Collage of Engineering
Materials Department

Third Class
Lecture (2)

GLASS

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3-Structure of Glass

Glass forming oxides**:** most inorganic glasses are based on the glass forming oxide. Silica is most widely used as glass forming constituent.

The fundamental subunit in silica based glasses is SiO_4 tetrahedron in which a silica si^4 atom ion in the tetrahedron is covalently ironically bonded to four oxygen atoms ions as shown in fig (2.a) .

- In crystalline silica cristobalite the si-o tetrahedra are joined corner to corner in a regular arrangement, producing long – range order as idealized in fig (2.b) .

- In a simple silica glass the tetrahedra are joined corner to corner to from a loose network with no long –range order fig (2.c) .

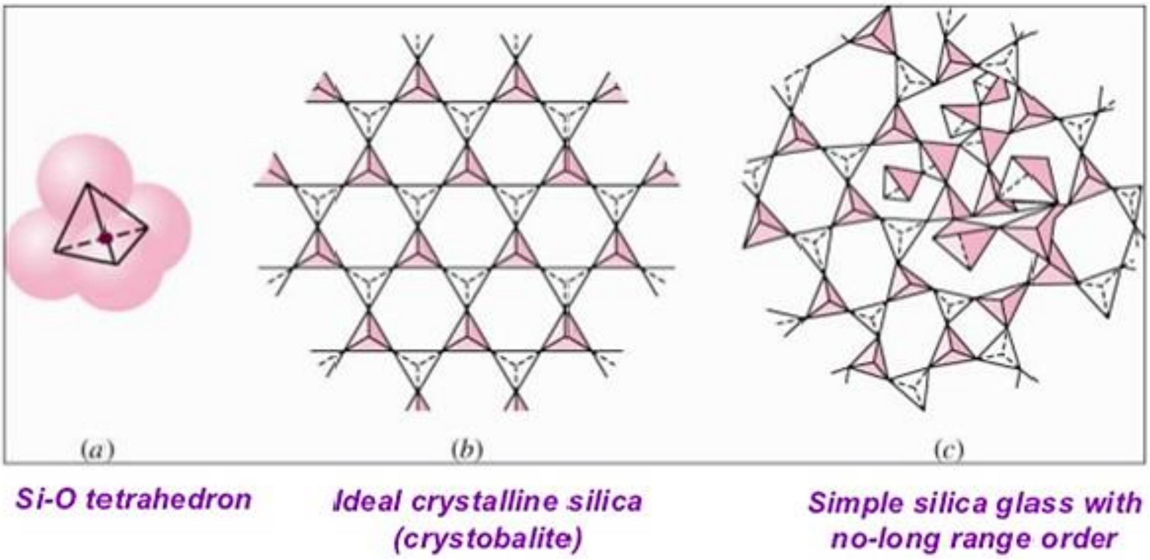

Figure 2: schematic representation of (a) a silicon-oxygen tetrahedron, (b) ideal crystalline silica (cristobalite)in which the tetrahedral have long range order, and (c) a simple silica glass in which the tetrahedral have no long range order.

The oxide components added in to a glass batch may be sub-divided as:

A. *Glass formers.*
B. *Intermediated.*
C. *Modifiers.*

These are groped on the basis of functions that they perform within the glass. However, the silicate glasses contain additional oxide as shown in (table 1) .

Table 1 Division of the oxides into glass former, intermediates, and modifiers		
Glass formers	Intermediates	Modifiers
B_2O_3 SiO_2 GeO_2 P_2O_5 V_2O_3	TiO_2 ZnO PbO_2 Al_2O_3 BeO	Y_2O_3 MgO CaO PbO Na_2O

A- Glass formers

Glass formers and network formers include oxides such as SiO_2 ,B_2O_3 , GeO_2 , P_3O_5 , V_2O_5 and AS_2O_3 which are indispensable in the formation of glass since they form the basis the random three dimensional network of glass.

Boron oxide, B_2O_3 ,is a glass- forming oxide and by itself from subunit that are flat triangle with boron atom slightly out of the plane of the oxygen atoms .

However, in borosilicate glasses that have additions of alkali and alkaline earth oxides , BO_3 triangles can be converted to BO_4

tetrahedra with the alkali or alkaline earth cationsproviding the necessary electroneutrality .

Boron oxide is an important addition to many types of commercial glass such as borosilicate and aluminoborosilicate glasses.

B- Intermediate oxide in glasses :

Intermediates include AL_2O_3 ,Sb_3O_2 ,ZrO_2 ,TiO_3 ,PbO, and ZnO , these oxides are added in high proportion for linking up with the basic glass network to retain structural continuity .

Some oxidescannot from a glass network by themselves but can join into an existing network. These oxides are known as intermediate oxides.

For example, aluminum oxides, silica network as AlO_4tetrahedra replacing some of the SiO_4 gropes (fig .3b) . However since the valence of Al is 3 instead of the necessary 4 for the tetrahedral , alkali cantions must supply the necessary other electrons to produce electrical neutrality .

Intermediate oxides are added to silica glass to obtain special properties. For example alaminosicate glasses can withstand higher temperature than common glasses.

Depending on the composition of the glass, intermediate oxides may sometimes act as network modifiers as well as taking part in the network of the glass .

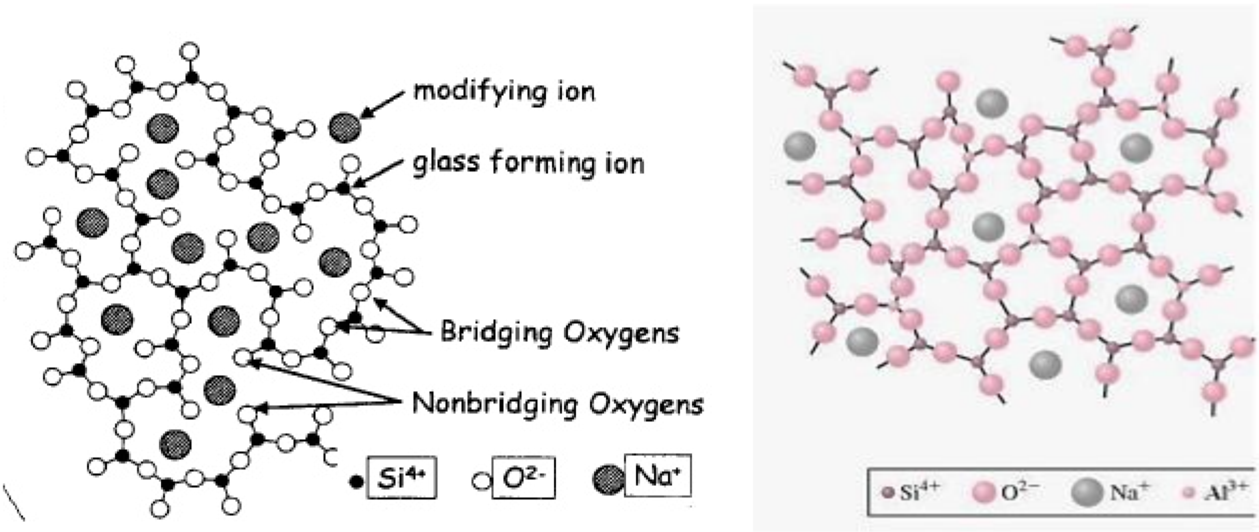

figure 3: (a) network modified glass (soda-limeglass); note that the metallic (Na+)ions do not form part of the network (b)intermediate oxides glass(alumina-silica) glass ; note that the small metallic (Al^{+3}) ions form part of the network

C- Glass – modifying oxides :

Modifiers include MGO, Li_2O, BaO, CaO, SrO, Na_2O, and K_2O. The oxides are added to modify the properties of glass oxides that break up the glass network are know as network modifiers.

Alkali oxides such as Na_2O and K_2O and alkaline earth oxides such as CaO and MgO are added to silica glass to lower its viscosity so that it can be worked and formed more easily.

The oxygen atoms from these oxide enter the silica network at points joining the tetrahadra and break up the network,producing oxygen atoms withan unshared electron (fig .4a) .

The Na and K ions from the Na_2O and K_2O do not enter the network but remain as metal ions ionically bonded in the interstices of the network.by filling some of the interstices, these ions promote crystallization of the glass .

Modifiers break up the silica network if the oxygen to silica ratio (O:Si) increases significantly when Na_2O is added , the sodium ions enter holes within the network , rather then becoming part of the network ,however , the oxygen ion that enters with Na_2O does become part of the network as shown in fig (fig 4).

When this happenes, there are not enough silica ions to combine with the extra oxygen ions and keep the network intact.

A high O:Si ratio causes the remaining silica tetrahedral to from chain , rings , or compound and the silica no longer transforms to a glass when the O:Si ratio is above about 2.5 , silica glasses are difficult to form , above a ratio of three , aglass forms only when special precaution are taken such as the use of rapid cooling rates .

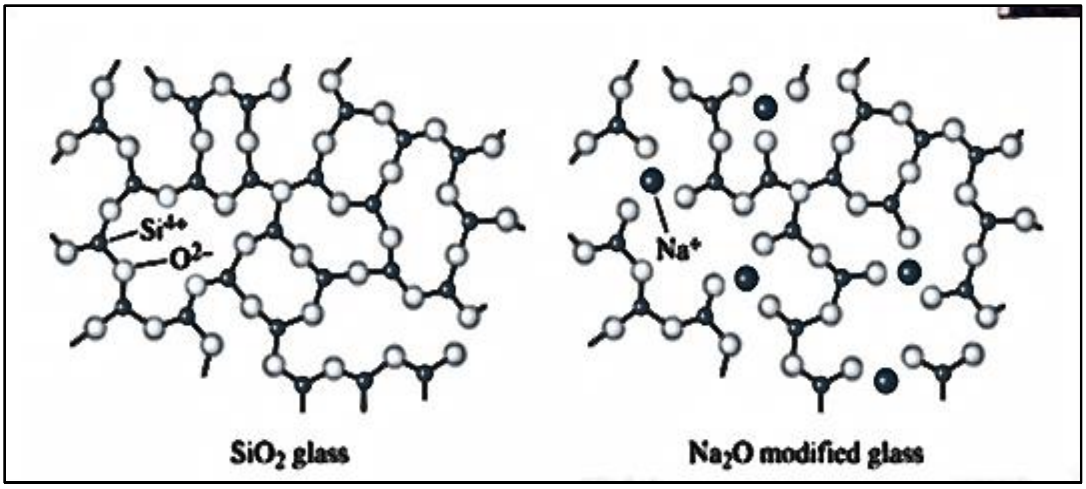

Figure 4: the effect of Na_2O on the silica glass network. Sodium oxide is a modifier disrupting the glassy network and reducing the ability to form a glass.

The other addition in glass are the fluxes which lower the fusion temperature of the glass batch and render the molten glass workable at reasonable temperature , modification lower the melting point and viscosity of silica, making it possible to produce glass at lower temperature .

The effect of Na_2O .addition to silica is shown in (fig5) the addition of Na_2O produces eutectics with very low melting temperature .

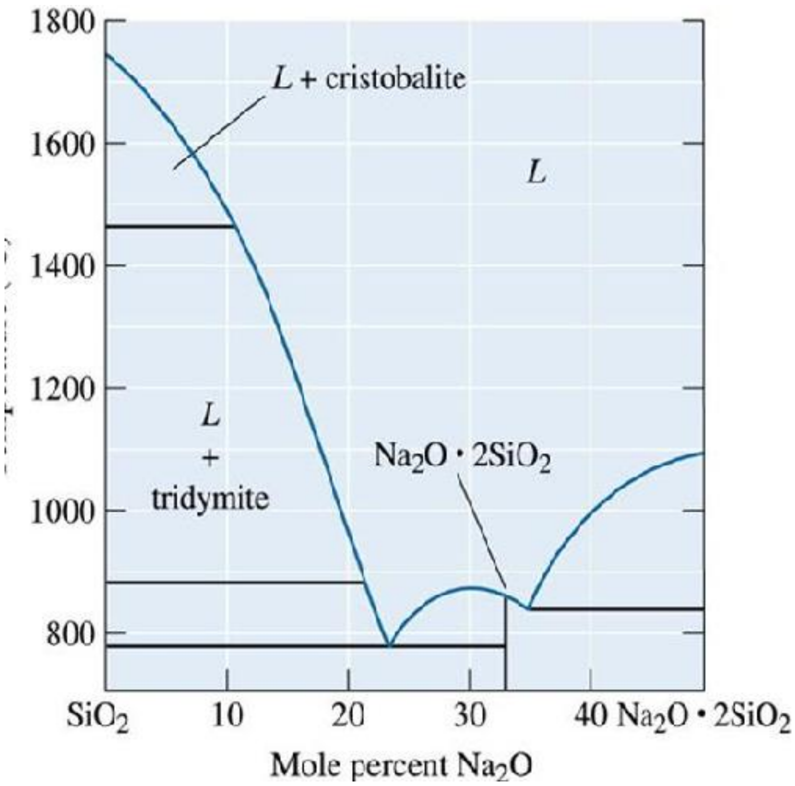

Figure 5: the SiO_2-Na_2O phase diagram

Addition of soda (Na_2O) to silica dramatically reduce the melting temperature of silica by forming eutectics.

Modifiers fluxes may reduce the resistance of glass to chemical attack, render it water soluble or make it subject to partial or complete devitrification. Devitrified glass is undesirable since the crystalline areas are externally weak and brittle, stabilizers are therefor, added to the glass batch overcome these problems.

Adding CaO which reduces the solubility of the glassin water further modifies these glasses.

3.1 Structure of some glasses

3.1.1 Silicate glasses:

Vitreous silica is the disordered structure of the ordered silica. The building blocks of vitreous silica are tetraherdra of $SiO_{4,}$ which link together by oxygen ions at the tetraherda corners. These oxygens are called bridging oxygens. Bonding angels in this structure are distributing over a wide range. Structure analysis indicates that the shortest Si-O distance in this structure is ≈ 0.162 nm and that the shortest O-O distance is ≈ 0.265 nm. While the bond of two silicon atoms is 0.312 nm. These distributions of atom-atom distances can be explained by assuming a distribution in the Si-O-Si bond angles. The maximum in this distribution occurs at ≈ 144°, with a range in angles from 120° to 180°.

Introduction of alkali oxides like Na_2O , K_2O etc. leads to lowering the melting temperatures by forming nonbridging oxygen .each nonbridging oxygen must be associated with a nearby alkali ion to maintain local charge neutrality see in fig(4). These alkali ions occupy the interstices in the network, reducing the unoccupied free-volume of the structure.

Ternary glasses containing alkaline earthoxides in combination with silica and alkali oxides, which are commonly called soda -lime-silica glasses, usually contain 10-20%mol alkali oxide, primarily in the form of Na_2O or soda, 5-15% molCaO or lime,and 70-75% mol silica .the replacement of the more mobile alkali ions by the less mobile divalent alkaline earth ions reduces the net mobility of modifier ions through the structure, improving the chemical durability and reducing the ionic contributing to the electrical conductivity of the glass.

3.1.2 Aluminosilicate glasses

Aluminum and gallium ions routinely occur in both tetrahedral and octahedral coordination in crystalline materials.

Since these ions assumed to have the same coordination in glass structure, the following explanation is applicable for both the glasses that contain aluminum and gallium ions. It is generally assumed that most, if not all, of the aluminumin these glasses will occur in aluminum - oxygen tetrahedral, so long as the total concentration of alkali and /or alkaline earth oxides equals or exceed that of aluminum i.e $[Al_2O_3/M_2O] \leq 1$. These tetrahedra substitute directly into the network for silicon-oxygentetrahedra.it follows that alumina, which does not readily form a glass by it self, can; however, easily replace silica in the vitreous network. Oxides which act in this manner are said to be intermediate in behavior between glass formers and modifier oxides. If the $[Al_2O_3/M_2O]$ ratio>1, aluminum enters the glass network as modifier. The two most commonly discussed models suggest that either (a) excess aluminum ions occur in octahedral coordination, with three BO and three NBO in each octahedron, or (b) tri-clusters of aluminum – oxygen and silicon –oxygen tetrahedral occur,with three coordination oxygen connects corners of three tetrahedral i.e AlO_4 and $2SiO_4$ or $2AlO_4$ and SiO_4 if the tri-cluster contains AlO_4 and $2SiO_4$ the overall unit will be charge neutral. If however, the unit contains $2AlO_4$ and SiO_4, the unit will have a net charge of -1 and will require an associated modifier cation for charge neutrality.

3.1.3 boric glasses

Triangles of boron ions and oxygen ions form the building units of the boric glass vitreous structure. All such triangles are connected by BO at all three corners to form a completely linked network. Basic building block of this network is planar 2D rather than 3D, the 3D linkage, which occurs in a network of tetrahedra, does not exist for vitreous boric oxide.

A 3Dstructure is developed by "crumpling" of the network, in much the same way that two dimensional drawing on sheet of paper develops a third dimension when the paper is crumpled into ball. Since the primary bonds exist only within the plane of the paper, bonds in third dimension (van der waals bonds) are very weak and the structure is easily disrupted.one result of this structure, for example, can be found in the glass transformation temperature (T_g) of vitreous boric oxide, which is only ≈ 260 $^\circ$C, as opposed to the T_g of vitreous silica , which is ≈ 1100° C. the structure of vitreous boric oxide is also believed to contain a large concentration of an intermediate unit, consisting of three boron-oxygen triangle joined to form a structure known as a boroxol ring or boroxol group. These well-defined units are connected by oxygen so that the B-O-B angle is variable, and twisting out of the plane of the boroxol group can occur see fig. (6)

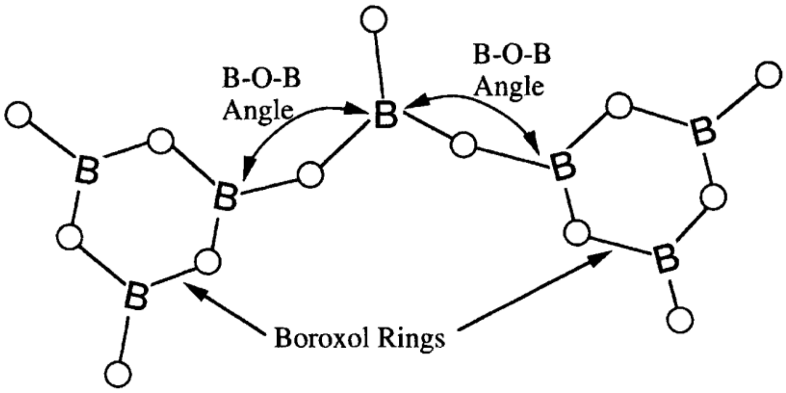

Figure (6): boroxol ring structure in vitreous boric oxide and alkali borate glasses

Addition of alkali oxides to vitreous silica result in the formation of NBO. Examination of property trends for alkali silicate versus alkali borate glasses suggests that this is not the cases for alkali borate glasses. Small addition of silica causes a decrease in T_g while similar additions to boric oxide cause an increase in T_g. conversely, small additions alkali oxides to silica cause an increase in the thermal expansion coefficient, while similar additions to boron oxide cause a decrease in the thermal expansion coefficient. The reason is that the boron coordination in existence of alkalis will be changed from $[BO_3]$ to $[BO_4]$.