

CHAPTER 2 THEORY

2.1 Glasses [1,25-27,46,47]

2.1.1 Definitions of Glass

The origin of the word glass is the late Latin term *glaesum*, which refers to a lustrous and transparent or translucent body. Glassy substances are also called *vitreous*, originating from the word *vitrum*, again denoting a clear, transparent body. Although glass became a popular commodity in the growth of civilization, perhaps because of its transparency, luster (or shine), and durability, the understanding of glass no longer requires any of these characteristics to distinguish it current from other substances. Glass can be inorganic (non-carbon-based) as well as organic (carbon-based), and fusion is not the only method to make a glass. Thus, the old American Society for Testing and Materials (ASTM) definition that glass is an inorganic product of fusion which has been cooled to a rigid condition without crystallizing is not appropriate.

Unlike a crystal, glass may not be represented by a simple chemical formula. There are no restrictions with regard to the relative numbers of chemically different atoms other than the fact that the valences and/or coordination requirements may need to be satisfied. Unlike a crystal, glass does not have a sharp melting point when heated. The seemingly rigid solid gradually softens and flows at higher temperatures. At ambient temperatures, however, the *viscosity* of glass may be sufficiently high that measurable flow does not occur over millennia certainly not over practical time scales in typical laboratory experiments. It is doubtful that glass windows in building structures of the middle ages have flowed to become thicker at the bottom. Chunks of glass do not have habit planes, nor does glass have identifiable cleavage planes. In the absence of externally applied mechanical, electrical, thermal, magnetic, and gravitational fields, *the properties of glass are essentially isotropic like those of a typical liquid.*

The isotropic of physical properties makes glasses resemble liquids. It follows that the atomic arrangements in glass must display the long-range order typical of liquids. In order not to be overly restrictive, we are left to define glass as a solid with liquid like structure, a *non-crystalline solids or simply as an amorphous solids*, with the understanding that the amorphous characteristic here is intended to describe atomic disorder as evidenced by an X-ray diffraction (XRD) analysis; it excludes substances such as “amorphous” powders that may simply be “micro-crystals” and that display more or less sharp peaks in XRD analysis. To get a clearer picture of the fundamentals of glass, we devoted to consideration of the volume-temperature relationship (the V-T diagram) of the glass with respect to a liquid and a crystal.

2.1.2 Types of Glass

The properties of glass can be modified or changed with the addition of other compounds or heat treatment. Since glass was developed on the basis of major commercial used, a large percentage of these are silica-based and more than 99% of glass compositions are oxides. Most glasses contain about 70–72 % by weight of silicon dioxide (SiO_2). The most common form of glass is the soda-lime glass, which contains nearly 30 % sodium and calcium oxides or carbonates. Pyrex is a borosilicate glass

containing about 10 % boric oxide. Lead glass is commonly contains a minimum of 24 % lead oxide.

2.1.2.1 Pure silica glass: Chiefly used for its low thermal expansion and high service temperature, and when very pure, for its transparency to a wide range of wavelengths in the electromagnetic spectrum and to sound waves. It also has good chemical, electrical and dielectric resistance. Its disadvantage is the very high temperature needed for manufacture, although it can also be made by hydrolysis of SiCl_4 ; in either case it is expensive. It is used for lightweight mirrors for satellite borne telescopes, laser beam reflectors, special crucibles for the manufacture of pure single crystals of silica for transistors, and as a molecular sieve that lets hydrogen and helium through.

2.1.2.2 Soda-lime glass: The addition of soda (Na_2O) and sometimes potash (K_2O) to silica lowers the softening point by 800-900°C. Lime (CaO) and sometimes magnesia (MgO) and alumina (Al_2O_3) are added to improve the chemical resistance. Electrical properties can vary quite widely with composition. This is the most common of all glasses, used in huge quantities for plate and sheet, containers and lamp bulbs. Crown glass is of this type.

2.1.2.3 Lead glass: Lead oxide reduces the softening point even more than lime and also increases the refractive index and dispersive power. Flint glass for optical purposes and crystal glass for tableware are both lead glass. They are also used for thermometer tube, part of electric lamp and neon-sign tube. Compositions vary widely; a glass of high electrical resistance contains about 25% PbO and 6 or 7 % each of Na_2O and K_2O ; for high refractive index the PbO content may be as much as 65%.

2.1.2.4 Borosilicate glass: Low thermal expansion, about one third that of sodalime glass, can be made with good chemical resistance and high dielectric strength, and is used where combinations of these are needed. Its high softening temperature makes it harder to work than soda-lime or lead glasses. Used for laboratory glassware, industrial piping, high-temperature thermometer, large telescope mirror, household cooking ware, enclosure for very hot lamp and electric tube of high wattage.

2.1.2.5 Aluminosilicate glass: Another low-expansion, chemically resistant glass that has a higher service temperature than borosilicate glass but is correspondingly harder to fabricate. It is used for high-performance military power tube, traveling wave tube and many applications similar to those of borosilicate glass.

2.2 The Enthalpy-Temperature Diagram

Any material which exhibits glass transformation behavior is a glass. Then the glass transformation will be discussed on the basis of either enthalpy or volume versus temperature diagrams, such as that shown in Figure 2.1. Since enthalpy and volume behave in a similar fashion, the choice of the ordinate is somewhat arbitrary. In either case, a small volume of a liquid at a temperature well above the melting temperature of that substance. As the liquid is cooled, the atomic structure of the melt will gradually change and will be characteristic of the exact temperature at which the melt is held. Cooling to any temperature below the melting temperature of the crystal would normally result in the conversion of the material to the crystalline state, with the formation of a long range, periodic atomic arrangement. If this occurs, the enthalpy will

decrease abruptly to the value appropriate for the crystal. Continued cooling of the crystal will result in a further decrease in enthalpy due to the heat capacity of the crystal.

If the liquid can be cooled below the melting temperature of the crystal without crystallization, a supercooled liquid is obtained. The structure of the liquid continues to rearrange as the temperature decreases, but there is no abrupt decrease in enthalpy due to discontinuous structural rearrangement. As the liquid is cooled further, the viscosity increases. This increase in viscosity eventually becomes so great that the atoms can no longer completely rearrange to the equilibrium liquid structure, during the time allowed by the experiment. The structure begins to lag behind that which would be present if sufficient time were allowed to reach equilibrium. The enthalpy begins to deviate from the equilibrium line, following a curve of gradually decreasing slope, until it eventually becomes determined by the heat capacity of the frozen liquid, *i.e.*, the viscosity becomes so great that the structure of the liquid becomes fixed and is no longer temperature-dependent. The temperature region lying between the limits where the enthalpy is that of the equilibrium liquid and that of the frozen solid, is known as the *glass transformation region*. The frozen liquid is now a glass.

Since the temperature where the enthalpy departs from the equilibrium curve is controlled by the viscosity of the liquid, *i. e.*, by kinetic factors, use of a slower cooling rate will allow the enthalpy to follow the equilibrium curve to a lower temperature. The glass transformation region will shift to lower temperatures and the formation of a completely frozen liquid, or glass, will not occur until a lower temperature. The glass obtained will have a lower enthalpy than that obtained using a faster cooling rate. The atomic arrangement will be that characteristic of the equilibrium liquid at a lower temperature than that of the more rapidly cooled glass.

Although the glass transformation actually occurs over a temperature range, it is convenient to define a term which allows us to express the difference in thermal history between these two glasses. If the glass and supercooled liquid lines were extrapolated, they intersect at a temperature defined as the *fictive temperature*. The structure of the glass is considered to be that of the equilibrium liquid at the fictive temperature. Although the fictive temperature concept is not a completely satisfactory method for characterizing the thermal history of glasses, it does provide a useful parameter for discussion of the effect of changes in cooling rate on glass structure and properties.

As indicated above, the glass transformation occurs over a range of temperatures and cannot be characterized by any single temperature. It is, however, convenient to be able to use just such a single temperature as an indication of the onset of the glass transformation region during heating of a glass. This temperature, which is termed either the *glass transformation temperature*, or the *glass transition temperature*, (T_g), is rather vaguely defined by changes in either thermal analysis curves or thermal expansion curves. The values obtained from these two methods, while similar, are not identical. The value obtained for T_g is also a function of the heating rate used to produce these curves. Since T_g is a function of both the experimental method used for the measurement and the heating rate used in that measurement, it cannot be considered to be a true property of the glass. However, T_g as a useful indicator of the approximate temperature where the supercooled liquid converts to a solid on cooling, or, conversely, of which the solid begins to behave as a viscoelastic solid on heating.

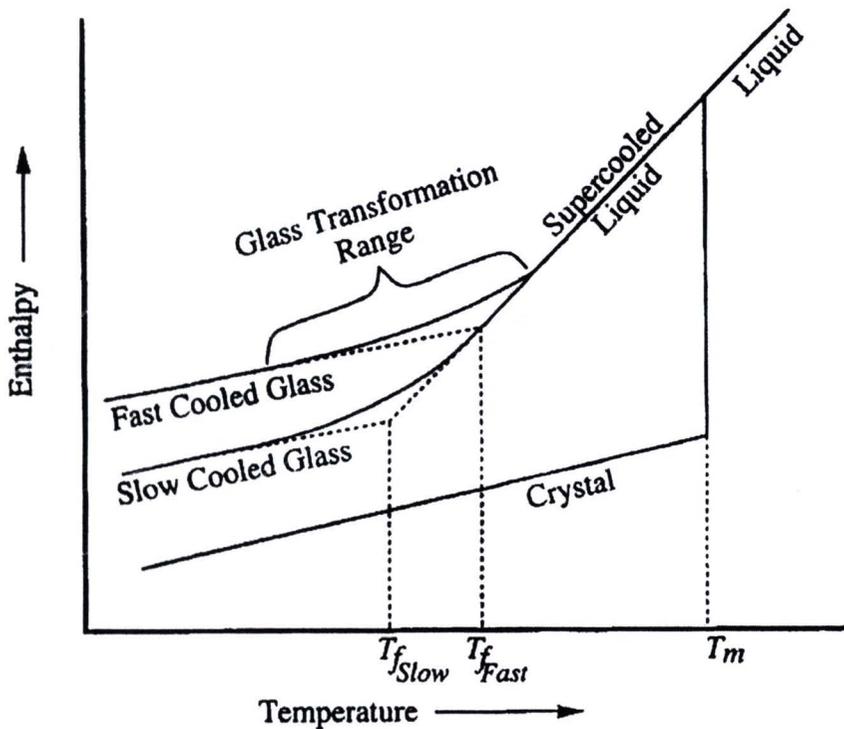


Figure 2.1 The enthalpy-temperature diagram (adapted from [1])

2.2.1 Raw Materials

In general, glasses are either produced from high quality, chemically pure components, or from a mixture of far less pure minerals. Research specimens, optical glasses, and many glasses used for low volume, high technology applications are produced using those chemicals we might routinely encounter in any chemical laboratory.

Regardless of the source of the components used to produce a specific glass, the batch materials can be divided into five categories on the basis of their role in the process: glassformer, flux, property modifier, colorant, and fining agent. The same compound may be classed into different categories when used for different purposes. Alumina, for example, serves as a glassformer in aluminate glasses, but is considered a property modifier in most silicate glasses. Arsenic oxide may be either a glassformer or a fining agent, depending upon the purpose for which it has been added to the batch.

2.2.1.1 Network formers or glass formers

In silicate glasses, the network is comprised of silica which is probably present in the form of anionic irregular ring structures. The quantity of silica in a silicate glass is normally between 50 to 75 mass %. Lower amounts (up to 5 mass %) of the glass forming oxides B_2O_3 and P_2O_5 may also be present in a silicate glass.

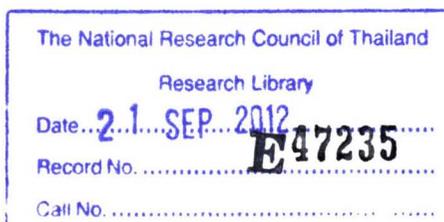
The most essential component of any glass batch is always the glass former. Every glass contains one or more components which serve as the primary source of the structure. While these components are commonly designated as glass formers, they are also called *network formers* or *glassforming oxides* [1] in many oxide glasses. The identity of these components usually serves as the basis for the generic name used for the glass. If most of the glass former present in a specific sample is silica, for example, that glass is called a silicate. If a significant amount of boric oxide is also present in addition to silica, the sample is termed a borosilicate glass.

The primary glass formers in commercial oxide glasses are silica (SiO_2), boric oxide (B_2O_3) and phosphoric oxide (P_2O_5) which all readily form single component glasses. A large number of other compounds may act as glass formers under certain circumstances, including GeO_2 , Bi_2O_3 , As_2O_3 , Sb_2O_3 , TeO_2 , Al_2O_3 , Ga_2O_3 and V_2O_5 . With the exception of GeO_2 , these oxides do not readily form glasses by themselves unless very rapidly quenched or vapor deposited, but can serve as glass formers when mixed with other oxides. The elements S, Se and Te act as glass formers in chalcogenide glasses. Although halide glasses can be made in many systems, with many different compounds acting as glass formers, the two most common halide glass formers are BeF_2 and ZrF_4 .

2.2.1.2 Fluxes

The melting point of quartz sand is approximately 1700 °C. To facilitate the melting, or more strictly, to lower the viscosity of the melt, Si-O-Si bond breaking compounds are introduced. This is achieved using a variety of elements termed fluxes; however the most commonly used are the alkali metals. The quantity of fluxes present ranges from 10 to 20 mass %. For cost reasons, lithium, sodium, and potassium carbonates are the only ingredients normally used in a glass batch.

Although the number of possible glass compositions is effectively unlimited, the vast bulk of commercial glasses are based on silica as the glassformer. While silica itself forms an excellent glass, with a wide range of applications, the use of pure silica glass for bottles, windows and other bulk commercial application would be prohibitively expensive due to the high melting temperature (> 2000 °C) required to produce vitreous silica. Production of silicate glasses requires the addition of a *flux* to reduce the processing temperature to within practical limits, e.g., < 1600 °C. The most common fluxes are the alkali oxides, especially Na_2O (soda) and PbO . Most commercial glasses contain soda, including those used for containers and window glasses. Potassium oxide is also used extensively in commercial glasses, while lithium oxide is used in a number of commercial glass-ceramics. Rubidium and cesium oxides are frequently used in laboratory studies of trends in behavior due to changes in the identity of the alkali oxide present in glasses, but are very rarely used in commercial products due to their high cost. PbO , which is an excellent flux, is becoming much more limited in use due to concerns regarding the toxicity of heavy metals. PbO is especially useful in dissolving any refractory or other impurity particles which might otherwise result in flaws in the final glass.



2.2.1.3 Modifiers

While the addition of fluxes to silica leads to decrease cost of glass formation, the addition of large amounts of alkali oxides results in serious degradation in many properties. In particular, the chemical durability of silicate glasses containing large concentrations of alkali oxides is degraded to the point where they can no longer be used for containers, windows or insulation fibers. The degradation in properties is usually countered by addition of *property modifiers*, which include the alkaline earth and transition metal oxides, and, most importantly, aluminum oxide (alumina). While these oxides partially counter the reduction in processing temperature obtained by the addition of fluxes, they also improve many of the properties of the resulting glasses. The properties and thus modified, or adjusted, by careful control of the amount and concentration of these oxides to obtain precisely the desired results. Since many of these oxides are actually very weak fluxes for silica, and the properly modifier are usually added in lesser quantities than the fluxes, their use does not lead to excessively high processing temperatures.

A two component alkali silicate glass is also known as water glass and is water soluble. The introduction of di-, tri-, tetra- or penta-valent elements renders the glass durable towards attack by water. The introduction of additional components, i.e. modifiers, affects the chemical and physical properties of the glass. From 10 to 35 mass % of modifiers may be presented. Non-coloring modifying elements for silicate glasses may be classified in terms of the oxide groups;

Divalent:	MgO, CaO, SrO, BaO, ZnO and PbO
Trivalent:	Al ₂ O ₃ , Bi ₂ O ₃ , Y ₂ O ₃ and La ₂ O ₃
Tetravalent:	TiO ₂ , ZrO ₂ and SnO ₂
Pentavalent:	Ta ₂ O ₅ and Nb ₂ O ₅

However, the glass batch contains compounds in which binary anions, typically carbonates, are present. Melting of the batch, at temperature up to 1500°C causes decomposition and carbon dioxide evolution. Most of the gas will be transported away by the flue gases in the furnace, however some remains, together with air and batch boundary, as gaseous inclusions in the melt. The removal of the gas bubbles is called refining and operates by two mechanisms. One is pure physical bubble-rise according to Stoke's law, the other is chemical dissolution of the remaining gas in the melt. Both mechanisms are facilitated by the addition to the batch of compounds referred to as refining agents; these result in gas evolution or sublimes. They also affect the redox chemistry of the melt. Three of the most commonly used combinations are;

Redox active:	As ₂ O ₃ and/or Sb ₂ O ₃ or CeO ₂ in combination with an oxidizing agent, most frequently sodium or potassium nitrate.
Sulfate:	sodium or calcium, often in combination with coke.
Salts:	various chlorides or fluorides, nowadays rarely used due to their adverse environmental impact

2.2.1.4 Colorants

Colorants are used to control the color of the final glass. In most cases, colorants are oxides of either the 3d transition metals or the 4f rare earths. Uranium oxides were once used as colorants, but their radioactivity obviously reduces their desirability for most applications. Gold and silver are also used to produce colors by formation of colloids in glasses. Colorants are only used if control of the color of the glass is desired, and are usually present in small quantities. Iron oxides, which are common impurities in the sand used to produce commercial silicate glasses, act as unintentional colorants in many products. When colorants are used to counteract the effect of other colorants to produce a slightly gray glass, they are referred to as decolorants.

2.2.1.5 Fining agent

Finally, fining agents are added to glass forming batches to promote the removal of bubbles from the melt. Fining agents include the arsenic and antimony oxides, potassium and sodium nitrates, sodium chloride (NaCl), fluorides such as CaF₂, NaF and Na₃AlF₆ and a number of sulfates. These materials are usually present in very small quantities (< 1 wt %) and are usually treated as if they have only minor effects on the properties of the final glasses. Their presence, however, is essential in many commercial glasses, which would be prohibitively expensive to produce without the aid of fining agents in reducing the content of unwanted bubbles in the final product [1, 46].

2.2.2 Batch melting reactions

Conversion of batch to glass can be described as a process of three main stages: the first stage is characterized by the absence of any melt. In this stage, all free and most of the bonded water is removed. If water or steam are present, batch components may undergo hydrothermal reactions. Most of the crystalline inversions occur during this stage. Also, organic materials burn, reacted with oxidants, or decomposed. Solid state reactions result in development of new crystalline phases. Evolution of gases, such as water, carbon dioxide, nitrogen, or oxygen is typical.

In the second stage, the melting reactions approach equilibrium in the presence of melt. More crystalline compounds precipitate and are eventually dissolved in the melt. Inorganic salts, if they were present in the batch, melt and decompose or partially dissolve in the glass melt. All gases except refining gases are liberated. At the end of this stage, the mixture consists of a melt with suspended refractory particles and gas bubbles.

In the third stage, the remains of refractory particles are dissolved and bubbles are removed. Dissolution of particles and bubble removal, or fining, are often dealt with as two separate processes. However, since bubbles are nucleated on solid surfaces, it is convenient to think about grain dissolving and fining as one process.

2.2.3. Atomic hypothesis of glass formation

According to Zachariasen's rules, it has been considered that a substance can form extended three-dimensional networks lacking of periodicity with energy content comparable with that of the corresponding crystal network. These rules were

remarkably successful in predicting new glass-forming oxides. The rules are as follows (Doremus, 1973);

- (1) An oxygen atom links to not more than two cations.
- (2) The number of oxygens surrounding these cations must be small.
- (3) The oxygen polyhedra share with one another by their corners, not by their edges or faces.
- (4) At least three corners of each polyhedra should be shared.

Oxides, such as SiO_2 , B_2O_3 , P_2O_5 , GeO_2 and BeF_2 , are called network formers because of their ability to form branching network structures. These network formers are generally 3 to 4 in coordination numbers. Goldschmidt also considered the crystal structures and their relation to the ionic sizes, and postulated a correlation between the ability to form glass and the relative sizes of the oxygen and cation atoms. The ratios between the radius of cation (R_C) and radius of anion (R_O) in glass-forming oxides are in the range of about 0.2 to 0.4. The radius ratios of typical glass formers are shown in Table 2.1.

Table 2.1 Radius ratios for typical network-formers [48].

Compounds	Radius ratio(R_C/R_O)
SiO_2	$R_{\text{Si}} : R_O = 0.39 \text{ \AA} : 1.4 \text{ \AA} \approx 0.28$
B_2O_3	$R_B : R_O = 0.20 \text{ \AA} : 1.4 \text{ \AA} \approx 0.15$
P_2O_5	$R_P : R_O = 0.34 \text{ \AA} : 1.4 \text{ \AA} \approx 0.25$
GeO_2	$R_{\text{Ge}} : R_O = 0.44 \text{ \AA} : 1.4 \text{ \AA} \approx 0.31$
BeF_2	$R_{\text{Be}} : R_O = 0.34 \text{ \AA} : 1.36 \text{ \AA} \approx 0.25$

2.3 GLASS FORMATION

2.3.1 Structural Concepts of Glass Formation

A variety of materials form glass readily by cooling from the molten state. It may be recognized that the glass formation range is quite extensive. Many other materials, on the other hand, form a noncrystalline solid only when special techniques, such as cooling from the vapor state, are used. A prime example of this is a-Si:H (amorphous hydrogenated silicon), used extensively for solar cell applications. It is not clear whether most of these amorphous solids are, in fact, glassy solids with a thermodynamic continuity to a supercooled liquid state.

The question of what characteristics make a substance a ready glass former has been the subject of intense research. Historically, the most prevalent thoughts were advanced by Zachariasen, who suggested four rules for an oxide, A_mO_n , to form a glass readily:

1. The oxygen is linked to no more than two atoms of A.
2. Coordination of the oxygen about A is small, say 3 or 4.
3. Oxygen polyhedra share corners, and not edges or faces.
4. At least three corners are shared.

Application of the above “random network theory” concepts suggests why oxides such as SiO_2 , GeO_2 and B_2O_3 , where the oxygen formed tetrahedra or triangles, are ready glass formers, and why compounds such as A_2O and AO have to be ruled out. Figure 2.2 shows a two-dimensional representation of the atomic arrangements in an A_2O_3 glass versus its corresponding crystalline form. (The figure may also correspond to AO_2 , where A is tetrahedrally bonded to oxygens, the fourth oxygen being out of the plane of the paper.) Whereas the local oxygen coordination is almost the same as that in a corresponding crystalline solid, the intermediate range order described by ring structures clearly differs considerably between the crystalline and the glassy forms. The glass network consists of holes that are larger than those in the crystal. (The aggregate of the holes yields the free volume discussed above.) When a compound such as Na_2O is introduced in silica, the arrangement of atoms in a two-dimensional plane is believed to look somewhat like that in Figure. 2.3. Those oxygens, which connect two silicon tetrahedral at corners, are called bridging oxygens (BOs). Some oxygens are linked to only one silicon; these are called the nonbridging oxygens (NBOs). Since oxygen is a bivalent ion, its connection to only one silicon ion leaves one negative charge, which is satisfied by a univalent positive sodium ion in the interstitial spaces.

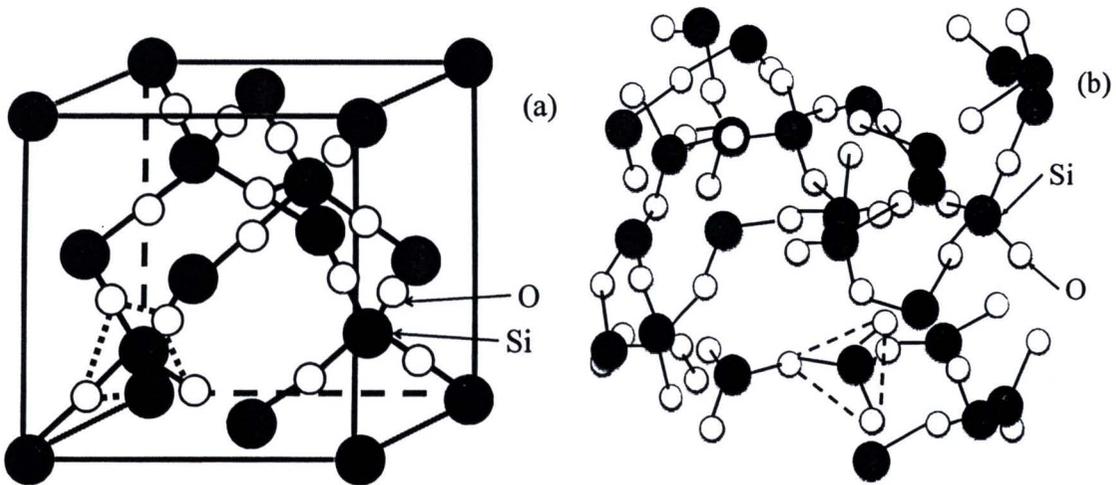


Figure 2.2 Dimensional representation of SiO_2 : (a) crystal and (b) glass (adapted from [27]).

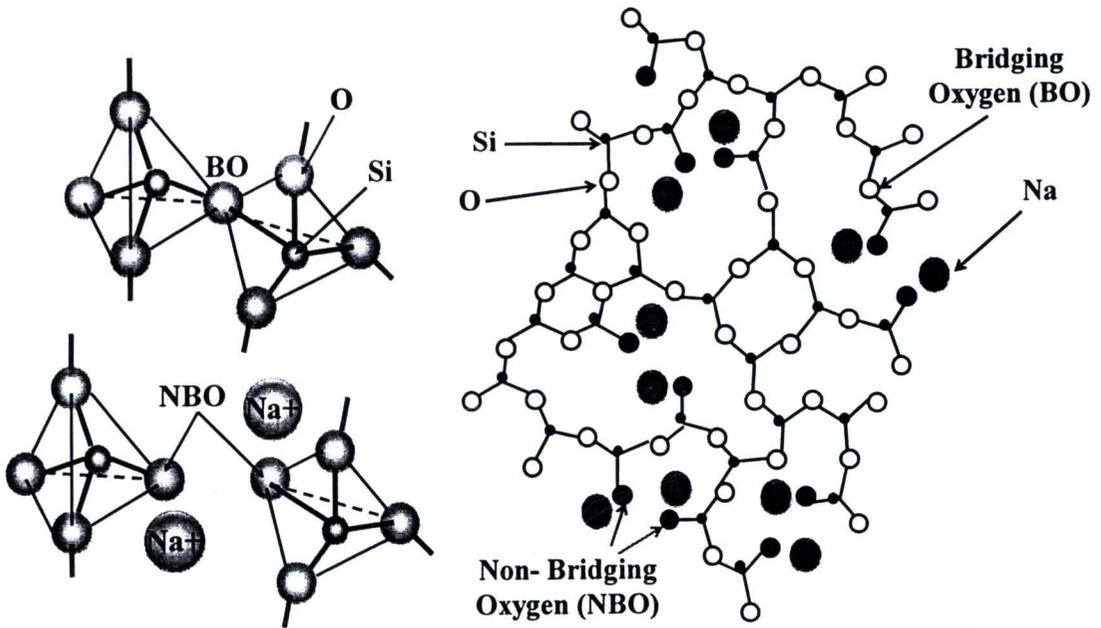


Figure 2.3 Dimensional representation of a sodium silicate glass (adapted from [26]).

Much of the early criticism of Zachariasen was based on the discussion of how random is random and, of course, the observation that elements such as S and Se make good glasses yet they did not fit Zachariasen's criteria. Electron microscopy of several otherwise transparent glasses has shown that glass may not be as random as Zachariasen thought and that some type of phase segregation exists in many glasses.

On the basis of the calculation of single bond strengths in an oxide AO_x , Sun suggested that oxides such as B_2O_3 , SiO_2 , GeO_2 , P_2O_5 , V_2O_5 , and As_2O_5 should be classified as *glass network formers* (NWFs), as they ought to be able to form the glass skeleton on their own. Oxides such as Li_2O , Na_2O , K_2O , CaO , BaO , ZnO , CdO , Ga_2O_3 , In_2O_3 , and PbO_2 were classified as *glass network modifiers* (NWMs); the cations of these oxides occupied the interstitial spaces in the network formed by the NWF oxides and, hence, acted as network modifiers only. Oxides such as BeO , Al_2O_3 , TiO_2 , and ZrO_2 were termed *intermediates*; these did not make glass readily on their own, but did make a glass when present in large quantities mixed with the NWF or NWM oxides.

SiO_2 is the most important raw material in glass manufacture. It is a basic glass former (network former). Crystalline silica has a very high melting point and liquid silica has high viscosity compare to the other glasses. High concentration of silica in glasses gives high softening temperature, low thermal expansion, and good chemical durability.

B_2O_3 normally functions as a network former in glasses. It is an important composition in special glasses which are used in electrotechnology, especially in the fields of heat and chemical resistance, excellent electrical insulation, low electrical loss, and gaseous impermeability. B_2O_3 will join the network structure of silica glasses without producing adverse change in the thermal expansion and durability. In the Kovar sealing, the higher percentages of B_2O_3 (17%-23%) are necessary if the glass-transition temperature of glasses must be reduced below $510^\circ C$ (Pfaender, 1983).

Na_2O is a network modifier which normally added in the form of soda ash (Na_2CO_3). This fluxing agent lowers softening point in glasses, raises thermal expansion and ionic conductivity, and reduces the glass durability.

K_2O , normally added in the form of potassium carbonate (K_2CO_3), is a network modifier similar to the Na_2O . It does not only contribute to the optical or thermal properties that are often desired, but also increases the workability of the glass by increasing its fluidity (van Vlack, 1964).

Al_2O_3 is an intermediate. It is usually added to the glass batch in the form of feldspars to join the network as AlO_4 tetrahedra. Al_2O_3 improves the chemical durability and increases viscosity in the lower temperature ranges, strongly suppresses devitrification, and makes melting and refining of the glasses more difficult.

2.3.2 Structural models for silicate glasses [1]

Discussions of the structural models for oxide glasses almost always begin with vitreous silica and the alkali silicate glasses. Structural models for most other silica-based glasses are derived from those for these systems, as is most of the terminology used in discussing glass structural models in general.

2.3.2.1 Vitreous Silica

The classic theory of glass structure dates from the 1930s and was formulated by Zachariasen that described glass as a network and postulated both coordination and bonding criteria for the components in the glass (Zachariasen's Rules). While the ideas and work of Zachariasen are still valid today, modern X-ray and spectroscopic techniques in combination with kinetic and thermodynamic considerations have contributed significantly to our current knowledge of glass structure in terms of bonding distances, atom distances and coordination polyhedra.

The structure of vitreous silica is readily described by the network structural rules of Zachariasen. The silicon-oxygen tetrahedron, with a coordination number of 4, serves as the basic building block for the network, as required by the second of Zachariasen's rules. Since these tetrahedra have a high degree of internal order, the short range order of the glass is preserved. These tetrahedra are linked at all four corners (rules 3 and 4) to form a continuous, 3-dimensional network. Each oxygen atom is shared between two silicon atoms, which occupy the centers of linked tetrahedra. Disorder in this structure is obtained by allowing variability in the Si-O-Si angle connecting adjacent tetrahedra. Additional disorder is introduced by allowing rotation of adjacent tetrahedra around the point occupied by the oxygen atom linking the tetrahedra, and by rotation of the tetrahedra around the line connecting the linking oxygen with one of the silicon atoms. Since the Si-O-Si angle and the rotations are described by distributions of values rather than the single values found in crystal lattices, no long range periodicity exists.

A 2-dimensional representation of such a structure is shown in Figure 2.4, where the fourth oxygen, which would sit directly above the small silicon ion, is not shown. Note the existence of rings consisting of three or more tetrahedra, and interstices of various sizes and shapes.

Diffraction studies indicate that the shortest Si-O distance in this structure is 0.162 nm and that the shortest O-O distance is 0.265 nm. These distances are consistent with those found within silicon oxygen tetrahedra in crystalline forms of silica and in silicate minerals. These distances exhibit very small variations, illustrating the high degree of order within the short range represented by the basic tetrahedral building block. The next distance in the structure, which should be between silicon atoms in the centers of linked tetrahedra, however, displays a considerable range of values clustered around a distance of 0.312 nm, as a result of the distribution in Si-O-Si angles. Even broader distributions are found for atom pair distances such as the silicon-2nd oxygen (0.415 nm) and oxygen-2nd oxygen (= 0.51 nm) distances.

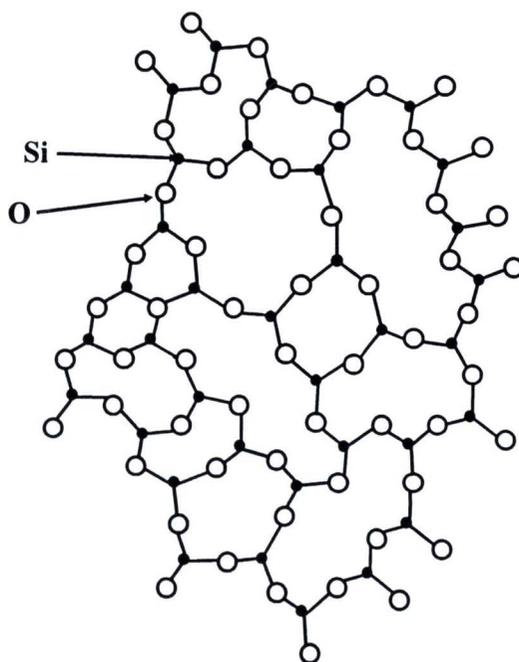


Figure 2.4 Schematic drawing of a 2-dimensional structure for a pure glass former. A fourth oxygen would be located above each cation in vitreous silica (adapted from [46]).

For glass where silica is the dominant component, a model using the concept of a depolymerised silica structure can be useful. Two principal types of Si-O bonds can be found: bonding, i.e. those bonding to additional Si atoms and nonbonding, i.e. those bonding to order components of the material. Adding additional components to silica, i.e. making a silicate glass, increases the degree of silica depolymerization and consequently the average number of non-bonding Si-O per Si. The latter number can be used for a description of the glass in terms of the expected structural units.

Following Zachariasen's constraints, the network structure of pure SiO₂ glass is such that each silicon ions bonded to four oxygen ions and each oxygen ions bonded to two silicon ions with the oxygen-silicon-oxygen bond at the ϕ angle of approximately $109^{\circ}28'$, as shown in Figure 2.5. The continuous random network structure occurs through corner-to-corner connections of the SiO₄ tetrahedra. The β angle is the bond angle between two adjacent SiO₄ tetrahedra. The mutual orientation of the adjacent tetrahedral is defined by ψ angle [49].

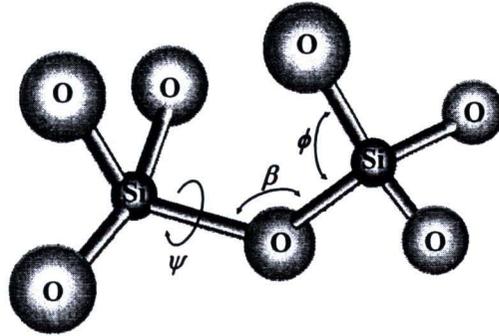


Figure 2.5 The structure of pure SiO_2 glass. A bond-and-stick model of two SiO_4 tetrahedra, $\phi \approx 109^\circ 28'$ (adapted from [49]).

In three dimensions (3D), Si and O atoms arrange to form oxygen tetrahedral elements with a Si atom at the centre. This is in terms of chemistry the resulting bonding through four sp^3 hybrid orbital of silicon and two $2p$ orbital of oxygen atoms (Figure. 2.6, 2.7). Then the structure can be thought of as built up by the sharing of corners by pairs of these oxygen tetrahedral. Two tetrahedral meet at only one corner, but all corners of all tetrahedral are actually shared.

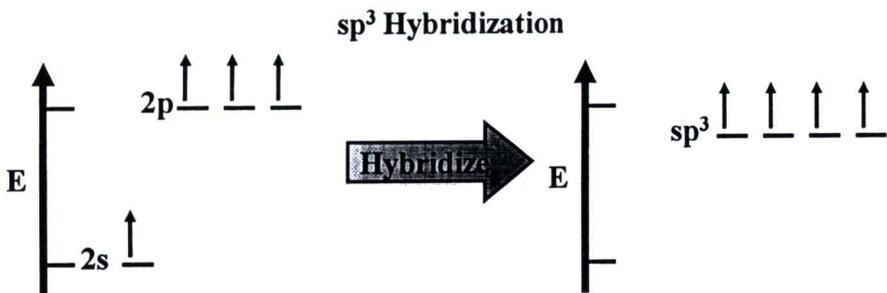


Figure 2.6 The sp^3 hybridization (adapted from [50]).

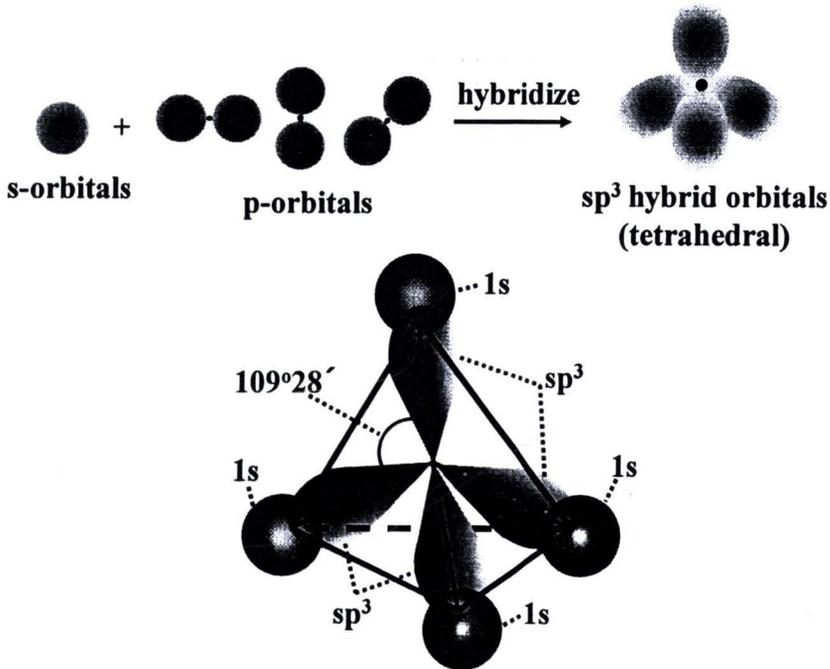


Figure 2.7 Three dimensions (3D) hybrid sp^3 orbital (adapted from [51]).

2.3.2.2 Structure of Alkali Silicate Glasses

Alkali silicate glasses, containing large concentrations of alkali oxides, can be easily produced by melting silica with alkali carbonates or nitrates. Glasses containing less than ≈ 10 mol% alkali oxide are considerably more difficult to melt due to their high viscosities. Metastable immiscibility occurs in the lithium and sodium silicate systems, with immiscibility limits extending to ≈ 33 mol% for the lithium silicate system and to ≈ 20 mol% for the sodium silicate system. There is little evidence for liquid-liquid immiscibility in the other alkali silicate systems (K, Rb, Cs), although there is some controversy concerning a report of a small region of metastable immiscibility in the potassium silicate system.

If we avoid the regions of metastable immiscibility, we find that the addition of any alkali oxide to silica to form a binary glass results in major reductions in the viscosity of the melt (many orders of magnitude) and the glass transformation temperature (≈ 500 K). The densities and refractive indices and the thermal expansion coefficients of the glasses increase with increasing alkali oxide concentration, and with the atomic number/mass of the particular alkali present. The electrical conductivity of the alkali silicate glasses, which is due to diffusion of alkali ions, increases by orders of magnitude with increasing alkali oxide content.

These trends in properties are due to the formation of non-bridging oxygens, which decrease the connectivity of the melt. The structure can be viewed as a network of silicon-oxygen tetrahedra with occasional breaks in connectivity due to the non-bridging oxygens. Each nonbridging oxygen must be associated with a nearby alkali ion to maintain local charge neutrality. These alkali ions occupy the interstices in the network, reducing the unoccupied free volume of the structure. The concentration of non-bridging oxygens increases, and the concentration of bridging oxygens decreases,

directly in proportion to the alkali oxide content, until a network can no longer be maintained. A 2-dimensional drawing of such a structure is shown in Figure 2.8, which includes alkaline earth ions as well as alkali ions.

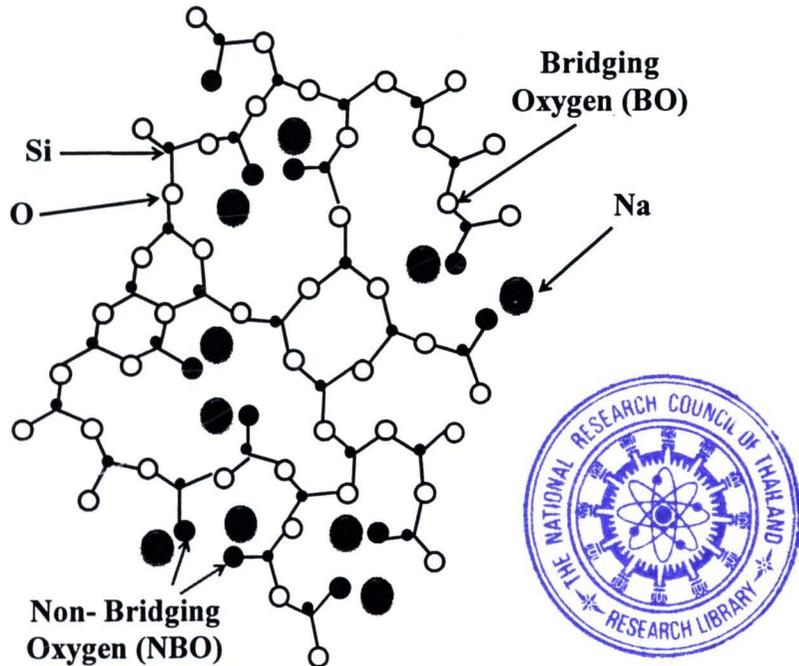


Figure 2.8 Schematic drawing of a 2-dimensional structure for a soda - silicate glass. A fourth oxygen would be located above each silicon in the 3-dimensional structure (adapted from [26]).

The addition of one molecule of sodium oxide (Na_2O) to silica glass breaks up a bridge and creates two *non-bridging oxygen* (NBO) as follows:



Each added sodium ion is attached more or less ionically to one non-bridging oxygen. The overall electrical neutrality of the structure is thus maintained. (The reader should note that each BO is counted as a half and each NBO is counted full, and thus mass balance exists between the two sides of the above equation.) If the oxygen bridges are broken up, the structure begins to lose connectivity and, as a result, becomes more fluid relative to the fully connected silica glass at comparable temperatures.

2.3.2.3 Structure of Alka/Alkaline Earth Silicate Glasses

The pure SiO_2 structure is a very dense network structure and has a very high glass transition temperature of about 1430 K (Table 2.2). The uniformly connected atomic arrangement represents the crystalline silica. On the other hand, the formation of disordered structure represents the vitreous structure. To reduce the glass transition temperature of the SiO_2 glass, network modifiers, such as Na_2O , K_2O , CaO , and BaO , have been added to the glass. The coordination numbers of these network modifier cations are generally equal to or more than 6. These modifiers weaken the pure SiO_2

network structure by alternating the bonding of the oxygen atoms. When an alkaline earth ion containing oxide, such as CaO, is added to silica, the bivalent alkaline earth ion is attached to two NBOs. The bridge via the Ca^{2+} ion is not as strong as the direct O-bridge, but is not as weak as the broken bridge with alkalis. The increased stability of a soda lime silica glass relative to the sodium silicate glass may be explained in such qualitative terms. Excellent glasses are formed in the $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$ primary phase field (shown as 1:3:6) around the $15\text{Na}_2\text{O} \cdot 10\text{CaO} \cdot 75\text{SiO}_2$ composition in the soda-lime-silica phase equilibrium diagram (Figure. 2.8). These form the basis of most of the commercial container, flat, and household lamp (both incandescent and fluorescent) glass industry. A 2-dimensional drawing of such a structure is shown in Figure 2.9, which includes alkaline earth ions as well as alkali ions.

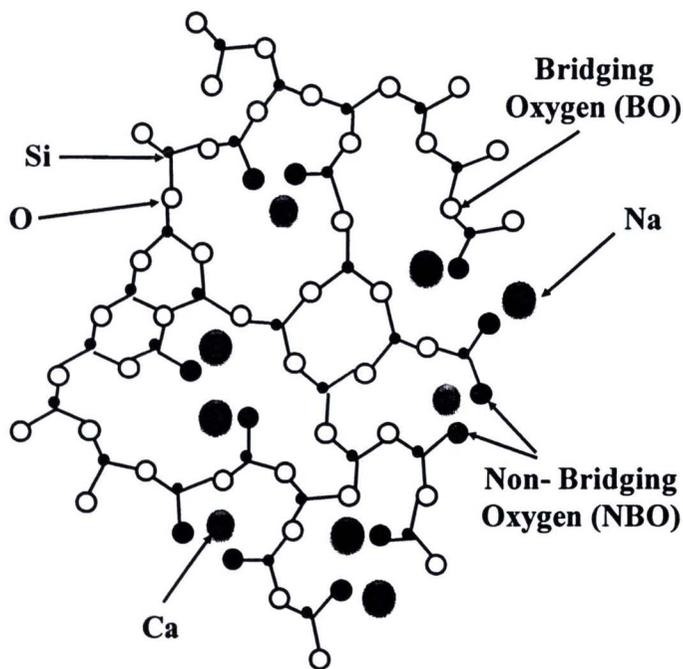


Figure 2.9 Schematic drawing of a 2-dimensional structure for a soda - lime - silicate glass. A fourth oxygen would be located above each silicon in the 3-dimensional structure (adapted from [26]).

2.4 Density and Molar Volume [47,51,52]

2.4.1 Definitions

Density of a substance is defined as the mass per unit volume, and is an intensive property. Appropriate units are g/cm^3 or g/cc (in cgs system) and kg.m^{-3} in SI system. Relative density is defined as density with respect to water 4°C and is, hence, unitless. Because the density is inversely proportional to the volume, a change ΔT in temperature changes the density by $-3\alpha_T\Delta T$, where α_T is the linear thermal expansion coefficient.

Since glasses may, in general, be regarded as solutions, a more useful property is the molar volume V_M , defined as the volume of one gram mole of glass, and then proceed to

define partial molar volumes of the various structural units constitution the glass. The partial molar volume v_i of a species i in a solution is defined by

$$v_i = \left(\partial V / \partial n_i \right)_{n_j, T, P} \quad (2.2)$$

And hence,
$$V_M = n_i v_i + n_j v_j \quad (2.3)$$

In essence, the total molar volume is treated as an extensive property in terms of the partial molar volumes of individual species or structural groups. The partial molar volume information can be extracted from the density data of glasses where the constituents have been systematically varied. If a Na^+ is replaced by K^+ in the glass and occupies the same interstice (without changing its size), it is clear that, although the glass density would increase because of the higher atomic weight of K^+ , the partial molar volume of the alkali ion would not change. Any increase in the molar volume would be an increase in the partial molar volume of K^+ relative to Na^+ . This is likely to have some relation to the relative ionic sizes of the two ions. One may readily note that, although the measurement of density changes in a family of glasses may provide only the trends, the extraction of the partial molar volumes from the density data provides further insight into structure while canceling out the effect of atomic masses.

2.4.2 Measurement of Density

Density is traditionally measure with a pycnometer, which allows the measurement of volume of a known mass of the specimen. Commercially available gas pycnometers measure the volume by measuring glass pressure changes in a compartment with and without the specimen. Using Archimedes's principle, one may measure the specimen volume as the buoyancy (the decrease in weight) when the specimen is immersed in 4 °C water. The buoyancy equals the weight of displaced fluid, which, for water, equals the volume in cm^3 . If the glass is attacked by water, and then it is advisable to use odorless kerosene as the immersion fluid, and multiply by the density of kerosene to obtain the specimen density.

Thus, if w_a is the weight of the specimen in air, and w_b in water, then the buoyancy is $w_a - w_b$ and the density

$$\rho = w_a / (w_a - w_b) \quad (2.4)$$

Occasionally, the glass may be affected by water immersion, in which case a suitable inert liquid such as kerosene may be selected. The specimen volume in this case is given by $(w_a - w_m) / \rho_m$ where ρ_m is the density of the immersion medium. A kit supplied by scientific balance manufacturers can be utilized to obtain density measurements accurate to 0.001 g/cc.

Density of silica glass is 2.20 g/cm^3 at room temperature. There is no detectable difference observed in density of silica regardless of the different methods of production. Of the various forms of crystalline silica, the density of silica glass closest to that β -cristobalite (high-temperature form), which is 2.25 g/cm^3 . Since density of α -quartz is 2.65 g/cm^3 , it is apparent that large structural changes occur during the melting of sand. Addition of alkalis to silica increases the density steadily: The alkali ions go

inside the interstices as NWM, take up holes. Heavier alkali ions generally are more effective in increasing the density, as shown in Figure 2.10. Likewise heavy elements such as Ba, Cd, Pb, and Bi bring large increases in the density.

Because density can be measured readily and accurately to the third decimal place, and because it is extremely sensitive to composition, density charts are often used to control the quality of glass production in a commercial environment.

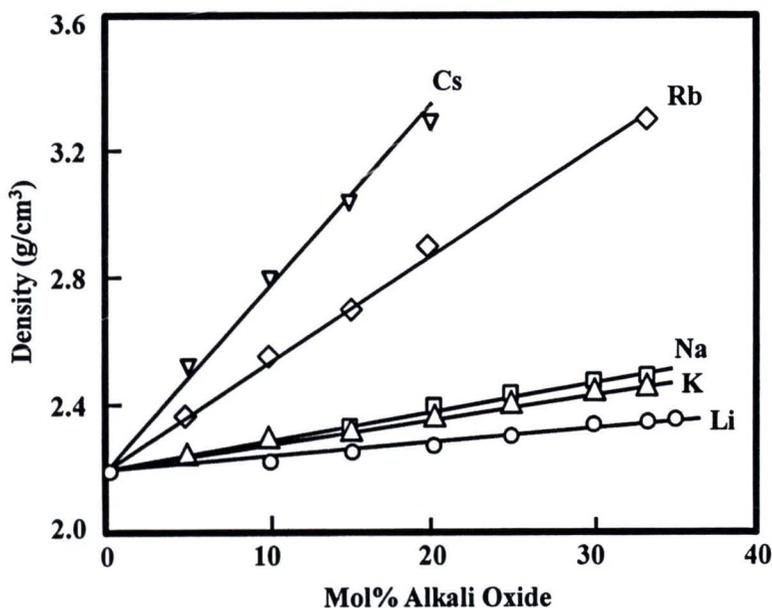


Figure 2.10 Density of binary silicate glasses [1].

Automatic measurements of density can be carried out using pycnometers that utilize He gas as the displacement fluid. A small sample, of the order of a few milligrams, is all that is needed to make the measurement. The accuracy of such instruments is generally about 0.002 g/cc. In a manufacturing environment, a comparative density (easily accurate to 0.0002 g/cc) is more rapidly obtained using a gradient column. The gradient column consists of a vertically held long (often 1-1.5 m), glass tube with one end closed. The tube contains a liquid with a linear density gradient. To prepare the density gradient, a heavy liquid such as *sym*-tetrabromoethane ($\rho = 2.96$ g/cc) or methylene iodide ($\rho = 3.32$ g/cc) is first poured into the tube, and then a lighter liquid such as isopropyl salicylate ($\rho = 1.1$ g/cc) is gently poured to float above the heavy liquid. With time, the liquids diffuse into each other, establishing a gradient with the help of gravity. The gradient is calibrated by allowing density standards to gently float in the column at different heights. The density of an unknown glass is obtained by reading its flotation level against a recalibrated scale placed adjacent to the column.

Another method also used commonly is the sink-float method, where the unknown specimen is gently dropped into a tube containing a slightly denser solution of organic liquids such as the ones just named. The temperature around the tube is gradually changed until the previously floating specimen begins to sink. Calibration of the liquid's density against temperature yields the density of the unknown.

2.5 Optical Properties [13-17, 53-55]

2.5.1 Refraction, reflection and absorption of light

There are many advanced and exciting applications of glasses in optics: optical fibers as waveguides for long and fast telecommunications, laser hosts, and optical components for medical and outer space studies. Other modern glasses are glasses that change absorption with light level (photochromic) and electric field (electrochromic), glasses for gradient index lenses, new glasses such as fluorides with different optical properties for silicate planar waveguides, sensors, and chalcogenide glasses with high non-linear optical properties for switching, all-optic devices and photonic applications.

For the glass window and the glass bulb to function, the optical transmission property is important. The correction for the failing vision and glass fiber communication are based upon the refractive, optical dispersion and transmission properties of glass. Beside these, there are many more technological advances where the optical properties of glass play a pivotal role.

The linear refractive index, n , and its dispersive wavelength dependence are important parameters that determine the suitability of oxide glasses as optical materials. The propagation of electromagnetic waves dependences on the optical constants of materials n and k (the extinction coefficient), where n affects the phase of light waves propagate in the material while k affects its amplitude. Fused silica glass for instant is used extensively in the fiber optics industry because the absorption and scattering losses are so small that light can travel many kilometers down the fiber before being fully attenuated. The presence of chemical additives can alter the refractive index and the transmission range. Glasses are differ considerably in structure and thus in the position and intensity distribution of their electronic absorption and vibrational spectra. Color glass filters are made by adding semiconductors with the band gaps in the visible spectral region during the fusion process.

If one were to list the major technological developments that added to the comforts of living, glass lenses as an aid to failing vision, glass windows to bring daylight into housing structures while providing protection from the harsh elements of nature, glass in the light bulb to provide a similar function after dark, and glass fibers foe enhanced communication capabilities would perhaps rank very high.

Before we begin, we should note that, in the visible (VIS) region, light rays are generally referred to by their wavelength λ stated in nanometers (SI units) or angstroms. In the infrared (IR) region, the wave number ($=1/\lambda$) with units cm^{-1} is used. In the ultraviolet (UV) region, sometimes the energy E (eV) of the photons is used. For conversion, $1 \text{ eV} = 1239.8/\lambda$ (nm).

When light travels through a medium, a part of it is reflected from the front surface, a part is absorbed, and the balance is transmitted. The reflectance R at normal incidence for light waves traveling from one dielectric medium to another is given by

$$R = \left[\frac{(n_1 - n_2)}{(n_1 + n_2)} \right]^2 \quad (2.5)$$

where the refractive index, n , is ratio of the velocities of light in vacuum to that in the medium; it is unit less.

When light waves travel from one medium of refractive index n_1 into another medium of refractive index n_2 , the incident and the refracted rays remain in the same plane and angles of incidence i and refraction r (angles between the ray and the surface normal) are related through Snell's law:

$$\sin r / \sin i = n_1 / n_2 \quad (2.6)$$

when $n_1 > n_2$, $r = 90^\circ$ at the critical angle of incidence ϕ_c (called Brewster's angle). Upon $i > \phi_c$, the incident ray is total internally reflected. The bending of light rays as they pass from one medium to another is the key to the design of lenses in eyeglasses, microscopes, telescopes, and cameras.

The absorption coefficient, α , is defined by Beer-Lambert's law for intensity I transmitted through a distance z in a medium:

$$I = I_0 \exp[-\alpha z] \quad (2.7)$$

where I_0 is the incident intensity. The units of α are cm^{-1} . (Note: this unit has yet to be replaced by m^{-1} .) Occasionally, the Beer-Lambert law is written as

$$I = I_0 10^{-\alpha z} \quad (2.8)$$

We may think of the absorption as due to a solution of the absorbing species in the medium, in which case it is useful to define a molar extinction coefficient δ as

$$\alpha = \delta c \quad (2.9)$$

where c is the concentration (mol L^{-1}) of the absorbing centers. δ is expressed as $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. The absorbance A and the optical density D are given by

$$A = -\ln[I/I_0], \quad (2.10)$$

$$D = -\log[I/I_0] \quad (2.11)$$

One other important criterion in the design of optical components to be considered is the correction for chromatic aberration resulting from the dispersion of light, i.e., the variation of n with wavelength λ . Away from an absorption peak, n may be expressed by Cauchy's dispersion formula: [13]

$$n = A' + \frac{B'}{\lambda^2} + \frac{C'}{\lambda^4} + \dots, \quad (2.12)$$

where A' , B' , C' ,... are known as Cauchy coefficients which are characteristic of the material. These coefficients are defined as

$$A' = 1 + \sum_{j=i+1}^{\infty} a_{ij}, \quad B' = 1 + \sum_{j=i+1}^{\infty} a_{ij} \lambda_{ij}^2, \quad C' = 1 + \sum_{j=i+1}^{\infty} a_{ij} \lambda_{ij}^4 \quad (2.13)$$

where $a_{ij} = r_e N f_{ij} \lambda_{ij}^2 / 2\pi$, $r_e = 2.818 \times 10^{-13}$ cm is the radius of an excited electron experiencing a transition from a lower energy level, i , to a higher energy level, j , when it absorbs a photon associated with a (transition) wavelength λ_{ij} . N is the atomic number density. The oscillator strength, f_{ij} , is a fraction of N , which takes part in a given $i \rightarrow j$ transition.

It may be noted that, according to this relation, the refractive index decreases with increasing wavelength. While this is true for the most part, the relation breaks down in the region where the material strongly absorbs light rays.

For practical purposes, the useful parameters in the correction for chromatic aberration are the Abbe number ν_d and the partial dispersion. The Abbe number is defined by

$$\nu_d = (n_d - 1) / (n_F - n_C), \quad (2.14)$$

where the F-line is the blue $\lambda = 486.1327$ nm line from the hydrogen spectrum, the C-line is red $\lambda = 656.2725$ nm line, also from the hydrogen spectrum, and the d-line is the yellow $\lambda = 587.5618$ nm line from the He spectrum. The partial dispersion for any two wavelengths x and y is given by

$$P_{x,y} = (n_x - n_y) / (n_F - n_C). \quad (2.15)$$

In optical applications of glasses, a map of the variation of refractive index as a function of Abbe number (dispersion) is used. In conventional maps, the designations of the glasses are given as ‘‘Crown’’ and ‘‘Flint’’, which is somewhat confusing [20]. Highly refractive glasses tend to have smaller Abbe numbers, i.e., high relative dispersion. A high refractive index is desirable to increase glass reflectivity (shiny appearance).

The factors affecting refractive-index of the glass are [15]:

1. Polarizability of the first neighbor ions coordinated with it (anion).
2. Field intensity Z/a^2 (i.e., polarization power), where Z is the valence of the ion (ionic charge) and a is the distance of separation (ionic radius).
3. Coordination number of the ion.
4. Non-bridging oxygen bonds (NBO's).
5. Electronic polarizability of the oxide ion.
6. Optical basicity of the glasses.

According to Fajan's rules [15] the first two factors mean that to increase electronic polarizability of the material a small positive ion (cation), a large negative ion (anion), and large charges on either ion are required. In the scope of previous factors, the refractive indices behavior of the different glass samples can be analyzed and explained.

2.5.2. Dispersion [47]

Because light waves are electromagnetic in nature, and glass is a dielectric, the interaction of light with glass is closely related to its dielectric properties. Maxwell's relations may be used to derive the relationship between the refractive index, n , and the dielectric constant, ϵ :

$$n = [\epsilon\mu/\epsilon_0\mu_0]^{1/2} = [\epsilon_s\mu_s]^{1/2} \quad (2.16)$$

where ϵ_0 is the absolute permittivity of the free space, ϵ is the electric permittivity of the medium, ϵ_s is the relative dielectric constant, and μ_0 , μ and μ_s represent the corresponding terms for magnetic permeability. It happens that for most nonferromagnetic materials, μ_s is nearly 1, so that we get the relation

$$n = [\epsilon_s]^{1/2} \quad (2.17)$$

Apparently, this relation works only for some simple gases. The reason for the apparent non-obedience is the frequency dependence of both the ϵ_s and n . Then, we described ϵ_s as a complex number ϵ^* :

$$\epsilon^* = \epsilon' - j\epsilon'', \quad j \equiv \sqrt{-1} \quad (2.18)$$

In a similar manner, we may write the complex refractive index n^* as

$$n^* = n_R - jn_I \quad (2.19)$$

The imaginary refractive index n_I is called the extinction coefficient. It causes attenuation: the amplitude of an electromagnetic wave traveling through the medium decrease by a factor $\exp[-2\pi n_I/n_R]$. The absorption coefficient in the medium as defined in Eq. (2.7) can be shown to be

$$a = 4\pi n_I/\lambda n_R = 4\pi n_I/\lambda_0 \quad (2.20)$$

where λ_0 and λ are the wavelengths of the incident radiation in vacuum and medium, respectively. For light waves traveling from one medium and falling at the surface of a dielectric at normal incidence, the reflectance R is given by

$$R = (n_1^* - n_2^*)^2 / (n_1^* + n_2^*)^2 \quad (2.21)$$

where n_1^* and n_2^* are the complex refractive indices of the two media, For air, $n_2^*=1$, such that Eq. (2.21) can be approximated to

$$R = [(n_R - 1)^2 + n_I^2] / [(n_R + 1)^2 + n_I^2] \quad (2.22)$$

which reduces to (2.5) for case of highly transparent media such as glass. For most metal, $n_R \rightarrow 0$, and hence, $R \rightarrow 1$.

From Maxwell's equations, the relationship between the complex dielectric constant and the complex refractive index may be written as

$$\epsilon^* = n^{*2} = [n_R - jn_I]^2 = (n_R^2 - n_I^2) - 2jn_R n_I \quad (2.23)$$

Thus,

$$\epsilon' = (n_R^2 - n_I^2), \text{ and } \epsilon'' = 2jn_R n_I \quad (2.24)$$

We assume that the total polarizability P is due to N_L dipoles per unit volume, each contributing an average polarizability α' , then

$$P = N_L \alpha' E' \quad (2.25)$$

where E' is the local electric field on the average dipole. In dense dielectrics such as a glass, E' is the sum of the macroscopic field E and a Lorentz field contribution equal to $P/3\epsilon_0$, i.e.,

$$E' = E + P/3\epsilon_0 \quad (2.26)$$

The polarization value may be define in term of

$$P = [\epsilon^* - 1]\epsilon_0 E \quad (2.27)$$

Equations (2.25), (2.26) and (2.27) yield

$$[\epsilon^* - 1]/\{N_L [\epsilon^* + 2]\} = \alpha'/3\epsilon_0 \quad (2.28)$$

which is called the Clausius-Mosotti relation, N_L is the number of dipoles per unit volume and is identified as the Loschmidt number (= the number per unit volume in an ideal gas at 0°C and 760 mm Hg = $2.687 \times 10^{25} \text{ m}^{-3}$). Avogadro's number N is related to N_L by

$$N = N_L V_M, \quad (2.29)$$

where V_M is molar volume. Hence, form (2.23) and (2.28),

$$N\alpha'/3\epsilon_0 = V_M (n^{*2} - 1)/(n^{*2} + 2) = R_m \quad (2.30)$$

which is called the Lorentz-Lorenz relation, R_m is called the molar refractivity. According to these relations, we could determine α' in the gas phase by measuring the refractive index, and then calculate the dielectric constant in the condensed phases at much higher density. Equation (2.30) may be also be written as

$$n^{*2} = (1 + 2Y)/(1 - Y) \text{ where } Y = N\alpha'/3V_M\epsilon_0 \quad (2.31)$$

which shows that a low value of V_M and high α' result in a high n^* .

2.6 Oxygen Ion Activity; Basicity [56-59]

The chemical interactions between the glass components are of acid-base character. The oxygen atoms in glasses behave as Lewis' bases and they can transfer part of their negative charge to the cations. The ability of oxygen to transfer the negative charges is the greatest when it is situated in the surroundings of weak cations, such as the alkalis. Duffy et al., proposed the concept of optical basicity based on the experimental shift of the ultraviolet spectrum of a probe incorporated in various oxides. Duffy proposed a parameter Λ that permits a comparison of the acid-base character of oxides. The optical basicity Λ , of an oxidic medium, is the average electron donor power of all the oxide atoms comprising the medium. Increasing basicity results in increasing negative charge on the oxygen atoms and, thus, increasing covalency in the cation oxygen bonding.

The optical basicity could be predicted from the glass compositions and from the basicity moderating parameters of the various cations present. It is possible to calculate the so-called theoretical optical basicity of multi-component glass on the basis of the following equation proposed by Duffy and Ingram :

$$\Lambda_{th} = \sum_{i=1}^n x_i \Lambda_i \quad (2.32)$$

where x_1, x_2, \dots, x_n are equivalent fractions of different oxides, i.e., the amount of oxygen each oxide contributes to the overall glass stoichiometry and $\Lambda_1, \Lambda_2, \dots, \Lambda_n$ are optical basicity values assigned to the constituent oxides.

In case of the present study, the values of optical basicity for oxide have been taken from the literature. The optical basicity evaluated for the glasses decreases when soda is replaced by one of the divalent metal oxides magnesia or barium oxide. Such low optical basicity means a reduced ability of oxide ions to transfer electrons to the surrounding cations.

Since the polarizability of oxide ions is closely related to the optical basicity of oxide materials, the studied glasses possess a relatively low optical basicity with the increase in the value of x . This may be understood according to the relation:

$$\Lambda_{th} = 1.67 \left(1 - \frac{1}{\alpha_0^{2-}} \right) \quad (2.33)$$

where α_0^{2-} is polarizability of oxide ions, and Eq. (2.33) shows that with decrease in polarizability, the optical basicity also decreases leading to a decrease in refractive index. Some theoretical values of optical basicity and related parameters for calculated of glass samples and are listed in Table 2.2 and Table 2.3, respectively.

Table 2.2 Optical basicities according to Dimitrov and Sakka calculated from refractive index ($\Lambda(n_0)$) and energy gap ($\Lambda(E_g)$), their average (Λ_{av}), optical basicity according to Duffy (Λ_{Duffy}), optical basicity according to Leboutellier and Courtine (Λ_{LS}), and O1s binding energy (E_b) of simple oxides [60].

Oxide	$\Lambda(n_0)$	$\Lambda(E_g)$	Λ_{av}	$\Lambda(Duffy)$	Λ_{LS}	E_b (eV)
BeO			0.375		0.48	
B ₂ O ₃	0.43		0.43	0.42	0.42	533.2
P ₂ O ₅				0.33(0.40)	0.33	533.5
SiO ₂	0.48	0.52	0.50	0.48	0.48	532.8
Al ₂ O ₃				0.60	0.60	531.2
MgO	0.69	0.67	0.68	0.78	0.78	530.9
GeO ₂	0.70		0.70	0.60	0.54	531.3
Ga ₂ O ₃	0.71	0.80	0.755			530.6
Li ₂ O	0.87		0.87	1.00	0.48	
CaO	1.00	0.95	0.975	1.00	1.00	529.8
Sc ₂ O ₃		0.87	0.87			
TiO ₂	0.96	0.91	0.97	1.00	0.75	529.7
V ₂ O ₅		1.04	1.04		0.63	530.0
MnO	0.94	0.96	0.95	1.00	0.96	529.8
Fe ₂ O ₃	1.04	0.99	1.02		0.77	530.0
CoO		0.98	0.98		0.98	529.9
NiO	0.91	0.92	0.915		0.91	530.0
CuO	1.08	1.11	1.10		0.56	530.3
ZnO	1.03	1.13	1.08	0.95	0.92	530.3
Y ₂ O ₃	0.99		0.99		0.72	529.3
ZrO ₂	0.86	0.79	0.825	0.90	0.71	529.9
Nb ₂ O ₅		1.05	1.05		0.61	
MoO ₃	1.07	1.07	1.07		0.52	530.4
In ₂ O ₃		1.07	1.07			530.1
SnO ₂	0.79	0.91	0.85		0.87	530.1
TeO ₂	0.99	0.96	0.975			530.5
CeO ₂		1.01	1.01		0.65	529.1
Ta ₂ O ₅		0.94	0.94			
WO ₃	1.05	1.04	1.045		0.51	530.2
Na ₂ O				1.15	1.15	529.7
SrO	1.10	1.18	1.14	1.10	1.10	529.0
CdO	1.10	1.13	1.115		1.12	528.6
Sb ₂ O ₃	1.14	1.22	1.18			
Cs ₂ O				1.70	< 1.70	529.4
BaO	1.21	1.23	1.22	1.15	1.20	528.2
PbO	1.19	1.17	1.18	0.95		529.7
Bi ₂ O ₃		1.19	1.19		1.19	

Table 2.3 Electronic polarizabilities of oxide ion calculated from refractive index ($\alpha_0^{2-}(n_0)$) and energy gap ($\alpha_0^{2-}(E_g)$), their average (${}^{av}\alpha_0^{2-}$), and O1s binding energy (E_b) of simple oxides [60].

Oxide	$\alpha_0^{2-}(n_0)(\text{Å}^3)$	$\alpha_0^{2-}(E_g)(\text{Å}^3)$	${}^{av}\alpha_0^{2-}(\text{Å}^3)$	$E_b(\text{eV})$
BeO			1.290	
B ₂ O ₃	1.345		1.345	533.2
P ₂ O ₅			1.350	533.5
SiO ₂	1.401	1.454	1.427	532.8
Al ₂ O ₃	1.460 ^b		1.460	531.2
MgO	1.699	1.675	1.687	530.9
GeO ₂	1.720		1.720	531.3
Ga ₂ O ₃	1.732	1.913	1.822	530.6
Li ₂ O	2.090		2.090	
CaO	2.505	2.334	2.420	529.8
Sc ₂ O ₃		2.075	2.075	
TiO ₂	2.368	2.188	2.278	529.7
V ₂ O ₅		2.643	2.643	530
MnO	2.303	2.357	2.330	529.8
Fe ₂ O ₃	2.647	2.467	2.557	530
CoO		2.405	2.405	529.9
NiO	2.202	2.218	2.210	530
CuO	2.838	2.963	2.900	530.3
ZnO	2.612	3.105	2.859	530.3
Y ₂ O ₃	2.458		2.458	529.3
ZrO ₂	2.054	1.897	1.975	529.9
Nb ₂ O ₅		2.679	2.679	
MoO ₃	2.769	2.769	2.769	530.4
In ₂ O ₃		2.762	2.762	530.1
SnO ₂	1.908	2.191	2.050	530.1
TeO ₂	2.444	2.358	2.401	530.5
CeO ₂		2.522	2.522	529.1
Ta ₂ O ₅		2.291	2.291	
WO ₃	2.677	2.662	2.670	530.2
SrO	2.918	3.382	3.150	529.0
CdO	2.909	3.078	2.993	528.6
Sb ₂ O ₃	3.172	3.686	3.429	
BaO	3.652	3.830	3.741	528.2
PbO	3.450	3.311	3.381	529.7
Bi ₂ O ₃		3.507	3.507	

2.7 Color of glasses [24,46]

Another important optical property of a glass is its color. Color is imparted to glasses by several methods. One is by dissolving transition metal ions into glasses, which give rise to optical absorption due to the well-known d-d optical transitions. The other is to dissolve a material in the molten glass, which gets precipitated out as extremely fine particles, and scatter light of particular frequencies in the resulting glass, thus imparting color to it. There are also glasses in which the absorption gets altered when the intensity of light falling on it changes so that the net light transmitted by the glass can be controlled. When the effect is reversible, the phenomenon is known as photochromism. Unlike in photochromic glasses, the incident light brings about permanent (irreversible) changes in the photo-sensitive glasses. In the latter, reactions similar to those occurring in photographic plates take place. We discuss in the following sections some salient features of color and absorption of light in glasses.

2.7.1 Color due to transition metal ions

Coloration of glasses by 3d transition metal ions is due to electronic transitions between normally degenerate energy levels of d-electrons. Since a detailed description of the mechanism leading to these electronic transitions (called ligand field or crystal field theory) can be found in many places, only a brief qualitative discussion will be provided here.

The 3d electronic levels are identical in energy for free ions. However, when a transition metal ion is surrounded by a few anions, called ligands, as in a crystal or glass, the interaction of the electric fields causes a small splitting of the energy levels. The magnitude of this splitting is a function of the field strength, number, and geometric arrangement of the neighboring anions. The number of different levels formed is a function of the electronic configuration and coordination number of the cation. Since the energy differences which commonly result for 3d transition metal ions from ligand fields are in the range of 1 to 3 eV, the absorption of photons by electronic transitions between split 3d levels results in visible coloration.

Similar arguments apply to the 4f electronic levels of the rare earth ions, where splitting of the 4f levels also produces absorption bands in the visible. Differences in the nature of the 3d and 4f ions result in less intense absorptions for the rare earth ions, as well as more complex spectra, which are due to the greater number of possible configurations of the seven 4f levels, as compared to the five 3d levels of the transition metal ions.

All of these electronic transitions are technically forbidden by Laporte's rule, which states that electronic transitions can only occur if the orbital angular momentum changes by ± 1 during the transition. Since this does not occur for transitions from one d state to another d state or from one f state to another f state, no absorption should occur for these ions. Fortunately, Laporte's rule is relaxed in solids due to the lack of perfect spherical symmetry, which results from the presence of a limited number of point sources, so that electronic transitions can occur with a low probability between 3d or 4f levels which are split by the fields of the neighboring ligands. The low probability of these transitions, however, does reduce the intensity of the absorption. As a result, ligand field induced transitions are much weaker than the charge transfer effects which occur in the ultraviolet.

Since the coloration of glasses by transition metal and rare earth ions results from ligand field effects, several general trends can be predicted. First, a change in oxidation state results in a change in the number of 3d or 4f electrons, resulting in a different number of possible electronic transitions for otherwise identical conditions. Since each possible electronic transition represents absorption with a different energy, a difference in oxidation state will result in a different absorption spectrum.

Most 3d transition metal ions are found in either octahedral or tetrahedral coordination in oxide glasses. A change in coordination number will result in a difference in splitting energy and, depending upon the number of 3d electrons present, possibly a change in the number and relative positions of the potential electronic transitions.

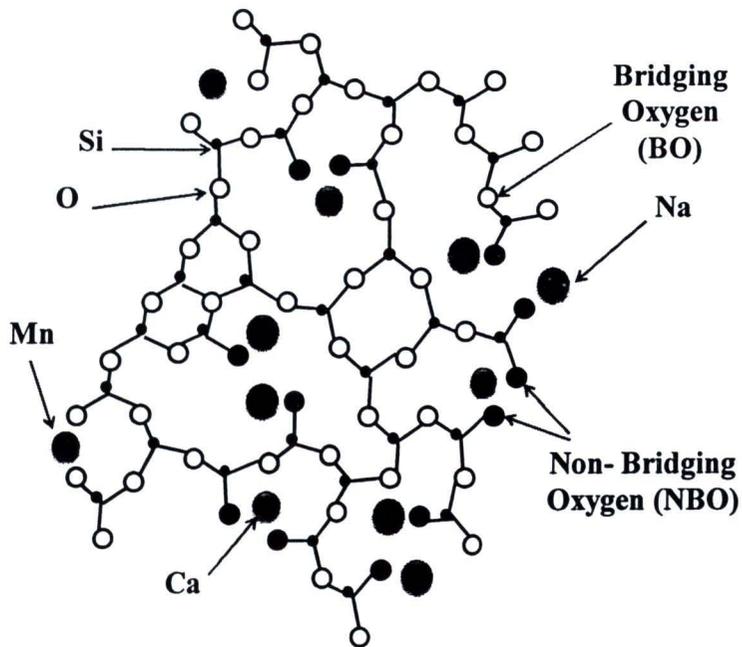
Changes in the identity of the anions results in a change in their ligand field strength, and thus a shift in the positions of the absorption bands with no change in their number or relative positions. The ligand field strength of the common anions decreases in the order $O^{2-} > F^- > Cl^- > Br^- > I^-$. In many cases, the transition metals appear to prefer to be associated with halide ions instead of oxygen ions in nominally oxide glasses. For example, the substitution of a small amount of NaCl for Na₂O in a sodium borate glass containing cobalt oxide can cause the color due to Co²⁺ ions to change from a dark blue-purple to lighter blue-green, due to a small shift in the absorption band positions to longer wavelengths. Addition of a small amount of NaBr can result in a green glass, while additions of NaI can yield a red-brown glass. The Co²⁺ ions must preferentially associate with the small number of halide ions, since the color of the glass is actually due to a very small concentration of the transition metal ions.

The color is also altered by changes in concentration of the coloring cation, in the identity of the network former, and in the identity and concentration of the modifiers present. The effect of the concentration of the coloring ion is obvious; more chromophores, or coloring species, result in more absorption. The effects of changes in the network former and the modifier ions present are due to alterations in bond distance and bond strength between the coloring ions and the surrounding ligands. Replacement of a small diameter modifier ion by a larger one can also occasionally cause a change in the most favorable coordination number for the coloring ion.

Details of the coloration of glasses due to ligand field effects are further complicated by the possibility of redox interactions between two or more different transition metal ions. Other elements such as arsenic and antimony, which do not directly affect color, may alter the oxidation state of a coloring ion and alter the color of the glass. Changes in furnace atmosphere can also inadvertently alter the oxidation state of coloring ions due to changes in the concentrations of O₂, CO, CO₂, and H₂O vapor. Table 2.4 shows the colors generated by some of the transition metal and rare earth ions in glass [51]. It may be noted that different valences impart different colors.

Table 2.4 Colors Generated by Transition-Metal and Rare-Earth Ions in Glass [46]

Transition metal ions			Rare earth ions		
Configurat ion	Ion	Color	Configurat ion	Ion	Color
d^0	Ti ⁴⁺	Colorless	$4f^0$	La ³⁺	None
	V ⁵⁺	Faint yellow to colorless		Ce ⁴⁺	Weak yellow
	Cr ⁶⁺	Faint yellow to colorless		Ce ³⁺	Weak yellow
d^1	Ti ³⁺	Violet-purple	$4f^1$	Pr ³⁺	Green
	V ⁴⁺	Blue	$4f^2$	Nd ³⁺	Violet-pink
	Mn ⁶⁺	Colorless	$4f^4$	Pm ³⁺	None
d^2	V ³⁺	Yellow-green	$4f^4$	Sm ³⁺	None
	Cr ³⁺	Green	$4f^5$	Sm ²⁺	Green
d^3	Cr ²⁺	Faint blue	$4f^6$	Eu ³⁺	None
	Mn ³⁺	Purple	$4f^7$	Eu ²⁺	Brown
d^4	Mn ²⁺	Light yellow		$4f^8$	Gd ³⁺
	Fe ³⁺	Faint yellow	$4f^9$	Tb ³⁺	None
d^5	Fe ²⁺	Blue-green	$4f^{10}$	Dy ³⁺	None
	Co ³⁺	Faint yellow	$4f^{11}$	Dy ²⁺	Brown
d^6	Co ²⁺	Blue-pink		$4f^{12}$	Ho ³⁺
	Ni ²⁺	Brown-purple	$4f^{13}$	Er ³⁺	Weak pink
d^7	Cu ²⁺	Blue-green	$4f^{14}$	Tm ³⁺	None
	Cu ⁺	Colorless		Tm ²⁺	None
d^8				Yb ³⁺	None
d^9				Lu ³⁺	None
d^{10}					

**Figure 2.11** Possible Schematic drawing of a 2-dimensional structure for a soda lime silicate glass doped MnO₂ (adapted from [26]).

2.8 CIELAB

CIELAB is the second of two systems adopted by CIE in 1976 as models that better showed uniform color spacing in their values. CIELAB is an opponent color system based on the earlier (1942) system of Richard Hunter called L, a, b. Color opposition correlates with discoveries in the mid-1960s that somewhere between the optical nerve and the brain, retinal color stimuli are translated into distinctions between light and dark, red and green, and blue and yellow. CIELAB indicates these values with three axes: L^* , a^* , and b^* . (The full nomenclature is 1976 CIE $L^*a^*b^*$ Space.)

The central vertical axis represents lightness (signified as L^*) whose values run from 0 (black) to 100 (white). This scale is closely related to Munsell's value axis except that the value of each step is much greater. This is the same lightness valuation used in CIELUV.

The color axes are based on the fact that a color can't be both red and green, or both blue and yellow, because these colors oppose each other. On each axis the values run from positive to negative. On the a - a' axis, positive values indicate amounts of red while negative values indicate amounts of green. On the b - b' axis, yellow is positive and blue is negative. For both axes, zero is neutral gray:

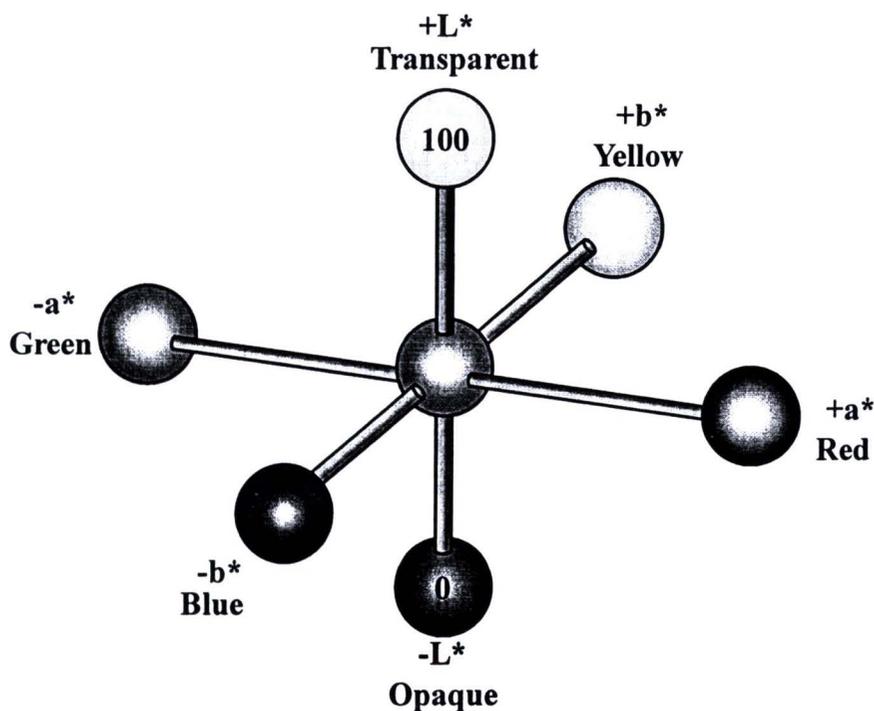


Figure 2.12 CIE Lab color space (adapted from [61]).

Therefore, values are only needed for two color axes and for the lightness or grayscale axis (L^*), which is separate (unlike in RGB, CMY or XYZ where lightness depends on relative amounts of the three color channels).

CIELAB has become very important for desktop color. Like all CIE models, it is device independent (unlike RGB and CMYK), is the basic color model in Adobe PostScript (level 2 and level 3), and is used for color management as the device independent model of the ICC (International Color Consortium) device profiles.

2.8.1 Measuring differences

The nonlinear relations for L^* , a^* , and b^* are intended to mimic the nonlinear response of the eye. Furthermore, uniform changes of components in the $L^*a^*b^*$ color space aim to correspond to uniform changes in perceived color, so the relative perceptual differences between any two colors in $L^*a^*b^*$ can be approximated by treating each color as a point in a three dimensional space (with three components: L^* , a^* , b^*) and taking the Euclidean distance between them.

2.8.2 RGB and CMYK conversions

There are no simple formulas for conversion between RGB or CMYK values and $L^*a^*b^*$, because the RGB and CMYK color models are device dependent. The RGB or CMYK values first need to be transformed to a specific absolute color space, such as RGB or Adobe RGB. This adjustment will be device dependent, but the resulting data from the transform will be device independent, allowing data to be transformed to the CIE 1931 color space and then transformed into $L^*a^*b^*$.

2.9 Manganese Characteristics [5,8,10,11,23,24,28,30-36]

Manganese is a chemical element, designated by the symbol **Mn**. It has the atomic number 25. It is found as a free element in nature (often in combination with iron), and in many minerals. As a free element, manganese is a metal with important industrial metal alloy uses, particularly in stainless steels.

The most common oxidation states of manganese are +2, +3, +4, +6 and +7, though oxidation states from +3 to +7 are observed. Mn^{2+} often competes with Mg^{2+} in biological systems. Manganese compounds where manganese is in oxidation state +7, which are restricted to the oxide Mn_2O_7 and compounds of the intensely purple permanganate anion MnO_4^- , are powerful oxidizing agents. Oxidation states +5 (blue) and +6 (green) are both oxidizing and vulnerable to disproportionate.

The most stable oxidation state for manganese is +2, which has a pink to red color, and many manganese (II) compounds are known, such as manganese (II) sulfate ($MnSO_4$) and manganese (II) chloride ($MnCl_2$). This oxidation state is also seen in the mineral rhodochrosite, (manganese (II) carbonate). The +2 oxidation state is the state used in living organisms for essential functions; all of the other states are much more toxic.

The +3 oxidation state is known, in compounds such as manganese(III) acetate, but these are quite powerful oxidizing agents and also disproportionate in solution to Mn(II) and Mn(IV) Solid compounds of Mn(III) are characterized by its preference for distorted octahedral coordination due to the Jahn-Teller effect and its strong purple-red color.

Manganese (IV) oxide is the inorganic compound with the formula MnO_2 . This blackish or brown solid occurs naturally as the mineral pyrolusite, which is the main ore of manganese and a component of manganese nodules. The principal use for MnO_2 is for dry-cell batteries, such as the alkaline battery and the zinc-carbon battery. MnO_2 is also used as a pigment and as a precursor to other manganese compounds, such as KMnO_4 . It is used a reagent in organic synthesis, for example, for the oxidation of allylic alcohols.

The oxidation state 5+ can be obtained if manganese dioxide is dissolved in molten sodium nitrite. Manganate (VI) salts can also be produced by dissolving Mn compounds in alkaline melts in air.

Permanganate (+7 oxidation state) manganese compounds are purple, and can color glass an amethyst color. Potassium permanganate, sodium permanganate and barium permanganate are all potent oxidizers. Potassium permanganate, also called Condy's crystals, is a commonly used laboratory reagent because of its oxidizing properties and finds use as a topical medicine (for example, in the treatment of fish diseases). Solutions of potassium permanganate were among the first stains and fixatives to be used in the preparation of biological cells and tissues for electron microscopy.