Chapter 1

INTRODUCTION

1.1 Preliminary Remarks

Inorganic glasses have been of interest for many hundreds of years due to their special mechanical and optical properties. Ancient man fashioned obsidian, a naturally occurring glassy silicate, into arrow and spear heads for hunting and other uses. Later, when glasses were made, their compositions were varied from time to time in search of new types of glasses which could be used for ornamental purposes. These investigations led to a systematic study of the relation of the composition, strength, glass forming ability and chemical durability. In the last two centuries extensive research has been made into the development of new glassy systems to meet the changing requirements of the present age. This has resulted in glasses with improved chemical durability, strength and other physical properties. In the present century, rapid industrialization and advanced technology have opened new frontiers for glasses applied to Electronics and Medicine. In such uses, glass often does not have the properties ascribed to it by the layman for whom it is a transparent material made from silica and used for windows, lenses, prisms and optical instruments. In reality, glasses can be formed from many different inorganic and organic materials under a host of different conditions. It is thus useful to define the term glass.
1.2 Glass structure and formation

Any solid chemical substance may broadly be categorized as either crystalline or amorphous. Glass is a subset of the amorphous category. In the conventional method of glass preparation, the melt is quenched rapidly enough so that it bypasses the crystallization temperature and enter the supercooled liquid phase. Figure 1.1 [Jones (1956)] shows the variation of specific volume with temperature of a glass. Continuous cooling below the supercooled phase leads to formation of a glass whose volume depends on the speed of cooling. Thus in Fig. 1.1, glass A results from a faster rate of cooling than glass B.

The growing demand for glassy materials for various applications had led to an interest in the relationship between physical properties such as ionic conductivity, hardness, chemical durability, glass transition temperature and the atomic scale structure of glasses. Since these properties ultimately depend on the structure, a knowledge of the latter is useful in optimizing any particular property. Thus, the optical and diffraction spectra of rare-earth doped glasses, for example, depend on the type of host matrix and the immediate environment of the rare-earth ion. This is also true of the nuclear-waste glasses studied here viz. several heavy metal oxides in a boro-silicate host network.

1.3 Structural theories

Various theories were established to understand the process of glass formation related to kinetics and structure. Structural theory deals with various types of structural models that were proposed to explain the formation of glass. These can widely be categorized as models based on randomness and models based on crystallographic order. Properties of glass vary slightly from those of crystals and can be seen from the density and the internal energy.
Figure 1.1: Formation of Glass (after Jones [1956])
1.3.1 Random Close Packing (RCP)

This model derives from a random packing of classical hard spheres. It was proposed for monatomic liquids and modified later for binary liquids. Non-crystalline models could be produced by constraining the outer surface to be irregular. Interatomic arrangement can then be explained in terms of irregular polyhedra. Computer modelling of such liquids [Finney and Wallace (1981)] minimized the number of large polyhedra with most of the structure arising from tetrahedra and octahedra. Usefulness of this model was tested for a binary system. Although such models can be constructed for polyatomic species of any shape and size, few attempts have been made to construct such a network.

1.3.2 Continuous Random Network (CRN)

A model, which is closely similar to RCP was proposed by Zachariasen for covalent glasses where the structural unit can be defined e.g. SiO₄ for silicon dioxide glass, BO₃ triangles for boron trioxide glass etc.. The random network can be constructed by connecting such polyhedra, with their relative orientations unconstrained. The restrictions such as choice of ring statistics and minimum strain energy can be added at a later stage after the construction of such a network. This model is very useful for construction of structures in that the random connection of these units provides a realistic non-crystalline model. Most of the successful models are from this category. This model [proposed by Zachariasen (1932)] which says that the atomic arrangement in a glass is characterized by a continuous network which lacks symmetry and periodicity, was further supported by the work on silica [Warren et al. (1936)] using X-ray diffraction. Incorporation of species such as alkali or alkaline earth atoms can be made by addition of these to the network. The latter approach was subsequently challenged by several researchers and will be discussed later.
1.3.3 Models derived from crystallographic order

Similarity between structures through comparisons of pair correlation functions for glasses and compositionally equivalent crystals provides the idea that the glasses may be formed from microcrystals. Strain induced from lattice mismatch at grain boundaries, defects such as dislocations and the presence of disordered interfacial regions may all give rise to regions of disorder smaller than the grain size.

Simple microcrystalline model

This model [Cargill (1970)] originated from a possible model for amorphous Ni—P alloys which predicted that Ni atoms are hexagonally close packed in the region of 20 Å. Similarly, RDF's obtained from amorphous Ge and crystalline Ge were not found to be in agreement beyond second neighbours.

Quasi-crystalline model

This model is based on crystalline polymorphs with variable correlation length [Leadbetter and Wright (1972)]. According to this, glass is made of quasi-crystals in which the crystallinity gradually decreases as the length approaches a correlation length which is of the order of 10 Å to 20 Å. These quasi-crystals are embedded in an homogeneous disordered matrix. Although this model gives close agreement with experiment for the structure of the local environment, large differences at higher values of \( r \) are observed.

Paracrystalline model

Hosemann et al. [1986] and Phillips [1982] have used the term 'paracrystalline' while describing models for amorphous solids. This is based on disordered regions over inter-planar distances. From cation/anion ratios of some glass forming oxides in the range 0.2 to 0.4, and the presence of tetrahedral bonding in crystals having the same radius ratios, Goldschmidt [1926] considered that tetrahedral bonding was necessary for the formation of
glasses. Several authors have considered the process of glass formation based on the nature of interatomic bonds rather than the structure. Stanworth's electronegativity criterion led to the rediscovery of Tellurite glasses [Stanworth (1946), (1948a, b), (1952)].

1.4 Zachariasen's model of glass

For oxide glass formation, Zachariasen proposed that the structure of glass may be considered to be made up of oxygen polyhedra which connect together in a 3-D arrangement to form a glass. For the internal energy of a glass to be only slightly higher than that of a crystal, it must contain polyhedra of the same type as the crystal and must be joined together in a similar way. Thus, since the crystalline forms of silica are made up of SiO$_4$ tetrahedra, its vitreous form must also be constituted of these units. However unlike a crystal, a glass would have a variation in relative orientation of adjacent tetrahedra. Zachariasen formulated the following rules for oxides to be glass formers: They are:

1. No oxygen atom may be linked to more than two cation atoms A.
2. The number of oxygen atoms surrounding each cation must be small.
3. The oxygen polyhedra share corners with each other, not edges or faces.

Oxides of the type AO and A$_2$O cannot satisfy these conditions and therefore should not form glasses and indeed the oxides of Groups I and II do not form glasses with the exception of water.

Rules 1, 2, and 3 are satisfied by

1. the oxide type A$_2$O$_3$ if the oxygens form a triangle around A
2. the oxides AO$_2$ or A$_2$O$_5$ if the oxygens form tetrahedra and
3. by oxides AO$_3$, A$_2$O$_7$ and AO$_4$ if the oxygens form octahedra.
The nonoxide BeF$_2$ also satisfies the above rules when ‘oxygen’ is replaced by ‘fluorine’. Thus BeF$_2$ glass is made up of BeF$_4$ tetrahedra.

For more complex oxide glasses, Zachariasen proposed that glass formation occurred:

1. if the sample contains a high percentage of cations which are surrounded by oxygen tetrahedra or oxygen triangles

2. if the tetrahedra or triangles share corners with each other and

3. if the oxygen is linked with only two cations and does not make further bonds.

These rules imply that the sample must contain a high percentage of glass forming cations or any other cations which are able to replace them isomorphically. The cation Al$^{3+}$ for example can replace Si$^{4+}$ since it resembles many silicate structures. Such cations form the network of the glass and are therefore termed as ‘network-forming-oxides’. The oxides which do not take part in the formation of a network are called ‘network-modifiers’. After the publication of the theory by Zachariasen, Warren (1941) studied simple binary glasses and the results were interpreted using the CRN model explaining the way in which alkali and alkaline earth cations are incorporated in the network. The conclusions drawn from this study were that each Si is surrounded by four oxygens as per Zachariasen’s formulation. The structure of silicate glass containing Na$_2$O was considered to be made up of Si tetrahedra with Na atoms partially bonded to a tetrahedral oxygen thereby modifying the network. The oxygens connected to two Si atoms were termed ‘bridging’ oxygens while those connected to the Na atom were ‘non-bridging’ oxygens.

1.4.1 Limitations of Zachariasen’s model

According to Zachariasen’s model for glasses, network-modifying elements which adjust the connectivity and dimensionality of the network have weak, ionic and non-directional bonds [Gaskell (1985)]. Their coordination environments are considered to be more distorted and variable than in crystals, and their spatial distributions are regarded as random or
homogeneous [Rawson (1967)]. This view of the structure of glass developed by Zachariasen and Warren of ‘CRN’ has been questioned by several researchers in recent years by new experimental findings from elemental specific EXAFS [Brown et al. (1986), Greaves (1990)] as well as neutron and X-ray scattering measurements [Wright et al. (1982), Milberg and Peters (1969), Yasui et al. (1983)]. Both techniques supply environmental information around a particular element, be it glass former or modifier.

1.5 Kinetic theory

Kinetic theory basically deals with the processes of crystal nucleation and growth, and the limiting values of these processes. Their values, when exceeded, affect glass formation. Turnbull and Cohen [1958, 1960, 1961] proposed the theory of vitrification based on the formation of crystal nuclei. One of the important results of this theory is the determination of minimum activation energy for glass formation and is stated as [Turnbull and Cohen (1958)]:

\[
\frac{\Delta T'}{T_m} = \left( \frac{2\pi}{3} \frac{RT_m}{80RT' - \Delta G'} \right)^{1/2}
\]

where \( T_m \) is the melting temperature, \( \Delta G' \) is the free energy of crystallization and \( T' \) is the temperature at which the value of the rate of nucleation is \( 1 \text{ cm}^{-3} \text{ sec}^{-1} \). A glass will be formed if the rate of crystal growth at \( T' \) is less than \( 10^{-5} \) atom spacings per second. A value of \( T' \) satisfying the above equation can be found if \( \Delta G' \) is less than \( 40RT_m \). The condition for rate of nucleation is satisfied when \( \Delta G' \geq 40RT_m \). The velocity of crystal growth however, will be less than \( 10^{-5} \) atomic spacings per second if \( \Delta G' \) is greater than \( 30RT_m \). Thus for glass formation in this description, the activation energy must exceed \( 30RT_m \). From this theory which leads to the relation \( T_m = \Delta v_m / \Delta S_m \) (where \( \Delta v_m \) is the energy and \( \Delta S_m \) is the entropy of crystallization), it follows that “the greater the glass forming ability, the lower are the values of energy required to produce a given amount of disorder”.

Sun [1947] postulated that the process of melting and crystallization depends upon the
strength of the bonds. If the bonds are stronger, the material is likely to be more viscous thereby increasing the probability of forming a glass. Using this criterion, bond strength was calculated for many oxides and was found to be higher for silica, boron trioxide etc.

Rawson [1967] after pointing out that the ratio of bond strength to melting temperature should be taken into account, explained glass formation in multicomponent systems. In such systems, he observed that glass formation is seen where the liquidus temperature of the system is low.

Kinetic theory in general explains the dependence of glass formation on the strength of bonds which have to be broken during crystallization, and the thermal energy available for this.

1.6 Techniques for probing structures

Structures may be probed by the following experimental techniques;

1. Diffraction: X-ray, Neutron and Electron

2. Scattering: Small Angle X-ray and Small Angle Neutron Scattering

3. Spectroscopy: IR, Raman, UV/visible, EXAFS, ESCA

4. Macroscopic measurements: Density, Molar volume etc.

The diffraction technique yields an overall Radial Distribution Function (RDF) that can be interpreted up to a few angstrom units for simple systems. The RDF is a superposition of various constituent pair distribution functions. X-rays, neutrons and electrons are scattered respectively by core electrons, nuclei and the atomic electron clouds. With all three probes, the relative positions of atoms are obtained through real space correlation functions to yield one dimensional average projections. The overall structure may then be deduced from a comparison of data from such experiments and the construction of models through computer simulation methods such as Reverse Monte Carlo (RMC) and Molecular Dynamics (MD).
Since these techniques produce one-dimensional RDF, knowledge of the chemical bonding in the structure is necessary to identify the features in the component correlation functions. Crystal structures of analogous compounds provide this information. Computer modelling studies such as MD can probe short range order of the glasses when a good interaction potential function is available. This is generally obtained by trial and error or ab-initio methods until a good fit between the experimental and theoretically simulated values for some physical properties is obtained.

The Reverse Monte Carlo (RMC) technique [McGreevy and Pusztai (1988)] is based on the Monte Carlo algorithm, in which instead of minimizing the energy, the squared difference between the experimental and calculated structure factor from an initial configuration is minimized. The structure is modified by moving the atoms until the calculated structure factor agrees with the experimental one within some acceptable limit of error.

Several researchers [Momiuchi (1986), Hosokawa et al. (1991)] have demonstrated Energy Dispersive X-ray Diffraction (EDXD) in studying disordered systems. Here the energy dependence of scattered intensity is detected by utilizing white radiation at a fixed diffraction angle. Subsequent to correction for Compton scattering, the scattered signal as a function of momentum transfer is calculated. This method has many advantages such as measurement of the intensity function $i(s)$ up to a relatively high value of momentum transfer e.g. 25 Å$^{-1}$. Mechanical movement is not necessary minimizing the errors due to optical misalignment. However, the availability of a detector having good energy resolution may sometimes be difficult.

Small angle X-ray and neutron scattering yield information on longer range order, formation of clusters in glasses or microstructure due to phase separation in a glass. Many spectroscopic measurements such as IR, UV/visible, EXAFS, ESCA can be used for structure determination. EXAFS is an atom specific technique and can be used to study the structural environment of any particular atom giving accurate information of interatomic distances in the first shell. Techniques such as IR, Raman mainly deal with molecular vibra-
tions and can be sensitive in probing the structure of glasses. In these methods, structural information can be obtained by comparing calculated vibrational characteristics of an assumed structure with those obtained from the measurements. ESCA provides information about the number of non-bridging oxygen atoms in oxide glasses and the valence state of an atom. Macroscopic measurements such as density, molar volume yield information about the compactness of glass. In the present work, X-ray and neutron diffraction, IR and UV/visible techniques have been used.

1.7 Nuclear-Waste glasses

The residual solutions produced by the reprocessing of spent nuclear reactor fuel have a high level of radioactivity and constitute high-level waste. The radioactivity may be of the order of a thousand Curies per litre. Storage of this waste presents a serious current problem of nuclear power. The half lives of many radionuclides in high-level waste are of the order of hundreds, thousands and hundreds of thousands of years. Thus, any scheme for the storage of such waste requires long-term mechanical integrity and chemical inertness with the objective of minimizing the interaction of radioactive waste with the environment. In recent times, a widely accepted technique for such storage has been the vitrification of the nuclear waste from reprocessing. Glass is a suitable candidate for it has a number of advantages:

a) It is capable of bonding with all of the chemically different fission product elements at high temperatures and can be used with considerable flexibility.

b) It is a homogeneous, isotropic material which is also impermeable and thus presents only a limited exchange surface area.

c) It is highly resistant to heat and radiation.

d) It is easy to manufacture with a minimum of intermediate process steps liable to generate secondary wastes.
1.8 Phosphate glasses

Phosphate glasses are used presently in a number of applications. P_2O_5 has attracted glass researchers due to its comparatively low melting temperature and ease of glass formation. The disadvantage in using phosphate glasses is that they are hygroscopic. Addition of Al_2O_3 or B_2O_3 increases the degree of cross-linked bonds in the glass and reduces the hygroscopic nature of the phosphate. Some borophosphates and aluminophosphates with a chemical durability similar to that of silicate glasses can be prepared. The hygroscopic nature of P_2O_5 has been used in the treatment of crops and animals suffering from trace element deficiencies [Knott (1989)]. These glasses dissolve at a controlled rate releasing transition metal additives. Glasses doped with halides have high ionic conductivities and are under study for battery applications [Ravaine (1985)]. The discovery of laser action in glass [Snitzer (1961)] initiated a new chapter in the world of glass research. Subsequent to this discovery, glass lasers use trivalent lanthanides as active ions whose wavelengths vary with the host matrix. Among all glasses, phosphates were found to offer the best overall combination of properties for many laser applications [Weber (1990)].

1.9 Objectives of the present work

The major hazard in the long term storage of nuclear waste arises from the action of water on the stored waste and possible subsequent contamination of the environment. Thus it becomes essential to know the chemical stability of the glass. Several studies have been performed to understand the leaching behaviour [Bault et al.(1978), Mcvay and Buckwalter (1980)] of glass subjected to boiling water for extended periods of time. In these measurements, the loss in weight is measured. This determines the 'leaching rate' of a particular composition. Thermal stability also plays a major role in the selection of a suitable candidate for the waste storage. Knowledge of the structure of such a system becomes essential in understanding some of its chemical and physical properties. Diffraction is a powerful technique
to study the structure of a glass in the short and medium range. In order to study the effects of added nuclear waste on the host boro-silicate network, glasses having high concentrations of simulated (non-radioactive) nuclear waste were studied using X-ray and neutron diffraction. A system having \( n \) components gives rise to \( n(n + 1)/2 \) different correlations. Thus, for the complete elucidation of the structure, \( n(n + 1)/2 \) independent diffraction experiments are necessary with a variation in the parameters such as the scattering factor, wavelength etc. Thus, only major changes in the boro-silicate host network caused by waste inclusion can be followed in the relatively low resolution diffraction experiments reported here.

In order to gain a better understanding of the effect that the elements constituting nuclear waste have on the host network, a phosphate glass former was incorporated with oxides of the lanthanides. It was intended to study the effect of these inclusions on the \( \text{P}_2\text{O}_5 \) network by X-ray and neutron diffraction. Topologically, vitreous silica and \( \text{P}_2\text{O}_5 \) have similar structures where the basic unit is a tetrahedron. As stable glasses doped with high concentrations of rare-earths find many applications, an additional incentive in studying these phosphates was to have insight into some of their basic physical properties. In the present work, such glasses were prepared and structurally characterized using diffraction, spectroscopic and other techniques.