

Collage of Engineering
Materials Department

Third Class
Lecture (2- B)

GLASS

Asst. Lect. Shireen Hasan

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 tetrahedra of SiO_4 , which link together by oxygen ions at the tetrahedra corners. These oxygens are called bridging oxygens. Bonding angles in this structure are distributed 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 $\approx 144^\circ$, 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% mol CaO 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 contribution 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 are 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 aluminum in these glasses will occur in aluminum - oxygen tetrahedral, so long as the total concentration of alkali and /or alkaline earth oxides equals or exceeds that of aluminum i.e $[\text{Al}_2\text{O}_3/\text{M}_2\text{O}] \leq 1$. These tetrahedra substitute directly into the network for silicon-oxygen tetrahedra. It follows that alumina, which does not readily form a glass by itself,

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 3D structure 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 $\approx 260^\circ\text{C}$, as opposed to the T_g of vitreous silica, which is $\approx 1100^\circ\text{C}$. 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)

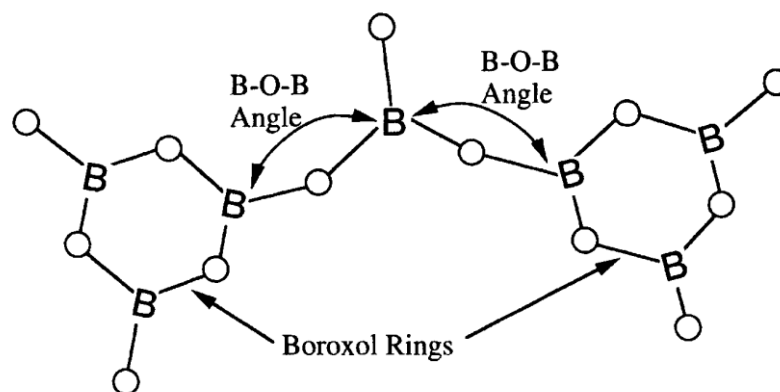


Figure (6): boroxol ring structure in vitreous boric oxide and alkali borate glasses

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 $[BO_4]$.