Collage of Engineering

Materials Department

Third Class

Lecture (2-A)

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) .

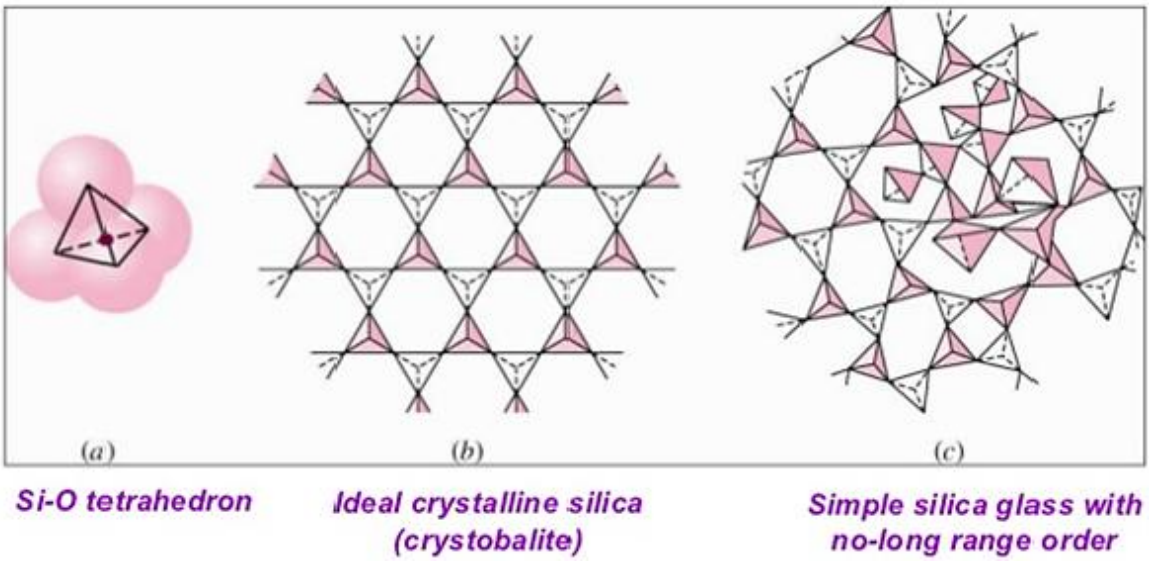

Figure 2: schematic representation of (a) a silicon-oxygen

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	TiO_2	Y_2O_3
SiO_2	ZnO	MgO
GeO_2	PbO_2	CaO
P_2O_5	Al_2O_3	PbO
V_2O_3	BeO	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 sometimesact as network modifiers as well as taking part in the network of the glass .

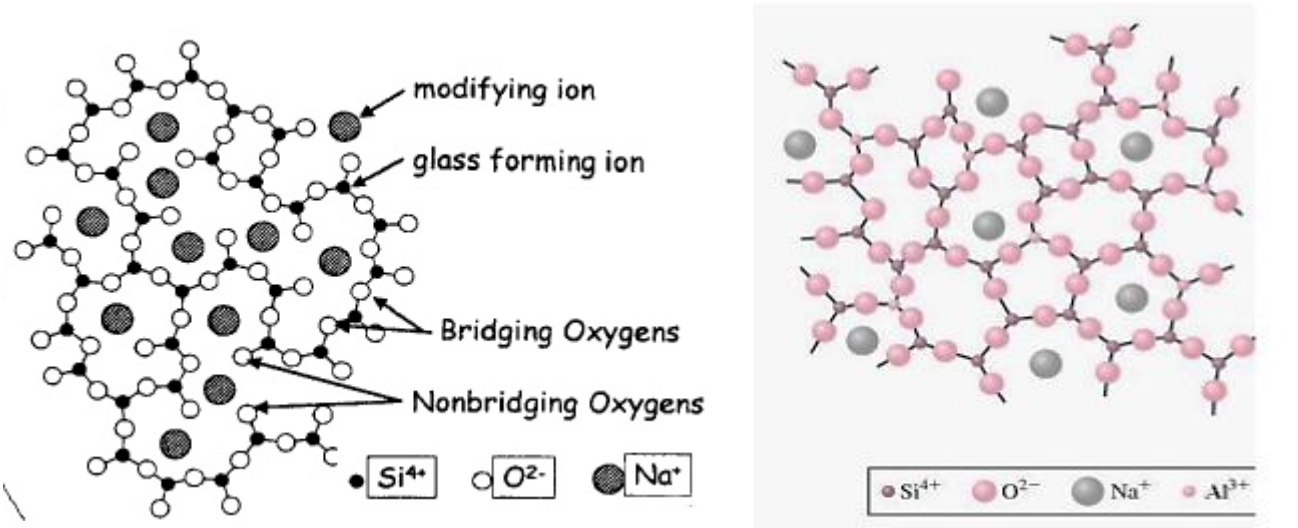

figure 3: (a) network modified glass (soda-limeglass); note that the metallic (Na+)ions do not form part of the network (b)intermediate oxides glass(alumina-silica) glass ; note that the small metallic (Al^{+3}) ions form part of the network

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 .

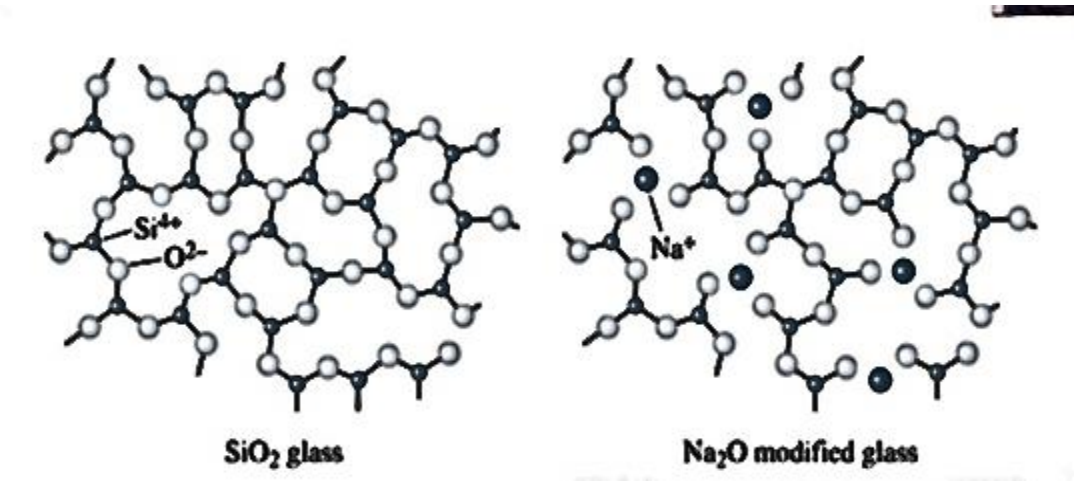

Figure 4: the effect of Na_2O on the silica glass network.
Sodium oxide is a modifier disrupting the glassy network and reducing the ability to form a glass.

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 .

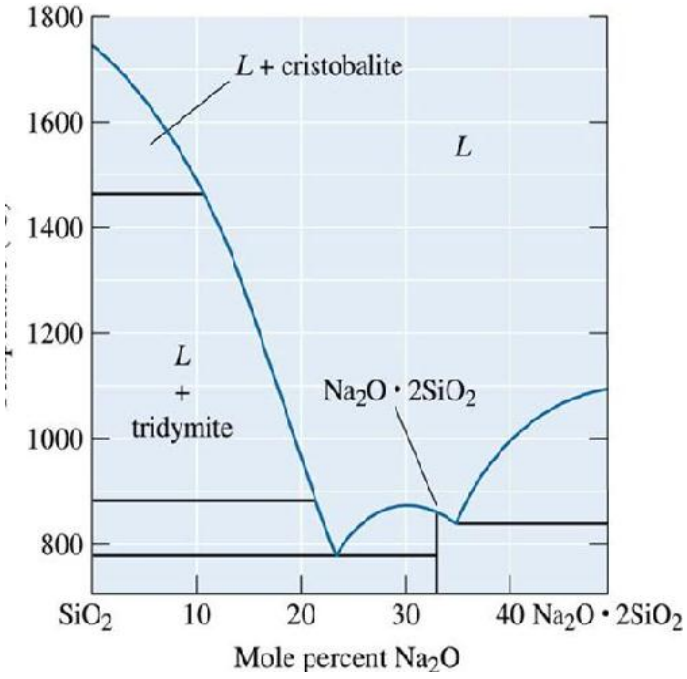

Figure 5: the SiO_2-Na_2O phase diagram

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.