Chapter I

INTRODUCTION

1.1 GENERAL INTRODUCTION

Glass is a transparent material, particularly in the visible region of electromagnetic spectrum. The transparent and colouration have made the glasses best suitable for decorative and illumination purposes in the early days of their invention. Today glasses find applications in various fields’ viz., electrical transmission, optical instruments, laboratory glassware, domestic appliances, textiles, optical fibers, electrochemical devices, solid electrolytes, biological systems (bioactive glasses) etc. The isotropic properties of glasses have given an edge in variety of applications.

Glasses are structurally disordered materials. They broadly fall under the category of amorphous materials. Amorphous materials show many properties that are unique to them and are not exhibited by crystalline solids.

Glass is a non-crystalline solid. This means that the regular periodic arrangement of motifs (groups of atoms, molecules or ions) is absent in glasses. The crystalline characteristic of long-range order of motifs is lacked and short-range order prevails in glassy materials.

Glasses are formed by quenching a material in liquid state sufficiently fast so that atoms cannot re-arrange themselves in a crystalline form and
form glasses. Amorphous materials prepared only by quenching a liquid are generally referred as glass. However several unconventional methods like neutron bombardment, sol-gel process etc., are becoming popular in the preparation of glasses. Hence glassy materials are not just prepared by melt quenching.

1.2 DEFINITION OF GLASS

Glass has been defined in several ways.

“Glass is an inorganic product of fusion, which has been cooled to a solid state condition without crystallizing [1] - ASTM.

Glass is a non-crystalline solid that exhibits a glass transition temperature [2]. Above the glass transition temperature \([T_g]\) glass exhibits properties of liquid and below \(T_g\), it retains liquid structure in rigid form.

It is now known that glasses can be formed from almost any material either organic or inorganic if cooled rapidly by avoiding crystallization.

1.3 GLASS FORMING

The formation of crystal, liquid and glass can be explained from the temperature volume relationship as shown in the Fig. 1.1. It is clear from the figure that slow cooling process leads to formation of crystal nuclei and crystallization takes place. If the cooling rate is fast, leaving no time to the formation of crystal nuclei, structure of super cooled liquid state turns to rigid and forms a glass.
Figure 1.1 Volume – temperature characteristics (schematic) for crystals, liquid and glass
Some oxides easily form glasses. These substances which form glass are generally called “Glass formers” or “Glass network formers”. The Oxides SiO$_2$, B$_2$O$_3$, P$_2$O$_5$, SiO$_2$ GeO$_2$ and As$_2$O$_3$ can form glass by their own. These oxides can also form glasses when mixed with other oxides in various proportions.

Some oxides such as Na$_2$O, Li$_2$O, K$_2$O, Bi$_2$O$_3$, Al$_2$O$_3$, V$_2$O$_5$, PbO, TeO$_2$, MoO$_3$, WO$_3$ etc which cannot form glasses by themselves can disrupt the glass forming oxides network and extend the glass forming region. These oxides are called ‘glass-modifiers’ or ‘glass network modifiers’. Glass-modifier oxides form glass when combined with appropriate quantity of second oxide. Hence glass modifier oxides are also known as conditional glass formers.

Fig.1.2 shows the disruption of silica (glass former) structure by alkali oxide Na$_2$O (glass modifier) and thereby formation of non-bridging oxygens (NBO).

Zachariasen pointed out that an oxide of general formula A$_n$O$_m$ should satisfy some rules to form glass [3]. The original set of rules are modified,
after Cooper’s remarks, by Zachariasen himself and are given by [2, 4]

1. A high proportion of (network-forming) cations are surrounded by oxygen tetrahedra or triangles.
2. The oxygen polyhedra only share corners with each other.
3. Some oxygen atoms are linked to only two cations and do not form additional bonds with any other actions.

It is well known that covalent bond is directional and ionic or metallic bonds show no directional property. According to Smekal [5], for glass formation, existence of mixed chemical bonding in a material is a must. He divided glass-forming substances with mixed bonding into three categories as

1. Inorganic compounds such as \( \text{SiO}_2, \text{B}_2\text{O}_3 \) having A-O bonds partly covalent and partly ionic.
2. Elements like S, Se etc having chain structures with covalent bonds within the chain and van der waal’s forces between the chain.
3. Organic compounds having large molecules with covalent bonds within the molecules and Van der waal’s forces between them.

1.4 TYPES OF GLASSES

Based on the composition of glasses (or sometimes based on their applications) they are classified broadly into two categories as oxide glasses and non-oxide glasses. The constituents in the glass composition play major role in the application and classification of glasses.
Oxide glasses may be single component glasses (SiO$_2$, GeO$_2$ etc) binary systems (SiO$_2$-Na$_2$O, PbO-GeO$_2$, B$_2$O$_3$-Na$_2$O, B$_2$O$_3$-K$_2$O), ternary systems(B$_2$O$_3$-Na$_2$O-K$_2$O, Na$_2$O-CaO-SiO$_2$, K$_2$O-MgO-SiO$_2$ etc) quaternary glass systems (LiF-Li$_2$O-P$_2$O$_5$-Nb$_2$O$_5$, Li$_2$SO$_4$-ZnSO$_4$-B$_2$O$_3$-VOSO$_4$, AgI-Ag$_2$O-B$_2$O$_3$-AS$_2$O$_3$ etc or multi component glass systems like SiO$_2$-Al$_2$O$_3$-CaO-MgO-Na$_2$O, SiO$_2$-Al$_2$O$_3$-CaO-MgO-K$_2$O).

Similarly non-oxide glasses are also prepared in many compositions. Some important non-oxide glasses are chalcogenide glasses. Non-oxide glasses such as Flurozirconate and Fluroaluminate groups are popular for making glass fibers. These glasses are used in electrical and optical memories [5].

Oxide glasses depending on composition may be further classified and some of these oxide glass systems are discussed briefly here.

1.4.1 Soda-Lime Glasses

The less expensive commercial glass is soda – lime glass. These are used as window glasses because of their good light transmission. Soda – lime glasses are also used as glass containers, jars etc. The chief constituents in soda-lime glass are silica (SiO$_2$-60-75%), soda(Na$_2$CO$_3$-12-18%) and lime (Ca$_2$CO$_3$ or MgCO$_3$-5-12%). Other materials are also added to these constituents to get required properties. The main disadvantage of these glasses is they are not resistant to high temperatures and sudden thermal changes.
1.4.2 Borosilicate Glasses

Borosilicate glass is widely used in the manufacture of laboratory glassware, pharmaceutical containers, high-power electric bulbs etc. Because of their good heat resistant properties and thermal shock resistance they are used in chemical industry, domestic kitchen cooking utensils (microwave or oven ware). The main ingredients of borosilicate glass are silica (SiO$_2$-70-80%) and boric acid (7-13%). Oxides of sodium, potassium and aluminum are added to borosilicate composition to get good chemical durability.

1.4.3 Lead Glasses

Lead glasses are widely used for decorative purposes because of their bright brilliance due to high refractive index. Generally lead glasses contain SiO$_2$ (54-65%), PbO (18-38%) Na$_2$O (13-15%) and other oxides in small proportions. If the PbO content is less than 18% in the glass it is called as crystal glass. If the lead content is high (65%), the glass can be used for radiation shield glass as lead absorb-rays.

Lead glass also is not resistant to high temperatures and sudden thermal changes like soda-lime glass.

1.4.4 Glass Ceramics

Controlled crystallization of glass lead to glass-ceramic which contains crystal phases within the glass. Some glass ceramics are Li$_2$O-ZnO-PbO-Si$_2$O$_2$ and Li$_2$O-Al$_2$O$_3$-SiO$_2$ with P$_2$O$_5$ as nucleation agent. Glass ceramics
have improved properties like extremely resistant to thermal shock, high mechanical strength, chemical stability etc.

Stookey discovered the controlled crystallization of glasses [6]. Later a number of nucleation agents or catalysts have been found viz., TiO$_2$, P$_2$O$_5$, SnO$_2$, ZrO$_2$, V$_2$O$_5$, etc.

Glass ceramics found applications in the fields of missile nose technology, astronomical telescopes, cooking ware etc.

**1.4.5 Other Technical Glasses**

There are many other glass systems that have applications due to their added advantages like optical absorption, ionic and electronic conductivity, semi-conducting nature (Phosphate and chalcogenide glasses), IR transmission materials and memory devices. Some glasses system that have scientific, technical and research applications are briefly discussed here under.

Alkali-oxide glasses have been prepared by many researchers. alkali-germanate glasses(Ge$_2$O-R$_2$O), alkali-tellurite (Te$_2$O-R$_2$O), alkali-Phosphate glasses (P$_2$O$_5$-R$_2$O), alkali-borate(B$_2$O$_3$-R$_2$O) glass systems are some of the important alkali-oxide glass [7-10].

In addition to glass formers and glass modifiers which form the host glass, dopant salts are added to a glass to get required properties such as ionic conductivity.
1.5 DOPING SALTS

Dopants like halides or sulfates are introduced in the host glass to vary the properties of the glass like the conductivity. The salts such as AgI, NaI, NaF, NaCl, NaBr, KI, KF, LiI, LiF, LiCl etc. are added to the host glass matrix to produce mobile ion species Li+, Ag+, Na+, K+ etc. It was observed from various studies that the dopant salts do not enter into macromolecular chain of the glass [11]. Therefore glasses are good solvents of metal ions [12].

1.6 ION CONDUCTION IN GLASSES

Glasses are known to be insulators offering high resistance to electricity. In the year 1884, Warburg established the ion conducting nature of oxide glasses [13].

Sodium β-alumina is one of the best ion conducting hard refractory materials. In very short time, number of oxide and non-oxide glasses were reported with their ionic conductivity reaching as high as $10^{-1}$ S/cm. The conductivity by ion motion in the glasses can be increased either by increasing doping salts (upto a certain extent) concentration or glass network modifiers that produce mobile ions such as Ag+, Li+, Na+, K+, Mg2+, etc. The progressive replacement of one glass former by the other which leads to mixed oxide/former effect can also sometimes enhances electrical conductivity.

In oxide glasses depending on the number of glass modifiers or doping salts there may be one or more than one mobile ions. The conductivity ($\sigma$) due to a single mobile ion is given by the relation
\[ \sigma = n(Ze) \text{ S.cm}^{-1} \quad \ldots \ldots (1) \]

where \( \sigma \) is the mobility of the mobile ion with charge \( Ze \) and \( n \) is the concentration of charge carriers. The Temperature dependence of electrical conduction in ionic conductors is best explained by the Arrhenius relation.

\[ \sigma = \frac{\sigma_0}{T} \exp(-E/KT) \quad \ldots \ldots (2) \]

In the above relation \( T \) is the absolute temperature, \( K \) is Boltzmann constant, \( \sigma_0 \) is the pre-exponential factor and \( E \) is the activation energy of mobile ion. The ionic conductivity of oxide glasses containing doping slats vary either in linear or non-linear manner when the composition is varied. Hence conductivity of ion conducting glasses is a function of both composition of glass and temperature.

Depending on the type of mobile ions in the host glass matrix, ion conducting glasses can be grouped under various names. A brief discussion on important ion conducting oxide glasses are given hereunder.

**1.6.1 Silver Ion Conducting Glasses**

The fast ion conducting phase -AgI at high temperature is stabilized at ambient temperature in AgI – Ag_2SeO_4 oxide glass [14-16]. Silver ion (Ag+) conducting oxide glasses have been studied extensively. Ag+ ion conductivity is found to be high at room temperature. These glasses are used as electrolytes in solid state cells. But these cells have disadvantages of low open circuit voltages and low energy density.
Important silver ion conducting glasses are $\text{AgI} - \text{Ag}_2\text{O} - \text{AnO}_m (\text{AnO}_m - \text{B}_2\text{O}_3, \text{P}_2\text{O}_5, \text{Cr}_2\text{O}_3, \text{MoO}_3, \text{etc.}), \text{AgI} - \text{Ag}_2\text{O} - \text{M}_x\text{O}_y (\text{M}_x\text{O}_y \rightarrow \text{B}_2\text{O}_3 - \text{As}_2\text{O}_3, \text{V}_2\text{O}_5 - \text{P}_2\text{O}_5, \text{MoO}_3 - \text{WO}_3 \text{ etc}), \text{AgI} - \text{Ag}_2\text{SeO}_4, \text{AgI} - \text{AgTeO}_4, \text{AgI} - \text{Ag}_3\text{AsO}_4 \text{ etc.} \ [16-19].$

1.6.2 Copper Ion Conducting Glasses

Copper ion ($\text{Cu}^+$) conducting glasses are also used to fabricate solid state cells. However, like $\text{Ag}^+$ ion conducting glasses, these cells also have suffered from the disadvantage of low open circuit voltage and low energy density. Non-oxide $\text{Cu}^+$ ion all halide superionic glasses were also reported. $\text{CuCl-Cul-RbCl-KCl}, \text{Cul, CuPO}_3, \text{Cul-CsI-BaI}, \text{CuBr-KBr-CsBr-BaBr}_2$ [20-22]. But $\text{Cu}^{2+}$ ion containing glasses as have attracted less attention.

1.6.3 Alkali Ion Conducting Glasses

Alkali ion ($\text{Li}^+, \text{K}^+, \text{Na}^+$) conduction in various oxide glasses is studied very extensively. Alkali silicates, Alkali borates, Alkali Phosphates, Alkali niobates, mixed alkali borate and tellurite glass systems have shown fast ion or super ion conduction [23-24].

Lithium ion conduction in oxide glasses have been studied and found that $\text{Ag}^+$ ion gives higher conductivity than $\text{Li}^+$ ions. But solid state cells with $\text{Li}^+$ ion conductivity glasses have shown good solid state cell parameters.

There are several theories to explain the ionic conductivity in glasses. Many theories could not present a consolidated phenomenon for ion
conduction including alkali borate and alkali halo-borate glasses. Theories of ion conduction in oxide glasses are briefly discussed below.

1.7 THEORIES OF ION CONDUCTION IN GLASSES

The addition of glass modifiers and doping salts breaks the continuous random network of glass former and as a result produce non-bridging oxygen's (NBOs). Hence the structure of alkali ion conducting glass consists of [25-27].

i. Broken network of glass former with NBOs or discrete glass former anion units (MO$_{n}^{m}$).

ii. Glass former anion units are in tetragonal structure in many cases and polyhedra shapes in higher coordination.

iii. Halide ions are dispersed in the glass matrix without any long-range order.

iv. The added alkali ions may either bonded to NBO sites by forming covalent bond or to holide ions by ionic bond.

Ion conduction in oxide glasses may be explained based on long range motion in which an ion may move at least several atomic orders and/or short range order in which the ion moves a distance less than a unit jump distance [28]. A few important ion conduction theories are briefly discussed below.

1.7.1 Weak Electrolyte Theory

Glasses can be regarded as weak electrolytes since the number of mobile ions is less than the stoichiometric concentration [29].
All mobile ions for example all Li$^+$ or Na$^+$ or K$^+$ or Ag$^+$ in the glass matrix are not mobile. This theory attributes the change in conductivity with composition to change in carrier concentration [30]. For SiO$_2$-Na$_2$O glass system, sodium oxide is assumed to dissociate as

$$\text{Na}_2\text{O} \rightarrow \text{Na}^+ + \text{ONa}^- \quad \ldots \ldots \text{(3)}$$

Then activity of sodium oxide a (Na$_2$O) is

$$a(\text{Na}_2\text{O}) = K.a(\text{Na}^+).a(\text{ONa}^-) \quad \ldots \ldots \text{(4)}$$

where K is Boltzmann constant. Since in the glass system only Na$^+$ and ONa$^-$ ions are present, their concentrations must be equal and hence

$$a(\text{Na}_2\text{O}) = K [\text{Na}^+]^2$$

For many glass systems at constant temperature, it is found that conductivity varies with metal oxide concentration.

1.7.2 Free Volume Theory

When the concentration of doping salts such as metal halides is high in the glass matrix, then glass can no more be treated as weak electrolyte. In such cases glass can be treated as strong electrolyte. This theory assumes that additional free volume is created by the addition of metal halides. Free volume theory is successfully applied to lithium sodium and silver borate glasses containing higher concentration of Li, Na and Ag metal halides.

1.7.3 Anderson and Stuart Model

According this model, the activation energy (Ea) of a mobile ion is the sum of strain energy (Es) associated with the long-range mobility and
colulombic energy \((E_b)\) which is required to move an ion. The activation energy is now given by

\[ E_a = E_s + E_b \]

\[ = \frac{ZZ}{\varepsilon_\infty} e^2 \left( \frac{1}{r + r_j} - \frac{1}{\lambda / 2} \right) + \pi \eta (r - r_D)^2 \lambda / 2 \]

where

- Jump distance between equivalent sites near NBOs
- \(r_D\) - radius of interstice or doorway opening
- \(r\) - carrier cation radius
- \(r_j\) - radius of NBO
- \(\varepsilon_\infty\) - high frequency dielectric constant

The doorway radius depends on alkali modifier content [31-32].

1.7.4 Modified Random Network Model

Fig.1.3 shows the path ways or channels for mobile ion migration. According Greaves modified random network model throughout the glass structure percolation paths due to channels established by conversion of bridging anions into non-bridging anions exists. This channels facilitates steady state diffusive transport of ions [33].

1.8 ELECTRON PARAMAGNETIC RESONANCE (EPR) AND OPTICAL ABSORPTION SPECTRA

Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) is a sensitive experimental technique to detect species that have
Figure 1.3 Two dimensional representation of modified random network model
unpaired electrons. i.e., one can detect free radicals in organic molecules or transition metal ions (like Cu$^{2+}$, VO$^{2+}$, Fe$^{3+}$, Cr$^{3+}$, etc.) in inorganic complex. The electron spin resonance (ESR) was first reported by the Russian scientist E.Zavoisky in 1945 [34]. Atoms or molecules that have one or more unpaired electrons can only show electron spin resonance (ESR). Such substances do also exhibit paramagnetism.

ESR deals with the interaction of electromagnetic radiation with magnetic moments arising from unpaired electrons. A magnetic dipole moment in an atom or molecule (neutral or charged) may arise from unpaired electrons as well as from nuclei. The magnetic dipole moments of these particles give rise to electronic and nuclear angular momenta respectively.

Electron with its intrinsic spin possesses a magnetic moment. The electrons will precess (like a symmetric top) in an applied magnetic field with a precise precessional frequency and undergo transitions between spin states if energy of correct frequency is applied. The resultant spin angular momentum of an unpaired electron is given by $\sqrt{S(S+1)}\hbar$. The value of this spin magnetic moment is given by

$$\mu_S = -g_e \frac{e\hbar}{4\pi m_e c} \sqrt{S(S+1)}$$

or

$$\mu_S = -g_e \beta S$$
Here $\beta = \frac{e h}{4 m c}$ is Bohr magneton which is a unit of angular momentum and for electron, $\beta = 9.2732 \times 10^{-21}$ erg/gauss and $g_e$ is the free electron $g$-factor whose value is 2.0023. When the free electron (or unpaired electron) is placed in a magnetic field $H$, the energy is given by

$$E = -\mu_s H \text{(ve sign since electron carries a unit negative charge)}$$

$$= g_e \beta S H.$$ 

Above expression gives the quantum mechanical Hamiltonian $H$ and is called spin Hamiltonian.

$$\mathcal{H} = g_e \beta S H.$$ 

The Eigen values of the above Hamiltonian are given by

$$E = \frac{1}{2} g_e \beta H \quad \text{(since } S = \pm 1/2)$$

i.e., there are two energy states. The lowest state has a -ve sign and corresponds to the magnetic moment aligned parallel to the field and hence spins anti-parallel to the field. The difference of the energy between the states is

$$\Delta E = h\nu = g_e \beta H,$$

which is the resonance condition

EPR studies of transition metal ions (TM) such as Cu$^{2+}$, VO$^{2+}$, Mn$^{2+}$ in glassy materials will yield valuable information about the magnetic properties of the unpaired electron [35, 36, 37]. From the EPR results, the coordination and environment of paramagnetic ion can be determined. Glasses containing TM ions have attracted considerable interest because of their technological applications [38, 39].
Significant research work has been carried out on EPR studies of TM ions in oxide glasses [40-44].

Another important aspect is the optical absorption studies of glasses containing transition metal ions [45-48]. By correlating the EPR and optical data, the metal ligand bond nature can be determined [49-54].

1.9 AIM AND OBJECTIVES OF THE PRESENT STUDY

(1) To prepare the following glass systems with the general formula

\[ xKR-(30-x) \text{K}_2\text{O}-35\text{B}_2\text{O}_3-35\text{P}_2\text{O}_5 \]
\[ x\text{NaR}-(30-x) \text{Na}_2\text{O}-35\text{B}_2\text{O}_3-35\text{P}_2\text{O}_5 \]
\[ xKR-(30-x) \text{K}_2\text{O}-35\text{B}_2\text{O}_3-34\text{P}_2\text{O}_5-1\text{CuO} \]
\[ x\text{NaR}-(30-x) \text{Na}_2\text{O}-35\text{B}_2\text{O}_3-34\text{P}_2\text{O}_5-1\text{CuO} \]
\[ xKR-(30-x) \text{K}_2\text{O}-35\text{B}_2\text{O}_3-33\text{P}_2\text{O}_5-2\text{V}_2\text{O}_5 \]
\[ x\text{NaR}-(30-x) \text{K}_2\text{O}-35\text{B}_2\text{O}_3-33\text{P}_2\text{O}_5-2\text{V}_2\text{O}_5 \]

where (R= Cl, Br, I) using melt quenching method.

(2) X-Ray diffraction of the glass samples prepared to confirm the amorphous nature.

(3) DSC investigations to determine the glass transition temperature \( T_g \).

(4) Ionic conductivity studies at different temperatures to draw the log \( T \) vs \( 10^3/T \) plots. Determination of activation energies from the conductivity plots and study the variation of isothermal conductivity and activation energy with the alkali halide content.
EPR and optical absorption studies of the glass system containing the transition metal ion Cu$^{2+}$ and EPR studies of the glass systems containing the transition metal ion VO$^{2+}$. Determination of the spin-Hamiltonian parameters, bond parameters, $\tau_\pi$ and $\tau_\sigma$ and covalency rates. Study of the variation of the spin-Hamiltonian parameters, $\tau_\pi$ and $\tau_\sigma$ with the alkali halide content. Determination of ground state, of Cu$^{2+}$ and VO$^{2+}$ in the glass samples studied.
1.10 REFERENCES

1. ASTM Glass designation C162-166.

