CHAPTER 1

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1.1. Introduction

The term 'glass' is commonly used to mean the fusion products of inorganic materials which have been cooled to a rigid condition without crystallization. Glass is one of the oldest synthetic materials used by man and the present knowledge of glass has been acquired over many centuries. Scientific study of glass began with Faraday and others at the beginning of nineteenth century and today it is still a rapidly developing subject, both in the development of new glassy materials with special properties for specific applications and in the application of new scientific techniques to improve our understanding of the structure and behaviour of 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 indispensible for many practical
applications. Glasses are generally good electrical insulators. Also glassy metals are more resistant to chemicals attack such as corrosion than polycrystalline metals[1].

Recently, there has been renewed interest in the properties of glassy ionic conductors[2-7]. In part this reflects a demand for new fast ion conductors and the growth of the new field of solid state ionics. Glasses have acknowledged advantages over crystalline electrolytes including physical isotropy, the absence of grain boundaries, continuously variable composition and good workability.

1.2. Definitions of Glass

The increase in the scientific knowledge about glasses caused a change in the definition of glasses. In 1930, glass was defined as an amorphous solid, i.e., a structureless solid[8]. 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[9]. 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[10]. Later in 1960, glass was defined as a non-crystalline solid[11].

Again in 1968, glass was redefined as an amorphous solid which exhibits a glass transition[12]. Glass transition exhibits more or less an abrupt change in the thermodynamic properties, such as heat capacity, thermal expansivity etc.

1.3. Differences Between Crystalline and Amorphous Solids

On the basis of atomic arrangement, solids may be broadly classified into two categories. (i) crystalline and (ii) amorphous.

In crystalline solids, both long-range and short-range order exist in the arrangement of atoms while in amorphous solids only short-range order exists. Figure 1.1 represents the schematic representation of the ordered crystalline form and random network amorphous form of the same composition. Due to the short-range periodicity in the atomic arrangement, the degree of disorder will be greater in an amorphous solid than its crystalline counterpart and it will be having a higher entropy.
Fig. 1.1. Schematic representation of (a) ordered crystalline form and (b) random network amorphous form of the same composition.
compared to the crystalline phase. Therefore amorphous state is a non-equilibrium state. So, on cooling from liquid phase to the solid phase, a crystalline solid is obtained as a transformation from one equilibrium state to another while in amorphous solid, the transformation is from an equilibrium state to a non-equilibrium state. Due to the random arrangement of atoms, amorphous materials exhibit isotropic properties while crystalline solids exhibit anisotropic properties.

1.4. Formation of Glasses

There exist certain well-defined properties which are common to all types of glasses (oxides, halides, chalcogenides, etc) and are different from those of liquids and crystalline solids. Diffraction studies using X-rays and electrons have shown that glasses lack long range periodicity. The atomic arrangement in glass is just as in the liquid phase.

Unlike crystals, glasses do not have a sharp melting point and do not cleave in preferred directions. Like crystalline solids they show elasticity - a glass fibre can be bent almost double in the hand and, when released, springs back to its original shape; like liquids, they flow under a shear stress but only if it is very high.
Thus one can see that the glassy form of matter combines the 'short-time' rigidity characteristic of the crystalline state with a little of the long-time fluidity of the liquid state. Glasses like liquids are isotropic, a property which is of immense value in their use for a variety of purposes.

1.4.1. Thermodynamics of glass formation

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. Figure 1.2 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
Fig. 1.2. Volume-temperature characteristics for crystal, liquid and glass.
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 (transformation) 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, $T_g$ cannot be reduced indefinitely. Angell[13] in 1970 pointed out that $T_g$ cannot be lower than a particular minimum temperature called the ideal glass transition temperature, $T_o$. The explanation for this is found by considering the relative heat capacities and entropies of liquid and crystalline phases of the same composition.
The glass transition temperature can be determined by differential thermal analysis (DTA) or differential scanning calorimetry (DSC).

1.4.2. Glass or network formers and network modifiers

Glasses have been prepared using different types of materials. The ability of a substance to form a glass does not depend upon any particular physical or chemical property. It is now generally agreed that almost any substance, if cooled sufficiently fast could be obtained in the glassy state although in practice crystallization intervenes in many substances.

$B_2O_3$, $SiO_2$, $GeO_2$ and $P_2O_5$, all of which come from a certain area of the periodic table readily form glasses on their own when their melts are cooled and are commonly known as 'glass formers'. These are oxides of elements with intermediate electronegativity: these elements are sufficiently electropositive to form ionic structures, such as $MgO$ and $NaCl$, but also are not sufficiently electronegative to form covalently bonded, small molecular structures, such as $CO_2$. Instead, bonding is usually a mixture of ionic and covalent and the structures are best regarded as three-dimensional polymeric structures. $As_2O_3$
and Sb$_2$O$_3$ also produce glass on their own when cooled very rapidly. TeO$_2$, SeO$_2$, MoO$_3$, WO$_3$, Bi$_2$O$_3$, Al$_2$O$_3$, Ga$_2$O$_3$ and V$_2$O$_5$ will not form glasses on their own, but each will do so when melted with a suitable quantity of certain other non-glass forming oxide. Hence they are known as 'conditional glass formers' according to Rawson[14].

There are some oxides like Na$_2$O, Li$_2$O, K$_2$O, PbO and CaO which when added in small quantities (10 mol% to 15 mol%) to the glass network forming oxides produce drastic changes (melting point, conductivity, etc.) in the properties of the later. Such oxides also modify the network structure of the glass and hence they are termed as 'glass or network modifiers'. The changes that are produced by these modifiers in the glass network is shown in figure 1.3.

Various attempts were made to explain the glass forming tendency of the oxides. Goldschmidt's criterion[15] 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
Fig. 1.3. Two-dimensional network of sodium-silicate glass.
corners of a tetrahedron. In other words, a tetrahedral configuration of the oxide is a pre-requisite for glass formation.

Zachariasen[16] in 1932, 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; \text{R}_{Be} - \text{Radius of Be and } R_{O} - \text{Radius of oxygen}). Zachariasen 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[16] 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 whereas 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 and supported by the X-ray diffraction results of Warren[17]. Zachariasen 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 $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, $\text{Li}_2\text{O}$, $\text{BaO}$, $\text{CaO}$, $\text{MgO}$ which do not satisfy Zachariasen's rules cannot form glasses. Oxides like $\text{SiO}_2$, $\text{B}_2\text{O}_3$, $\text{GeO}_2$, etc. satisfy these empirical rules and are good glass forming oxides. Zachariasen extended these rules to multicomponent 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, and (iii) some oxygen atoms are linked to only two such cations and do not form further bonds with any other cations. In terms of Zachariasen's model for glass formation, a 'network forming oxide' is an oxide which forms part of 'vitreous framework' and 'network modifying oxide' is an oxide which does not form part of the network.

Another important hypothesis regarding glass formation was put forward by Smekal[18], 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 otherhand, 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 $\text{B}_2\text{O}_3$, $\text{SiO}_2$; 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 and (iii) organic compounds containing large molecules with covalent bonds within the molecule and van der Waals forces between them.

Sun[19] in 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[19]. The stronger the bonds, the more sluggish will be the rearrangement process and hence more readily will a glass be formed. Sun[19] showed that the glass forming oxides have bond strength greater than 330 KJ mol$^{-1}$, whereas modifier ions, which are not part of the network structures, have bond-strengths that are below this value.
Rawson[14] modified Sun's criterion 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 $\text{B}_2\text{O}_3$ glass and thus can be understood from Rawson's criterion, since $\text{B}_2\text{O}_3$ has a relatively low melting point, $400^\circ\text{C}$. This criterion may also explain why, in binary systems, the glass forming compositions are often located around the low melting eutectics.

1.5. Kinetics 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 figure 1.4. 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 (figure 1.4) corresponds to the situation 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.
Dependence of rate of crystallization of an undercooled liquid on temperature.
In considering the crystallization of undercooled liquids (figure 1.4) 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.

1.6. Preparation of amorphous materials (glasses)

There are at least a dozen different techniques that can be used to prepare materials in the amorphous state. Of these, the following are commonly used in one form or another to produce most non-crystalline (amorphous) materials of commercial or academic interest. They are

(i) thermal evaporation
(ii) melt quenching method
(iii) sputtering
(iv) glow discharge decomposition
(v) chemical vapour deposition
(vi) sol-gel method

(a) splat quenching
(b) melt spinning
(c) roller quenching
The commercially used methods for the preparation of glasses are briefly discussed below.

(i) Thermal evaporation

This method is widely used to prepare amorphous thin films of semiconductors and chalcogenide glasses. It is one of the several ways of producing amorphous solids from a vapour. In this method, the starting material is vaporised and is collected on a substrate. The thermal evaporation technique is performed in vacuum (about $10^{-6}$ Torr) to reduce contamination and to avoid the effect due to scattering. The material is evaporated by heating in a molybdenum or tungsten 'boat' or by bombarding with high energy electrons from an electron gun and the vapours are collected on a cold substrate. The essential feature of thermal evaporation is that atomic surface mobility is greatly diminished because of the cold substrate, causing the atom to be frozen in the random positions at which they arrive. The principal advantage of thermal evaporation as a preparative technique lies in the variability in purity and composition of the films. The quality of the resulting film developed by this method depends on (a) the substrate temperature (b) distance between the source and substrate and their orientation (c) pressure in the chamber and (d) the filament (boat) temperature.
(ii) Melt-quenching technique

Many materials need sufficiently rapid quenching in order that the melt solidifies into glass. Commonly used melt quenching methods are (a) splat quenching (b) melt-spinning and (c) roller quenching.

(a) Splat quenching: This is the oldest but most established method for the preparation of amorphous materials. In this method the melt is cooled sufficiently quickly, which is referred to as 'quick cooling'. The method is particularly useful in the preparation of metallic glasses and the cooling rates may lie in the range $10^5$ to $10^8$ K/sec. This is the method used for the preparation of glasses in the present study and is discussed in detail in chapter 3.

(b) Melt spinning method: This is the most commonly used rapid liquid quenching technique (figure 1.5) to obtain glasses in the form of long ribbons of uniform cross section and having reproducible properties. This method is widely used for the commercial production of amorphous alloys.
A melt-spinner consists of a disc, usually of copper, which is to be rotated at high speed (figure 1.5). The alloy is melted by r.f. induction heating under an inert helium or argon atmosphere. The ejection of the alloy melt is achieved by increasing the inert gas pressure through a fine nozzle at the bottom of a refractory tube of the spinning disc. The dynamic melt puddle impinging on the moving substrate is solidified and is thrown out of the wheel in the form of a ribbon by the centrifugal force after travelling with it over a short distance. Some of the main process variables affecting the properties of the ribbons are the amount of superheating, i.e., the temperature in excess of the liquidus temperature of the alloy, the jet velocity, the angle of ejection, the dimension and shape of the orifice, the speed of the spinning disc, the temperature and nature of the surface finish of the substrate, and the atmosphere.

(c) Roller quenching method: In this method, the melt is propelled onto a cooled rotating drum as shown in figure 1.6. The amorphous material (glass) thus obtained is in the form of a thin ribbon. This method has the advantage of producing glassy ribbons of uniform thickness. Usually this method is used to prepare glassy metals. In this method the cooling rates are of the order of $10^6$ to $10^8$ K/sec.
Fig. 1.5. Schematic diagram of melt-spinning technique.

Fig. 1.6. Schematic diagram of roller-quenching technique.
(iii) Sputtering

Besides the rapid liquid quenching, the most commonly used technique for the preparation of glassy semiconductors and metals is sputtering. Sputtering is the process by which atoms or molecular groups are released from a target under the bombardment of positive ions. The major advantage of this technique is that it is not regulated by classical thermodynamics and Gibbs phase rule. Hence, unlike methods involving rapid quenching of liquids which require homogeneous melt, this technique can be used to make new materials without regard to solid solubility and immisibility. Further, the process of sputtering does not degrade the properties of substrate. The simplest way to induce sputtering is to apply a high negative voltage to the target surface, thereby attracting positive ions from the plasma. However, this d.c. sputtering process is only feasible for targets composed of metals, or at least consisting of materials which are sufficiently electrically conducting so that the target can act as an electrode. In sputtering process, the following factors are very significant. (i) sputtering gas pressure (ii) r.f. power applied to target (iii) bias voltage of target or substrate (iv) ratio of partial pressures of reactive gas to inert gas.
(iv) Glow-discharge decomposition

This method is also used to prepare amorphous solids of semiconductors in the form of thin films. This technique, like sputtering relies on the production of a plasma in a low pressure gas, but instead of ions from a plasma ejecting materials from the target, chemical decomposition of the gas itself takes place leading to deposition of a solid film on a substrate placed in the plasma.

(v) Chemical vapour deposition (CVD)

This method is used to prepare amorphous solids of polycrystalline materials. Chemical vapour deposition is similar to the glow discharge method in that both depend on the decomposition of vapour species. In this CVD method, chemical decomposition of a vapour takes place leading to deposition of a solid film on a substrate placed in plasma.

(vi) Sol-gel method

This is a new method for preparing glassy materials. The advantage of this technique is that, it is a low temperature glass preparation method. The method for
producing amorphous materials via sol-gel method has considerable technological promises [20]. The sol-gel method has its greatest usefulness for those system which give rise to very viscous melts near the melting point, or alternatively which have extremely high melting points and hence pose considerable technical problems in actually being able to make glass by melt quenching.

Recently, a technique called ion implantation has been extensively used for modifying the properties of the surface layers of thin films especially of semiconductors. In this technique high speed ions are allowed to impinge on the surface. These ions travel a short distance and get embedded within the top few atomic layers of the material. In this process the quenching rate is estimated to be about $10^{14}$ K/sec. It is possible to produce amorphous para-surface layers in crystalline solids by implanting ions in high dose. In electropolished Fe, Co and Ni foils by implanting $B^+$ and $P^+$ at low energy of 40 KeV and high dose of $10^{17}$ ions/cm$^2$ amorphous thin films at the surface of the samples can be produced without much difficulty.

In addition, there are methods like laser glazing technique, electrolytic deposition, etc. to prepare amorphous materials.
1.7. Types of glasses

Glasses are not restricted to inorganic silicates but form in widely different types of materials. Glasses may be broadly classified into different groups according to their chemical composition and their type of bond (Table 1.1) as follows.

(i) Oxide glasses (silicates, borates, phosphates, etc.)
(ii) Chalcogenide glasses
(iii) Metallic glasses.

Table 1.1. Classification of glass forming materials in terms of chemical bonding

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Glass-forming materials</th>
</tr>
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<tbody>
<tr>
<td>Covalent</td>
<td>Oxide glasses (silicates, borates, phosphates etc), chalcogenides, organic high polymers.</td>
</tr>
<tr>
<td>Hydrated ionic</td>
<td>Aqueous salt solutions</td>
</tr>
<tr>
<td>Ionic</td>
<td>Halides, nitrides, sulphates</td>
</tr>
<tr>
<td>Molecular or vander Waals</td>
<td>Splat-cooled alloys</td>
</tr>
<tr>
<td>or metallic</td>
<td></td>
</tr>
</tbody>
</table>
(i) Oxide glasses

Silicate glasses: Among oxide glasses, commercially important and extensively studied are the silicate glasses (SiO₂ based glasses). In silicate glasses SiO₂ is the glass former and the study of its structure and properties has been very important in understanding the chemically more complex silicate glasses. These glasses have immense applications in various fields due to its chemical and weathering stability.

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 H₃BO₃ or Na₂B₄O₇. Boron oxide (B₂O₃) usually occurs in the glassy form which is virtually incapable of direct crystallization. The crystalline forms of B₂O₃ can only be prepared by special procedure. Although borate glasses are of little commercial importance because they are water soluble, B₂O₃ is an important constituent of borosilicate glasses such as Pyrex. In contrast to SiO₂ and silicate glasses in which the silicon is present as SiO₄ tetrahedra, B₂O₃ glasses contain BO₃ triangular units and BO₄ tetrahedra depending on the composition. Addition of alkali oxide to
glassy $\text{B}_2\text{O}_3$ gives rather different results from those obtained in the corresponding alkali silicates. The structure of borate glasses are explained in detail in section 1.8.

(ii) 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. 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 $10^{-3}$ to $10^{-13}$ ohm$^{-1}$ cm$^{-1}$. These glasses are used as optical elements in the instruments for the infrared region, where they transmit radiation of considerably longer wavelengths than oxide glasses; however they show very strong absorption in the visible region.

(iii) Metallic glasses

Usually, liquid metals do not form glasses, but recently certain compositions have been shown to do so.
Some particular metallic compositions may be quenched very fast to yield glasses and usually, at least two elements must be present in the melt composition. One of these is a conventional metal, e.g., a transition-metal element such as iron or palladium and the other is an element on the metal insulator border line. In order to prepare glassy metals, special ultra rapid quenching techniques like splat quenching or roller quenching are necessary. The cooling rates are usually of the order of $10^6$ to $10^8$ K/sec.

Glassy metals are much stronger than crystalline metals. These are resistant to chemical attack. Some glasses containing cobalt and iron have low coercivity and may be easily magnetized and demagnetized.

1.8. Structure of glasses

Several techniques, both microscopic and macroscopic, have been developed for the study of the structure and properties of glasses. By measuring the viscosity, density and electrical conductivity of glass system, one can get an insight into the structure of the glass[21-26]. Structural studies have been carried out by several investigators[27-31], using electron spin resonance (ESR), nuclear magnetic resonance (NMR), Raman, IR and Mossbauer spectroscopy, and X-ray diffraction.
1.8.1. Structure of silicate glasses

Structure of glasses lacks long-range periodicity in the atomic arrangement. The X-ray and spectroscopic studies may be used for obtaining information about the structure of glass systems. The generally accepted view of the structure of glassy SiO$_2$ is largely the same as that proposed by Zachariasen[16] and supported by the X-ray diffraction results of Warren[8]. The structure is built up of corner-sharing SiO$_4$ tetrahedra which link up to form a three-dimensional network that lacks long-range periodicity. In order to maintain electroneutrality, each corner oxygen is shared between only two tetrahedra and consequently the structure is rather open.

Due to the absence of a unit cell in a glass structure, the X-ray diffraction pattern of glasses is very diffuse, consisting of broad humps rather than sharp peaks. (The comparison of glassy and crystalline X-ray diffraction patterns of SiO$_2$ is shown in figure 1.7). The only information that can be obtained from the X-ray studies is the radial distribution curve (figure 1.8). This is a curve plotted between pair distribution function and the interatomic distance. From this one can find out the probability of finding a second atom as a function of
Fig. 1.7. X-ray powder diffraction pattern of (a) crystalline SiO$_2$ and (b) glassy SiO$_2$.

Fig. 1.8. X-ray diffraction results for SiO$_2$ glass.
distance from a chosen atom. From the figure 1.8, it is obvious that the probability of finding a second atom is represented on the ordinate by a pair distribution function and the straight line gives the results expected for the hypothetical material that consists of a random array of non-interacting point atoms.

The structure and properties of silica based glasses (binary, ternary, etc.) is not only dependent on SiO\textsubscript{2} structure, but also on the nature and concentration of other oxides (modifier oxides) which are added to SiO\textsubscript{2}. Addition of modifier oxides like alkali or alkaline-earth oxides to the network forming oxides leads to the breakage of Si-O-Si bonds creating non-bridging oxygens and the modifier cations remain at the interstitials of the network. In otherwords, the silica network is gradually broken up as more of the alkali or alkaline-earth oxide is added. If the concentration of the modifier oxide is increased, the ratio of silicon to oxygen will be decreased. That means more and more non-bridging oxygen atoms will be formed and the network will be rather open. In otherwords, if the alkali concentration is more (eg., if there are two sodium ions to each silicon ion as in Na\textsubscript{2}O - SiO\textsubscript{2} glass system) some of the tetrahedra will be unlinked from the network of the linked tetrahedra.
In this case, the viscosity of the liquid phase will be markedly lower and it becomes increasingly difficult to form glasses at higher alkali concentrations.

1.8.2. Structure of borate glasses

In contrast to silicate glass in which silicon is present as \( \text{SiO}_4 \) tetrahedra, borate glass contains a mixture of \( \text{BO}_3 \) triangles and \( \text{BO}_4 \) tetrahedra depending on composition. An important constituent of vitreous \( \text{B}_2\text{O}_3 \) is boroxol group (figure 1.9). It is a planar, six membered ring of alternate boron and oxygen atoms which are randomly connected in a three-dimensional network by sharing all the three oxygen atoms with adjacent \( \text{BO}_3 \) units. However, with the planar coordination of boron, in comparison with the tetrahedral coordination of silicon in \( \text{SiO}_2 \), glassy \( \text{B}_2\text{O}_3 \) has a rather open structure. Molten \( \text{B}_2\text{O}_3 \) is also more fluid than molten \( \text{SiO}_2 \). Using X-ray diffraction and various spectroscopic studies, the triangular coordination of boron in \( \text{B}_2\text{O}_3 \) glass can be deduced.

The addition of alkali oxide to glassy \( \text{B}_2\text{O}_3 \) gives rather different results than those obtained in the corresponding alkali silicates and an effect known as the boron oxide anomaly is observed. It was shown that a
Fig. 1.9. Schematic representation of boroxol group
B = Boron, O = Oxygen.
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. Figure 1.10 shows the several structural groups present in various borate compounds.

Pure $\text{B}_2\text{O}_3$ consists of planar $\text{BO}_3$ units which are randomly distributed in a three-dimensional network by sharing all the three oxygen atoms with adjacent $\text{BO}_3$ units. The planar $\text{BO}_3$ unit presumably involved in $sp^2$ hybridization, with the third orbital being vacant and extending in direction perpendicular to the $\text{BO}_3$ 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
Fig. 1.10. Structural groupings in borate glasses.
BO$_4$ tetrahedron with three bridging and one non-bridging oxygen, (c) an oxygen atom may contribute an electron pair to two BO$_3$ units changing the coordination of the two borons from sp$^2$ to sp$^3$ hybridization and with no non-bridging oxygen.

Several attempts[32] 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 state. However NMR studies[33,34] 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 behaviour in the critical range 15-20 mol% of modifier oxide. The BO$_4$ 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[26,28] using $^1$H 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$_3$. 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[20] who proposed a new model for the structure of borate glass. Krough-Moe 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[35] and infrared[36] studies the structural groupings in borate glasses can be classified into four different groupings. viz., boroxol, pentaborate, triborate and diborate groups (figure 1.10). the pentaborate and triborate groups will always occur in pairs and these pairs are referred to as tetraborate groups.
Boron oxide anomaly

This is a peculiar property of borate glasses and which cannot be seen in the boron-free glasses. In the system \( \text{Na}_2\text{O-B}_2\text{O}_3 \), for example, viscosity of the melt increases with increase in the alkali oxide content and passes through a maximum at 16 mol\% Na\(_2\)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 \( \text{B}_2\text{O}_3 \), increases towards the value 1:2, which is the value in the vitreous \( \text{B}_2\text{O}_3 \), 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.
1.9. Research work undertaken in the present investigation

Preparation of glassy materials and the study of their physical properties have gained much importance due to their immense applications. Continued efforts which may throw more light on the properties of already prepared glasses and to synthesize new glassy materials exhibiting practically useful properties are relevant in view of the role glassy materials are expected to play in technological and scientific areas.

The research work presented in this thesis consist of the properties of the quarternary glass systems CaO-B₂O₃-Al₂O₃-Na₂O and CaO-B₂O₃-Al₂O₃-Fe₂O₃. The glass system CaO-B₂O₃-Al₂O₃ usually known as cabal glasses is characterized by a very high electrical resistance due to the lack of mobile charge carriers. The incorporation of an alkali oxide like Na₂O or a transition-metal oxide like Fe₂O₃ in cabal glass is expected to generate either mobile ions or electrons, respectively, which may enhance the conductivity of the glass system. In the present investigation, the d.c and a.c conductivity, and dielectric constant of the glass systems CaO-B₂O₃-Al₂O₃-Na₂O and CaO-B₂O₃-Al₂O₃-Fe₂O₃ are systematically studied for different compositions of the glasses and over a wide range of temperature. The structure of the glasses is
investigated using laser Raman spectroscopy. Ultrasonic velocities in the glass samples have been measured using ultrasonic pulse-echo overlap technique and thereby the elastic constants of the glasses of different compositions have been estimated.
References