. Upon absorption of light, the silver ion reduces to metallic silver, which nucleates to form colloids about 120 angstroms in size. This is small enough to keep the glass transparent, but the colloids are dense enough to make the glass look gray or brown. In photochromic eyeglasses, darkening is reversed either by the removal of light (optical bleaching) or by raising the temperature (thermal bleaching).

Properties of glass Optical properties Refraction and reflection of light

A ray of light, on passing from one transparent medium to another transparent medium of different density, will be transmitted through the second medium with no loss of intensity or change in direction if it strikes the boundary between the two mediums at a right angle (90°). In geometric terms, the right angle at which the light ray meets the boundary is called the normal. If the light ray meets the boundary at an angle other than the normal, then it will be partially reflected back into the first medium and partially refracted, or deflected, in its path through the second medium. The extent to which the light is reflected and refracted depends on the relative densities of the two mediums involved (usually glass and air) and on the angle at which the light ray meets the boundary (known as the angle of incidence). As is shown in Figure 7, if the light ray meets the boundary at less than a certain critical angle (θc), most of the light will be refracted while a small amount is reflected. If it arrives at the boundary at the critical angle, then the emerging light will be of diminished intensity and will assume a direction parallel and close to the boundary; most of the light will be reflected. Finally, if the critical angle is exceeded, all of the light will be reflected back into the glass without suffering any loss of intensity. Known as total internal reflection, this phenomenon is widely exploited in single-lens reflex cameras and in fibre optics, in which light signals are piped for great distances before signal boosting is required.

Refraction can be expressed as a constant, known as the refractive index, which is derived mathematically from the ratio of the sine of the angle of incidence on the medium to the sine of the angle of refraction within the medium. The refractive index of a particular type of glass depends on its composition and on the wavelength of the light. The refractive indices of various oxide glasses are shown in

Glass treating Strengthening Polishing and glazing

Etching of most silicate glasses can be carried out using a solution of 6–30 percent hydrofluoric acid with a small amount of sulfuric acid—although, for safety reasons, this treatment is not recommended. Strengthening by overlay glazing is carried out by firing onto the glass product a thin layer of another glass that has lower thermal expansion properties than the substrate.

Glass treating Strengthening Thermal tempering

Thermal tempering is achieved by quenching (or rapid-cooling) the glass from a temperature well above the transition range using symmetrically placed air jets. Since the outer layers of the glass are cooled faster than the inside and pass through the glass transition range sooner, they shrink at a higher rate and are compressed (in effect strengthening the glass), while the interior is stretched. Many commercial glass products can be strengthened significantly by thermal tempering. However, thick glasses may fracture spontaneously, beginning at a flaw in the interior, owing to the high tension that tempering creates in that region. Such glass may break, or dice, violently into a larger number of pieces. Since diced glass is unlikely to cause serious injury, tempered glass products may be legally required in certain applications, as in bathroom shower doors.

Glass treating Strengthening Ion exchange

Ion-exchange strengthening is applicable only to alkali-containing glasses. It is carried out by immersing the glass in a bath of molten alkali salt (generally a nitrate) at temperatures below the transition range. The salt must be selected to have ions greater in size than the host alkali ions in glass. Through a diffusion mechanism, the larger invading ions from the alkali bath exchange relatively smaller sites with the smaller alkali ions in the surface regions of the glass—thus producing, as in thermal tempering, compression in the surface and tension in the interior. Because the invading ions penetrate only 40 to 300 micrometres into the host glass, the magnitude of the balancing internal tension is generally small. Thin glass specimens may be strengthened using the ion-exchange process. However, it is a slow process, generally requiring 2 to 24 hours of immersion in the salt bath.

Glass treating Strengthening Lamination

In lamination, the mechanical energy associated with applied stress is absorbed by successive layers of glass and laminate, leaving less energy for crack development. Most glass products are laminated by bonding sheets of tough polymers such as polyvinyl butyral, polyurethane, ethylene terpolymer, and polytetrafluoroethane (sold under the trademark Teflon) to glass surfaces, generally by heat-shrinking. For windshield applications, paired sheets of glass, 3 to 6 millimetres (0.12 to 0.5 inch) thick, with a fine coating of talc to keep them from fusing, are placed over a metal support frame. The two plies are heated almost to softening, at which point bending occurs basically by gravity action. After cooling, the plies are separated and a polymer interlayer introduced, and the entire laminated assembly is gently heated in an electric furnace and either squeezed through a pair of rollers or pressed between molds. Not only does the interlayer help to absorb the energy of an impacting object, but the adhesion of glass to the polymer minimizes the risk of flying shards upon fracture. For aircraft, windshields may have several laminates, sometimes as many as three glass plies and two plastic interlayers. At least one of the inner glass plies is strengthened by ion exchange (see above) in order to withstand the impact of flying objects such as birds. Bulletproof glass is often laminated, although a single ply of dead-annealed glass as thick as 20 to 25 millimetres is used in some applications. The reason for having dead-annealed glass is the absence of tension in the interior; internal tension would cause the glass to shatter upon impact of the first bullet, thereby rendering the person behind the glass vulnerable to the second bullet.

Tempered glass

Tempered glass is one of two kinds of safety glass regularly used in applications in which standard glass could pose a potential danger. Tempered glass is four to five times stronger than standard glass and does not break into sharp shards when it fails. Tempered glass is manufactured through a process of extreme heating and rapid cooling, making it harder than normal glass. The brittle nature of tempered glass causes it to shatter into small oval-shaped pebbles when broken. This eliminates the danger of sharp edges. Due to this property, along with its strength, tempered glass is often referred to as safety glass.

The thermal process that cures tempered glass also makes it heat resistant. Tempered glass is used to make the carafes in automatic coffee makers and the windows in ovens. Computer screens, skylights, door windows, tub enclosures and shower doors are more examples of places you will find tempered glass. Building codes also require the windows of many public structures to be made of tempered glass.

Automobiles use a different type of safety glass for the windshield and tempered glass for the back and side windows. Windshields are made from laminated glass, which sandwiches a sheet of plastic between two panels of glass. When the windshield breaks, the glass panels stick to the plastic film, rather than falling away to possibly injure the driver or other passengers.

Tempered glass breaks in a unique way. If any part of the glass fails, the entire panel shatters at once. This distinguishes it from normal glass, which might experience a small crack or localized breakage from an isolated impact. Tempered glass might also fail long after the event that caused the failure. Stresses continue to play until the defect erupts, triggering breakage of the entire panel.

In recent years, acrylic has replaced tempered glass in many applications in which heat is not a factor. Acrylic is 20 times more impact resistant than glass and does not shatter like tempered glass. Instead, acrylic dents if the impact is strong enough. If the force is sufficient to cause acrylic to fail, it will crack without shattering. Acrylic is also half the weight of glass and has many other advantages. However, it is flammable. Therefore, you won’t find an acrylic coffee carafe or oven door.

Low E glass:

Low emissivity glass, commonly called low **E glass,** is a type of reflective glass that is gaining in popularity, especially in residential and office applications. Low E coatings are very thin metallic coatings that reduce visible light transmission by about 10 percent compared to uncoated glass. They are applied using either the vacuum (sputter) or pyrolytic process.
Characteristics include:

- Reduces heat loss through windows.
- Re-radiates the heat absorbed from sunlight back inside the room.
- Allows sunlight into a room without letting heat escape outdoors.
- Resists ultraviolet light, which results in less damage to carpets, draperies and other furnishings.
- Reduces glare.

The main reason low **E** glass has these advantages is that it reflects sensible heat. The heat generated by hot water or steam radiators or the heat from hot air ducts are examples of sensible heat. Low E glass retains more of this heat indoors than other types of reflective glass. In northern areas, low E coatings let in the heat from the winter sun while retaining the heat generated from inside the building. In southern areas, low E coatings are usually applied to bronze, green or gray tinted glass. They reduce glare and reflect the sun's heat away from the structure.

Insulating glass units, commonly called **ig** units, are made from two or more lites of glass separated by a sealed air space. The metal tube around the perimeter of the insulated unit which seperates the two lites of glass is called the spacer. This spacer comes in thicknesses of 3/16" and larger. It is filled with a special moisture absorbing material called a dessicant. The perimeter of the entire unit is sealed with a high grade sealant. Characteristics include:

IG Units:

- Reduce the tendency of condensation to form on the room side of the glass.
- Reduce cold transmittance at windows and helps maintain a uniform temperature. In the winter, ig units reduce heat loss and in the summer they reduce heat gain.
- Reduce the level of noise from the outside.