CHAPTER 1
INTRODUCTION

The word “glass” is derived from a Latin term ‘glaseum’ means a lustrous and transparent material. Glassy substances are also termed as ‘vitreous’. Early civilisations considered ‘lustre’ and ‘durability’ as most important characteristics of glasses. In the modern world too luster, transparency and durability of the glasses are exploited in the applications. But it can be emphasized that these properties of luster, transparency and durability are neither sufficient nor necessary to describe “glass”.

Glasses have some unique properties which are not found in other engineering materials. The combination of hardness and transparency at room temperature along with sufficient strength and excellent corrosion resistance make glasses indispensable for many practical applications. Glasses are generally good electrical insulators. Also, glassy metals are more resistant to chemical attack such as corrosion than polycrystalline metals (Doremus, 1973).

1.1 Brief History

Glasses are very common materials to seek attention towards their existence. The cave dwellers had their tools made of obsidian, a natural glass. Egyptians considered glass as precious materials. There are several artifacts found in the tombs of pharaohs displaying a great work in glasses of different colors. The earliest pure glass is evidenced to be found around 7000 B.C. Glassware developed some six thousand years ago. Then developed the art of glass window making around birth of Christ and then given the new level by Christian church around middle ages.

According to old suggestions, combination of sea salt (NaCl) and bones present in the embers of fire built on the sands (SiO2) at the edge of saltwater sea sufficiently reduced the melting point of the sand to temperature where crude, low quality glass could form. Eventually, some genius of old times discovered the combination of materials of the glass found in remains of such fires which led to the formation of first commercial glasses. Then the concept of moulding and pressing
jars and bottles replaced the earlier methods and quality of the glass improved. The invention of glass blowing around the first century B.C. generated a greatly expanded range of application for glasses. With advancement of technology, there is an increase in the application of glasses. Modern electronics exists because of invention of glass vacuum tubes. Recent invention of glass optical fibers revolutionised telecom industry.

1.2 Definition of Glass

Glass does not have a simple definition as it may seem. Due to structural peculiarities and properties of different glasses, it is difficult to keep a single definition for glasses.

In 1930, glass was defined as an amorphous solid, i.e., a structureless solid. In 1938, it was redefined as an inorganic substance in a condition which is continuous with and analogous to the liquid state of that substance, but which, as a result of reversible change in viscosity during cooling, has attained so high a degree of viscosity that for all practical purposes it may be treated as rigid (Morey, 1954). In 1949, American Society for Testing Materials (ASTM) defined glass as an inorganic product of fusion which is cooled to a rigid condition without crystallization (Stanworth, 1946). But this definition was too restrictive as many organic glasses are known and fusion is not only the method to make glass. Later in 1960, glass was defined as a non-crystalline solid (Secrist and Mackenzie, 1960). Again in 1968, glass was redefined as an amorphous solid which exhibits a glass transition (Elliot, 1982). So being reasonably lenient, a glass can be defined as “An amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behavior”. To be emphasized here that glass transformation is a time dependent behavior and occurs over a temperature range.
1.3 Glasses in Nature

Natural glasses are quite abundant in nature. They are relics of past and can be studied to find durability as a result of glass composition. Some of the natural glasses reported are discussed below.

*Obsidian:* It is perhaps the oldest and most familiar example. They are less than 65 million years old and have a volcanic origin. They contain water upto 1% which is the reason for their foaming behavior when heated. The chemical composition of typical California obsidian is:

\[
74SiO_2, 13.5Al_2O_3, 1.6FeO/Fe_2O_3, 1.4CaO, 0.3Na_2O, 0.5K_2O, 0.7MnO \text{ (wt %)}
\]

makes it member of alkali aluminosilicate family.

*Fulgarites:* Another example is of fulgarites, formed when lightning strikes the soil.

*Meteoritic origin:* Glasses of meteoritic origin:
Impact glasses: These glasses have been forms either during the meteoritic impact event by “shock transformation” or by fusion of local minerals and rocks due to absorbed heat.

Tektites: This is the most intriguing natural glass. Few known tektites are described below.

*Australasian tektites:* They are around 700,000 years old. Specimens found are generally liquid splash forms- spheres, teardrops, dumbbells and buttons. They are black to dark brown in color. Dimensions are around 1-2 cm. The chemical composition is:

\[
75SiO_2, 13Al_2O_3, 4FeO/Fe_2O_3, 3.5MgO/CaO, 0.4Na_2O/K_2O, 0.7TiO_2 \text{ (wt%)}
\]

According to O’Keefe, homogeneity of these tektites are of lunar volcanic origin.
**Microtektites**: They appear to be clear to light yellow-brown in color. Dimensions are generally less than 1mm in diameter.

**Moldavites**: They are found to be pale yellow to yellowish green in color. They are estimated to be 15 million years old and are result of fused ejecta of meteoritic impact that formed a Ries crater in Germany. The chemical composition:

\[ 75 - 80\% SiO_2, 9 - 12\% Al_2O_3, 1 - 3\% FeO / Fe_2O_3, 2 - 3CaO, 0.3\% Na_2O, 3.5\% K_2O \]

**The Libyan desert glass**: They are pale yellow to yellowish green in color. They contain ≥ 97% SiO₂ and around 0.5% FeO. They are dated around 28 million years old. The scientists suggest that they have been formed by sol-gel process.

**Lunar glasses from the Apollo expeditions**: They are found to be in different shapes like irregular fragments, teardrops, dumbbell of various sizes as small as few microns. The composition of some of these particles:

\[ 38 - 50\% SiO_2, 10 - 27\% Al_2O_3, 4 - 20\% FeO, 9 - 14\% CaO, 0.4\% Na_2O / K_2O, 0.6 - 13\% MgO, 0.2 - 4\% TiO_2 \]

Some inhomogeneities having as much as 89% of SiO₂ have been found in these specimens. They have high FeO and low alkali content.

### 1.4 Glass Families

There cannot be a typical classification for glasses. They can be classified according to types of bonding or chemical composition as given in Table 1.1.
According to chemical composition, the glass families can be broadly classified into following categories:

- Oxide glasses (silicates, borates, phosphates etc.)
- Chalcogenide glasses
- Halide glasses
- Metallic glasses

Following are some glass families of importance:

**Vitreous Silica**: Most refractory glass in commercial use. It is highly resistant to corrosion particularly due to chemical attack of acids. It has very low electrical conductivity, a nearly zero (\(\sim 5.5 \times 10^{-7} \text{ohm} \cdot \text{cm}\)) coefficient to thermal expansion and a good UV transparency. It has quite high manufacturing cost thus limiting its use for making astronomical mirrors, optical fibres and crucibles for melting high purity silica.

**Soda Lime glass**: It is least expensive and most widely used glass. Good chemical durability, high electrical resistivity and good spectral transmission in visible region are its luring features. Its high coefficient of thermal expansion (\(\sim 100 \times 10^{-7} / \text{°C}\)) makes it prone to shock failure. It is used in making beverage containers, glass windows and fluorescent light envelopes.
**Borosilicate glass:** It contains small amount of alkali added to silica and boron oxide. It has low thermal expansion coefficient (\(~30-60\times10^{-7}/°C\)) and high resistance to chemical attack. It is useful in making laboratory glassware, household cooking utensils and automobile headlamps.

**Lead Silicate glass:** This family contains PbO and SiO\(_2\) as principal components with small amounts of soda or potash. They have high degree of brilliance, large working range and high electrical resistivity. Adding PbO increases the fluidity of glass and wettability to oxide ceramics. Mostly used in microelectronics eg. For conductor, resistor and dielectric pastes.

**Borate glasses:** Boron trioxide is a significant component of glasses, enamels and glazes. It is very rarely added to the raw material mixtures in the form of oxide, more frequent use being made of H\(_3\)BO\(_3\) or Na\(_2\)B\(_4\)O\(_7\). Boron oxide usually occurs in the glassy form which is virtually incapable of direct crystallization. The crystalline forms of B\(_2\)O\(_3\) can only be prepared by special procedure. Although borate glasses are of little commercial importance because they are water soluble. In contrast to SiO\(_2\) and silicate glasses in which silicon is present as SiO\(_4\) tetrahedra. B\(_2\)O\(_3\) glasses contain BO\(_3\) triangular units and BO\(_4\) tetrahedra depending on the composition. Addition of alkali oxide to glassy B\(_2\)O\(_3\) gives rather different results from those obtained in the corresponding alkali silicates.

**Chalcogenide glasses:** Chalcogenides (elements of group 6A in the periodic table) like sulphur and selenium give viscous liquids on melting which rapidly form glasses on cooling. Glassy or amorphous semiconductors can be made from the chalcogens either alone or in combination with other elements (mostly group 4 or 5 elements). In this type of glasses, the bonding is fairly covalent and the melt contain rings and chains of sulphur and selenium atoms. The chalcogenide based glasses are semiconductors and usually have electronic conductivities in the range 10-13 ohm\(^{-1}\) cm\(^{-1}\). These glasses are opaque in visible light appearing grey or black in color but begin to transmit in the near IR region and continue till 18-20 µm. Therefore used as fibre material for transport of CO\(_2\) laser wavelength (10.6 µm) used in laser
assisted microsurgery. But they require O₂⁻ and OH free melting conditions to ensure good transmission behavior.

*Oxyhalide, Oxynitride and Oxycarbide glasses:* These glasses are hybrids where oxygen is substituted in part by halogen, nitrogen or carbon. Melt viscosities of the oxyhalides are generally lower than those of oxides making it useful for making ultra-low temperature sealing glass. They are used as solid electrolytes because of high anionic electrical conductivity.

*Glassy metals:* Generally, noncrystalline materials composed of either pure metals or combinations of metals and metalloids. Their resistivity often decreases with temperature but they are not semiconductors. An example is Fe₄₀Ni₄₀P₁₄B₆ named as Metglas. These materials are good for ferromagnets providing flexible magnetic shielding and power transformer core laminations. These materials have low B-H hysteresis curve losses and about three times higher electrical resistivity than their crystalline counterparts. High mechanical strength of these glasses makes them useful to make fiber reinforced composites in high strength to weight ratio applications such as high speed aircraft, space vehicles etc.

1.5 Glass Components

Glass components are mainly divided into three categories depending upon the functions and general characteristics. The main difference between them is the bond strength.

**Network Formers (NWF) or Glass Formers**

Glass formers generally have cation–oxygen bond strength greater than 80 kcal/mol. Some important glass formers are SiO₂, B₂O₃, P₂O₅, GeO₂, Sb₂O₅, V₂O₅ and As₂O₅. The number of intermediate neighbors or co-ordination number is three for B₂O₃ and four for the rest of the oxides. All the above oxides form tetrahedral units, which share corners in their crystalline forms except B₂O₃, which forms triangular structure.
Network Modifiers (NWM)

In multi-component systems, oxides with lower bond strengths don’t become part of the network and are called modifiers. The network modifiers don’t form a glass under ordinary conditions but are introduced into the glass to modify its properties. Some of the important modifiers are Na$_2$O, K$_2$O, MgO, HgO, CaO, BaO, Li$_2$O, SrO and ZnO. The bond strength of the modifiers is usually in the range between 10 to 40 k cal/mol and the co-ordination number varies from 4 to 10. The choice of a modifier cation to the glass network results in glasses, which posses a large variety of potential applications such as bioactive materials, sensor applications, optoelectronic devices and solid-state ionic conductors. Therefore, the selection of a modifier is most important for the preparation of a particular type of glass for particular applications.

Intermediates

Intermediates occupy a position somewhere between the glass formers and the modifiers. Examples of intermediates are TiO$_2$, ZnO, PbO, Al$_2$O$_3$, ThO$_2$, BeO, ZnO$_2$ and CdO.

The network formers retain the tetrahedral structures of their crystalline forms with the long-range order destroyed. The network modifiers do not form glasses by themselves as the bond strength of atoms or ions in their chains are insufficient to prevent or hinder effectively their orderly orientation. In multi-component glasses, the terms formers, modifiers and intermediates are frequently used to define the role of the individual oxides. However an element such as Pb may be either a modifier or an intermediate depending upon its co-ordination number and the glass system considered. The larger co-ordination numbers of these modifier oxides also weaken the bonds as the probability of the localized concentration of electron clouds in certain definite directions gets reduced. The modifiers may, therefore be added to the glass formers as these allow the glass forming ability of the latter to be retained, though in a modified structure. In the complete structure, the electrical neutrality of the system has to be preserved so that
mode of packing of the glass forming and the glass modifying groups gets changed, giving new properties to the product of fusion.

In glass formation bond strength is important. Glass former generally have cation-oxygen bond strengths greater 335 KJ/mol (80 Kcal/mol). In multiple-component system, oxides with lower bond strengths do not become part of network are called modifiers. Oxides with energies bout 335 KJ/mole may not become part of network are referred to as intermediates.

Different formers, intermediates and modifiers are listed in Table 1.2 alongwith their single bond strength.
<table>
<thead>
<tr>
<th>Oxide</th>
<th>Single Bond Strength KJ/MOLE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formers</strong></td>
<td></td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>496</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>443</td>
</tr>
<tr>
<td>GeO$_2$</td>
<td>450</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>420-332</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>372</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>462-370</td>
</tr>
<tr>
<td><strong>Intermediates</strong></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>301</td>
</tr>
<tr>
<td>PbO</td>
<td>303</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>280-221</td>
</tr>
<tr>
<td>BeO</td>
<td>261</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>253</td>
</tr>
<tr>
<td>CdO</td>
<td>248</td>
</tr>
<tr>
<td><strong>Modifiers</strong></td>
<td></td>
</tr>
<tr>
<td>ThO$_2$</td>
<td>179</td>
</tr>
<tr>
<td>PbO$_2$</td>
<td>161</td>
</tr>
<tr>
<td>MgO</td>
<td>154</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>150</td>
</tr>
<tr>
<td>PbO</td>
<td>151</td>
</tr>
<tr>
<td>ZnO</td>
<td>130</td>
</tr>
<tr>
<td>BaO</td>
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</tr>
<tr>
<td>CaO</td>
<td>134</td>
</tr>
<tr>
<td>SrO</td>
<td>133</td>
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<tr>
<td>CdO</td>
<td>124</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>83</td>
</tr>
<tr>
<td>CdO</td>
<td>82</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>53</td>
</tr>
<tr>
<td>Rb$_2$O</td>
<td>48</td>
</tr>
</tbody>
</table>
1.6 Formation of Glass:

Some properties of glasses are similar to the corresponding crystals but some of the properties resemble that of liquids. The fundamentals of glass can be understood by having the knowledge of thermodynamics and structural theories of glass formation.

1.6.1 Thermodynamics of Glass Formation (The V-T diagram)

There are two main types of pathways that a liquid may follow on cooling to the solid state: either it may crystallize at or below the melting temperature, \( T_m \) or it may undercool sufficiently to form a glass without crystallization. A glass is generally obtained by cooling a liquid below its freezing point. The classical explanation for the glass formation is that, when a liquid is cooled, its fluidity which is the reciprocal of viscosity decreases and, at a certain temperature, below the freezing point, becomes nearly zero. That is, the liquid becomes rigid. Fig. 1.1 represents the volume-temperature characteristics for crystal, liquid and glass. When a liquid is cooled to form a solid, the resulting cooling curve shows distinct differences from those of the crystalline and amorphous solids. When a liquid solidifies into a crystalline state there is a marked discontinuity in the volume at a well-defined temperature called the 'melting point' (\( T_m \)) of the material. However, if no crystallization occurs, the volume of the liquid decreases at about the same rate as above the melting point until there is a decrease in the expansion coefficient in a range of temperature called glass transformation range. In other words, the liquid-glass cooling curve does not show any discontinuity. The curve, however, shows a change of slope at a temperature called 'glass transition temperature' (\( T_g \)). Below this temperature range the glass structure does not relax at the cooling rate used. The expansion coefficient for the glassy state is usually about the same as that for the crystalline solid. Glass transition temperature mainly depends on the rate of cooling of the melt. i.e., \( T_g \) is not a well-defined one and is a function of cooling rate. Slower the rate of cooling, lower is the value of \( T_g \). However, it cannot be reduced indefinitely. Angell (1970) pointed out that \( T_g \) cannot be lower than a particular minimum temperature called the ideal glass transition temperature, \( T_O \).
Fig. 1.1 Volume- Temperature Characteristics for Crystal, Liquid and Glass
1.6.2 Glass Formation Theories

1.6.2.1 Structural Theories

Formation of glass is a simple process. Still on examining two closely related compositions, they seem to display different glass forming tendencies under different conditions. For example, small change in melt size can lead to crystallization in one composition while forming glass in the other. The ease of glass formation or glass forming ability of a composition can be defined by the critical cooling rate required to prevent crystallization of a specified volume fraction of the sample. The smaller the critical cooling rate better is the glass forming ability. Various theories were given to explain the glass forming tendency of the oxides. Goldschmidt's criterion (Goldschmidt, 1929) gives a correlation between the ability to form a glass and the relative sizes of the oxygen anion and cation. According to him, glass forming oxides are those for which the ratio of ionic radii of anion and cation lie in the range 0.2 to 0.4 and have four anions around each cation, the anions being situated at the corners of a tetrahedron. In other words, a tetrahedral configuration of the oxide is a pre-requisite for glass formation according to him.

One of the most important theories which influenced glass science enormously was given by Zachariasen (1932). He pointed out that the Goldschmidt's criterion was not satisfactory even as an empirical rule, since not all oxides having a radius ratio in the specified range are glass formers, BeO being one such case ($R_{Be}/R_O=0.221$; $R_{Be}$-Radius of Be and $R_O$-Radius of oxygen). Zachariasen (1932) considered the relative glass-forming ability of simple oxides and concluded that the ideal condition for glass formation is that the material should be capable of forming an extended three dimensional network structure without any long-range order. Since, the mechanical properties and density of an oxide glass are similar to those of the corresponding crystal, the interatomic distances and interatomic forces in crystals and glassy state must be similar. Zachariasen (1932) pointed out that because of the random network; internal energy of glass is slightly higher than that of the corresponding crystal which suggests that the polyhedra of the same type as
in the crystal must be joined together in a similar way in the glass. For example, consider the glass which is made up of silicon dioxide (SiO$_2$) which not only illustrates many structural features but also is a major constituent of most commercial glasses. The crystalline form of silica contains SiO$_4$ tetrahedra joined at the corners. Glassy (vitreous) silica must also contain SiO$_4$ tetrahedra joined at their corners. The only difference between crystalline and vitreous silica is that the relative orientation of adjacent tetrahedra is variable in the former where as in the later it is constant throughout the structure. The generally accepted view of the structure of SiO$_2$ glass is largely same as that proposed by Zachariasen (1932) and supported by the X-ray diffraction results of Warren (1969). Zachariasen (1932) has put forward a set of empirical rules known as Zachariasen's rules which an oxide must satisfy if it is to be a glass former:

(i) No oxygen atom may be linked to more than two atoms.
(ii) The coordination number of oxygen atoms is small (probably 3 or 4).
(iii) The oxygen polyhedra share corners with each other, not edges or faces.
(iv) The polyhedra link up to form a three-dimensional network. i.e., at least three corners of each polyhedron should be shared.

Zachariasen's hypothesis for glass formation has been more or less universally accepted. The alkali and alkaline-earth oxides like Na$_2$O, K$_2$O, Li$_2$O, BaO, CaO, MgO which do not satisfy Zachariasen's rules cannot form glasses. Oxides like SiO$_2$, B$_2$O$_3$, GeO$_2$, etc. satisfy these empirical rules and are good glasses forming oxides. Zachariasen extended these rules to multi component glasses also with a few additional modifications viz.,

(i) The sample contains high percentage of cations which are surrounded by oxygen tetrahedra or triangles,
(ii) These tetrahedra or triangles share only corners with each other
(iii) Some oxygen atoms are linked to only two such cations and do not form further bonds with any other cations.

Another important hypothesis regarding glass formation was put forward by Smekal (1951), known as Smekal's mixed bonding hypothesis. According to Smekal, pure covalent bonds have sharply defined bond-lengths and bond angles
and these are incompatible with the random arrangement of the atoms in glass. On the other hand, purely ionic or metallic bonds completely lack any directional characteristics. Thus the presence of 'mixed' chemical bonding in a material is necessary for glass formation. Glass forming substances with mixed bonding are divided into three categories by Smekal:

(i) Inorganic compounds like B$_2$O$_3$, SiO$_2$; in this case the bonds are partly covalent and partly ionic.
(ii) Elements like S, Se having chain structures with covalent bonds within the chains and van der Waals forces between the chains.
(iii) Organic compounds containing large molecules with covalent bonds within the molecule and van der Waals forces between them.

Stanworth used partial ionic character model of Pauling to quantify the mixed bond concept. According to him, oxides can be classified into three groups on the basis of electronegativity of the cation:

- **Group 1**: This group contains oxides having fractional ionic character of the cation-anion bond (nearly 50%). These act as *network formers* and form good glasses.
- **Group 2**: In this category, cations with slightly lower electronegativities are placed. They form slightly more ionic bond with oxygen. They cannot form glasses by themselves but partially replace cations from group 1. They are known as *intermediates*.
- **Group 3**: Cations with very low electronegativities and which form highly ionic bonds with oxygen are put here. As they just modify the network structure, they are known as *modifiers*.

Sun (1947) proposed a criterion for the correlation between the structural features and the glass forming tendency of simple oxides. Since the process of atomic rearrangement which takes place during the crystallization of a material may involve the breaking and reforming of interatomic bonds, it may be reasonable to expect a correlation between the strength of these bonds and the ability of the material to form a glass. The stronger the bonds, the more sluggish will be the rearrangement process and hence more readily will a glass be formed. Sun showed the glass forming oxides have bond strength greater than 330 KJmol$^{-1}$, whereas
modifier ions, which are not part of the network structures, have bond-strengths that are below this value. This gave similar results as that of Stanworth but no result to provide insight for glass formation.

Rawson (1956) modified Sun's criterion (1947) and related glass forming tendency to the ratio of bond-strength to melting temperature. This ratio accounts for both the bond strength and the thermal energy available to break the bonds, which depends on temperature. It is virtually impossible to crystallize B$_2$O$_3$ glass and thus can be understood from Rawson's criterion, since B$_2$O$_3$ has a relatively low melting point, 400°C. This criterion may also explain why, in binary systems, the glass forming compositions are often located around the low melting eutectics.

1.6.2.2 Kinetic Theory of Glass Formation

In order for a glass to form, the rate of crystallization of the undercooled liquid must be sufficiently slow that crystallization does not occur during cooling. Crystallization of an undercooled liquid is a two stage process that involves the formation of crystal nuclei followed by their subsequent growth. A kinetic condition for glass formation is that the rate of nucleation and/or the rate of crystal growth should be slow. In some undercooled liquids, nucleation is easy because there are plenty of nucleation sites available; foreign particles, container surfaces, etc. can act as nucleation sites. The rate of crystallization is then largely controlled by the rate of growth, which varies with temperature in a manner shown in Fig. 1.2. The rate is zero at the melting point, increases to a maximum at a certain degree of undercooling and then falls to zero again at still lower temperatures. At lower temperatures, especially for glass forming liquids, the viscosity of the undercooled liquid becomes increasingly important. With increasing viscosity, the diffusion of atoms or ions through the liquid to the surface of the growing nuclei becomes increasingly difficult and the rate of crystallization tends to decrease accordingly. With decreasing temperature, there are two competing effects. The increased difference in free energy between crystals and liquid favours crystallization whereas the increased viscosity of the undercooled liquid reduces the tendency for crystallization. The peak in the crystallization (Fig. 1.2) corresponds to the situation
Fig. 1.2 Dependence of Rate of Crystallisation of an Undercooled Liquid on Temperature
where these two competing effects have equal weight. On the low temperature side of the peak, the viscosity effect dominates whereas on the high temperature side it is the difference in free energy between crystals and the liquid that predominates. In considering the crystallization of undercooled liquids and the ability to form a glass, there is a 'danger zone' for glass formation that corresponds to the maximum in the crystallization rates. If it is possible to undercool a liquid through this danger zone, it should be relatively safe from subsequent crystallization (or devitrification) and the liquid will form a kinetically stable glass.

1.7 Structure of Glasses

Earlier all the discussions regarding glass structures centered on silicate glasses especially vitreous silica and alkali silicate glasses. One of the first models considers microcrystal approach according to which glasses are simply masses of very small or micro crystals. The small size of these crystals explains the lack of structure in X-Ray Diffraction pattern. Another model favored by Lebedev and other Russian scientists named “crystallite model”. These crystallites differ from microcrystals in that “the structures are deformed version i.e. not perfect lattices, of those crystals and are not merely small sized version of normal crystals”. A glass then was assumed to consist of crystallites connected by amorphous region. Few other models were also given to explain structure of glasses but all seem incomplete. Fundamental law of structural models states that “No model can be considered to be valid unless that model can explain “ALL” the available data”. Basic elements for any complete structural model for glasses:

Coordination no. of all network cations: Network cations are the building blocks of the vitreous network. So, their coordination no. provides the most basic element of the any model of glass structure.

Distribution of bond angles and rotations: After determining the building blocks of glass structure, we must find out how these blocks are connected. This includes distribution in bond angles and rotations which introduce randomness in structure.
The concept of bond angle distribution is important part of glass structure models but very little quantitative information is available about it.

*Connectivity of all network units:* Connectivity of network i.e. the no. of bridging and non-bridging bonds which link the building blocks to their neighbors is quite important in describing the glass network.

*Dimensionality of network:* Since networks can exist in two or three dimensions, we must specify the dimensionality of network. It affects the properties of the glass. No quantitative model to describe dimensionality exists, challenging scientists to design one.

*Nature of any intermediate range order:* The concept of dimensionality points that these blocks may be connected into slightly larger units which have a more ordered arrangement than that predicted by a purely random connection scheme. These blocks may contain rings or chains as found in crystals but extend order to the structure. These intermediate range order models are not yet proven to be unique thereby must be treated as potential description of glass structure.

*Morphology:* It results from phase separation is frequently neglected in proposing glass structure models. As a result, systems having large immisicibility regions are incorrectly explained by no. of structural models.

*Properties of specific ions:* Field strength of both network forming and network modifying cations must be included to explain trends in properties with glass compositional variations. Since many modern studies include variations in the identity of the anions which link the structure, their field strengths and ionic radii are also important. Atomic radii of cations and anions are also useful in models explaining transport properties.
Nature of interstitial or free volume: Knowledge of interstitial or free volume is quite important in understanding of diffusion based processes and behavior of volume dependent properties such as density, refractive index and thermal expansion co-efficient, yet it is ignored in designing structural models.

Role of minor constituents, impurities and defects: The role of minor constituents and defects must also be included in vitreous structural models. In many cases, the local structure around these sites play important role in determining certain properties of glass. The effect of impurities is especially important if the impurity is water, as hydroxyl has a large effect on properties of oxide glasses. Even if ignored, must be quoted to ensure the validity of the study.

1.7.1 Structural Models of Borate Glasses

There are many types of borate glasses. Below are discussed the structural models of the glasses related to present research work.

1.7.1.1 Vitreous Boric Oxide

Boron occurs in both triangular and tetrahedral coordination in crystalline compounds; however it is believed to occur only in triangular state in vitreous boric oxide. All such triangles are connected by BO at all three corners to form a completely linked network. Since the basic building block of this network is planar rather than 3-dimensional, three dimensional linkage doesnot exist for vitreous boric oxide. A 3-D network is forms in this case by crumpling of the network. The primary bonds exist only within the plane of paper, Vander Waals bond exists in the third dimension. As these bonds are weak, this structure is easily disrupted leading to low glass transformation temperature i.e. just 260°C.

The structure of vitreous boric oxide also contains a large concentration of an intermediate unit consisting of three boron oxygen triangles joined to form a structure known as boroxol ring or boroxol group (Fig.1.3). These well defined units are connected by oxygens so that the B-O-B angle is variable and twisting out
of plane of the boroxol group can occur. (Note: Existence of boroxol groups is supported by the observed 808 cm\(^{-1}\) in the Raman spectra of vitreous boric oxide)

1.7.1.2 Alkali Borate Glasses

Addition of alkali oxide to vitreous silica results in formation of NBO which is not the case with alkali borate glasses. Small additions of alkali oxide to silica cause a decrease in \(T_g\) while similar additions to boric oxide cause an increase in \(T_g\) and decrease in thermal expansion coefficient. The addition of alkali oxide to glassy borate gives rather different results than those obtained in the corresponding alkali silicates and an effect known as the borate anomaly is observed. It was shown that a gradual change in the coordination number of boron from three to four occurs as alkali oxide is added. By combining Raman scattering studies and the NMR investigations with the available crystallographic data, structural groups present in these glasses have been clearly identified. Pure B\(_2\)O\(_3\) consists of planar BO units which are 3 randomly distributed in a three-dimensional network by sharing all the three oxygen atoms with adjacent BO\(_3\) units. The planar BO\(_3\) unit presumably involved in \(sp^2\) hybridization, with the third orbital being vacant and extending in direction perpendicular to the BO\(_3\) plane. This vacant orbital accepts an electron from the unpaired electrons from the oxygen atoms, forming a partial double bond. The following modifications in the network can be enhanced by the addition of network modifying oxides. (a) Boron-oxygen-boron bonds may be broken by oxygen anions (as in the case of the breakdown of silica network) to form non-bridging atoms (b) a filled orbital of an oxygen anion may overlap with an empty p-orbital of a boron atom resulting in a change of hybridization of the boron atom to the \(sp^3\) tetrahedra arrangement leading to BO\(_4\) tetrahedron with three bridging and
one non-bridging oxygen, (c) an oxygen atom may contribute an electron pair to two BO units changing the coordination of the two borons from sp$^2$ to sp$^3$ hybridization and with no non-bridging oxygen.

Several attempts (Pye, 1977) were made to explain the structure of borate glass on the basis of a number of imaginative structural models, all of which were built around the relatively unique ability of boron to exist in two distinct coordination states. However NMR studies showed that the four coordinated boron varies smoothly as $x/(1-x)$ where $x$ varied from 0 to 30 mol% modifier oxide without any unusual behavior in the critical range 15-20 mol% of modifier oxide (Savabsib et al. 1962; Bray and O’Keefe, 1963). The BO$_3$ groups are bonded to the rest of the structure in four directions and the structure is therefore tied together in three dimensions rather than two. This will produce a marked increase in the strength and tightness of the Structure. Bray has shown using B 11 NMR spectroscopy that a gradual change in the coordination number of boron from three fold to four occurs as alkali oxide is added to B$_2$O$_3$ (Bray et al. 1972; Muller-Warmuth and Eckert, 1982). By the time about 30 mol% has been added, approximately 40 per cent of the borons would have changed to tetrahedral coordination and this is independent of the nature of the alkali. In triangular coordination, the B$^{11}$ nucleus shows strong quadrupole coupling with a broad resonance line whereas in tetrahedral coordination, the quadrupole coupling is weak and the resonance is narrow.

Extensive investigations have been carried out on crystalline and glassy borates by Krough-Moe (1960) who proposed a new model for the structure of borate glass. They suggested that borate glasses are not merely a random network of BO$_3$ triangles and BO$_4$ tetrahedra joined at the corners but, they actually contain well-defined and stable groups as segments of the disordered framework. These borate groups which are included in the glass structure should be identical with the groupings which occur in crystalline borates. From the experimental results of thermodynamic (Krough-Moe, 1962) and infrared (Krough-Moe, 1965) studies the structural groupings in borate glasses can be classified into four different groupings. viz., boroxol, pentaborate, triborate and diborate groups. The pentaborate and triborate groups will always occur in pairs and these pairs are referred to as tetraborate groups.
1.7.1.3 Borate Anomaly

This is a peculiar property of borate glasses and which cannot be seen in the boron-free glasses. In the system Na\textsubscript{2}O-B\textsubscript{2}O\textsubscript{3}, for example, viscosity of the melt increases with increase in the alkali oxide content and passes through a maximum at 16 mol\% Na\textsubscript{2}O. Similarly the properties like coefficient of thermal expansion also show either minimum or maximum around this composition. This peculiar effect is known as boron oxide anomaly. A fully accepted explanation of the boron oxide anomaly is not yet reported. A partial explanation of the boron oxide anomaly is that with small amounts of added alkali oxide, some boron atoms change to tetrahedral coordination and these act to 'tie-in' the network by increasing the viscosity. Thus the boron to oxygen ratio, which is 1:1.5 in B\textsubscript{2}O\textsubscript{3}, increases towards the value 1:2, which is the value in the vitreous B\textsubscript{2}O\textsubscript{3} as alkali oxide, is added. A fully tetrahedral network could be achieved, in theory even at 50 per cent alkali oxide, but it appears that long before this situation is reached; the viscosity will start to decrease again.

1.8 Transition Metal Ion in Glasses

Transition metal in glasses often exhibit coloration in glasses. The coloration originates in d-d transition and the phenomena is well discusses by using ligand-field theory. Fig. 1.4 shows splitting of d orbitals. If the ion is in glass, the ligand of the ion is not uniform but has distortion and its structure has some distribution, which results in shifts and/or broadening of absorption band due to transition. In case of oxide glasses, the ligand is influenced by states of the surrounding oxygen atoms. Thus, glass composition and process conditions affect the absorption of metal ion in the glass.
Fig. 1.4 Splitting of d- Orbitals in a) Octahedral Crystal Field and b) Tetrahedral Crystal Field