Kirk-Othmer Encyclopedia of Chemical Technology.

CERAMICS, GLASS STRUCTURE AND PROPERTIES

Inorganic glasses are important ceramic materials and glasses share many of the desirable properties of crystalline ceramics even though they lack long-range order (see Glass; Glass, ceramics). The structure of glasses is not completely random, however. Glasses do have short-range order in the arrangement of anions around cations.

Glasses, less thermodynamically stable than crystals, must be "captured" in a metastable state, and this is typically accomplished by rapid cooling of a liquid. Whereas virtually any inorganic material can form a glass if it can be cooled at a sufficiently rapid rate, glasses requiring extremely fast cooling rates such as those attained from splat quenching or twin-roller techniques are not discussed herein.

1. Types of Glasses

The simplest inorganic glasses are composed of only one element: B, C, P, As, S, or Se. Glassy selenium in thin-film form has been used extensively in the photocopying industry. Inorganic glasses containing more than one element can be broadly categorized according to the type of anion. There are two main categories: chalcogenide glasses and halide glasses. Chalcogenide glasses contain anions from Group 16 (VI A) of the Periodic Table O, S, Se, Te; halide glasses contain anions from Group 17 (VII A), F, Cl, Br, I. Although oxide glasses are, strictly speaking, a subset of the chalcogenide glasses, the family of oxide glasses is so large and so important that it is usually considered separately from the other chalcogenides.

1.1. Oxide Glasses

The oxides that form glass without the addition of any other agents are known as primary glass forming oxides. These are P_2O_5, As_2O_5, SiO_2, GeO_2, and B_2O_3. Vitreous arsenious oxide, As_2O_3, is obtained by condensing the vapor onto a cold surface. It is possible to form small amounts of antimony trioxide glass by sealing Sb_2O_3 into a silica ampul which is heated to 800°C for 30 minutes and then quenched by being held in contact with a cold metal plate. Sulfur trioxide also forms a glass when cooled rapidly to a temperature below its melting point of 16.8°C. The most important, by far, of all the glass forming oxides is silicon dioxide, SiO_2. The oxides V_2O_5 and TeO_2 form glasses with very small ($\leq$5 mol %) amounts of additives. In general, an oxide compound that is capable of contributing over 50 atom % of the cations in a glass is known as a conditional glass former. These include MoO_3, WO_3, TiO_2, Fe_2O_3, Al_2O_3, Ga_2O_3, Bi_2O_3, BeO, and PbO. The compounds Nb_2O_5 and Ta_2O_5 can form glasses in proportions up to 42.5 mol %.

1.2. Nonoxide Chalcogenide Glasses

Primary glass forming sulfides include As_2S_5, SiS_2, GeS_2, B_2S_3, Al_2S_3, Ge_2S_3, As_2S_3, and Sb_2S_3. Arsenic(III) sulfide is the most widely known and used sulfide glass, but its manufacture is problematic because of the toxicity and volatility of arsenic. The compounds P_2S_5, Ga_2S_3, and In_2S_3 are conditional glass forming sulfides. Some primary glass forming selenides are $SiSe_2$, $GeSe_2$, Ge_2Se_3, As_2Se_3, Sb_2Se_3, and TlSe. Examples of primary glass forming tellurides are $GeTe_2$, Si_2Te_3, GaTe, GeTe, and SnTe. The compound As_2Te_3 is glassforming (1), but the glass is difficult to obtain. Some compounds, such as Ge_2S_3, Ge_2Se_3, and $GeTe_2$, do not exist in crystalline form. In general, nonoxide chalcogenide glasses can exist over wide ranges of the component elements. For example, the S/Ge ratio in binary Ge–S glasses can range from 1.3 to 1.5 and from 2 to 9. Chalcogenide glasses containing various ratios of three elements include Ge–As–S, Ge–As–Se, Ge–As–Te, Ge–Sb–Se, As–Sb–Se, As–S–Se, As–S–Te, As–Se–Te, S–Se–Te, etc. Mixed chalcohalide glasses such as Se–Te–X ($X =$ Cl, Br, I) have also been developed.

1.3. Halide Glasses

Fluoride glasses are the most important of the halide glasses. The only primary fluoride glass former is beryllium fluoride, BeF_2 (see Beryllium compounds). Conditional fluoride glass formers are ZrF_4, HfF_4, ThF_4, UF_4, ScF_3, YF_3, CrF_3, FeF_3, AlF_3, GaF_3, InF_3, ZnF_2, CdF_2, and PbF_2. The only primary chloride glass former is zinc chloride, $ZnCl_2$. Conditional chloride glass formers include $ThCl_4$, $BiCl_3$, $CdCl_2$, $SnCl_2$, $PbCl_2$, CuCl, AgCl, and TlCl. The only primary bromide glass former is zinc bromide, $ZnBr_2$, which is more difficult to prepare than is $ZnCl_2$. Conditional bromide glass formers include $PbBr_2$, CuBr, and AgBr. Conditional iodide glass formers include ZnI_2, CdI_2, PbI_2, CuI, and AgI. There are many mixed-halide glasses (2, 3).

1.4. Oxyhalide Glasses

Many glasses contain both oxide and halide anions. The introduction of halides into an oxide glass typically serves to reduce the glass-transition temperature, T_g, and to increase the coefficient of thermal expansion. Oxyfluorophosphates have been investigated as laser host materials. The Sn–P–O–F system yields glasses having very low glass-transition temperatures and moderate durability in water. Relatively large amounts of halides can be incorporated into glasses based on tellurium(IV) oxide or antimony(III) oxide.

1.5. Oxynitride Glasses

Small concentrations of nitride ions, sometimes added as Si_3N_4 or AlN, increase the viscosity of oxide melts, the refractive index, T_g, and hardness of oxide glasses. Apparently the nitride anions are three-coordinate and cause more cross-linking and denser packing in the glass. The incorporation of large amounts of nitrogen also increases the tendency for the glasses to crystallize.

The first oxynitride glasses were aluminosilicates; these Si–Al–O–N glasses became known as sialons. Much greater concentrations of nitrogen (up to 15 atomic %) can be accommodated in magnesium, calcium, yttrium, or rare-earth sialons. The glasses are bluish gray, and the color intensifies with nitride concentration. The crystallization products are high melting oxynitride compounds, so it is possible that the sialon glasses could give rise to glass-ceramics with useful high temperature properties.

Other glasses, such as phosphates and borates, have also been nitrided. The nitridation improves the aqueous durability of the parent glass. In low melting nonsilicate glasses, the nitride ions are typically introduced into the glass by melting in an ammonia atmosphere or by bubbling ammonia through the melt.

1.6. Oxycarbide Glasses

Oxycarbide silicate glasses are made by adding SiC to the melt. The T_g and hardness of the glasses are increased to a greater extent than by nitride additions, because the carbide anion is four-coordinate and results in a greater degree of cross-linking. The density, elastic modulus, and fracture toughness increase with increasing carbon content.

1.7. Glasses Containing Polyatomic Anions

Carbonate, nitrate, nitrite, sulfate, dichromate(VI), and selenate(IV) glasses are interesting in that they contain discrete polyatomic anions rather than extended oxide networks (4). Structural interpretations of glass formation in these systems usually are based on the idea that unbalanced cation force fields prevent efficient packing of polyatomic anions, which are typically triangular, pyramidal, or tetrahedral. There are many cases of mixed-anion glasses containing combinations of halides and polyatomic anions (4). Most of these glasses are quite soluble in water.

1.7.1. Carbonate Glasses

Carbonate glasses must be melted under moderate pressures to prevent the escape of carbon dioxide gas. The simplest carbonate glass forming system is K_2CO_3–$MgCO_3$.

1.7.2. Nitrate and Nitrite Glasses

The best nitrate glasses result when the difference between the field strengths (Z/r^2) of the cations is 0.7 or more (4). Here, Z is the charge on the cation, and r is the cation radius in nm × 10^{-1}. Cations having high field strengths tend to cause perturbations of the symmetry of the nitrate ions. The most studied nitrate composition is $40Ca(NO_3)_2{\cdot}60KNO_3$. Nitrate glasses containing large amounts of thiocyanate (SCN^-) also exist. Nitrite glasses such as those in the $Ca(NO_2)_2$–KNO_2 system have been prepared, but decomposition of nitrite melts is a problem.

1.7.3. Sulfate Glasses

The sulfate ion is tetrahedral (quasispherical), so the formation of sulfate glasses is more difficult than the formation of nitrate glasses (4). The presence of cations of different valences appears to be necessary for sulfate glasses. An example is the $ZnSO_4$–K_2SO_4 system. Glass formation is enhanced upon the addition of chlorides.

1.7.4. Dichromate(VI) Glasses

Alkali dichromate(VI) glasses exist in systems such as $Li_2Cr_2O_7$–$Na_2Cr_2O_7$. The glass-transition temperatures of the dichromates are very low, about 0°C. The addition of chlorides or nitrates aids in glass formation.

1.7.5. Selenate(IV) Glasses

Selenate(IV) glasses, like carbonate glasses, are very volatile. They are best prepared under pressure. Sublimation from glasses in the K_2O–SeO_2 system, however, has been reported to be negligible. The selenate(IV) glasses have low glass-transition temperatures and are very hygroscopic.

2. Glass Structure

Several criteria for predicting which compounds form glasses have been proposed. The best known guidelines are those originally presented for oxide glasses and known as Zachariasen Rules (5). They can be summarized as: (*1*) an oxygen or anion must not be linked to more than two cations; (*2*) the oxygen or anion coordination number of the cations must be small; and (*3*) the cation–anion polyhedra must share corners rather than edges or faces. These rules are satisfied by glasses such as vitreous B_2O_3, which contains triangularly coordinated boron atoms, and by vitreous SiO_2 and vitreous BeF_2, which both contain tetrahedrally coordinated cations.

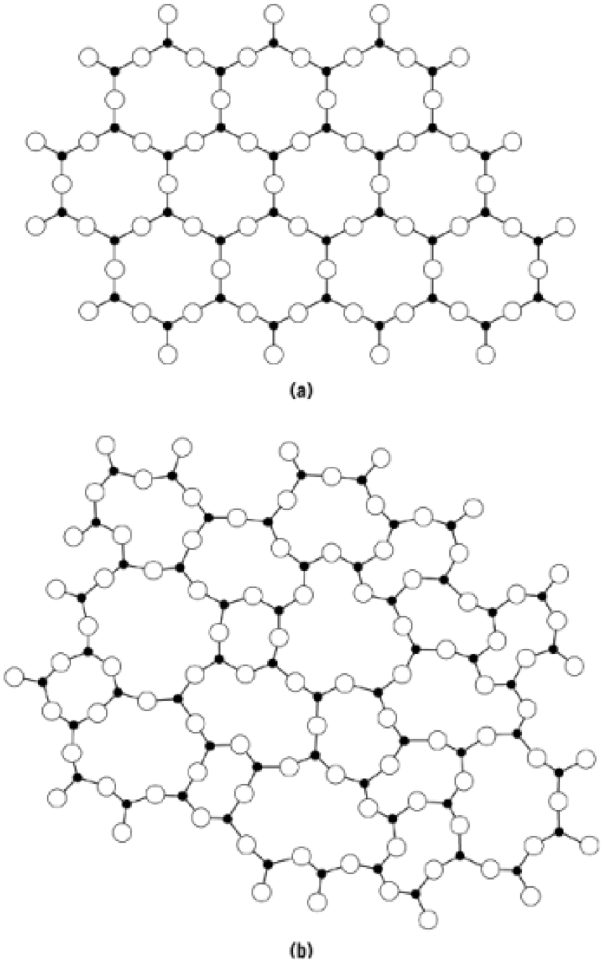

Fig. 1. Schematic two-dimensional representation of SiO_2 structures where ● represents Si atoms and ○, oxygen, (**a**) crystalline material; (**b**), glass (5).

Many fluoride glasses, such as those based on zirconium(IV) fluoride, ZrF_4, contain cations having high coordination numbers of 6, 7, or 8 (see Fluorine compounds, inorganic) and thus violate Rule 2. However, the fluoride ions are predominantly two-coordinate, as required by Rule 1. The importance of Rule 1 in glass formation is probably because a distribution of M–A–M angles, where M is a cation and A is an anion, is necessary to avoid imposing too much order in the system. If most of the anions were, for example, three-coordinate, there would be little structural freedom in the network, and the substance would crystallize. Both crystalline and vitreous SiO_2 are shown in Figure 1.

The radius ratio rule (6) can be used with Zachariasen Rule 1 to predict which compounds tend to form glass. For oxides with the formula MO_2, charge balancing requires that the cations must be four-coordinate if the oxygens are to be two-coordinate. For tetrahedral coordination of a cation by oxygen, the ratio of the cation radius to the oxygen radius must be ≤ 0.414 (6). Oxides satisfying this requirement are SiO_2 and GeO_2, which are glass forming. The radius ratio of TiO_2 is too large, but glasses containing substantial amounts of TiO_2 can be made if other agents are added. Whereas the radius ratio of Te^{4+} is much too large, glasses containing

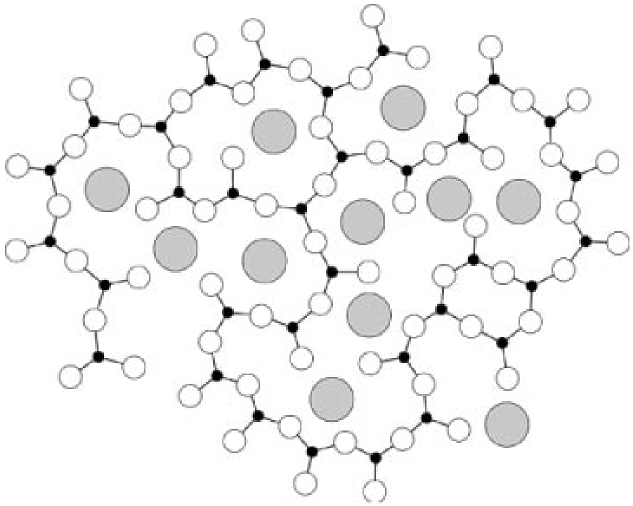

Fig. 2. Schematic two-dimensional representation of the structure of sodium silicate glass where● represents Si; ○, oxygen; and • sodium (5).

as much as 98 mol % TeO_2 have been reported, presumably because the Te^{4+} lone pair of electrons occupies a large amount of space allowing the tellurium cation to be four-coordinate.

For halides the cation should have a charge of 2+ rather than 4+ for tetrahedral coordination. The only fluoride compound capable of containing two-coordinate F and four-coordinate cations is BeF_2. For ZrF_4, the radius ratio rule predicts that Zr^{4+} is eight-coordinate if all fluorine atoms are two-coordinate.

In addition to the Zachariasen and radius ratio rules, for oxides the electronegativity of the predominant cation should be between 1.7 and 2.1 (7). If the cation electronegativity is too high, the compound tends to form molecules or discrete polyatomic ions rather than a connected network. For example, CrO_3 satisfies the radius ratio rule, but the highly electronegative Cr^{6+} ions promote the formation of discrete dichromate(VI) ions, $Cr_2O_7{}^{2-}$;, in the presence of other oxides.

Modifiers in glass are compounds that tend to donate anions to the network, whereas the cations occupy “holes” in the disordered structure. These conditions cause the formation of nonbridging anions, or anions that are connected to only one network-forming cation, as shown in Figure 2. Modifier compounds usually contain cations with low charge-to-radius ratios (*Z/r*), such as alkali or alkaline-earth ions.

3. Optical Properties

Probably the most striking and useful characteristic of common silicate glass is its transparency to visible light. This transparency results from the absence of grain boundaries and delocalized electrons, which tend to scatter and absorb light.

3.1. Transmission of Light

In the absence of an electromagnetic field, the electrons and atoms of a material oscillate at their natural, or resonance, frequencies. When the frequency of an incident electromagnetic field matches the resonance frequency of any of the components, some of the light is absorbed. This frequency is determined by the constituents and the chemical bonds. Absorption in the ultraviolet (uv) is primarily from electronic transitions associated with the oxygen atoms, particularly nonbridging oxygens. The addition of alkali or alkaline-earth oxides to a glass forming oxide shifts the uv absorption edge to lower energies (longer wavelengths). Conversely, the range of uv transmission is enhanced when the cations in the glass have a high charge-to-radius ratio, indicating a stronger cation–oxygen bond.

When equimolar quantities of a given modifier oxide are added to SiO_2 and B_2O_3, the uv cutoff of the silicate glass is at a lower energy than that of the borate; the value of *Z/r* for Si^{4+} is 10, and the *Z/r* of B^{3+} is 20. The addition of nitride ions to oxide glasses shifts the uv edge to longer wavelengths (lower energies), probably because of the greater polarizability of the trivalent nitrogen.

In the visible region, absorption by additives such as transition-metal or lanthanide ions is usually more important than contributions from the glass formers themselves. The solarization, ie, coloration of glass by uv radiation from sunlight, usually results from oxidation of transition-metal ions in the glass. However, gamma rays or x-rays can induce coloration even in undoped glass through the formation of separated electron-hole pairs. Binary phosphovanadate glasses are opaque in the visible region because of the movement (delocalization) of electrons between V^{5+} and V^{4+} sites. Chalcogenide glasses such as As_2S_3 are colored or even opaque, because of the small difference in energy between the conduction and valence bands.

Glasses having some absorption in the visible are used in products such as sunglasses. The visible transmission of photochromic glasses decreases with increasing frequency of light, and the effect is reversible. These glasses contain small ($\sim$10 nm in diameter) droplets of silver chloride, AgCl, or other silver halides doped with copper(I) ions (8). In the presence of uv radiation, the reaction $\mathrm{Ag(I)} + \mathrm{Cu(I)} \longrightarrow \mathrm{Ag} + \mathrm{Cu(II)}$ occurs, leading to the formation of small particles of metallic silver which cause the glass to darken.

Infrared (ir) transmission depends on the vibrational characteristics of the atoms rather than the electrons (see Infrared and Raman spectroscopy). For a diatomic harmonic oscillator, the vibrational frequency is described by

$$\nu = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

where ν is the frequency, c is the speed of light, k is the force constant of the bond, and μ is the reduced mass of the atoms. Thus the ir cutoff in a glass would be extended to lower energies as the atomic masses increase and as the bond strengths decrease and indeed germanate glasses transmit further into the ir than silicate glasses because germanium atoms are larger and heavier. Also, halide glasses have better ir transmission than oxide glasses; the -1 charge on the halide ions leads to weaker cation–anion bonds. Chalcogenide glasses combine the desirable features of heavy atoms and low valent ions. For example, the well-known infrared optical component material As_2S_3 transmits at longer wavelengths than GeO_2 does because As is heavier than Ge, S is heavier than O, and the arsenic ion has a charge of 3+ as opposed to the charge of 4+ on germanium.

3.2. Refractive Index

The refractive index n of a glass is defined as the ratio of the speed of light in vacuum to the speed of light in the glass, v ie, $n = c/v$. The value of n is always greater than 1, because light travels more slowly in dense media. The refractive index is governed almost exclusively by the nature of the electron-oscillators, with essentially no contribution from atomic vibrations. At visible frequencies, the electrons of an optically transparent glass can follow or move in phase with the applied field, but because of the small vibrational amplitudes of these induced oscillations, the light is reradiated rather than absorbed.

The loosely bound valence electrons make the greatest contribution to n, so large, many-electron atoms, eg, Pb(II) or Bi(III), are added to glass to increase the refractive index. For Pb(II) or Bi(III) additions, there is a lone pair of nonbonding electrons that are exceptionally polarizable and contribute to n even more effectively than the other valence electrons. In general, the refractive index of a glass also increases on addition of alkali oxides, because of the formation of polarizable nonbridging oxygens. The partial replacement of oxide ions by fluoride ions decreases n because the small, electronegative fluoride ions bind electrons tightly. The substitution of nitride ions for oxide ions results in an increased refractive index because of the greater negative charge and lower electronegativity of nitrogen. Addition of PbO to silicate glass creates lead crystal.

3.3. Dispersion

A glass prism separates white light into its component colors by virtue of the frequency dependence of n. The higher the frequency, the higher the refractive index for a given substance, ie, blue light is slowed to a greater extent than red light and deviated through a larger angle by a prism. It is this dependence of the refractive index on the frequency (color) of light that is known as dispersion. The measure of dispersion is the Abbé number, v_{d}, which is equal to $(n_d - 1)/(n_F - n_C)$ where n_{d}, n_{F}, and n_{C} are the indexes of refraction at the sodium d-line (587.6 nm), a wavelength in the blue (486.1 nm), and a wavelength in the red (656.3 nm), respectively. The greater the dispersion, the smaller the Abbé number.

A low dispersion is desirable in optical glasses used for lenses in cameras, telescopes, etc, because dispersion causes chromatic aberration, a condition which reduces the sharpness of an image. However, it is possible to correct for chromatic aberration by using a combination of glasses having different Abbé numbers (9).

The farther into the uv and the narrower the distribution of the resonant electron frequencies, the smaller the effect of dispersion in the visible region. The Pb(II) ion exhibits absorption in the near-uv, and addition of Pb(II) to a glass increases both n and dispersion. However, the use of Ba(II) and La(III) increases n without increasing dispersion. Fluorophosphates, having absorption bands located well into the uv, are examples of glasses with high Abbé numbers and low refractive indexes.

3.4. Fluorescence and Glass Lasers

Some ions absorb light of a certain frequency emitting light of lower frequency. This is known as fluorescence. Examples of ions that fluoresce in glass are Mn(IV), Pb(II), and the lanthanide ions.

The existence of glass lasers (qv) was first reported in 1961 (10). Optically pumped laser action has since been observed for several lanthanide ions in a variety of glass systems (11). Large, high power neodymium glass lasers have been used for inertial confinement fusion experiments (11). The best glass laser systems have the following qualities: the absorption spectrum of the lasing ion matches the spectrum of the pump radiation; the absorbed radiation efficiently produces excited-state ions; the excited state has a long lifetime; the probability of radiative decay is high; and the linewidth of the emitted radiation (fluorescence) is narrow. The linewidth of the fluorescence band of the lanthanide ion is affected by the glass matrix. In general, the smaller the field strength of the anions, the less the perturbation of the coordination shell of the fluorescing ion and the narrower the linewidth, ie, fluoride and chloride glasses promote narrower linewidths than those seen in oxide glasses. The stimulated-emission cross sections (efficiencies) of rare-earth sulfide glasses based on Ga_2S_3 are reported to be higher than those of oxide, oxyhalide, and halide glasses (12).

4. Electrical Properties

There are many applications in which glass is used as an electrical insulator. One example is glass-to-metal seals. Moreover, other glasses are useful as a result of ionic or electronic conductivity.

4.1. Ionic Conductivity

Ionic conductivity in oxide glasses is almost always because of the movement of monovalent cations, eg, in an alkali silicate glass, the small, univalent alkali ions are much more mobile than the Si^{4+} or O^{2-}; ions. In glasses containing appreciable amounts of hydroxide groups, charge can be carried by H^+ ions. The ions move through the glass network when subjected to an applied field, so the ionic conductivity of a glass depends on the distribution of ring sizes (or doorways) in the glass as well as on the size, charge, and polarizability (deformability) of the charge carriers. For a given glass network and a given charge on the mobile ions, smaller ions fit through the doorways more easily, but their higher field strength causes greater interactions with the network and tend to increase the activation energy for movement. For a given ion, sulfide glasses have higher ionic conductivities than oxide glasses, because the larger, more polarizable sulfide ions deform more easily than do oxide ions.

The electrical conductivities of many glasses containing monovalent ions are so high that such glasses are being considered for all-solid-state batteries (qv). An example of a highly conductive sulfide-based glass is the Li_2S–P_2S_5–LiI system. The glass family exhibiting the highest ionic conductivities is based on AgI–$AgMO_x$, where M = Cr, Mo, B, P, As, or Se. The conductivities of these glasses at 25°C can be as high as that of a 0.1 *M* aqueous solution of KCl. Batteries based on these systems have been made, but are not of commercial interest because of low energy density.

4.2. Semiconductivity

Amorphous selenium and other chalcogenide glasses form the basis for the multibillion dollar electrostatic copying industry (see Electrophotography). Although amorphous substances possess only short-range and a certain degree of intermediate-range order, they can exhibit extended electronic states similar to those found in crystals. Glassy semiconductors (qv) also possess localized electronic states. There is no energy gap between the localized and extended states, but at a certain boundary energy E_c there is an abrupt change in mobility between the states, leading to a mobility gap. This means that the localized states effectively act as traps for charge carriers. Conduction in chalcogenide glasses can occur by the activation of carriers across the mobility gap into the extended states, or by tunneling between the localized states. Conduction is favored if the atoms are close together and if the spatial extent of the overlapping orbitals is relatively large. For example, the conduction band is more likely to consist of *p*-orbitals than *s*-orbitals.

It has been known since the 1960s that certain chalcogenide glasses can be switched between low and high conductivity states using an applied voltage. There are two types of switching: threshold and memory. In the case of threshold switches, a small current is required to maintain the on (high conductivity) state. In contrast, memory switches remain on indefinitely in the absence of a current and require a short, high current pulse to return to the off state. A typical glass for a memory switch contains Ge, Te, and either As, S, or Sb. The on state in threshold switching is thought to arise from the saturation of charged defect centers. This same state in memory switching has been attributed to the formation of a conductive crystalline filament. The filament is remelted to the glassy state with the applied pulse.

Semiconductivity in oxide glasses involves polarons. An electron in a localized state distorts its surroundings to some extent, and this combination of the electron plus its distortion is called a polaron. As the electron moves, the distortion moves with it through the lattice. In oxide glasses the polarons are very localized, because of substantial electrostatic interactions between the electrons and the lattice. Conduction is assisted by electron-phonon coupling, ie, the lattice vibrations help transfer the charge carriers from one site to another. The polarons are said to "hop" between sites.

Cations capable of multiple valences facilitate small-polaron conductivity. Vanadium and tungsten ions readily assume multiple valences, and vanadium oxide and tungsten oxide glasses exhibit some of the highest electrical conductivities of any oxide glass. Phosphate and tellurate(IV) glasses containing substantial amounts of multiple-valent transition-metal ions such as iron or copper are also semiconducting. The conductivity is enhanced if the transition-metal ions are close together, the ionic charges are small, and the spatial extent of the *d*-orbitals is large.

4.3. Dielectric Constant

Capacitance, C, refers to the ability of two conductors to store charge, Q, in the presence of a potential difference, V; $C = Q/V$. In a vacuum, the charge density on the surfaces of the conductors is affected by the permittivity of free space, ϵ_0. When a dielectric material is placed between the conductors, the capacitance increases because of the higher permittivity, ϵ, of the material. The ratio of ϵ and ϵ_0 gives the dielectric constant, κ, of the material, $\kappa = \epsilon/\epsilon_0$. The dielectric constant of silica glass is 3.8.

The dielectric constant is a measure of the ease with which charged species in a material can be displaced to form dipoles. There are four primary mechanisms of polarization in glasses (13): electronic, atomic, orientational, and interfacial polarization. Electronic polarization arises from the displacement of electron clouds and is important at optical (ultraviolet) frequencies. At optical frequencies, the dielectric constant of a glass is related to the refractive index: $\kappa = n^2$. Atomic polarization occurs at infrared frequencies and involves the displacement of positive and negative ions.

At lower frequencies, orientational polarization may occur if the glass contains permanent ionic or molecular dipoles, such as H_2O or an Si–OH group, that can rotate or oscillate in the presence of an applied electric field. Another source of orientational polarization at even lower frequencies is the oscillatory movement of mobile ions such as Na^+. The higher the amount of alkali oxide in the glass, the higher the dielectric constant. When the movement of mobile charge carriers is obstructed by a barrier, the accumulation of carriers at the interface leads to interfacial polarization. Interfacial polarization can occur in phase-separated glasses if the phases have different dielectric constants.

Because κ is related to the polarizability per unit volume, denser glasses generally have higher dielectric constants. The dielectric constant also increases with increasing temperature, because ionic motion becomes faster. Similarly, κ is higher at lower frequencies, because the ions can follow the oscillations more readily.

In a sinusoidally varying field, there are dielectric losses arising from the long-range migration of charges and from overcoming the inertial resistance to the rotation or oscillation of dipoles. Energy losses are minimized when the dielectric constant is small.

5. Thermal Properties

5.1. Glass-Transition Temperature

When a typical liquid is cooled, its volume decreases slowly until the melting point, T_m, where the volume decreases abruptly as the liquid is transformed into a crystalline solid. This phenomenon is illustrated by the line ABCD in Figure 3. If a glass forming liquid is cooled below T_m (B in Fig. 3) without the occurrence of crystallization, it is considered to be a supercooled liquid until the glass-transition temperature, T_g, is reached. At temperatures below T_g, the material is a solid.

Unlike the abrupt melting of a crystalline solid, the glass transition is characterized by a continuous change in properties over a small temperature interval. When a solid glass is heated from below its glass-transition temperature, the volume and specific heat increase slowly. As the glass-transition temperature is reached, the rates of change of these quantities become larger, indicating that bonds are being broken and that some parts of the glass have become more mobile; ie, above T_g the behavior of the glass becomes more like that of a liquid, in that there are now opportunities for long-range molecular diffusion. Viewed in terms of percolation theory, the glass-transition temperature represents the point at which, upon heating, a single liquidlike cluster that spans the entire sample is created.

Glass-transition temperatures are usually proportional to melting temperatures and are dependent on similar factors. For instance, stronger bonds typically lead to higher values of T_g. Although SiO_2 and GeO_2 glasses have virtually the same structure, the T_g of SiO_2 is 1157°C as opposed to only 547°C for GeO_2 because the Ge–O bonds are longer and weaker than the Si–O bonds. The T_g is expected to decrease as modifying agents

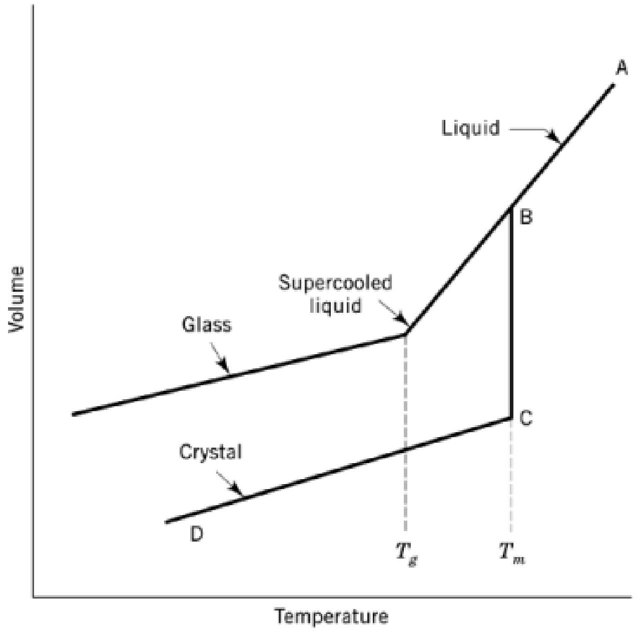

Fig. 3. Volume changes in the glassy, liquid, and solid states. Terms defined in the text.Courtesy of Chapman & Hall.

such as Na_2O are added because of the formation of nonbridging oxygen atoms. The longer-range structural features of a glass also affect transition temperatures.

5.2. Working, Softening, Annealing, and Strain Points

Although the glass-transition temperature is important in the scientific study of glass formation, other temperatures are more useful from a technological point of view. For example, the working point refers to the temperature at which the glass can be formed into some desired shape. The American Society for Testing and Materials (ASTM) defines such phrases in terms of viscosity. The working point of a glass corresponds to a viscosity of 10^6mPa·s(= cP). At the softening point (viscosity of $10^{6.6}$ Pa·s), a glass suspended at two points can begin to sag in a few minutes. The term annealing point is essentially the same as T_g. If annealing is carried out at the strain point, a temperature below T_g at which the viscosity is $10^{13.5}$ Pa·s, the reduction of stresses to acceptable levels takes about four hours.

5.3. Thermal Expansion

In general, solids expand when they are heated either through bond length expansion, bond angle changes, or expansion regulated by weak forces such as van der Waals bonding. In a covalently bonded glass such as vitreous SiO_2, which contains strong Si–O bonds and tetrahedrally coordinated Si atoms, the contribution to the coefficient of thermal expansion (CTE) from bond length expansion is relatively low. The Si–O–Si bond angle changes are important. High silica glasses such as Pyrex have low CTEs and are used in applications requiring good resistance to thermal shock. In fact, certain ultralow expansion SiO_2–TiO_2 glasses have CTEs of practically zero. Some applications, such as glass-to-metal seals, depend on glasses having high CTEs. Lead-containing glasses are appropriate for such purposes, because the Pb–O bonds are relatively weak and the Pb(II) coordination sphere is quite asymmetric, as a result of the presence of a lone pair of nonbonding electrons.

5.4. Thermal Conductivity

Like thermal expansion, thermal conductivity depends on bond anharmonicity, but thermal conductivity is reduced rather than enhanced by the anharmonic contributions. The thermal conductivity also appears to be greatly dependent on long-range order, meaning that an amorphous material has the same effect on phonons as would a greatly anharmonic crystal. The mean free path of a phonon in a glass is on the order of a few interatomic spacings, so phonons are damped out over very short distances, ie, glasses are good thermal insulators, making them ideal materials for windows in buildings. The thermal conductivity of a glass increases markedly as it is crystallized to form a glass–ceramic. The thermal conductivity of an aerogel is exceptionally low.

6. Processing

6.1. Melt Processing

In melt processing, the starting materials, such as powdered oxides or glass pieces from previous melts, are placed into a crucible and heated until the entire mixture is molten. After the melt becomes homogeneous, the liquid is poured into a mold and the resulting glass is then annealed at or slightly below its glass-transition temperature. This approach, although simple and convenient, has some drawbacks: (*1*) the amount of energy required to prepare the glass is fairly large, especially if the glass is high melting; (*2*) the temperatures involved can cause unwanted chemical reactions such as oxidation–reduction processes within the melt or with the atmosphere, as well as corrosion of the crucible; (*3*) some compounds become excessively volatile at elevated temperatures and are lost from the melt; and (*4*) glasses having relatively large coefficients of thermal expansion may crack before or during the annealing step.

Some ultrafast quenching procedures used for molten materials include: (*1*) melt spinning, in which a molten metal is ejected onto a rapidly spinning cylinder to form a thin ribbon; (*2*) splat quenching, in which the melt is smashed onto an anvil by a compressed-air-driven hammer; (*3*) twin-roller quenching, in which the melt is forced between two cylinders rotating in opposite directions at the same speed; (*4*) laser glazing, in which a short, intense laser pulse is focused onto a very small volume of a sample; and (*5*) laser-spin melting, in which a rapidly rotating rod of the starting material is introduced into a high power laser beam, eg, a CO_2 laser, causing molten droplets to spin off and form into small glass spheres (14).

6.2. Sol-Gel Processing

In the sol–gel method, a room temperature solution of one or more soluble glass precursor compounds, typically metal alkoxides (see Alkoxides, metal), undergoes hydrolysis to form a metal hydroxide or metal oxide (see Sol–gel technology) (15). The by-product is an alcohol that is removed by subsequent heating. The hydrolysis reaction sometimes requires an acid or base catalyst. If unstable metal hydroxides are formed, they can condense together to form M–O–M linkages. Eventually, the colloidal suspension (sol) polymerizes to such an extent that it becomes insoluble and forms a gel. The gel must be dried and then heated to a temperature slightly above the T_g of the corresponding melt-prepared glass to effect densification. If the gel is dried by evaporation under normal conditions, the resulting product is called a xerogel. If instead the gel is dried under supercritical conditions in an autoclave by a fluid such as CO_2, the resulting product is an aerogel. The preparation of aerogels results in considerably less shrinkage because the surface tension of a supercritical fluid is zero, so it is easier to prepare crack-free samples from aerogels.

Glasses formed by the sol–gel method are very homogeneous and can be made very pure. In general, there is little or no difference between the physical properties of sol–gel and melt-formed glasses of identical composition, but some researchers have reported structural differences. One drawback to the sol–gel method is the possibility of a higher content of hydroxyl groups or the presence of organic residue in the resulting glass. Another is the expense of the raw materials. An advantage of sol–gel processing is the ability to form thin films (qv) and coatings (qv), in addition to bulk glass articles.

6.3. Vapor-Phase Processing

Optical fiber preforms are prepared by vapor-phase techniques because of the superior clarity of the products. This technology also allows the control of refractive index profiles by doping. All vapor-phase techniques use a vapor stream of volatile halides such as $SiCl_4$, $GeCl_4$, BCl_3, or $POCl_3$, and gases such as Cl_2 or O_2. The reactants are oxidized and deposited onto a substrate to produce a solid glass preform which is then drawn into a fiber. The variations of the technique differ in the way the reactants are oxidized (16).

In flame hydrolysis, the halide vapors are converted to oxides in a methane/oxygen flame. The finely divided oxide soot is deposited onto a substrate such as a rotating alumina rod. The refractive index of the glass layers is changed during the deposition by controlling the relative amounts of the halides added to the flame. When the deposition is complete, the rod, which has a higher coefficient of thermal expansion than the deposited material, is removed. The porous glass preform is baked to remove impurities such as water, then sintered into bulk glass.

In the modified chemical vapor deposition (MCVD) technique, the reactants are deposited on the inside of a rotating silica tube. The hollow tube is heated from the outside by a moving oxyhydrogen torch. The oxide soot condenses onto the tube walls ahead of the burner, and the soot is then sintered into a glassy layer as the burner passes over it. When deposition is complete, the tube and its contents are collapsed to form a solid preform rod.

In plasma chemical vapor deposition (PCVD), the starting materials are typically $SiCl_4$, O_2, C_2F_6, and $GeCl_4$ (see Plasma technology). Plasma chemical vapor deposition is similar to MCVD in that the reactants are carried into a hollow silica tube, but PCVD uses a moving microwave cavity rather than a torch. The plasma formed inside the microwave cavity results in the deposition of a compact glass layer along the inner wall of the tube. The temperatures involved in PCVD are lower than those in MCVD, and no oxide soots are formed. Also, the PCVD method is not affected by the heat capacities or thermal conductivities of the deposits.

6.4. Thin-Film Techniques

Many integrated optical and electronic components require thin films (qv), usually 5–50 μm deep, of materials. Amorphous thin films can be prepared by chemical vapor deposition, evaporation, and sputtering, in addition to the sol–gel process. In both evaporation and sputtering, the target is vaporized and redeposited onto a cold substrate. Vapor deposition can be carried out by using electron beams. It frequently results in porous films, and it can cause compositional changes in multicomponent glasses, because of differing vapor pressures at the deposition temperature. Vacuum evaporation can cause nonstoichiometry, but this problem can be alleviated for oxides by adding oxygen to the evaporation chamber. Sputtering is typically carried out by radio-frequency heating of argon gas to produce beams of argon ions that are directed at the sample. Some glasses prepared by thin-film techniques differ from bulk glasses in that they crystallize before reaching T_g (14).

7. Applications

Silicate glass is a familiar, ubiquitous material, used in beverage containers, window panes, and automobile windshields. Increasingly, however, unusual glasses are being employed in high technology applications.

7.1. Optical and Electrical Applications

7.1.1. Optical Fibers for Telecommunications

There are several advantages in using light pulses through silica glass fibers for telecommunications (16). Signals sent through copper wires require repeaters or signal boosters at intervals of about 2 km; the repeaters in commercial fiber optic systems are 30 km apart (see Fiber optics). Also, the glass fibers are so small (typically dia $\sim 100\ \mu\mathrm{m}$) that more of them fit into a cable of a given size. The glass fibers are not susceptible to electromagnetic interference, so the signal is clearer. Finally, the information carried on optical fibers can be modulated at very high frequencies, so many more simultaneous transmissions, eg, telephone conversations, are possible.

Communication by light rather than electricity required the development of suitable light sources as well as extremely pure, ultratransparent glass fibers. The use of long-wavelength radiation reduces intrinsic scattering from inhomogeneous density distributions, so infrared-transmitting fibers are desirable. The infrared light is usually produced by small semiconductor lasers (qv) or by light-emitting diodes (see Light generation). The fibers must be coated with a substance of lower refractive index in order to minimize losses. The fibers are also coated with a polymer immediately after drawing in order to prevent abrasion and hydroxyl formation at the surface. Fluorozirconate glasses transmit into the mid-ir, and they may be suitable for applications requiring relatively short lengths of fiber.

7.1.2. Graded-Refractive-Index Glasses

Light-focusing glass fibers and rods having radially parabolic refractive-index distributions are known as graded-refractive-index (GRIN) devices (18, 19). These GRIN lenses can be made by ion-exchange (qv) techniques. In such a process, the glass is immersed in a bath of a suitable molten salt, and monovalent cations are replaced by other cations. Typically, nitrate or sulfate melts of lithium, potassium, or silver are used. GRIN glasses can also be made by chemical vapor deposition methods and by sol–gel processing. GRIN glasses are used as waveguides for coupling optical fibers and as lenses for compact photocopiers and compact disk players. The use of graded-refractive-index lenses could also reduce the number of elements needed in complicated optical systems such as cameras and microscopes.

7.1.3. Infrared Optics

Although the standard wavelength of transmission used in silica optical fiber networks is in the infrared (1.55 μm), there are applications in which glasses transmitting to longer wavelengths are preferable. These include nose cones for heat-seeking missiles; noninvasive monitoring of bodily fluids, eg, analysis of blood by transmitting ir radiation through an earlobe; and lenses for night vision equipment. Some chalcogenide and halide glasses transmit to the far-ir region (up to about 20 μm), but the relatively difficult preparation techniques and the relatively poor chemical, thermal, and mechanical properties of these glasses can complicate use. For example, some commercially available chalcogenide glasses must be sealed with a polymer coating to prevent slow reaction with air and water vapor.

7.1.4. Nonlinear Optical Glasses

Optoelectronic applications such as optical switches and modulators require materials having nonlinear optical (NLO) properties (see Nonlinear optical materials) (20, 21). Such properties are dependent on the square, cube, etc, of the intensity of the applied electric field and are noticeable only when high-energy sources such as lasers are used. It has been found that glasses containing small amounts of semiconducting microcrystals exhibit large optical nonlinearities (22, 23). If the crystalline particles are less than about 5 to 10 nm in diameter, the movement of the charge carriers is greatly restricted, resulting in quantum confinement effects. Some examples of semiconductors where the quantum-dot effects in glass have been studied are CdS, CdSe, CuCl, and CuBr (22, 23).

7.1.5. Acousto-Optic Glasses

In the acousto-optic effect, a surface acoustic wave (SAW) produced by transducers causes photoelastic index fluctuations that can diffract light. The SAW therefore acts as a traveling diffraction grating, and a guided optical wave is scattered by the SAW. The scanning of the scattered beam can be controlled by changing the frequency of the transducer drive signal. Chalcogenide glasses such as those in the Ge–As–S system have high indexes of refraction, low acoustical losses, and low sound velocities, making them candidates for acousto-optical applications. Acousto-optic microscanning devices could be used in laser printing, optical memory addressing, and information processing (24).

7.1.6. Fast-Ion-Conducting Glasses

One possible application of fast-ion-conducting glasses is in solid-state batteries (qv) for automobiles. The glasses might also be used in electrochromic displays or as sensors (qv) (25).

7.2. Glass–Ceramics

Glass–ceramic materials are first formed as glasses and then converted to polycrystalline ceramics by suitable heat treatments (26). The heat treatment schedule usually consists of a nucleation stage at lower temperatures, followed by a growth stage at higher temperatures. In general, glass-ceramics (qv) are stronger, harder, and more stable at high temperatures than are the parent glasses. One advantage of glass–ceramics over conventionally prepared ceramics is their fine-grained, nonporous, uniform structure. Another is the ability to form the parent glass into complex shapes before the crystallization occurs.

7.3. Glass Microspheres

It has long been known that plastics can be reinforced by the inclusion of glass fibers. A more recent development is the use of large amounts of small, hollow glass spheres as lightweight fillers to improve the mechanical properties of plastic insulators. High quality, hollow glass microspheresare also being used as containers for hydrogen (qv), deuterium, and tritium in inertial confinement nuclear fusion experiments (see Fusion energy). Small glass beads containing short-lived radioactive elements can be injected into cancerous tumors, thereby providing higher and more localized doses of radiation (27).

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